Stability of Reference Masses VIII: X-Ray Fluorescence (XRF) as a Noncontact, Nondestructive Measurement Method for Trace Mercury Contamination of Platinum-Group Metal Surfaces

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ABSTRACT: We apply X-ray Fluorescence (XRF) to the assessment of contamination on platinum-group metal mass standard surfaces for the first time. XRF has a sampling depth suitable for detection of mercury contamination that we previously conjectured would diffuse into surfaces of platinum and platinum-iridium prototypes along defects and grain-boundaries introduced by polishing. XRF shows mercury contamination on a 19th century platinum reference weight of $0.96\pm0.19\mu g/cm^2$, equivalent to around 70µg on a Pt-10%Ir prototype kilogram, confirming that this diffusion into the surface does take place. The mass of contamination does not reach a limit, but continues to increase as the square-root of time since manufacture, probably for several hundreds of years.

We review the implications of mercury accumulation for the study of the stability of platinum-iridium standard weights, in particular the kilogram prototypes that still stand at the heart of the SI, and look at the implications after redefinition of the kilogram when stable transfer standards and stable medium-term storage will be needed.

We anticipate that the methods developed in this work to detect extremely small amounts of mercury at platinum surfaces by XRF may be useful in other applications, for example the detection of mercury poisoning of platinum group catalysts "in the field" using portable XRF instruments.

Keywords: kilogram, metrology, mercury contamination, platinum catalyst poisoning, XPS, XRF, surface analysis

I. INTRODUCTION

Of all the Système international d'unités (SI units) base units only the kilogram remains as an artefact standard[1] and even though this will not be the case for much longer[2,3,4,5] the stability of transfer standards will be crucial in future. It has been known for many years that the mass of prototype kilogram standards increases over time[6], and surface effects have long been suspected as being responsible[7]. Surface analytical techniques, such as x-ray photoelectron spectroscopy (XPS) were first applied to the analysis of mass standard surfaces by Ikeda *et al*[8]. Later XPS at the National Physical Laboratory (NPL) in the UK was particularly valuable in showing for the first time the unexpected presence of mercury on samples of platinum-iridium alloy foil stored in the same laboratory environments as kilogram weights. We were able to demonstrate that (a) atmospheric mercury contamination[9] is likely to be a problem in causing part of the monotonic increase[10] in platinum-iridium prototype masses and (b) the remaining mass increase is largely due to the growth of a carbonaceous layer[11]. Adsorption of mercury onto the surfaces of platinum-group metals has been known for a century[13,14]. Recently the presence of mercury at the surface of a 19th century platinum kilogram prototype in Switzerland has been confirmed[15]. More recently we examined the surfaces of six other platinum mass standards manufactured in the mid-19th century, using x-ray photoelectron spectroscopy (XPS). XPS showed mercury on all six[16], with the most contamination observed being equivalent to around 249µg on a Pt-10%Ir prototype.

With XPS we were able to probe only the top few nanometres of the surface directly, whereas from earlier work[9] we would expect mercury to diffuse more deeply into the surface. In other applications (for example semiconductor oxide layer depth-profiling by XPS) it is possible to remove the surface layer-by-layer to record XPS peaks as a function of depth into the material. In our application the value of the weights we are analysing (more in terms of historical significance and metrological effort invested than materials costs) make

such destructive techniques impossible to apply, so we were limited to detecting and quantifying the mercury within the top few nanometres of the surface[16].

Thus there are two critical questions that we now address in this work;
1. Does mercury penetrate more deeply than the first atomic layers of metal atoms?
2. Is there a convenient non-destructive technique that can be used to assess how contaminants (in particular but not limited to mercury) have been taken-up by a kilogram prototype in service?

If mercury does penetrate further than the first few nanometres of the surface then the mercury contamination will extend beyond the depth range accessible to XPS, and there will be more mercury than XPS has so far indicated. More worryingly it will continue to increase in a diffusion-like "root-time" manner, without saturating or ever becoming stable, at least for the time it takes to saturate the polishing damage layer, which is likely to mean hundreds of years[9,17].

As the SI system moves to an absolute definition of the unit of mass, a much wider range of materials beyond platinum-iridium alloy are being assessed as potential transfer standards[18]. Yet *no material is completely inert*. All materials interact with an environment *via* their surfaces, and even if that environment is Ultra High Vacuum, the rate of arrival of residual gas, if immobilised, would cause mass increases beyond any reasonable or acceptable limit within the SI. Surfaces of these new materials become crucial, and it would be foolish to expect that new effects (analogous to the chemical reaction between mercury and platinum) will not emerge. Gold and its alloys, for example, react with atmospheric mercury even more strongly than platinum. New surface assessment techniques are needed to cope with this wider range of putative material transfer standards, preferably non-destructive and non-contact methods that operate in both air and vacuum[19,20]. Without them we have only drifts in weighing results with many potential sources, providing little or no guidance as to the source of the problems. For these reasons we have investigated X-ray Fluorescence (XRF) as a potential method of qualitative and quantitative analysis of the outermost few micrometres of mass standard surfaces.

