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ABSTRACT

In a previous study (Part I) we showed that the material used for national prototype and reference masses, Pt/10%Ir, was susceptible to mercury contamination even at the very low levels of mercury present in air in weighing laboratories. In this study we measure the mass uptake per unit area of Pt/10%Ir exposed to mercury vapour, as a function of time, using the mass response of a quartz crystal microbalance with electrodes of Pt/10%Ir. This system can detect mass increases equivalent to less than 0.1 μg on a prototype kilogram with accuracy. It is shown that there is a rapid adsorption of the first monolayer of mercury, but this mercury then diffuses into the solid allowing further mercury to adsorb. The quantity of mercury absorbed does not tend towards any immediate limit, but instead continues to grow in proportion to the square-root of time. A consideration of the morphology of polished surfaces suggests this growth will continue for between 10 and 600 years. We conclude that our earlier recommendation of cleaning all environments where reference masses are housed, particularly with regard to mercury, is essential for maintaining the stability of Pt/10%Ir masses. Significant mass instability due to mercury sorption will occur for atmospheric mercury levels well below current health and safety limits.
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1 INTRODUCTION

An alloy consisting of platinum with 10wt% iridium is used for the manufacture of prototype kilograms\(^1\) which are the basis for realisation of the unit of mass in the SI system. The kilogram is defined as the mass of the PtIr international prototype, held by the BIPM (Bureau International des Poids et Mesures) at Sèvres near Paris. BIPM routinely use copies of this kilogram as reference standards, and similar prototypes are held by national metrology laboratories (such as NPL in the UK) as national standards\(^2\). This measurement system, especially as it relates to mass and related quantities in the UK, is shown in Fig 1 of reference (2). Mass is the only SI quantity still defined by means of a physical artefact; for the moment there is no accepted method which permits the definition of the kilogram in terms of atomic constants with equivalent accuracy. A redefinition in terms of fundamental constants is an important objective for developing the basic SI system. When it is achieved we may hope for greater accuracy, but even greater stress will then be focused on the stability of the masses needed to disseminate the standard.

The design of the prototypes was the result of careful thought and experimentation when this system was set up in late 19th Century. Platinum and iridium are noble metals, and are relatively simple to purify, so that prototypes of repeatable density could be manufactured. This density is high, so that PtIr prototypes have a low buoyancy correction and also a much smaller surface area than, for example, prototypes fabricated from stainless steel. This surface area is further minimised by manufacturing each prototype in the form of a circular cylinder, of height equal to its diameter. Since the early 19th Century prototypes have been manufactured from high purity platinum; however an alloy containing 10% iridium improves hardness and resistance to abrasion. Great care has always been taken to produce a good finish on these prototypes\(^1\), originally (numbers 1-63) by hand polishing using fine emery paper, but for prototypes produced in the last 10 years or so (numbers 64 onwards) by diamond machining, producing a smooth and repeatable "mirror" finish\(^1\). Thus the design of the prototypes which constitute the most fundamental level of our system of mass measurement represent a great achievement of 19th Century applied science and technology. However, two developments have renewed interest in the surface state of these prototypes;

Balances in routine use at a number of national metrological laboratories now have precisions of about 0.5 µg for the comparison of 1 kg prototypes. Further improvements seem likely, the theoretical limit to precision being at least a factor of 10 lower, set by "microseismic" ground vibrations\(^3\).

2 USING SUCH PRECISE BALANCES, INSTABILITIES IN THE MASS OF PtIr PROTOTYPES CAN EASILY BE MEASURED, AND HAVE BEEN A SUBJECT OF DISCUSSION FOR AT LEAST TWO DECADES\(^4\). The consensus is that these are due to surface effects. Thus the precision with which the SI unit of mass can be realised is currently limited by the surface-state of the prototypes, and not by balance technology.

2 ANALYSIS OF AS-RECEIVED DIAMOND-MACHINED SPECIMENS

To elucidate the surface state of PtIr prototypes we have examined 3 specimens of diamond machined PtIr alloys, machined by BIPM under the same conditions as is now used for the manufacture of kilogram prototypes. These are discs of 1.1 cm diameter and thickness ~1 mm. Though originally received by us in 1987 and 1990, they were re-machined by BIPM in 1990 in an attempt to improve the surface finish; the form and roughness of these surfaces was the subject of a separate study, and is published in part V\(^5\).

In preliminary studies sputter depth profiles through the surface by Auger electron spectroscopy (AES) showed a carbonaceous contamination which was only a few nanometres thick, so that later work was all by angle-resolved X-ray photoelectron spectroscopy (ARXPS);
this technique is appropriate for very thin contaminant films and gives additional oxidation state information on each of the elements detected. ARXPS, which has a sensitivity of ~ 1%, revealed the presence of 5 elements; platinum, iridium, carbon, oxygen and mercury. The presence of carbon and oxygen was expected, since these elements are observed in carbonaceous contamination on a wide range of substrates. The presence of mercury came as a surprise; we shall first examine its likely source.

3 SOURCE OF MERCURY CONTAMINATION

Mercury is more important than any of the other contaminants detected on the PtIr specimens for 3 reasons.

1. It has large atomic mass; a thickness of 1 nm of carbon, oxygen or mercury atoms would increase the mass of a PtIr prototype (of 71.5 cm² surface area) by 16, 10 or 97 µg, respectively.

2. Platinum is known to react with mercury, so that the formation of a thin layer of a ternary Pt-Ir-Hg alloy at the surface might be expected, rather than a distinct surface layer (such as formed by carbonaceous contamination) which would allow easier removal or cleaning.

3. Gold-mercury alloys are known to have very poor abrasion resistance, so (though no data seem to be available on abrasion resistance of Pt-Ir-Hg alloys) by analogy there is the possibility that contamination by mercury may make some loss of mass from a prototype during handling more likely.

