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# THE USE OF UV ACTIVATED OZONE FOR THE CLEANING OF PRIMARY PLATINUM-IRIDIUM KILOGRAM MASS STANDARDS

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**Abstract:** The cleaning of primary platinum-iridium mass standards is traditionally achieved using the nettoyage-lavage process developed at the BIPM. This manual cleaning method is notoriously difficult to reproduce, particularly at laboratories other than the BIPM. An alternative, operator independent, method for the cleaning of primary mass standards, using UV activated ozone, has been investigated and the results are reported.

**Keywords:** Mass, standard, cleaning.

## 1. INTRODUCTION

The kilogram is the last of the seven base SI units to be defined in terms of an artefact rather than with relation to a fundamental physical constant. The values of all national mass standards, an ultimately all weights calibrated worldwide, must be traceable to the International Prototype of the Kilogram, which is held at the Bureau International des Poids et Mesures (BIPM) at Sevres near Paris, France. Each time a national standard is returned for calibration to the BIPM for verification it is cleaned using a method known as nettoyage-lavage to return it to a nominally contamination free condition. The nettoyage-lavage process involves manual cleaning using chamois and alcohol followed by washing with a jet of steam (figure 1). As a result of this cleaning the national standards are relatively unstable for a period of approximately 12 months.

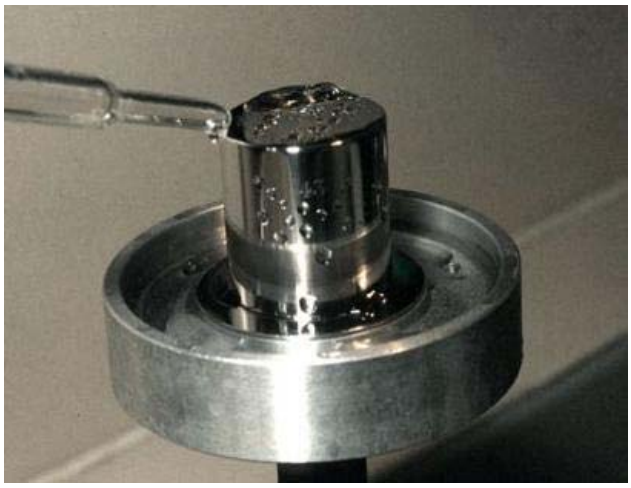

**Fig. 1. Steam cleaning of a Pt-Ir kilogram**

An artefact-based definition thus presents a unique set of problems both to do with the stability of the International Prototype and the national copies, and with the dissemination of the unit of mass worldwide. The only way in which national standard kilograms can be checked is by returning them to the BIPM for calibration. This, combined with the fact that the national prototypes are known to gain between 1 and 5 micrograms every year, makes maintaining the stability of national mass scales a major concern for all national measurement institutes (NMIs) [1]. Figure 2 shows the relative temporal stability of seven of the copies of the International prototype.

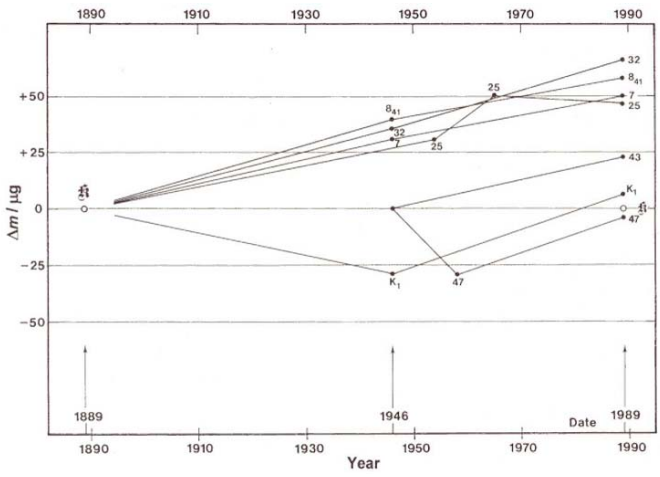


**Fig. 2. Stability of some national standard kilograms**

A number of NMIs have experimented with various methods of cleaning primary standard kilograms in order to return them to the nominally contamination free state achieved at the BIPM [2]. However the repeatability achieved has always been relatively poor and the absolute changes in mass with various methods used is difficult to predict.