II. X-RAY FLUORESCENCE

XRF is the emission of characteristic X-rays from a material that has been excited by X-rays of higher energy. XRF spectrometers capture the spectrum of energy of the emitted X-rays, showing peaks characteristic of the elements present in the sample. XRF instruments are widely used for elemental analysis, particularly in the investigation of metals, glass, ceramics and minerals, for research in geosciences, archaeology and heritage artwork studies[21]. For our purposes the technique is useful because it has the potential to solve both issues listed above;

1. XRF has a deeper sampling depth than XPS due to the greater ability of characteristic x-rays to escape from the surface under analysis compared to photoelectrons. Whereas the region accessible to XPS is typically a few nanometres thick, the region accessible to XRF of metals it is typically a few micrometres. This would, in principle, allow the mercury that has diffused in along defects and grain boundaries to be detected. This is illustrated schematically in Fig 1.

2. XRF can be performed in air at room temperature and pressure using a thin X-ray window of a low atomic number metal (often beryllium) to allow X-rays to pass out of the vacuum tube in which they are generated. Thus XRF can be a non-destructive, noncontact analysis technique that (unlike XPS) does not require us to put the sample in vacuum.
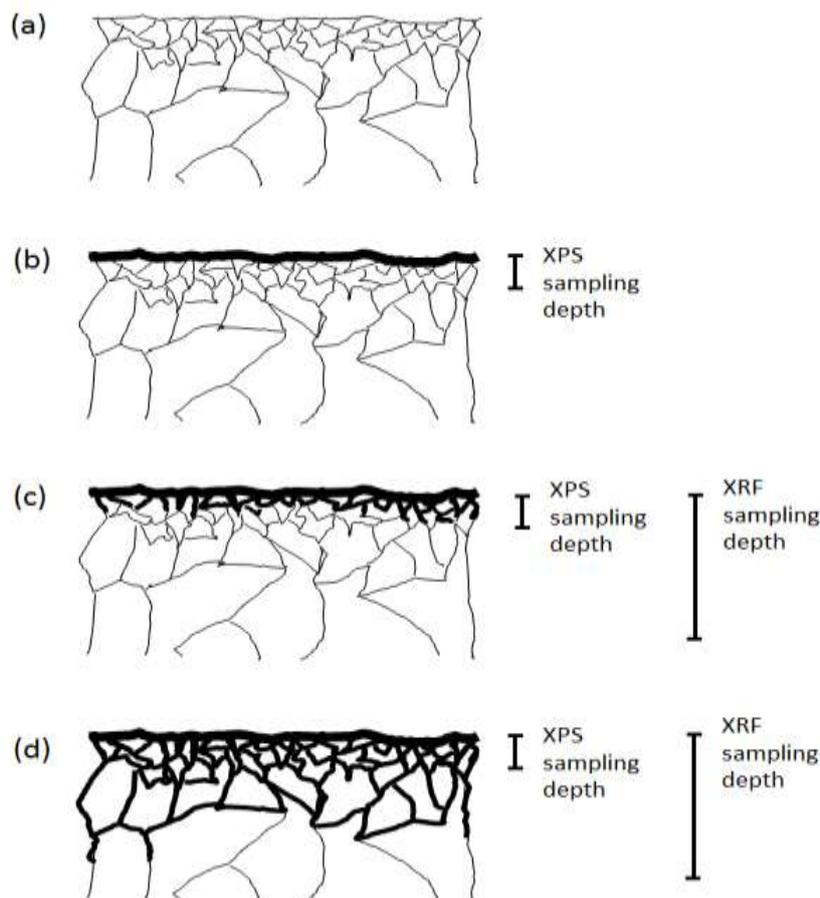
Figure 1 Schematic cross-section of a polished prototype kilogram, (a) immediately after manufacture, (b) Some tens of days after manufacture, (c) about 10 years after manufacture and (d) about 100 years after manufacture. Darker lines represent a high mercury concentration. XRF is able to capture mercury signal from a much deeper region than XPS. This diagram is schematic: in reality the XRF sampling depth is around 2,000 times larger than the XPS sampling depth.

XRF is less sensitive to thin surface layers than XPS, so the question arises as to whether it is sufficiently sensitive to meet the need of surveying kilogram prototype surfaces for mercury. Previously[9] we used Quartz Crystal Microbalance (QCM) measurements to show that atmospheric mercury is adsorbed onto, and then absorbed into, platinum-10 % iridium alloy surfaces deposited on quartz, but this method could not be applied directly to prototypes. Therefore in that paper we recommended that a nondestructive, chemically-specific technique is required to measure the sub-surface mercury on reference kilograms in service, and we suggested careful XRF measurements at that time. We also suggested[10] Nuclear Activation Analysis as a possible method, though this is much more expensive and much less readily available than XRF, so that if XRF is capable of the measurement then XRF is much preferred.