For these reasons it is important to identify the source of mercury contamination, and determine whether it is absorbed into, or merely adsorbed onto, the surface of a prototype. There are only 5 possible sources of mercury;

1) segregation of a bulk mercury impurity to the surface during or after manufacture;

2) contamination from the diamond cutting tool;

3) contamination from the cutting oil;

4) contamination from the environment between machining and analysis, and

5) contamination in the ultra-high vacuum (UHV) chamber of the XPS instrument itself.

Segregation is implausible because of the low level of mercury in the bulk material (BIPM quote no value from their assay of impurities) and the fact that segregation to the surface will be extremely slow at room temperature. Diamond-point tools will not introduce mercury contamination. Measurements of many clean Pt, Pt/10%Ir and Au samples show no mercury contamination in the XPS instrument. We are therefore left with two plausible mercury sources; the cutting oil used during manufacture, and environmental contamination between manufacture and analysis. A specimen of the cutting oil was obtained from BIPM. This is a light cutting oil, Cimcool 5 star 45 supplied by Cincinnati Millacron, containing mineral oil, emulsifiers, deoxidisers and inhibitors, and is used as a 4% solution in distilled water.

An analysis by inductively-coupled plasma optical emission spectrometry (ICP-OES) was conducted. Initially the oil was dissolved in xylene, producing two phases, a xylene layer containing mainly organics and an aqueous phase. The only inorganic element detected in the organic phase was boron, and in the aqueous phase we found B, Na, S, Sn, Se, P, As, Ca, Fe, Pb, Cu and Zn in order of decreasing concentration, from 40 µg/ml for boron to
0.02 μg/ml for zinc. No mercury was found, even though the technique has the low detection limit of about 0.01 - 0.1 μg/ml for this element. Even assuming mercury to be present in the oil at a concentration somewhat below this detection limit, the quantity of mercury observed by XPS (~ 1 monolayer) would require the entire mercury content of about 50 ml of oil, equivalent to 1250 ml of the cutting oil solution used by BIPM, for each PtIr prototype. Thus the only remaining plausible source of mercury is environmental contamination.

To investigate the contamination of PtIr specimens by atmospheric mercury we exposed a number of pieces of carefully cleaned Pt/10%Ir rolled foil (supplied by Johnson Matthey Noble Metals Ltd, Royston, UK) to a range of environments typically encountered by PtIr prototype kilograms at NPL. A report of this work has been published elsewhere, but will be briefly summarised here. Five specimens of Pt/10%Ir foil were sputter-cleaned by Argon ion bombardment under UHV (Ultra High Vacuum) conditions; the effectiveness of this cleaning was checked by XPS analysis of each specimen which showed only Pt and Ir to be present at the cleaned surface. The group of cleaned foils were then distributed to (i) a balance room safe, usually housing stainless steel and PtIr reference masses, (ii) a cupboard adjacent to a frequently used balance, (iii) the safe in which the UK primary standard kilogram is normally kept, and (iv) inside the case of the UK primary precision balance. The fifth specimen was returned for immediate analysis after being transported with the other specimens to their venues, as a control to check if mercury contamination is occurring during the process of distribution. No mercury was detected on this sample. After 19 days exposure, each of the four stored specimens showed some mercury contamination, the greatest being specimen 4, which had been kept inside the case of the UK primary balance; XPS analysis of this specimen showed a quantity equivalent to 5 μg of mercury for the 71.5 cm² surface area of a PtIr prototype. The full results are summarised in the tables of Part I. Specimen 4 was exposed for a further 9 days to the environment of a cupboard which appeared to be very clean as judged by simple visual inspection. This led to a total mercury contamination equivalent to 14 μg. Washing in pure water, or washing together with rubbing with chamois leather impregnated with a 50% ethanol/50% ether solution (to mimic the BIPM "nettoyage" procedure) did not remove any significant quantity of this mercury contamination.

We concluded that atmospheric mercury is the source of the observed contamination on diamond machined specimens, and that it is not likely to be removed from PtIr prototypes by currently used cleaning procedures. Hashiguchi et al have observed mercury contamination on specimens of PtIr diamond-machined at BIPM, and we believe there is good reason to suppose this contamination is generic, and not a particular problem of NPL.

Having observed the mercury there are several questions to be answered: (i) what is the source of the atmospheric mercury, (ii) why does it adsorb, (iii) is it stable and (iv) what action should be taken.

The most likely source of the mercury, as noted in Part I, is from the spilt liquid metal from broken thermometers or barometers in the past. Monitoring of the laboratory air for health and safety purposes in areas close to the venues tested, but not the precise venues, showed mercury levels in the range 0 to 5 μg/m³. One should bear in mind that the mercury level in the air in closed drawers and compartments may be much higher than these levels.

At 1 μg/m³ the partial pressure of the mercury would be 10⁻¹⁰ of an atmosphere and even this amount of mercury could lead to the observed surface contamination in 10 seconds or so on clean Pt/10%Ir. In practice this high rate will not be achieved as the surface has C and O contamination prior to the Hg adsorption, making the retention probability of any impinging mercury atom rather small.
Why does mercury adsorb on Pt/10%Ir? The reason lies in two aspects: (i) there is a release of free energy in the interaction between Pt and Hg\(^{9,10}\) and (ii) there is no oxide on the Pt/10%Ir surface to form an inhibiting barrier layer. The reaction between Pt and Hg is similar to the better-known reaction between Au and Hg. In equilibrium with liquid mercury very large amounts would be taken up; but here, in equilibrium with a very low partial pressure it is likely that up to one monolayer could be adsorbed in a short time and, over long periods the atoms from that monolayer could diffuse into the bulk so leaving further sites for adsorption. A typical diffusion length for atoms diffusing with diffusivity, \(D \text{ m}^2/\text{s}\), after a time \(t\) is \((Dt)^{1/2}\). By this estimate, using reasonable values of \(D\) in metal crystals at room temperature, the time for diffusion by one atomic spacing exceeds 100 years\(^{11}\). Only dislocation or grain boundary diffusion could be active at these temperatures, by providing routes into the metal through which diffusion is much more rapid.