## 2. PURPOSE

The purpose of this work is to develop a repeatable, non-contact automated method for cleaning primary mass standards. The method will, in the first instance, be used for the platinum-iridium masses currently used for the majority of national mass standards. However, with suitable

modification, the method developed will be equally applicable to the silicon artefacts used in the International Avogadro Project and also to mass standards of stainless steel or similar materials.

## 3. METHOD

The method developed for the cleaning involves exposing the surface of the mass standards to UV light and ozone in air at room temperature. This method has been used for some time in the semi-conductor industry for the preparation of silicon wafers and has the advantages that it is a user-independent non-contact method and thus produces extremely reproducible results. The process operates at room temperature and pressure, and cleaning can be optimized by varying the ozone concentration and UV intensity at the surface of the weight (and also the exposure time).

A hermetically sealed vessel has been constructed in order to control the ozone level to which the weight is exposed (figure 3).

**Fig. 3. Enclosure for ozone/UV cleaning experiment**

A constant ozone flow rate through the vessel is achieved using a control valve attached to the ozone source. Contained within the vessel is a mounting system for the artifact to be cleaned. This consists of a turntable which is manually controlled from outside the enclosure and allows the artifact to be rotated, exposing each section for a pre-determined length of time. A UV lamp and a quartz guide are mounted in a moveable housing to allow accommodation of artifacts with different diameters (figure 4). By masking the quartz guide it is possible to regulate the UV intensity at the weight's surface.

An initial evaluation of the apparatus with an ozone meter suggested it would be difficult to reliably vary and control the level of ozone around the weight. However, a stable value of between 6 and 8 ppm could be maintained for extended periods. Previous work on UV ozone cleaning [3] sowed that the process was relatively insensitive to variations in ozone concentration. The concentration achieved was also near the optimum value (5ppm). The cleaning process could be optimized by varying UV intensity and exposure time.

**Fig. 4. Quartz UV guide and rotational turntable**

Preliminary tests were performed to allow optimization of the UV intensity and exposure time. This work was performed on platinum-iridium foil wrapped around a cylindrical former. Using foil not only eliminated the need to use primary mass standards for the initial evaluation of the apparatus but also made surface studies on the cleaned surface much easier to perform (see below). The foil was 40 mm x 120 mm in area and thus approximated the curved surface of a primary Pt-Ir mass standard. Thus experimentation on the foil effectively duplicated use of the UV cleaning technique on primary mass standard and allowed evaluation of the effects of varying the UV intensity and the exposure time.

The foil was left exposed to laboratory air for a period of six months to allow a build up of contamination on its surface. Before exposure to the cleaning process the contamination overlayer was measured using a scanning X-ray photoelectron spectroscopy (XPS) technique.

## 4. PRELINIMARY MEASUREMENTS

The surface contamination of the foil was cheeked at 20 points across its surface. Figure 5 shows a typical XPS scan

of the foil, with peaks for the substrate at 61 eV (iridium) and 71 eV (platinum) and for the overlayer at 285 eV (carbon) and 532 eV (oxygen).