As with many other analytical techniques the quality, sensitivity and portability of XRF instruments has improved enormously in the two decades since our original recommendation was published. Today small, handheld XRF instruments are available that can be carried easily to the sample to be analysed. We used a handheld XRF instrument (Model Niton XL3t-Ultra, Thermo Fisher Scientific, Portable Analytic Instruments Division, Munich, Germany). This instrument is shown in Figure 2. One simply points the XRF gun, presses the trigger, and waits for 10 to 60s for a spectrum to be recorded. An in-built microprocessor provides a preliminary quantitative analysis, but the spectra can also be transferred to computer very easily for more detailed analysis and display. For repeatable positioning a stand is available, if required, and measurements can be initiated from a remote PC rather than the built-in trigger.

Figure 2 Handheld, energy-dispersive X-ray fluorescence (XRF) instrument used in this work. It operates in air, and requires no vacuum. It is a non-destructive and non-contact chemical-element analysis instrument.

We chose this model because it has a larger x-ray detector acceptance solid angle than some others, and may therefore be expected to be one of the most sensitive types commercially available (though we did no systematic comparison to confirm this). Much better laboratory XRF instruments are available – however if we can show that mercury can be detected and quantified using this simple handheld device then we will have shown that virtually any lab-based XRF instrument will be capable of this too. The portability of the XRF instrument we used was also helpful, in that we could take the XRF instrument to the platinum weight; this will be helpful in many National Measurement Institutes where it is desirable keep to a minimum the movement of mass standard prototypes. The question we address below is whether XRF is sufficiently sensitive to measure mercury in the outermost few micrometres of prototype kilogram surfaces. Firstly we need to compare the likely depth of the mercury accumulated with the sampling depth of XRF.

Whereas the bulk alloy of a prototype kilogram consists of large, equiaxed grains (and therefore has a very low grain boundary density), polishing leaves a "damaged layer"[21] which, due to extreme plastic deformation, is broken into small grains with a very high density of both grain boundaries and dislocations. Most published studies of surface damage caused by polishing have involved 70:30 brass, which has good etching characteristics, allowing easy imaging of the damage region through selective chemical etching at defects. We would expect the damaged region of PtIr to be much the same in dimensions, due to a similar material hardness. For example, Samuels[22] examined 70:30 brass polished with diamond paste; he found a damaged layer around 700 nm thick which he further classified as consisting of a "fragmented layer" around 100 nm thick, and a deformed layer from a depth of 100 nm to about 700 nm. The issue is how this corresponds to the sampling depths of XPS and XRF. We can estimate the depth of the region sampled by XRF in a typical experiment as follows. The primary X-rays are (in a typical commercial instrument) around 50-60keV, and penetrate many micrometres. The sampled depth is limited (considering mercury in a platinum matrix) by the attenuation length of mercury characteristic X-rays escaping from the platinum surface. For example, Hg $L_{\alpha 1}$ x-rays (one of the strongest peaks in the mercury XRF spectrum) having an energy of 9.99 keV has an attenuation length of around 4.2μm in platinum[23]. Therefore XRF is able to capture a very large fraction of the signal from mercury within the assumed 700nm damaged layer at this energy. By comparison XPS is limited to a sampling depth of a few nanometres. This is illustrated schematically in Fig. 1.

Finally it is worth noting that there is a trend in the XPS community to use higher X-ray energies, often in the range 5keV to 10keV, a technique known as HAXPES – "Hard X-ray Photoemission Spectroscopy". This would have a sampling depth several times that of conventional XPS using monochromated aluminium X-rays, and therefore may provide further information as to the depth of mercury present.

III. XRF ANALYSIS OF A STANDARD MASS SURFACE

The XRF instrument we used was kindly calibrated by the manufacturer a few days before it was used, and internal instrument calibration sequences were run before and after each set of measurements. Not having access to prototype kilograms we analysed an imperial standard weight made of platinum in the Victorian era, but which are now museum pieces; a platinum troy pound held by the Royal Society in London since the 1840's, which we refer to as "RS1". Details of what is known of its history have been reported previously[14]. This weight is a few decades older than those at the heart of the current SI system of mass. XPS showed the presence of approximately a single layer of mercury atoms at the surface of RS1[14], but (as discussed above) sampled only the top nanometres of the surface. The mass of mercury was calculated from the XPS results to be around

23µg for a surface area of a kilogram prototype. This mercury mass, of itself, is not a serious concern, especially if it were a stable layer formed soon after manufacture. However penetration is likely to be deeper, below the region accessible to XPS, and this is what we proceeded to examine by XRF. It is vital to recognise that variation in local mercury concentration in the atmosphere has no effect on the rate of mercury ingress in the long term. If the mercury ingress is diffusion-limited, as we expect, then one laboratory may have 1,000 times the atmospheric mercury concentration of another, yet both would see an identical rate of mass increase. Indeed, comparisons between these masses would show no *relative* mass increase at all.