4 MASS OF MERCURY CONTAMINATION AS A FUNCTION OF TIME

As noted above, the adsorption of the first monolayer (28 \(\mu\)g on a 71.5 cm\(^2\) area of Pt/10%Ir) of mercury is likely to be particularly rapid; half a monolayer was the most mercury observed within the 19 day test, but it is expected that adsorption will proceed at least to monolayer completion. The adsorption of this monolayer, of itself, may have little practical significance as far as PtIr prototypes are concerned; it has long been recognised that these prototypes require a period of "stabilisation" after manufacture, during which their mass varies relatively rapidly. The take-up of a monolayer of mercury may be one of the processes which occurs during this stabilisation period. The only implication for the maintenance of mass standards of this mercury monolayer may be a decreased abrasion resistance compared to the original PtIr surface. Even so, our simulation of the BIPM nettoyage indicates\(^{1}\) that the mercury layer's abrasion resistance may be adequate for the purposes required. Of much more significance is the long term mercury sorption behaviour. A number of possible types of behaviour can be conceived; three possibilities are shown schematically in Fig 1. The ideal behaviour as regards mass stability is illustrated in Fig 1(a), where only one monolayer of mercury adsorbs, and thenceforth the mass of the prototype remains constant. Other possibilities include (b) a linear increase after the initial monolayer take-up, or (c) a long term parabolic régime in which the additional mass of mercury is proportional to the square root of time since initial exposure. The square root dependence is characteristic of diffusion of any species into a semi-infinite bulk substrate, and the linear dependence is characteristic of a process limited by the rate of transfer of a species across an interface.

In our earlier report on mercury contamination we suggested\(^{1}\) the most probable behaviour is as shown in 1(a); bulk diffusion of Hg in Pt (and by analogy a PtIr solid solution) must take place, but is so slow at room temperature that the \(\sqrt{t}\) régime expected for diffusion will in practice be so slow as to be indistinguishable from the long term constant behaviour of Fig 1(a). Nevertheless, diffusion along dislocations and grain boundaries is likely to be much more rapid, and bearing in mind that the timescales reach 100 years, further experimental work was undertaken to elucidate the true long term behaviour. The quartz crystal microbalance\(^{12,13}\), which is extremely sensitive to small mass changes at its surface, was especially suited to these measurements. Unlike surface analysis techniques such as XPS, the microbalance gives mass changes directly in situ as the experiment proceeds without the need for a vacuum environment.

5 THE QUARTZ CRYSTAL MICROBALANCE MEASUREMENTS

The quartz crystal microbalance (QCM) is an extremely sensitive and accurate method for measuring changes in mass at a surface. First used by Sauerbrey\(^{12}\) in 1959, the QCM is today widely used in commercial vacuum thin film deposition monitors\(^{13}\), and is
increasingly being used in research into small changes of mass at surfaces exposed to gases\textsuperscript{(14)} or liquids\textsuperscript{(15)}.

The mass-sensitive component of the QCM is a quartz crystal resonator, consisting of a rectangular plate cut from a quartz crystal, onto which metal electrodes have been deposited. By connecting these electrodes to an appropriate oscillator circuit the crystal can be made to resonate mechanically, via the piezoelectric effect, at about 6 MHz.

Any change in areal density at the surface of the resonator results in a change of the resonant frequency. This may be readily monitored to an accuracy of 0.1 Hz, allowing, for example, 0.1\% of a monolayer of mercury be detected. In the present application, electrodes of Pt/10\%Ir alloy were deposited onto the surface of argon sputter cleaned 6 MHz quartz crystal plates (Brookes Crystals Ltd) by dc magnetron sputtering from a Pt/10\%Ir target (Johnson Matthey) of 99.99\% purity under ultra-high-vacuum (UHV) conditions. The iridium content was determined by assay as 9.99\%.

The confidence which we can place in the accuracy of areal density measurements made using the QCM depends largely on two aspects.

(i) The mass-sensitivity of the quartz resonator is a function of position on its surface, and if this function is not known, systematic errors may result. In an experiment to measure adsorption of mercury onto the PtIr electrodes, any sensitivity to changes in areal density outside the electrode (on the bare quartz) would lead to a systematic error.

(ii) Temperature variations and electrical noise are always present, and these limit the accuracy with which the resonant frequency can be determined.

The first source of uncertainty, the effect of the non-uniform sensitivity of the resonator (in particular to mass changes outside the electrode material) has been modelled mathematically in some detail in a previous work\textsuperscript{(16)}. A novel electrode structure has been developed which effectively eliminates this problem\textsuperscript{(17)}, and it is this type of QCM which has been used for all of the measurements described in this report. The QCM crystal sensor is shown schematically in Fig 2. The mass sensitivity is confined to the central circular thick region of the PtIr electrode; Fig 3 shows experimental measurements of sensitivity performed using a method previously described\textsuperscript{(16)}, and a continuous line representing the sensitivity predicted theoretically. One can see that, although much of the surface of the sensor is not covered with PtIr, the sensitivity is truly confined to the Pt/10\%Ir covered regions.

The merits of the QCM in comparison with a conventional kilogram balance for studying surface mass stability are given in Table 1.

The crystals were now exposed to a saturated vapour pressure of mercury at a temperature of 21.0 °C for 23 days. The temperature was measured using a platinum resistance thermometer, and maintained at 21.00 ± 0.05 °C by placing the entire apparatus in an airbath heated/cooled by two 70W Peltier devices under the control of a Eurotherm 810 temperature controller. Such careful temperature control is not very important to the mechanism of the mercury uptake but is necessary to utilise the full mass sensitivity of the QCM, due to its unwanted temperature sensitivity. A saturated vapour pressure of mercury is much higher than would be experienced in any laboratory, but was suitable for this "accelerated" test, and could be maintained using simple apparatus.