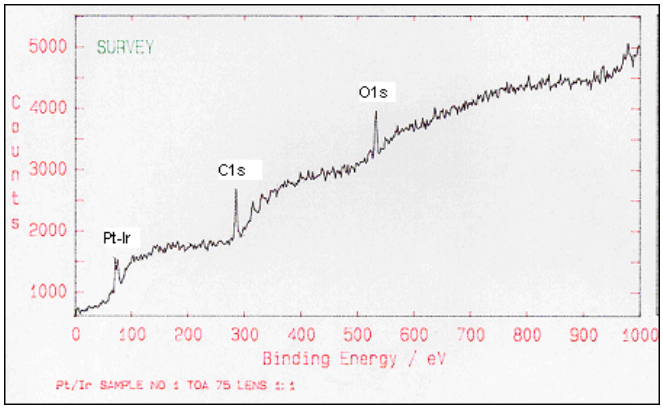


**Fig. 5. XPS survey scan of contaminated Pt-Ir foil**

Peak fitting on the carbon (C1s) and Oxygen (O1s) peaks showed the majority of the overlayer to consist of oxides of the substrate (PtO) and of hydrocarbons (H-C). The variation between the measured overlayer depths at each point was within the uncertainty of the XPS measurement (approximately ± 1.5%) indicating a uniform layer over the surface of the foil. The depth of the overlayer on the surface of the foil was approximately 6 nm. This consisted of an oxide of approximate depth 1.5 nm of and carbonaceous contamination of approximate depth 4.5 nm. The majority of the carbonaceous overlayer was hydrocarbon contamination. Figure 6 shows a typical distribution of species within the overlayer.

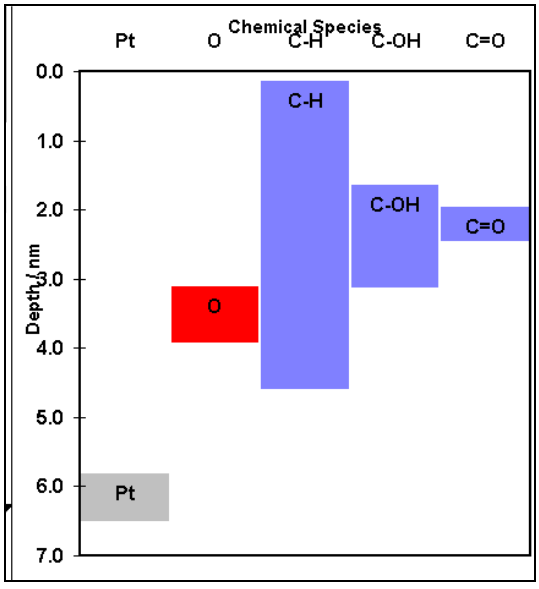


**Fig. 6. Typical extent and average depth of the overlayer on the contaminated Pt-Ir foil sample**

The plot shows the relative amounts and average depth of the various components of the overlayer on the Pt-Ir foil. Although there appears to be extensive overlap between the species this is partly a function of the analysis (and display) method which shows the average depth and amount of the individual species but may not reflect the overall extent of the contamination layers. It can be seen that in general the oxide lies below the carbonaceous contamination. Of the carbon layers, the H-C (hydrocarbon) contamination lies nearest the surface and is the thickest layer. It is predominantly this accreted layer that cleaning of Pt-Ir artifacts will remove.

The Pt-Ir foil, with the accreted surface overlayer, attached to the cylindrical former was the cleaned using the UV ozone process. The foil was exposed to UV at various intensities and for different amounts of time to evaluate the optimum parameters for cleaning. UV intensities were varied by masking off the quartz UV guide to produce a graduated intensity along the (vertical) surface of the foil attached to the cylinder. UV intensities in the range 1.2 to 12.2 mW/cm$^2$ were investigated. The cylinder was rotated on its mount and different sectors of the surface were subjected to varying lengths of UV exposure. Six exposure times were investigated; these were 10 minutes, 30 minutes, 1 hour, 2 hours, 4 hours and 10 hours. Figure 7 shows how this matrix of exposure time and UV intensity was set up on the Pt-Ir foil.

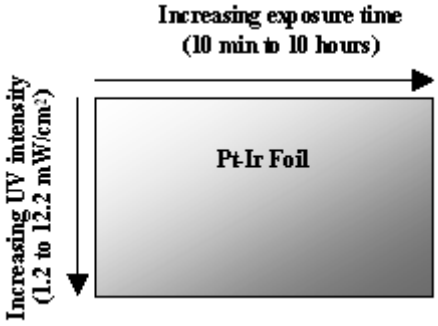


**Fig. 7. Variation in UV intensity and exposure time across the foil surface**

After the cleaning procedure was complete its effect on the surface overlayer was assessed by making a second set of XPS measurements across the surface of the foil. Initially the original measurements, made at 20 points across the surface of the foil, were repeated. Comparison of these results with the original measurements on the uncleaned foil gave an indication of where the UV/ozone cleaning process had been most effective.