The area of X-ray illumination is approximately 8mm in diameter, so all results represent an average over this area of the surface of the weight. We selected a number of points on the surface of the weight, typically acquiring spectra for 60s at each point. We did not use the internal software to identify mercury or other peaks in the XRF spectrum. If, as in our case, we are looking for a trace of one known element in what we know to be a virtually pure sample of another, then we can make more quantitative measurements at a much lower detection limit by careful analysis of the original XRF spectra rather than automatic interpretation of those spectra by the built-in software.

Figure 3 shows the XRF spectrum for a sample of pure platinum, 1mm in thickness (Pt 99.997%, Alfa Aesar Stock#12060). The principal peaks of Pt in this energy range are all clearly visible.
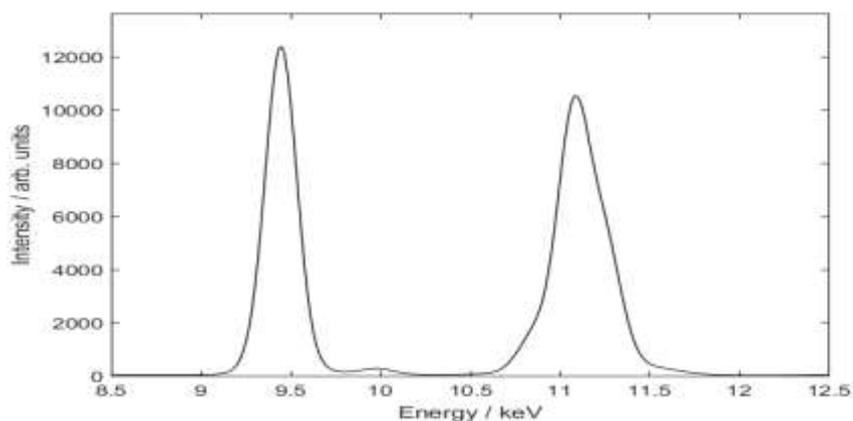
Figure 3: Region of the XRF spectrum containing the most intense Pt peaks. This spectrum is taken from a pure (>99.99%) platinum foil.

Because mercury is close to platinum in atomic number, it has similar XRF peaks in this energy range, but at slightly higher x-ray energies, making them a challenge to resolve and quantify in the presence of the strong platinum signal. Figure 4 compares the XRF spectrum of pure platinum with the XRF spectrum obtained when a mercury-containing reference film is placed on top of this pure platinum sample.
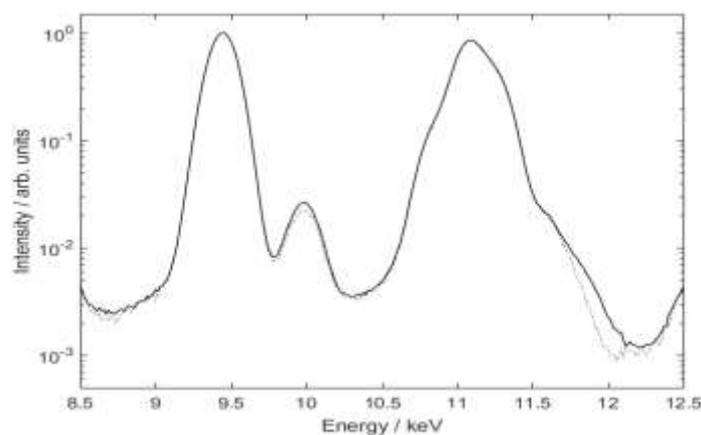
Figure 4: Semilogarithmic plot comparing XRF spectra from a pure platinum surface (stippled line) with a 20.5µg/cm^2 mercury reference material placed on that platinum reference. The main differences in XRF intensity are around 10keV and just below 12keV, where the most intense mercury lines occur. However the difference in intensity is small compared to the large, intense platinum peaks.

The mercury-containing reference film we used contains 20.5µg/cm^2 Hg and 14.7µg/cm^2 silver, deposited on 3.5µm polyester membrane (Micromatter Ltd, 130th Street, Surrey, British Columbia, Canada V3W 7X4). This is a certified XRF calibration reference that is NIST traceable. The reference material manufacturer states that the areal density of the AgHg deposit has been determined by precision weighing and checked by spectrometry. The largest peaks in these spectrum are the peaks corresponding to the Pt substrate beneath the film, and to make the presence of mercury clear at all we have needed to plot Fig 4 with a logarithmic intensity scale. The presence of mercury leads to small additional x-ray intensity at around 10keV and just under 12keV. The silver contributes small peaks to the XRF spectrum outside the plotted energy range, and the polyester support attenuates the signal to some extent.