The crystal sensor itself was contained in a 500 ml glass vessel, and connected to a Pierce oscillator circuit\textsuperscript{(18)} through copper wires running through a PTFE stopper, as shown in Fig 4. The frequency of the oscillator output signal was measured using a Racal-Dana digital counter, model 1991 with a high stability reference oscillator option, and logged using an
IEEE488 interface to an IBM compatible PC. Note that static mercury droplets tend to form surface oxides and adsorb hydrocarbons, both of which may cause the mercury vapour pressure to fall as time progresses. To prevent this, the mercury droplets were continuously agitated using a PTFE-sealed magnetic stirrer. This had to be driven by a vibrationless magnetic stirrer unit (i.e. one containing sequentially excited solenoids rather than a rotating permanent magnet) and be thermally insulated from it to prevent the formation of convection currents within the vessel. 5 ml of mercury was used.

The data acquired during QCM measurement are the shifts in the resonant frequency as a function of time. An increase in mass at the electrode surface results in a fall in this frequency. The equation relating mass to frequency is the Sauerbrey equation\(^{(12,16)}\), which for a uniform increase in mass per unit area, over the entire sensitive area on both crystal faces gives

\[
\Delta \sigma = \frac{-N_{AT} \rho_Q \Delta f}{f_0^2} \tag{1}
\]

where
- \(\Delta \sigma\) = areal density change at each electrode surfaces
- \(\Delta f\) = observed frequency shift
- \(\rho_Q\) = density of quartz
- \(N_{AT} = 1661 \text{ ms}^{-1}\), a constant for these "AT-cut" quartz crystals
- \(f_0\) = initial resonant frequency of the QCM.

Using a reference value for the density of quartz, \(\rho_Q = 2649 \text{ kgm}^{-3}\), and the measured resonant frequency of our (nominally 6 MHz) crystal after electrode deposition, \(f_0 = 5.891 \text{ MHz}\), we obtain

\[
\frac{\Delta \sigma}{\Delta f} = -63.4 \text{ } \mu g \text{ m}^{-2} \text{ Hz}^{-1}
\]

If we now assume the surface area of a 1 kg mass prototype is 71.5 cm\(^2\), we can find the change in mass of such a prototype, \(\Delta m_{\text{Hg}}\), equivalent to that experienced by the PtIr electrodes of a QCM

\[
\Delta m_{\text{Hg}} = -0.453 \text{ } \mu g \text{ Hz}^{-1} \Delta f
\]

This equation has been used to convert measured frequency values to mass shifts for a PtIr prototype. Fig 5 shows the rapid increase in mass immediately after exposure to the stirred mercury at 21 °C at atmospheric pressure, gaining the equivalent of 10 \(\mu g\) on a 71.5 cm\(^2\) surface area mass prototype in less than 1 hour. Fig 6 shows the results for the first 550 hours of exposure. There is a rapid initial mass increase, followed by a slower, but unmistakable, \(t^{1/4}\) regime. This \(t^{1/4}\) behaviour can be seen more clearly in Fig 7, where the abscissa is linear in \(t^{1/4}\). In this plot the mass increase is clearly proportional to \(t^{1/4}\) from 170 to 510 hours. Performing a linear regression in this range we obtain

\[
\Delta m_{\text{Hg}} / \mu g = 24.7 + 0.871 \sqrt{t/\text{hours}} \tag{4}
\]

The \(t = 0\) intercept, \(\Delta m = 24.7 \mu g\), can be interpreted as the mass of mercury taken-up during an initial, rapid adsorption phase. This compares well with the mass of a 71.5 cm\(^2\) monolayer of mercury atoms, 28 \(\mu g\), calculated from the bulk density and atomic mass of mercury. After 550 hours the QCM sensor was removed to a carefully cleaned mercury-free
environment, after which its frequency was stable for several days until the final termination of the test.

The initial rapid adsorption phase which terminates with about one monolayer of mercury at the surface is shown in Fig 8. This plot gives the difference between our "diffusional" fit and the measured data. This shows the surface sites unfilled by mercury. For an atomically clean PtIr surface we might expect this curve to be an exponential with a rapid decay constant (given the low ΔG for the Hg-Pt reaction, and therefore the likely low sticking probability) of at most a few minutes. Whilst the initial slope is of that order, we can conjecture that for the majority of the surface, physisorbed water and hydrocarbons force a range of different displacement mechanisms to occur before the mercury monolayer can complete, reducing the "effective" Hg sticking probability still further, and ensuring that no single exponential regime can be distinguished.

The important aspect of the results of Figs 6 and 7 is that a full monolayer is rapidly established. If we ignore changes in the first year and assume this to be our starting point, the mass increases in a saturated mercury vapour environment in the subsequent 1, 5 and 10 years would be, respectively 82, 184 and 260 μg, i.e. there is no asymptotic limit to the mass increase even over very long times.

6 MERCURY SORPTION BY PLATINUM-IRIDIUM PROTOTYPE SURFACES

There are two respects in which our quartz-crystal microbalance "accelerated test" of mercury uptake differs from the metrologically important problem of mercury uptake by a prototype in use as a reference mass;

1. The sputtered Pt/10%Ir alloy surface of the QCM sensor has a different structure and morphology to that of a polished or diamond machined reference kilogram, even though the materials are chemically identical.

2. The mercury vapour pressure used in our QCM accelerated test was much larger than would be present in any laboratory. The mass of mercury taken up must therefore be scaled according to the mechanism of mercury sorption in order to predict mercury uptake by a real prototype over the long term.

We shall deal with each point in turn.

