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EMRP SIB-05 Work Package 4
Deliverable 4.2.2

A method to enable on-demand preparation of controlled “contaminated” samples for evaluation of cleaning techniques

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Engineering Measurement Team

ABSTRACT

Two different approaches to enable on-demand preparation of controlled “contaminated” samples for evaluating cleaning techniques have been investigated using gravimetric weighing of mass artefacts and x-ray photoelectron spectroscopy on surface samples. The first method heated oil within a glass chamber to contaminate artefacts and the second method used an inverted magnetron vacuum gauge in a vacuum chamber to contaminate artefacts. Both methods applied a suitable controlled quantity of contamination to the surface of mass artefacts but the heated oil method also increased the surface temperature of the artefacts which may have an adverse effect on the surface properties.

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Approved on behalf of NPLML by Stuart Davidson, (Science Area Leader - Mass).

CONTENTS

1 INTRODUCTION

The aim of this task was to develop a method to prepare samples with controlled quantities of contamination for use in the evaluation of cleaning techniques. Kilogram prototypes manufactured from platinum-iridium (Pt-Ir) alloy were found to gain between 1 µg year^{-1} and 3.5 µg year^{-1} from hydrocarbon contaminants in the atmosphere [1], which over a thirty year period (typical time between prototype verifications [2]) amounts to between 30 µg and 105 µg of contamination. Due to the limited availability of samples with about ten years of surface contamination for use in testing the effectiveness of different cleaning techniques, a method of applying hydrocarbon contamination in controlled quantities is required.

The most commonly used method to artificially apply contamination to the surface of mass artefacts involves either rubbing the surface of the artefacts with an uncleaned chamois leather cloth or using chamois leather that has been impregnated with a hydrocarbon based oil. Schwartz [3] used an uncleaned chamois leather cloth to artificially add about 85 µg to a previously cleaned stainless steel kilogram and between 30 µg and 70 µg on stainless steel standards that were not cleaned. On inspection this appears to be an appropriate method of applying a suitable quantity of contamination to the surface of mass artefacts. However, Berry [4] also tried this method on two Pt-Ir kilograms and only added between 5 µg and 11 µg of mass suggesting that this technique is highly dependent on the cleanliness of the chamois leather supplied by the manufacturer.

Therefore in an attempt to improve on the production of samples with controlled amounts of contamination two different methods for applying quantities of hydrocarbon contamination to mass artefacts were evaluated. The first method involved heating up hydrocarbon oil so that the oil vapours produced would coat the surface of the artefact (heated oil method) and the second method involved using an inverted magnetron vacuum gauge with a small quantity of hydrocarbon oil in a vacuum (vacuum gauge method).

2 EQUIPMENT

2.1 HEATED OIL METHOD

The equipment used in the heated oil method is shown in Figure 1 and consisted of a glass desiccator vessel on top of a hot-plate with the desiccant replaced with a petroleum hydrocarbon oil identified as S60 (Paragon Scientific Ltd, Birkenhead, UK), a small fan to circulate the air within the vessel and a thermocouple to control the temperature of the oil. The test artefact was placed within the desiccator on a metal grating above the S60 oil. A thermocouple temperature probe was used to measure the surface temperature of the test artefacts before and after exposure in the glass desiccator contamination chamber.

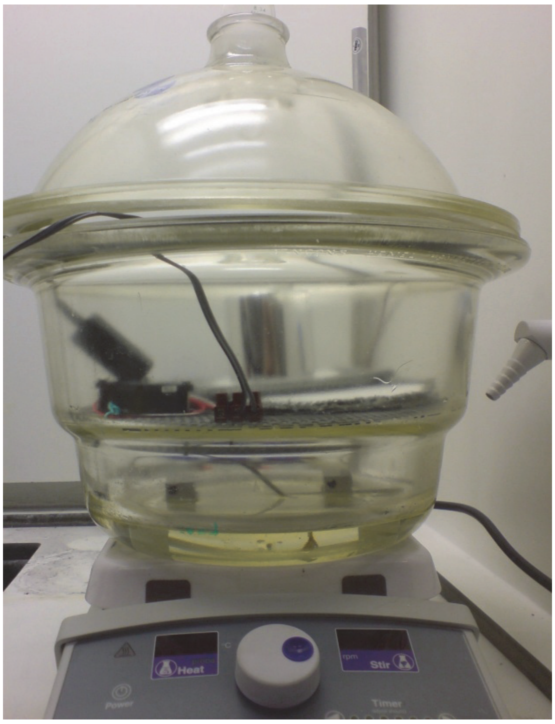


Figure 1. Apparatus used in the NPL heated oil method.

2.2 VACUUM GAUGE METHOD

The equipment used in the vacuum gauge method is shown in Figure 2 and consisted of a stainless steel vacuum chamber fitted with a rotary vacuum pump, Micropirani vacuum gauge (MKS Instruments), Leybold PR35 inverted magnetron vacuum gauge and a needle valve. A small quantity of S60 oil was spread across a section of the vacuum chamber wall using a q-tip. A schematic of the vacuum gauge contamination apparatus is shown in Figure 3. This method of contaminating artefacts has been developed from previous work [5] that investigated the contamination on stainless steel artefacts due to an inverted magnetron vacuum gauge.