To begin to isolate the contribution of mercury to this spectrum we first normalise both the platinum-alone and the platinum-with-Hg-film spectra so that the Pt L$_{\alpha 1}$ peak has unit intensity in each case. We then subtract the platinum spectrum from the film-covered platinum spectrum. Figure 5 shows this subtracted spectrum, with mercury peaks labelled (a) Hg L$_{\alpha 1}$ and (b) Hg L$_{\beta 1}$.
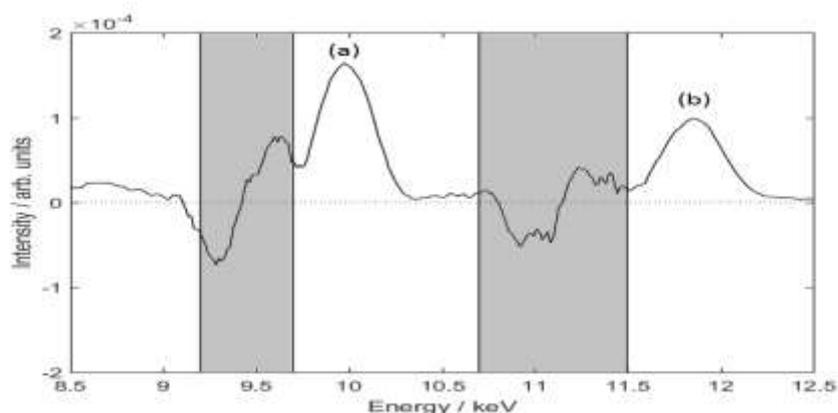
Figure 5: Spectrum for 20.5µg/cm^2 mercury on platinum with the platinum spectrum subtracted. The grey regions represent the locations of the strong Pt peaks, where these subtracted spectra are noisy and unreliable due to small drifts in energy and sensitivity of the XRF instrument. Nevertheless, outside these regions the mercury peaks (a) and (b) are clear and at the expected energies and relative intensity. These mercury peaks are the L$_{\alpha 1}$ and L$_{\beta 1}$ Hg x-ray lines at 9.99keV and 11.82keV respectively.

To check this subtraction method we performed measurements on platinum foil known to be mercury free, to ensure that the peaks in Fig 5 that we ascribed to mercury do not appear. Figure 6 shows this normalisation and spectrum subtraction applied to two pieces of pure platinum foil (freshly scraped to make sure no mercury is present at the surface). As one would expect, no mercury peaks appear.
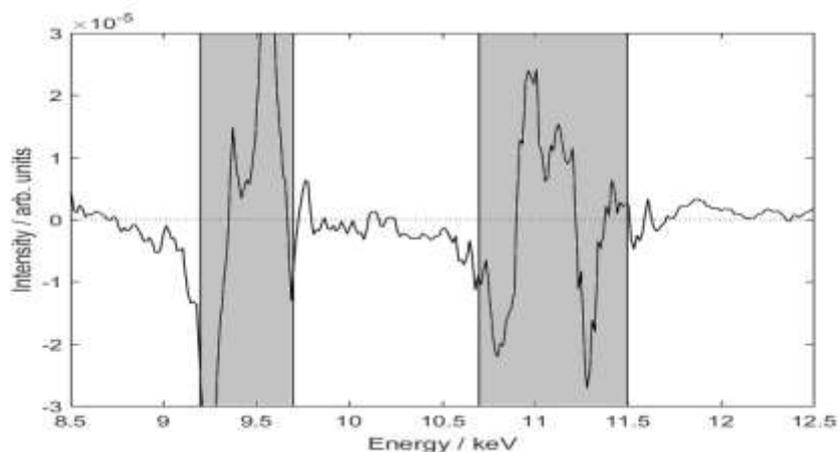

Figure 6: To check that there are no mercury peaks present in the reference platinum sample we show here subtracted spectra for two areas of the platinum reference foil. No mercury peaks are visible. As with the previous figure, the energy regions containing the strong platinum peaks are shaded to indicate that we would expect small changes in instrument energy scale and sensitivity to make these areas noisy and unreliable.

In Figs 5, 6 (and 7 about to be presented) there are regions around the energy of the platinum peaks that we must ignore, and which we have therefore shaded in these figures, the reason being as follows. This process of subtraction means that very small differences in the intensity of the platinum peaks from one spectrum to the next are accentuated. These are due to very small changes in the energy scale and sensitivity of the x-ray detector. Such detectors, their Peltier cooling temperature stability and power supplies are engineered to an extremely high standard, but of course cannot be perfect. For example, in Fig 5 a small shift in the energy scale of the instrument means that derivatives of the platinum peak shapes appear in the shaded regions. This is not really a concern, and we should focus primarily on the mercury peaks which emerge from this subtraction process. We should ignore the shaded regions.