6.1 SURFACE MORPHOLOGY

The surface of a PtIr single-crystal (such as those sometimes used in academic catalysis studies) would not absorb mercury, but would most likely adsorb a single monolayer. Diffusion of mercury into the crystal would be geologically slow, due to the extremely low diffusivity of mercury in platinum and its substitutional alloys, as discussed previously. However, both sputtered films and polished or machined surfaces are highly disordered on a sub-micron scale. Both will allow mercury ingress along defects such as grain boundaries and dislocations. A quantitative study of expected ingress rates would be expensive, requiring Transmission Electron Microscopy sectioning to determine the defect density and separate experiments to determine the grain-boundary diffusivity of mercury in PtIr. In any case, specimens taken from polished prototypes nos. 1-63 are not available. Nevertheless a qualitative comparison can be made based on typical surface morphologies as shown schematically in Fig 9. Figure 9(a) shows the morphology we would expect for our sputtered PtIr films on quartz crystals. All of our films have thicknesses between 200 and 300 nm and were deposited without any special heating of the quartz crystal substrate. Substrate temperature, T_s, was therefore not significantly above room temperature. It is known that in the absence of "shadowing" effects during film growth (which would not be expected
given our sputter target geometry, film morphology is determined by surface diffusion and bulk diffusion\(^{(19,20)}\). Both scale in proportion to the melting point \(T_m\) of the material being deposited; our conditions of \(T_s/T_m = 0.15\) lead to a so-called "zone I" morphology\(^{(19,20)}\), characterised by small equiaxed grains formed by renucleation after deposition, and a high dislocation density (which might be expected to present pathways for mercury diffusion). Columnar grain structures caused by epitaxial growth would not be expected below about 700 °C for Pt/10%Ir. For example, in TEM sectioning of Pt films formed by evaporation onto a room temperature substrate, Hentzell et al\(^{(19)}\) observed a distribution of equiaxed grains between about 5 nm and 30 nm.

Figure 9(b) shows schematically the surface of a polished PtIr prototype, such as nos 1-63. Whilst the bulk alloy consists of large, equiaxed grains (and therefore has a very low grain boundary density), we would expect polishing to leave a "damaged layer"\(^{(21)}\) which, due to extreme plastic deformation, has been broken into small grains with a very high density of both grain boundaries and dislocations. Most published studies of surface damage due to polishing have involved 70:30 brass, which has good etching characteristics, allowing easy imaging of the damage region. We would expect the damaged region of PtIr to be much the same, due to a similar material hardness. Samuels\(^{(21)}\) examined 70:30 brass polished with 0.1 μm diamond paste; he found a damaged layer ~ 700 nm thick which he further classified as consisting of a "fragmented layer" ~ 100 nm thick, and a total deformed layer from a depth of 100 nm to about 700 nm.

The conclusion is that despite the differences between these surface preparation methods, sputter deposition, diamond polishing, and diamond machining are likely to give very similar disordered surfaces consisting of small grains and high densities of both dislocations and grain boundaries. This means they will have similar mercury sorption properties.

### 6.2 EFFECT OF MERCURY CONCENTRATION IN AMBIENT AIR

The UK occupational health limit for ambient mercury in air is 50 μg m\(^{-3}\); our laboratories at NPL are surveyed periodically for health and safety purposes by instruments with a sensitivity of 1 μg m\(^{-3}\). Typical results are in the range 0-5 μg m\(^{-3}\), well within safety limits. By comparison our QCM measurements were performed at a saturated vapour pressure of mercury at 21 °C, corresponding to 0.187 Pa\(^{(23)}\), or 15.4 mg m\(^{-3}\). Figure 8 shows QCM results for the initial mercury monolayer adsorption phase; had this been a simple exponential then it would have provided a valuable "sticking probability" value for mercury adsorption. This in turn would allow us to predict the time taken for monolayer adsorption on kilogram prototypes by simple scaling of adsorption rate with ambient mercury concentration. However Fig 8 does not show exponential behaviour; mercury uptake in the very early stages of adsorption is extremely rapid, but the rate limiting step for much of the period shown in Fig 8 seems to be displacement of other adsorbed material such as water and carbonaceous contamination. Thus a better guide to the rate of the initial monolayer adsorption comes from our earlier XPS studies\(^{(6)}\); here, as in real prototype storage environments, monolayer adsorption rate will be limited by rate of mercury atom impingement rather than how rapidly other adsorbed species can move out of the way to expose virgin PtIr surface.

The damaged layer of a polished metal has a finite thickness, so that the grain boundary structure shown in Fig 9(b) must eventually saturate. The time taken to reach saturation is very important; if it is very short, then kilograms in service will contain a constant mass of absorbed mercury, and will be stable. If saturation only occurs after many decades, then all prototypes currently in service are likely to be gaining in mass of absorbed mercury. We can
estimate the mass of mercury which can be absorbed as follows; let \( N \) be the number of grains in the damaged layer thickness \( t \), on a kilogram prototype of surface area \( s \) (= 71.5 cm\(^2\)). Then approximating the grains as spheres of diameter \( 2r \) we get

\[
N = \frac{st}{4\pi r^3} \tag{5}
\]

so that the total grain boundary, \( A_{gb} \) area is about

\[
A_{gb} = 4\pi r^2 N/2 = \frac{3st}{2r} \tag{6}
\]

So that if monolayer adsorption occurs at all these grain boundaries on saturation of the damaged layer, we have a mass of mercury on saturation of \( m_{sat} \)

\[
\Delta m_{Hg}^{sat} = A_{gb} \left( \frac{m_{Hg}^{mono}}{s} \right) \tag{7}
\]

where \( m_{Hg}^{mono} \) = mass of mercury monolayer (= 28.4 µg), so

\[
\Delta m_{Hg}^{sat} = \left( \frac{3t}{2r} \right) m_{Hg}^{mono} \tag{8}
\]

