THE USE OF X-RAY PHOTOELECTRON SPECTROSCOPY TO ESTIMATE THE STABILITY OF PRIMARY MASS STANDARDS

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ABSTRACT

Because it is still defined in terms of an artefact, the limit on the accuracy with which the SI unit of mass can be realised is largely limited by the surface stability of the kilogram standard. Not only is this true on the case of the International Prototype used to define the unit but also for national standard copies and indeed for mass standards in general. This paper describes the use of x-ray photoelectron spectroscopy (XPS) to study the accretion of contamination of the surfaces of standard masses. Angle resolved X-ray photoelectron spectroscopy (AR XPS) was used to characterise the surfaces of platinum-iridium and stainless steel mass standards stored either in air or in vacuum, or which have been transferred between the two media. Various analysis methods for XPS data have been compared both in terms of providing an overlayer thickness on the mass standard and in terms of analysing the composition of this layer of contamination.

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1. BACKGROUND

The kilogram is the last of the seven base SI units which is defined by an artefact, rather than derived from naturally occurring physical phenomena. As such it presents a unique set of problems in both its maintenance and dissemination. The accuracy with which the SI unit of the kilogram can be realised in practice is dependant on the stability of the artefacts used to maintain and disseminate the unit, in particular the platinum-iridium national standards and the international prototype, kilogram K.

Monitoring the stability of such weights gravimetrically is difficult due to the limitations of the comparison process and the need for a suitable standard against which to monitor mass changes (this is particularly difficult when it comes to national copies of the prototype and the prototype itself!). A surface analysis technique such as X-ray photoelectron spectroscopy is potentially an independent (and much more sensitive) method for measuring surface contamination and therefore predicting mass gain on standard weights. Additionally an analysis of the stratification of contamination layers on the weight surface gives a useful insight into potential cleaning and storage methods and into the ongoing stability of the weights.

2. SURFACE ANALYSIS

X-ray photoelectron spectroscopy is one of several surface measurement techniques which are used to analyse surface layers of materials. The technique relies on the liberation of electrons from the material surface using an X-ray photon source. The (binding) energies of these liberated photoelectrons are analysed by a electron spectrometer and give information about the materials present in the surface layers (the analysis depth is limited to a few nanometres).

Initially a wide (survey) scan is performed over a range of binding energies (usually 0 eV to 2000 eV). The peaks in this scan indicate the binding energies of the elements present in the sample. More detailed narrow scans are then made over smaller energy ranges around the peaks of interest. Figure 1 shows a typical wide scan and a narrow scan of a carbon (C1S) peak.

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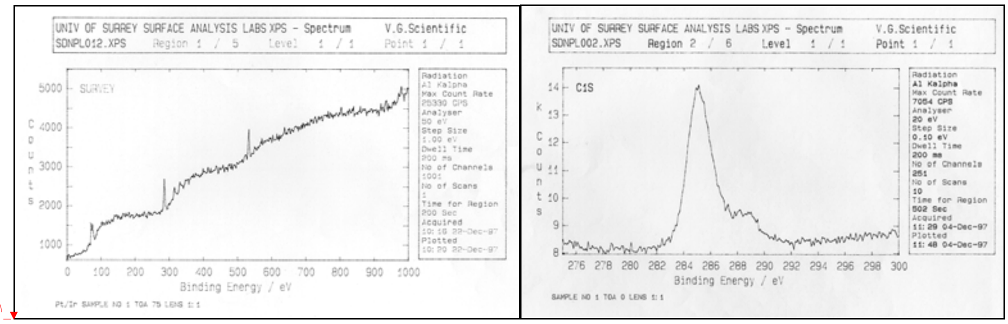

Figure 1: Wide (survey) scan and narrow scan (carbon peak) of surface sample

Different species of carbon and oxygen groups exist within the peak envelopes for these elements. Individual peaks can be fitted to the narrow scans of these peaks to allow examination of the individually attributed carbon and oxygen components described in Table 1. Figure 2 shows how the individual carbon peaks are fitted within the C1S peak envelope.