As expected the second set of XPS measurements showed that the cleaning process produced a reduction in the depth of the hydrocarbon overlayer. The depth of the oxide layer was slightly increased by the UV/ozone cleaning process. This could also be expected since the exposure of the (cleaned) Pt-Ir substrate to an ozone rich environment

would result in (further) oxidation of the Pt-Ir surface. Although an increase in the oxide depth will lead to a nominal increase in the depth of the overlayer (and the mass of a Pt-Ir artifact) it will in fact be beneficial to the stability of the mass standard in the long term since the oxide passivates the surface and inhibits the accretion of further contamination.

Figure 8 shows the effect of the cleaning process (plotted as a reduction in the overlayer depth) against UV intensity for the range of exposure times investigated.

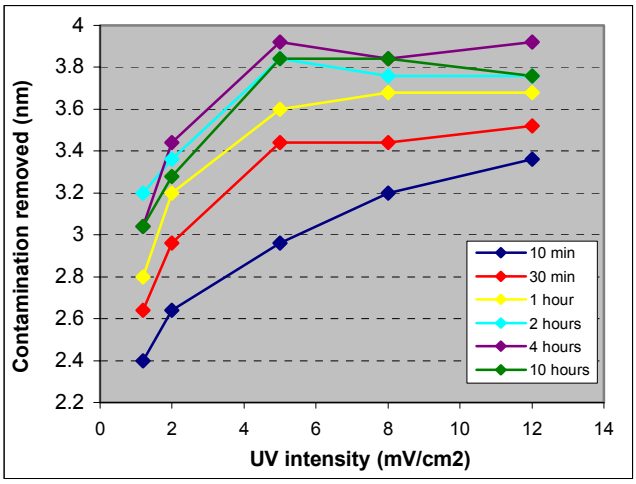


**Fig. 8. Reduction in overlayer depth as a function of UV intensity and exposure time**

The results show that the optimum UV intensity is about 5 mV/cm$^2$ and an exposure time of 2 hours provides the maximum cleaning effect. Any increase in UV intensity or exposure time above these figures shows no significant improvement in the overall reduction in the depth of the surface overlayer. As can be seen from the slop of the curves and their spacing the sensitivity to increase in UV exposure and exposure time for the cleaning process is relatively low, thus overexposure or increased UV intensity will not detrimentally affect the results.

It should be noted that the optimum cleaning conditions (6-8 ppm ozone concentration, 5 mW/cm$^2$ UV intensity and 2 hour cleaning time) apply to the foil sample which had been exposed to laboratory air and had a carbonaceous overlayer of 6.5 nm (equivalent to a mass gain of about 10 µg on a Pt-Ir kilogram). Further investigation is necessary to assess the effectiveness of UV/ozone cleaning on surfaces with a deeper contamination overlayer and to assess whether the cleaning parameters should be adjusted for different depths of contamination. (It should be noted however, that the UV intensity and the exposure time are not sensitive to small variations and thus it will be possible to use the selected cleaning parameters for a reasonable range of overlayer depth).

The effect of cleaning under the optimum conditions was a reduction in the carbonaceous overlayer of about 5 nm (i.e. about 85%). Previous studies [3] show that this is a significant improvement over the nettoyage-lavage process. As well as removing the carbonaceous contamination, the UV/ozone cleaning process had the effect of increasing the depth of the oxide layer. This increase was to a degree dependant on the exposure time but an average increase of 1 nm in the depth of the oxide layer was measured. As discussed earlier the increase in the depth of the oxide layer has the benefit of improving the long-term stability of the artifact.

## 5. PRACTICAL APPLICATION

Following its preliminary evaluation the cleaning apparatus was slightly modified. A stepper motor was attached to the turntable which supports the mass. This allows automatic rotation of the weight generating uniform exposure of the vertical face of the weight. An additional UV lamp was added above the weight when mounted on the turntable to effectively clean the top surface of the weight. As with the vertically mounted lamp, this lamp also illuminates the weight via quartz guide which is masked to produce a uniform exposure with time across the top of the weight. The cleaning of a cylindrical platinum-iridium kilogram is a two-stage process with the weight being inverted between cleaning rums. This ensures all surfaces are exposed to the similar UV/ozone conditions.