We can view the factor \((3t/2r)\) as an enhancement of the surface area of the prototype available for mercury adsorption. This is separate from the enhancement of surface area due to roughness described in part V\(^{(5)}\). For a careful diamond polish, using 0-1 µm diamond paste, Samuel\(^{(21)}\) work would suggest \(700 \geq t \geq 100\) nm, whereas the very limited annealing which could take place at room temperature after extreme plastic deformation of this region would give a grain size similar to that observed in the evaporated films of Hentzell et al\(^{(19)}\), \( r \leq 15\) nm. This gives a conservative estimate of the lower limit for the mass of mercury on saturation of

\[
280 \mu g \leq \Delta m_{Hg}^{sat} \leq 2 \text{ mg} \tag{9}
\]

Applying the diffusional growth law we derived from the fit to QCM measurements. This means no saturation can occur within the first 10 years of manufacture, and may continue for up to about 600 years, depending on the degree of subsurface damage during polishing. It is unsafe to assume that any polished prototype currently in service has yet reached mercury saturation. Close to the point of saturation, one would expect to see an exponential law as the mass of absorbed mercury tends to a limit, analogous to the theory underpinning studies of outgassing from thin layers\(^{(24,25)}\).

Might careful polishing lead to a lower rate of mercury uptake compared to our QCM experiments? We can generalise equation (4) to
\[ \Delta m_{\text{Hg}} = m_{\text{Hg}}^{\text{mono}} + k \sqrt{t/\text{hours}} \]

where \( k = 0.871 \) for our QCM data, in which the grain size \( \leq 30 \text{ nm} \). We must have \( k \propto 1/r^2 \), so a maximum credible grain size, in the subsurface damage of \( 2r = 100 \text{ nm} \) gives us a lower credible bound to the long-term growth rate of

\[ \Delta m_{\text{Hg}} = 28.4 \mu g + 0.09 \mu g \sqrt{t/\text{hours}} \]

These conclusions on the likely growth in mass of polished prototypes are summarised in Fig 10. A rather wide band of feasible behaviour has been necessary in this plot, essentially because (i) no specimens of actual prototype kg surfaces have been studied, (ii) no published mercury contamination measurements exist for the atmospheres in which PtIr prototypes are stored in the various national laboratories. Nevertheless, QCM measurements together with XPS spectra from specimens exposed at locations within NPL give us a good deal of confidence in the behaviour shown in Fig 10.

7 COMPARISON WITH HISTORICAL WEIGHING DATA FOR PLATINUM-IRIDIUM PROTOTYPES

Two points are important when discussing whether the mercury sorption model is in agreement with historical weighing data;

1. We are not interested here in the increases in mass of prototypes directly after cleaning/washing\(^{7,26,27}\). These probably measure the recontamination of the surface by hydrocarbons rather than having any relation to mercury sorption; XPS results\(^6\) indicate that cleaning/washing does not significantly reduce adsorbed mercury, and it is certain that it will not remove any mercury which has been absorbed into the damaged layer along defects and grain boundaries. We will here consider only weighing results from the 3 international verifications\(^{28}\) so far performed by BIPM, since these represent the masses of the prototypes after cleaning/washing, and therefore with little carbonaceous contamination. Reduction of carbon contamination will be the subject of a separate work\(^{29}\).

2. Only relative weighing data (ultimately traceable to the international prototype) are available. Prototypes with similar degrees of surface damage due to polishing, stored in atmospheres with similar trace levels of mercury, should increase in mass at much the same rate. Such differences may be barely detectable, even though, as shown in Fig 10, absolute mass increases of \( \geq 100 \mu g \) (0.1 ppm) are to be expected over a century if mercury sorption does take place. Instead we are limited to examining relative mass increase due to differences in mercury concentration in the air, or surface condition (i.e. the defect density at the surface of a prototype which allows mercury to be absorbed).

It will be useful to review what is known about the kilogram prototypes\(^1\). The oldest prototypes still in use are the international prototype \( k \), and a reference prototype \( K1 \), both held by BIPM. They were manufactured in 1878 from a single alloy melt, and polished in the workshop of M Collot, a Paris instrument-maker\(^1\), prior to the establishment of the BIPM. Most of the current national prototypes (nos 1-40) were made circa 1884, and again polished by Collot, this time in the newly-equipped BIPM. Further prototypes were manufactured after the Second World War, and polished using a procedure thought to be similar to that used by Collot\(^1,30\). All of these prototypes were polished using emery paper of 00 or 000 grade (the exact grade in uncertain), leaving a "satin" finish. In 1974 two new
prototypes were polished using diamond paste on a felt pad, which gave a better finish, but polishing was replaced in the 1980s by the new diamond-machining process(1) beginning with prototype 64. Diamond machining results in a "mirror" finish, and profilometer traces indicate a much reduced surface roughness compared to polished prototypes(1,5).

Figure 11(a) shows the mass of certain groups of PtIr prototypes as a function of time since they were manufactured. Each group was manufactured within a few years of each other, and therefore can be assumed to have been polished identically, or as near identically as can be judged by eye. The error bars in this plot do not represent weighing precision, but the standard deviations of the nominal mass values within each set; these bars therefore indicate the "spread" of values within each set. The four sets plotted are; (a) the 4 "témoins" manufactured in the 1880s, and held as reference kilograms by BIPM (filled circles in Fig 11(a)), (b) all remaining PtIr national standard kilograms manufactured in the 1880s, except the national standards of the USA, France, Japan and the UK (open circles), (c) 3 prototypes manufactured circa 1946 (filled square) and (d) 6 prototypes manufactured circa 1951 (filled triangle).