جدول منسّق

Carbon peaks	Oxygen peaks
PtC* (or IrC*)	PtO* / PtO_2*
C*-C, C*-H	Pt(O*H)$_4$
C*-OH	C=O*, C-O*
C*=O	H_2O*
C*OOH	

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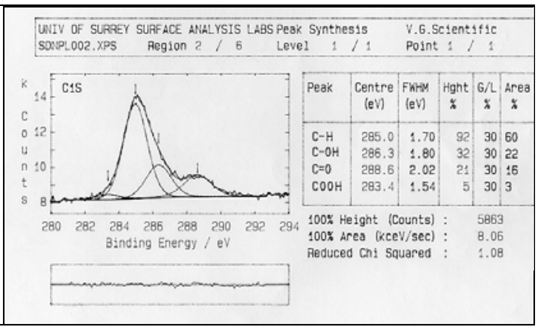
Table 1: Individual peaks within the C1S and O1S peak envelope.



Peak	Centre (eV)	FWHM (eV)	Hght %	G/L %	Area %
C-H	285.0	1.70	92	30	60
C-OH	286.3	1.80	32	30	22
C=0	288.6	2.02	21	30	16
COOH	283.4	1.54	5	30	3

100% Height (Counts) : 5863
100% Area (kceV/sec) : 8.06
Reduced Chi Squared : 1.08

Figure 2: Individual peaks fitted within the C1S peak envelope.

Having gathered data from the peaks of interest, this can be analysed in a number of ways in order to calculate the depth and extent of the elements in question. The most simple analysis method, devised by Hill et al [1], involves ratioing the substrate and overlayer peak intensities. This will give an indication of the depth of the overlayer but cannot discriminate between different forms of contamination.

A more powerful surface analysis tool is Angle Resolved XPS (AR XPS). Whereas the methods described above gather data at only one take off angle (the angle between the detector and the sample surface), AR XPS uses data from two take off angles (usually 0°, as used for the methods already described, and 75°). Analysis of data from the two take off angles allows information about the relative depths and extents of the overlayers to be derived. The stratification method for the analysis of AR XPS data, developed by Cumpson [2], allows the relative depths and amounts of two or more overlayers to be calculated by ratioing the peak intensities of overlayer and substrate at the two take off angles. The data can be displayed graphically (see Figure 3) allowing a more intuitive interpretation of the components of the overlayer.

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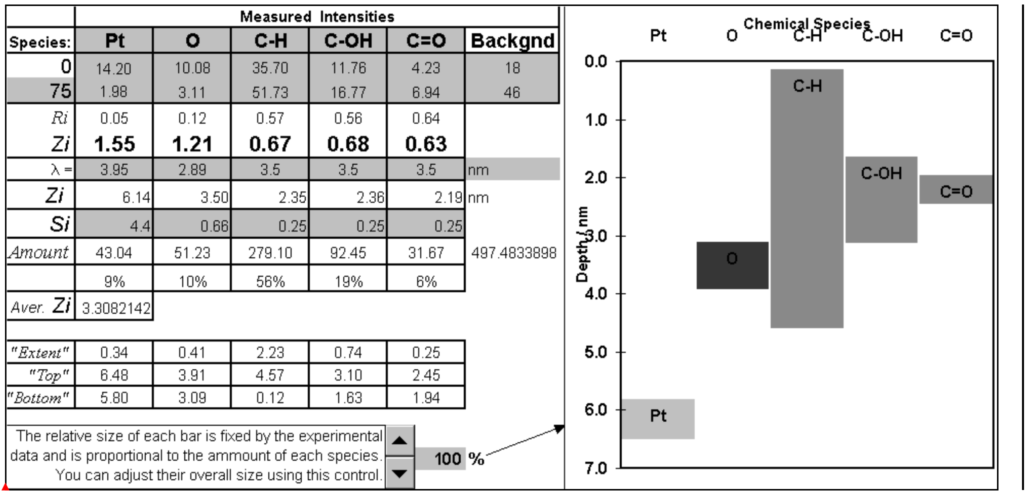