Figure 9 shows a platinum-iridium kilogram mass standard mounted on the turntable within the sealed enclosure. The weight is illuminated by the vertically mounted UV lamp.

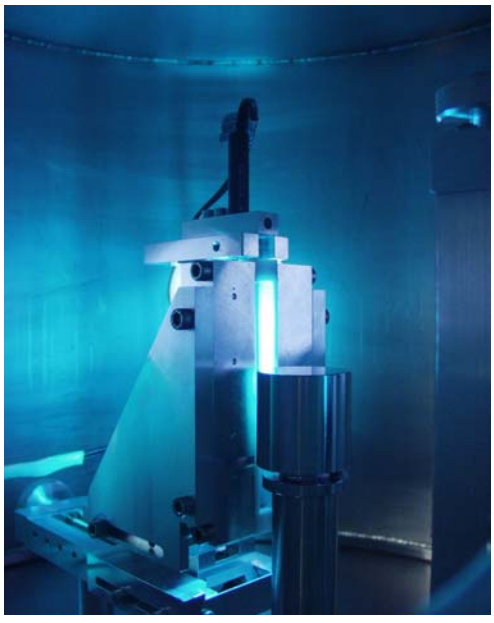

**Fig. 9. Pt-Ir kilogram and vertical UV lamp**

## 6. FURTHER WORK

Tests on platinum-iridium artifacts (rather than foil) are necessary to evaluate the apparatus under practical conditions. Surface analysis techniques such as XPS will be difficult to perform on kilogram artifacts so the effectiveness of the cleaning process will be evaluated gravimetrically. Previous work [4] has quantified the correlation between the increase in overlayer depth and mass gain for platinum-iridium mass standards.

The nettoyage-lavage process will be replicated on the Pt-Ir foil to allow XPS measurements to be made. A comparison between the contamination left by the UV/ozone and nettoyage-lavage approaches will be possible. Additionally a direct comparison between the existing nettoyage-lavage cleaning method and the UV/ozone process will be carried out on platinum-iridium mass standards. Gravimetric measurements will be made to evaluate the effectiveness of the two cleaning methods in removing the accreted contamination.

As well as the user dependency of the nettoyage-lavage cleaning process another major drawback is the relative instability of the mass standard after cleaning. For a period of several months after cleaning, platinum-iridium mass standards exhibit a relatively rapid mass gain of several micrograms. The medium to long-term stability (up to 1 year) of standards cleaned by the two process will be measured. It is anticipated that the increase in the oxide overlayer, which is an effect of the UV/ozone cleaning process, may have a beneficial effect on the stability of the standards.

## 7. CONCLUSIONS

A process for cleaning primary platinum-iridium mass standards has been developed. The process involves the use of UV and activated ozone to remove carbonaceous contamination for the surface of the weights. It has the advantages that it is totally automatic and is thus easily reproducible (a major drawback with current, nettoyage-lavage process is that it is extremely user dependant).

Initial evaluation of the process allowed optimization of the UV intensity and exposure time parameters and the results suggested that the process was significantly more effective than nettoyage-lavage and removed approximately 85% of the carbonaceous contamination overlayer. Additionally the process has been shown to enhanced the oxide layer on the weight surface which may result in an improvement in the stability of the cleaned mass standards when compared with those cleaned by nettoyage-lavage. This is particularly significant for the period directly after cleaning.

## ACKNOWLEDGMENTS

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## REFERENCES

[1] Girard G, The third verification of national prototypes of the kilogram, Metrologia, 31, 317-336, (1994)

[2] Knolle D, Firlus M, Glaeser M, Cleaning investigations on platinum-iridium prototypes, Proc. IMEKO TC3, 15, 139-144, (1996)

[3] Cumpson P, Seah M, Stability of reference masses IV: growth of carbonaceous contamination on platinum-iridium alloy surfaces, and cleaning by UV/ozone treatment Metrologia Vol. 33, 507-532 (1996)

[4] Davidson S, The use of X-ray photoelectron spectroscopy to estimate the stability of primary mass standards, Proc. IMEKO TC3, 19, (2005)