The spread within each set is smallest for (a), the set of 4 témoins held by BIPM, as one might expect, since they have been stored in a common environment for a century. Set (b), which comprises the majority of the national prototypes, shows the widest spread. On compiling this data it became clear that the mass changes observed for kilogram prototypes held by countries which have been industrialised over the whole of the past century fall significantly below the average; the average for those kilograms from the USA, France, Japan and the UK (the extant FRG prototypes are of mid-20th Century manufacture, and not included in this set at all) is just 5.5 ± 15 μg compared to 33.0 ± 21 μg for the rest, in the 1989-92 3rd verification. We think this may be due to increased abrasion resulting from higher than average frequency of handling, possibly aggravated by the mercury adsorption at their surfaces. This may have led to a fortuitous near-cancellation of the upward trend in prototype masses in these countries. The open circles plotted in Fig 11(a) represent the prototypes manufactured in the 1880s of all other nations participating in the 3rd verification.

The data plotted in Fig 11(a) is consistent with a mass increase for all post-1880 prototypes with respect to the international prototype k of

\[ \Delta m_{Hg} = 4.6 \, \mu g / \sqrt{t/\text{years}} \]  

(12)

However this historical weighing data provides no conclusive proof of mercury build-up, since many other curves would describe this data equally well. If we assume mercury to be the cause, then Fig 11(a) suggests a difference in mass of mercury absorbed between these prototypes and the international prototype k of about 50 μg. We could conjecture that this difference in mass of mercury absorbed is due to a minor difference in subsurface damage due to greater care being applied to the polishing of the first 3 prototypes (this is reasonable given that the prototype K1, polished before 1880 in Collot’s workshop along with k, shows no clear long-term drift with respect to k, as shown in Fig 11(b). However, the only definite conclusion we can draw from this weighing data is that mercury sorption is consistent with the observed long term drift. The scatter in the data of Fig 11(a) reflects the variability of the surface conditions and air quality relating to these stored prototypes. Many other curves would fit these measurements equally well, and other contaminants may indeed be more important than mercury for prototypes stored in particular locations. We present this data simply to show that it does not disprove the mercury accretion hypothesis.

The inability of existing weighing measurements to show convincingly whether mercury sorption is, or is not, a problem (even though the entire set of prototypes may be growing in unison at somewhere between 2 μg and 10 μg per year due to this effect) is compelling justification for further, chemically specific measurements of contamination on real polished
PtIr kilograms, or any similar specimens polished by Collot in the 1880s. Non-destructive analysis of the polished region should be possible in air at room temperature using modern X-ray fluorescence instruments especially those with high resolution wavelength dispersive detectors. Destructive analysis by Auger fractography would show definitively whether mercury is present at grain boundaries below the surface.

8 CONCLUSIONS

1. Quartz crystal microbalance measurements show that atmospheric mercury is adsorbed onto, and then absorbed into, platinum-10%iridium alloy surfaces.

2. Typical laboratory environments containing 1-5 µg/m³ of mercury can lead to significant, irreversible mass increases for reference masses made from platinum or platinum-10%iridium alloy.

3. There are two distinct phases in the sorption of mercury by the PtIr surface; (i) an initial, rapid chemisorption of a monolayer of mercury, followed by (ii) a slow mass increase proportional to the square root of time, caused by mercury diffusing into the layer of surface damage introduced by polishing or diamond machining.

4. For reference masses, the initial rapid monolayer mercury adsorption probably takes place within a few months of manufacture, during the "stabilisation" period in which the mass of a prototype is known to be unreliable and to increase measurably. This monolayer of mercury forms a Pt-Ir-Hg ternary alloy, increasing the mass of the prototype by 25 - 30 µg (more if the prototype is rough on the near atomic scale). Provided this layer is retained for the entire life of the prototype, it may not affect the accuracy of mass comparisons.

5. The long-term mass increase, proportional to the square root of time, is probably due to mercury diffusion along defects and grain boundaries into subsurface damage. This process is likely to continue for many years, and is unlikely to have terminated for any of the PtIr reference masses currently in service.

6. Quartz Crystal Microbalance (QCM) measurements indicate a magnitude of mercury diffusing into the bulk material consistent with historical observations of the long-term mass gain of prototypes. However, QCM results are only a qualitative guide to mercury defect diffusion behaviour in real reference kilograms; on the one hand the sputter deposited films will have a much smaller grain size than the reference masses (ie a higher defect density for grain boundaries) but on the other the polishing or machining of the masses ensures that the surface layers have all been deformed massively beyond the yield point and so they have a higher defect density for dislocations and point defects. The observed mass gains of PtIr prototypes may be partly due to mercury, partly due to accretion of physisorbed carbonaceous contamination, which may also be expected to display a "root t" time dependence.

9 RECOMMENDATIONS

1. Platinum and platinum-10%Ir reference masses should be kept in an environment as free as possible from atmospheric mercury. This requires mercury levels well below current health and safety limits.

2. Storage areas should be monitored for mercury contamination, for example by XPS analysis of test Pt/10%Ir specimens. This would also help to establish an acceptable upper limit for atmospheric mercury in prototype storage environments.
3. A non-destructive, chemically specific technique is required to measure the subsurface mercury on PtIr reference kilograms in service. Some modern X-ray fluorescence spectroscopy (XRF) instruments allow this to be done in air at room temperature and pressure. The quantities of mercury, whilst easily large enough to affect mass comparisons on balances with µg precision, are likely to be close to the XRF detectability limit, so very careful work will be needed.

4. For new prototypes, it may be possible to insert a processing step after diamond machining but before final cleaning/washing, which helps prevent mercury sorption by removing the damaged layer. This may be possible by

(i) A "heat treatment" (~ 400-500 °C) similar to that used to remove subsurface strain after cold-working of many small metal components;

or

(ii) An electrochemical polish which would remove the damaged layer and have the added advantage of leaving a much smoother surface on a nanometre scale. This was investigated by BIPM in about 1950(30), but deserves further work in view of improvements in polishing techniques since then.