Species:	Pt	O	C-H	C-OH	C=O	Backgnd
0	14.20	10.08	35.70	11.76	4.23	18
75	1.98	3.11	51.73	16.77	6.94	46
Ri	0.05	0.12	0.57	0.56	0.64	
Zi	**1.55**	**1.21**	**0.67**	**0.68**	**0.63**	
λ =	3.95	2.89	3.5	3.5	3.5	nm
Zi	6.14	3.50	2.35	2.36	2.19	nm
Si	4.4	0.66	0.25	0.25	0.25	
Amount	43.04	51.23	279.10	92.45	31.67	497.4833898
	9%	10%	56%	19%	6%	
Aver. Zi	3.3082142					
"Extent"	0.34	0.41	2.23	0.74	0.25	
"Top"	6.48	3.91	4.57	3.10	2.45	
"Bottom"	5.80	3.09	0.12	1.63	1.94	

The relative size of each bar is fixed by the experimental data and is proportional to the ammount of each species. You can adjust their overall size using this control.

100 %

Figure 3: Analysis of the Angle Resolved XPS data from a platinum-iridium surface

3. EXPERIMENTAL PROCEDURE

The stability of kilogram mass standards of stainless steel and platinum-iridium was studied over a period of approximately 3 years. Standards stored in air, in vacuum and transferred between air and vacuum were examined. While it is possible to make XPS measurements directly from the surfaces of the weights, it was more practical to use small (1 cm diameter) surface samples for these measurements. The samples were produced at the same time as the weights used for this research, from the same material, and to the same surface finish. The surface samples accompanied the mass standards at all times and thus were exposed to the same potential sources of contamination.

Initially the stainless steel mass standards were exposed to a variety of conditions for a period of approximately one month. Four weights (and surface samples) were stored under the following conditions:

- In water for one week (hydrostatic weighing to determine density) followed by storage in air
- Permanently in air
- Permanently in vacuum
- Transferred between air and vacuum weekly (used to give a traceable link between mass values in air and vacuum)

Figures 4 and 5 show the change in overlayer thickness (calculated using the basic Hill ratioing method) and mass for the weights stored in the conditions described. It can be seen that there is good correlation between the mass gain and increase in overlayer thickness for the weights and surface samples exposed to the same conditions. The largest mass gain (and overlayer depth increase) occurred on the sample immersed in water. Transfer of the weight between air and vacuum also appears to accelerate the accretion of contamination when compared with permanent storage in either medium. From the two sets of data an increase of 1.2 nm of contamination on the water and air sample equates to a mass gain of about 17 µg. Given that the surface area of a cylindrical kilogram mass standard is 146 cm^2 this gives a theoretical density for the overlayer of 0.97 g/cm^3.

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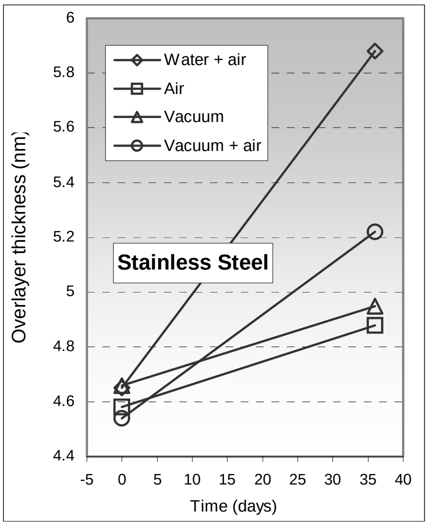

Figure 4: Increase in overlayer thickness

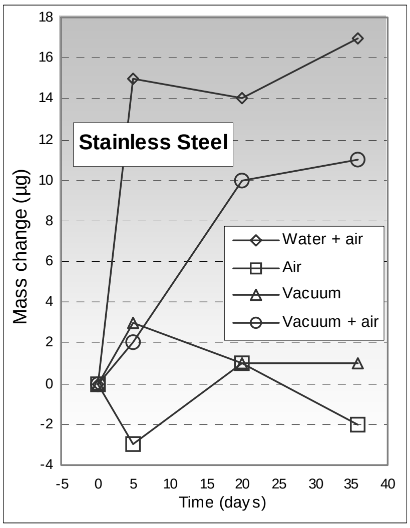

Figure 5: Mass change on weights

The experiment was repeated with platinum-iridium kilogram weights (and surface samples) and showed similar effects.