Figure 7 shows the result of normalising and subtracting the platinum spectra from the spectra recorded from RS1. In this case a further precaution was taken to help remove some of the effect of small drifts in x-ray detector response by performing repeated measurements on RS1 and reference platinum as follows. We performed five measurements of scraped platinum foil reference ("measurement A") and four measured spectra from a single position on the RS1 weight ("measurement B") in the order ABABABABA. Each spectrum took 60s to acquire, so that the total acquisition time for this series of measurements was 9 minutes, and the real time taken (considering the small time required to save the spectrum after each measurement) was around 11 minutes.

The "A" spectra were then added together, as were the "B" spectra. The A and B spectra were individually normalised using the intensity of the Pt $L_{\alpha 1}$ peak, and then the A spectrum subtracted from the B spectrum, the result being shown in Fig. 7.
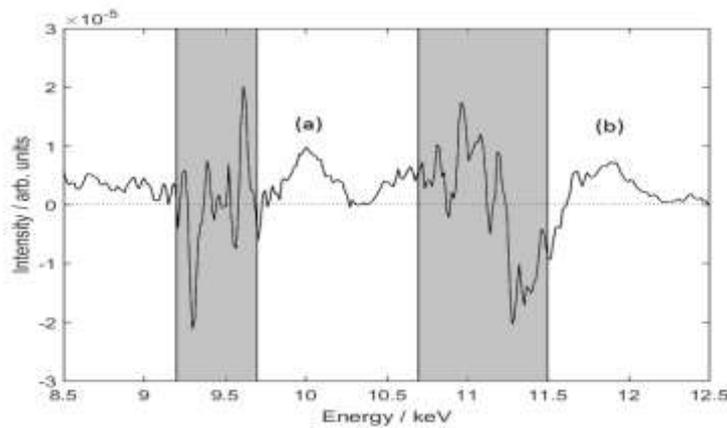
Figure 7: Spectrum from the Royal Society platinum Troy pound, with the spectrum of the pure platinum reference foil subtracted. Shaded areas are unreliable (for the same reason as in the above figures). Mercury x-ray peaks (a) and (b) are clearly visible. These mercury peaks are the $L_{\alpha 1}$ and $L_{\beta 1}$ Hg x-ray lines at 9.99keV and 11.82keV respectively.

Clearly mercury $L_{\alpha 1}$ and $L_{\beta 1}$ peaks are unambiguously present, though somewhat smaller than those in Figure 5, indicating that RS1 has an areal density of mercury below $20.5\mu g/cm^2$. We now make this quantitative, by taking the $Hg_{L\alpha 1}$ peak height in Fig 7; assuming a linear response to mercury we scale the areal density of the reference film according to;

$$\sigma_{RS1} = \frac{I_{RS1}}{I_{ref}} \times \sigma_{ref}$$

(1)

Where $\sigma_{ref}= 20.5\mu g/cm^2$, I_{RS1} and I_{ref} are the areas of the mercury $L_{\alpha 1}$ peaks (after normalisation of Pt $L_{\alpha 1}$ areas and spectrum subtraction) on RS1 and reference platinum foil respectively, and σ_{RS1} is the areal density of mercury on the RS1 weight. We can evaluate the equivalent mass of mercury on a Pt-10%Ir prototype by multiplying σ_{RS1} by the surface area of such a prototype, i.e.

$$\Delta m_{Hg} = \sigma_{RS1}A$$

(2)

Where A=71.5cm^2 is the surface area of a Pt-10%Ir prototype. The quantity of mercury calculated from these data by this means is σ_{RS1}=0.96µg/cm^2, equivalent to around $\Delta m_{Hg} \approx 70$µg over the 71.5cm^2 of a prototype Pt-10%Ir kilogram. We would expect a realistic uncertainty in this value of around ±20%, mostly arising from the unknown depth-distribution of the mercury. This measurement result is;

(a) Consistent with the range predicted from the diffusion model by our earlier studies[9].

(b) Around three times higher than 23µg observed to be at the surface of RS1 by XPS[14], showing that a substantial mass of mercury has diffused to a depth below the XPS accessible region. In fact, approximately two thirds of the mercury is below the XPS accessible depth.

Both of these conclusions confirm the diffusion-limited ingress of mercury along defects and grain boundaries very strongly. All that we have measured over the years, including this latest result, confirms the conclusions and models developed earlier in this series of papers regarding mercury contamination. XRF is clearly a powerful and valuable technique in the non-destructive assessment of mercury contamination at these surfaces.