ACKNOWLEDGEMENTS

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REFERENCES


2. D R Armitage, "One Measure, One Weight; The National Measurement System" in Proc. 2nd Conf. on Weighing, Calibration and Quality Standards in the 1990s, Ed M J Buckley (South Yorkshire Trading Standards Unit, Sheffield 1992).


17. P J Cumpson "Novel quartz crystal microbalance design eliminating sensitivity outside electrodes", submitted to Anal. Chem.


Table 1

Comparison of conventional kilogram balance and Quartz Crystal Microbalance as instruments for surface mass stability studies

<table>
<thead>
<tr>
<th>Nature of measurement</th>
<th>Conventional kg balance with kg prototype</th>
<th>QCM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Area of sensitivity</td>
<td>Mass comparison with (hopefully) stable reference</td>
<td>Absolute measurement of mass change</td>
</tr>
<tr>
<td>Minimum interval between measurements</td>
<td>≥ 1 hour</td>
<td>~ 1 cm²</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>0.5 - 1.0 μg</td>
<td>0.2 ng</td>
</tr>
<tr>
<td>Sensitivity per unit area</td>
<td>~ 10 ng/cm²</td>
<td>~ 0.2 ng/cm²</td>
</tr>
<tr>
<td>Unwanted temperature sensitivity</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Cost</td>
<td>£10,000 - £100,000</td>
<td>~ £100</td>
</tr>
</tbody>
</table>
FIGURE CAPTIONS

1. Possible models for mercury up-take on PtIr standard masses prior to the present work; (a) adsorption of a monolayer of mercury, followed by long-term stability, (b) adsorption of a monolayer followed by a linear increase with time, (c) adsorption of a monolayer followed by a parabolic increase in mass due to diffusion of mercury into the bulk. QCM measurements in the present work show case (c) is the most probable behaviour for PtIr prototypes.

2. Quartz crystal microbalance sensor used in the present work. Electrodes were sputter deposited Pt/10%Ir alloy to simulate the surface of a PtIr prototype. The crystal surface was highly polished, giving the PtIr electrodes a "mirror" finish.

3. Mass-sensitivity of the QCM was confined to near the centre of the sensor by deposition of a relatively thick PtIr layer in a circular disc of diameter 4.8 mm. Theoretical prediction\(^{16}\) (continuous line) and experimental measurements (points with error-bars) show that the sensor is virtually insensitive to any mass changes taking place outside the area of the PtIr electrodes.

4. Apparatus used for exposure of PtIr sensor surface to a saturated vapour pressure of mercury at 21 °C.

5. A large increase in mass at the PtIr surface occurs immediately upon exposure to mercury vapour, at \(t = 0\). Here \(\Delta m_{\text{Hg}}\) represents the mass increase of a PtIr kilogram prototype, calculated by scaling up the mass increase measured by the QCM to the 71.5 cm\(^2\) surface area of such a prototype.

6. Exposure for 550 hours indicated behaviour similar to that expected under the model shown in Fig 1(c). Again, \(\Delta m_{\text{Hg}}\) represents the mass increase of a prototype of surface area 71.5 cm\(^2\).

7. (a) A least-squares fit of QCM measurement to a \(t^{1/2}\) law characteristic of diffusional processes gives us a model for long-term mercury uptake. The abscissa is the square-root of time, so a fit to the measurements appears as a straight line on this plot.

(b) When plotted against a linear time axis, this \(t^{1/2}\) law is seen to provide a good fit, and suggests an initial rapid adsorption of \(\approx 24.7 \mu g\), close to the mass of 28.4 \(\mu g\) which would be expected for a single layer of Hg atoms.

8. The surface sites unfilled by mercury showing the initial, monolayer adsorption behaviour on the QCM sensor. Exponential adsorption would be a straight line on this plot; instead mercury adsorption rate is quickly dominated by desorption of other species, ie water and carbonaceous contamination.

9. (a) Schematic cross-section through sputter-deposited Pt/10%Ir films on QCM sensor crystal. Films were deposited onto the quartz substrate at \(T_s = 300\) K, much lower than the melting-point of PtIr, \(T_m\), leading to a film of small, equiaxed grains\(^{19,20}\).

(b) Schematic cross-section through a polished PtIr prototype surface, postulated from taper-section micrographs of Samuels\(^{21}\).

10. Mass increase of PtIr kilogram prototypes due to mercury uptake, \(\Delta m_{\text{Hg}}\) as a function of time since manufacture, \(t\), based on QCM results and XPS data (+) for specimens exposed to typical weighing environments\(^{6}\). Possible behaviour of any particular prototype depends on the mercury concentration in its surroundings in the initial
adsorption stage, and on the subsurface damage introduced by polishing during the long-term diffusion stage. The shaded band shows the range of behaviour possible, given typical Hg contamination levels and damage known to be introduced during careful polishing. Both axes are logarithmic in this plot.

11. (a) Increase in mass of 4 groups of PtIr prototypes manufactured together, compared to that of the international prototype\(^{(28)}\). The average mass of the members of each group are plotted using square-root of time since manufacture, as the abscissa, with vertical bars indicating the standard deviation "spread" of values within each group (not weighing precision, which is rather better). The mass-increase trend shown (- -) is consistent with the mercury contamination model proposed. These groups were manufactured (a) in 1880s, and held by BIPM, (b) in 1880s, and held by national laboratories, (c) circa 1946, (d) circa 1951.

(b) Mass of prototype K1 compared to the international prototype \( k \), as a function of time since their manufacture in 1878.
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A quartz crystal microbalance sensor used in the present work deposited Pt/10%Ir alloy to simulate the surface of a Pt prototype. The crystal surface was highly polished, giving the PtIr electrodes a "mirror" finish.
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(b) When plotted against a linear time axis, this law is seen to provide a good fit, and suggests an initial rapid adsorption of \( \approx 24.7 \) \( \mu \)g, close to the mass of \( 28 \) \( \mu \)g which would be expected for a single layer of Hg atoms.
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