The longer term effects of storage in air, in vacuum, and in weekly transfer between the two media was investigated using platinum-iridium kilogram mass standards (and surface samples). These were manufactured by the Bureau International des Poids et Mesures (BIPM). The three weights used for the test were kilograms A, 81, and 82, the latter two being official copies of the International Prototype Kilogram.

Figure 6 shows the change in overlayer contamination for the three mass standards over the period of the test as measured using AR XPS and calculated using the stratification analysis method.

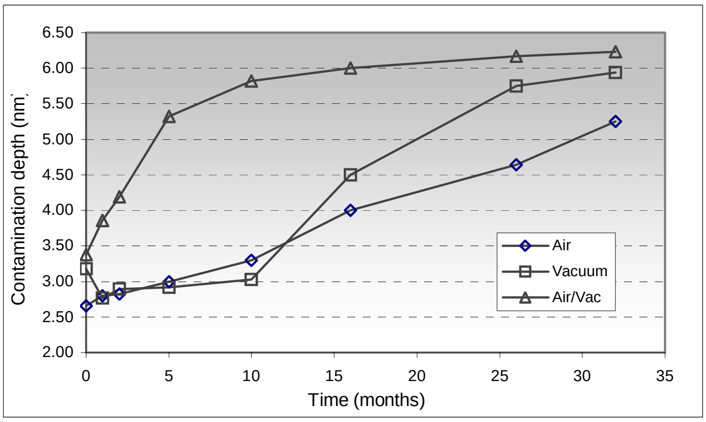

Figure 6: Increase in overlayer thickness for platinum-iridium samples

The weights stored in air and vacuum showed similar trends accreting surface contamination at an approximately linear rate (equal to about 1 nm per annum). Interestingly the vacuum sample showed a decrease in contamination after the first month possibly due to removal of previously accreted contaminants by exposure to the vacuum. Over the period of the test the vacuum stored sample accretes more contamination and in a less linear way than the sample stored in air. This may suggest a more dynamic surface with contaminants being removed and re-adsorbed due to the action of vacuum exposure. The sample transferred between air and vacuum shows a rapid increase in surface contamination over the first few months of the test followed by a period of minimal increase in overlayer depth. This suggests that the overlayer depth, and thus the mass increase of standard weights, reaches a maximum value and then becomes relatively stable, but the behaviour seen may also be a function of the AR XPS analysis technique and stratification calculation method which may become less sensitive as the overlayer depth increases. The relative stabilities of the three mass standards can be seen as a function of the surface water layer which exists on mass standards in air. At normal humidities (40 % RH to 60 % RH) a number of monolayers of water exist on the surface of the standards. This water layer acts as a buffer to the contaminants in the air so the standards remain relatively stable. While it is true that in vacuum there will be few contaminants present, the action of moving a weight into vacuum removes the surface water and so the surface becomes more susceptible to any contaminants present in the vacuum. By transferring a weight from air to vacuum, the surface water layer is removed; if the weight is subsequently brought back to ambient conditions, it is exposed to the contaminants in the air for the finite time it takes the water layer to re-establish itself on the surface. Thus the weight transferred between air and vacuum shows accelerated growth of the contamination layer.

As outlined in Section 2, AR XPS can be used to analyse individual carbon (and oxygen) peaks. Analysis of the data for the three platinum-iridium samples showed that the oxygen content of the overlayer remained relatively stable over the period of the test with the increase in depth predominantly due to increase in the carbonaceous contaminants. The individual groups which made up the carbonaceous contamination were analysed separately. Figures 7a and 7b show the growth of the overlayer for the in-air and transfer samples.