In this work we developed a normalisation and subtraction scheme to overcome the dominating intensity of the platinum signal in the XRF spectrum. This dominating signal is somewhat unavoidable when using a portable and inexpensive x-ray source such as that in the XRF instrument we used. A wavelength-dispersive XRF instrument, with greater energy resolution than our energy-dispersive one, would have made this easier, at the expense of portability. It also happens that in our laboratory we do not have easy access to a wavelength-dispersive instrument.

In the future it may be possible to reduce the platinum signal directly by using a synchrotron x-ray source with tunability of x-ray energy to select an incident x-ray energy able to excite Hg x-ray emission more strongly than platinum x-ray emission. This would require moving prototype kilogram(s) to a synchrotron to be studied, and these are rare within National Measurement Institutes. Nevertheless this approach may be open to, for example, the PTB laboratory at the BESSY II, or one of NIST's three beamlines at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.

IV. IMPLICATIONS OF DIFFUSIVE MERCURY INGRESS

As the SI makes a transition to an absolute method of realising the standard of mass, the question arises as to whether mercury ingress will continue to cause any problems given that prototypes will be periodically calibrated. If mercury is added between such absolute calibrations will the magnitude of such additions be significant? If not, then XRF monitoring of prototype surfaces has little value after redefinition of the SI unit of mass.

Whatever method is ultimately chosen, absolute calibrations are likely to be available in only a very small number of locations worldwide, so that most countries will rely on periodic absolute weighings of their national standards at these locations. Stability of the prototype kilograms between absolute weighings therefore becomes critical.

Storage conditions (though without any consideration of mercury) have been considered in a recent "Guide to the Storage of Primary Mass Standards" by Perkin and Davison[24]. They identify one of the key requirements of storage methods after redefinition as being the ability to "Store weights in optimal conditions in both the short and medium term (up to 10 years). This will provide on-going traceability for mass between primary realisations of the kilogram". It is important to realise the implications of the diffusion-limited nature of the way mercury reacts chemically with platinum alloy surfaces over this medium-term storage timescale of up to 10 years. Bulk diffusion through single-crystal platinum occurs at a negligible rate[8], so diffusion is instead along defects and grain boundaries, especially in surface polishing damage. Diffusion processes typically give rise to a "root time" dependence, so that no saturation occurs after any reasonable time (in this case probably centuries). Perhaps more important, even the rate of increase varies and does not reach a constant. New prototypes gain mercury more rapidly than old ones. For example, suppose we have two similar Pt-10%Ir prototypes, one 3 years old and another 100 years old. If these are weighed using an absolute instrument (for example a Kibble balance) and then stored for the medium term (the 10 years mentioned above) then we can predict the rate at which their masses will increase based on our previous QCM measurements[9];

$$\Delta m_{Hg}/\mu g = 24.7 + P\sqrt{t/hours}$$

(3)

where Δm_{Hg} is the mass gain due to mercury, t is the time since manufacture, and P is a parameter related to the density of defects and grain boundaries available to mercury diffusing into the surface. For our QCM measurements on a sputtered Pt-10%Ir film[9] we measured P=0.871 for Pt-10%Ir sputter deposited on

quartz. A consideration of the likely lower density of defects in polished films then led to an estimate for the value for a typical polished prototype kilogram of P=0.08 (see Eqn (11) of paper III[9]). The XRF measurements we have now made give P≈0.04 for RS1, in the range that we estimated in paper III on the basis of QCM and XPS experimental results at that time. PtIr alloys are harder than pure platinum, and therefore may be expected to have a larger defect density after polishing, so that we expect that for Pt-10%Ir prototypes 0.04<P<0.871.

Suppose we consider the divergence (due to mercury ingress) between two possible Pt-10%Ir kilogram prototypes, one made recently (perhaps as a transfer standard for use with a Kibble balance, say three years old) and another conventional Pt-10%Ir prototype that is a century old. Even if we assume that both have surfaces polished identically, over the subsequent 10 years the new and old masses will gain 7μg and 2μg of mercury respectively if P=0.04, 18μg and 5μg of mercury respectively if P=0.1, and 53μg and 14μg of mercury respectively if P=0.3. If the degree of surface damage is initially different in the two prototypes (e.g. one polished prototype, one diamond machined prototype) then the P value could be different between these two prototypes, and this mass difference could be significantly greater. Depending on how relative weighing data is interpreted (and especially if the comparison also includes other "young" prototypes gaining mass at a similar rate as the three-year-old one) this may appear as a (relative) mass loss by the 100 year-old prototype rather than various different mass gains, at least until the next absolute calibration takes place. Such a "mass loss" by some of the oldest and original prototypes, including the international prototype, has been recognised already, at least up to the time of the 3rd verification[25].

Therefore the degree of divergence among stored reference standards that would be suggested by mercury ingress may pose a significant problem even in the new era of mass being realised by absolute means.

V. SOURCES OF MERCURY

Mercury vapour from accidental spillages from barometers and thermometers is sufficient to explain the presence of mercury. Mercury has been used in a wide range of scientific instruments over the last 200 years. Davis[26] describes the current storage location of the international prototype kilogram. Figure 3 of that paper is a photograph of the safe where the international prototype and its six official copies have been stored since the late 1980s. Inside the safe, beside the bell jars enclosing the international prototype is a small white thermometer containing alcohol and mercury[27]. An online video recording is available from a recent BBC TV documentary showing the proximity of this thermometer to all of the prototypes at the top of the SI system of mass[28]. The mercury is fully enclosed and therefore no immediate danger to the prototypes around it. Nevertheless the presence, until very recently, of a glass tube containing liquid mercury even within the storage location of all the prototypes at the centre of the SI shows how pervasive the use of mercury within scientific instruments has been.

As some sources of mercury are eliminated others appear. Modern sources of mercury vapour make it almost impossible to remove completely from the laboratory environment. Fluorescent light fittings typically release between 1mg and 4mg of mercury when broken[29]. Mercury vapour has been measured in the breath of some of us that have mercury amalgam dental fillings[30]. Measurements of mercury released range from around 0.7ng[31] to 1.4ng[32] per breath.

VI. IMPLICATIONS FOR STORAGE OF REFERENCE MASSES

XRF and XPS results show that mercury is present at the surface, reacts chemically with, and diffuses into the polished 19th century platinum standard weight we examined. Mercury is virtually impossible to remove from the general laboratory environment to the extreme degree needed to interrupt the mass increase of prototype masses. Therefore it would be desirable to store kilogram prototypes under a thin, clean, gold foil or mesh to reduce mercury reaching the prototype kilogram[14]. Periodic XPS analysis of this gold foil, and periodic XRF of the stored prototype itself, would provide good confidence that mercury has been eliminated as a source of mass instability by this "getter". It may be that this simple and inexpensive measure alone would halt the divergence of the prototype kilograms[23] suspected since 1939 and confirmed since 1992.

As discussed already, work is underway internationally on SI redefinition so as to replace the current international prototype kilogram with an absolute standard at the top of the SI mass dissemination chain. Candidate methods include the Kibble balance (formerly known as the Watt balance) and the Avogadro method based on silicon sphere artefacts. Both require mass comparisons to take place in vacuum at some stage. Therefore storage in vacuum or inert gas may appear preferable to storage in air. However it should be emphasised that even an exceptionally low concentration of mercury in that inert gas or anything less than ultra-high vacuum would be enough to continue the increase in mercury in the prototype surface at the maximum possible rate limited by the polishing damage. Trace mercury is present in hydrocarbon oils and lubricants to which even ultra-high purity gas is exposed during manufacture. Vacuum oils have trace mercury content. Those in the chemical industry using platinum catalysts would expect "poisoning" of catalyst surfaces due to mercury if

used over a period of weeks or months under these conditions, even if the concentration of mercury in the feedstock gasses is very small and undetectable by all but the most sensitive equipment. Between manufacture of the inert gas, its distribution, introduction into a storage vessel for platinum alloy prototype masses, and its eventual release, the only material that trace mercury in the gas reacts-with chemically is the platinum surface. In that sense, mercury is being concentrated very efficiently at the surface of the stored prototype unless a mercury "getter" is used[14].

VII. CONCLUSIONS

X-ray fluorescence measurements on a 19th century artefact mass standards confirm the presence of significant amounts of mercury, the equivalent of around 70µg on a kilogram prototype. This mercury has diffused below the surface atoms. It now seems certain that the prototype kilograms that form the basis of the SI have accumulated significant quantities of mercury contamination, and that this may have caused the divergence between kilogram prototypes observed in recent years. It would be wise to remove any remaining mercury-containing thermometers and barometers from the vicinity of the places where prototypes are stored, and to store prototypes under a thin, clean, gold foil or mesh to act as a mercury "getter".

XPS and now XRF are powerful tools in monitoring this contamination. XRF in particular is a nondestructive, non-contact method that can be used in air or vacuum, is quite cheap and portable, and should be used for assessing the extent of this problem in real prototype kilograms. The risk of damage to those kilograms from XRF monitoring is negligible, and even less than the existing risks of handing in weighing studies. Software within XRF instruments is excellent, but given the very specific question of quantifying mercury in platinum we can gain extra sensitivity by the normalisation and spectrum subtraction method described here, even when (as one would expect) the built-in software can detect no mercury while the mercury signal is definitely present in the spectra. The authors would be very pleased to collaborate with any metrology organisation wishing to make XRF measurements on their own reference weights, or any application to the assessment of mercury poisoning of platinum group catalysts.

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