H-C ■ C-OH ░ C=O ▨ Oxygen □

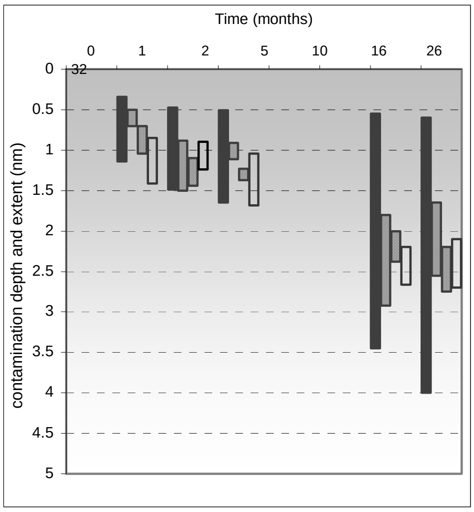

Figure 7a: Change in contamination on in-air sample

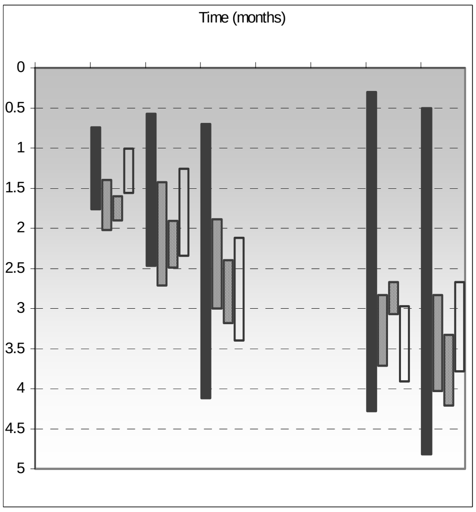

Figure 7b: Change in contamination on transfer sample

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The plots show the depth and extent of the H-C (hydrocarbon), C-OH, C=O, and combined oxygen groups. The stoichiometry of the results is broadly as expected with the oxide lying on the substrate followed by the oxidised carbon groups (C=O and C-OH) and finally the H-C groups lying nearest the surface. In both cases the increase in the depth of contamination is predominantly due to growth in the hydrocarbon overlayer.

The results for the mass gain and depth of contamination for the air/vacuum transfer standard were examined for the period of the test. Figure 8 shows the results of the two sets of measurements.

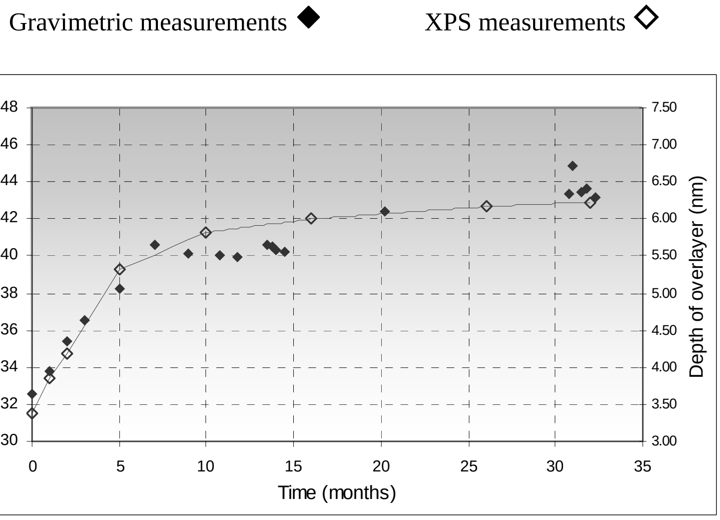

Figure 8: Increase in mass and depth of contamination for the air/vacuum transfer standard

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There is very good correlation between the mass gain figures measured gravimetrically and the contamination depth measured by XPS. Examining the data for the first five months shows a rapid mass gain of 5.7 µg which corresponds to an increase of 1.94 nm in the depth of the contamination layer. The surface area of a platinum-iridium kilogram weight is 71.5 cm^2 so the mean density of the contamination layer is 0.41 g/cm^3.

4. CONCLUSIONS

X-ray photoelectron spectroscopy has been shown to be a useful tool in the calculation of the contamination on standard masses. Correlation between gravimetric and surface studies was extremely good. XPS is potentially more sensitive than weighing as a means of determining the small changes in the values of primary mass standards and also provides additional data on the type and stoichiometry of surface contaminants.

REFERENCES

[1] Hill J, et al, Chem. Phys. Lett. 44, 225, (1976).
[2] Cumpson P, NPL Report CMMT(D)178, (1998).

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