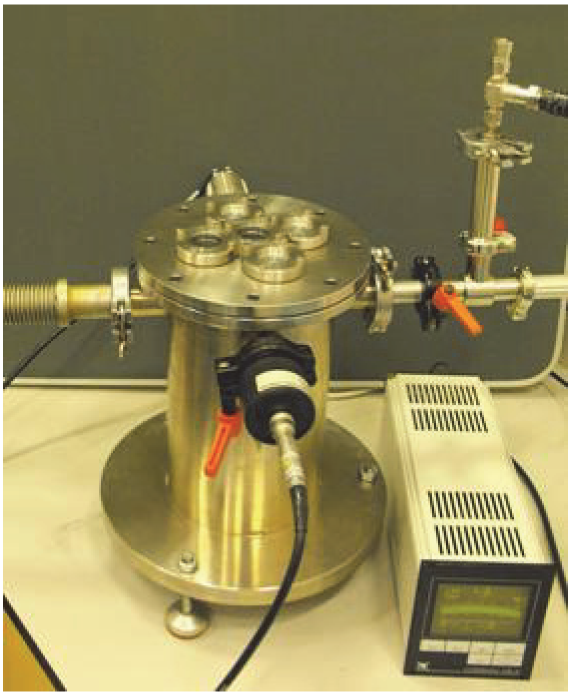


Figure 2. Apparatus used in the NPL vacuum contamination method.

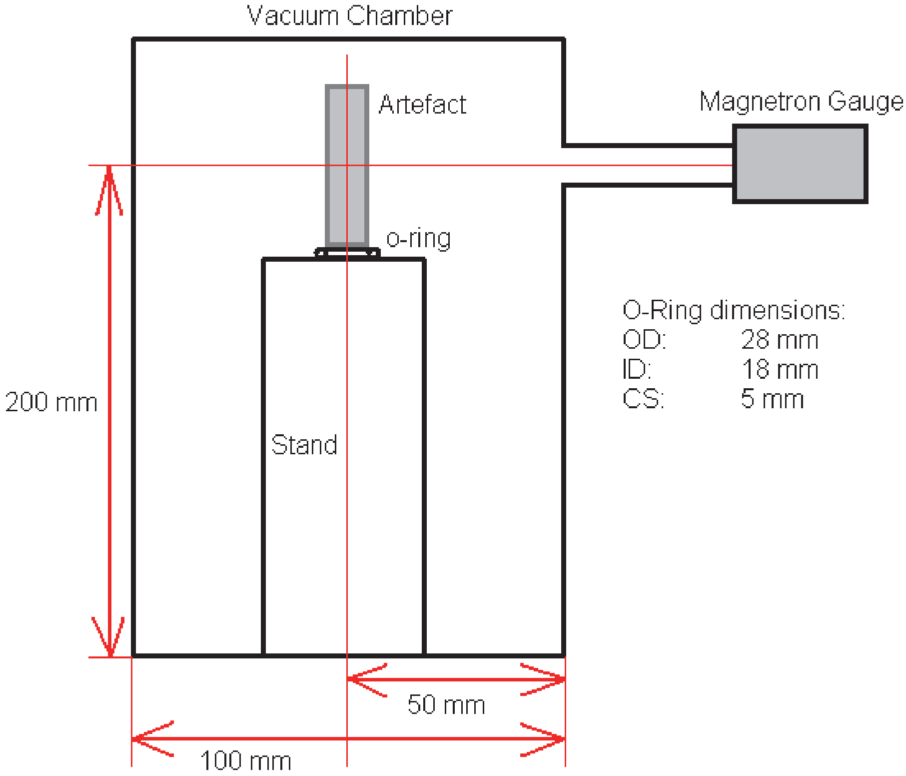


Figure 3. Schematic of the NPL vacuum contamination apparatus.

2.3 TEST MASS ARTEFACTS AND SURFACE SAMPLES

2.3.1 Mass artefacts used to test the heated oil method

Four cylindrical stainless steel kilogram masses were used to test the heated oil method and information on them is given in Table 1. 62D and 62TD were used in the heated oil chamber with 62 and 62DD used as reference weights to measure the change in mass of the two test weights.

Table 1. Mass artefacts used to test the heated oil method.

Identification	Nominal mass / g	Material	Volume at 20 °C / cm^3	Surface area / cm^2	Alpha / 10^{-6} °C^{-1}	Beta / 10^{-9} °C^{-2}
62	1000	Stainless Steel	124.279 5	140.02	46.0	0
62D	1000	Stainless Steel	124.279 8	140.02	46.0	0
62DD	1000	Stainless Steel	124.279 8	140.02	46.0	0
62TD	1000	Stainless Steel	124.279 2	140.02	46.0	0

2.3.2 Mass artefacts used to test the vacuum gauge method

Three stainless steel 200 g masses identified as 200(82), 200D(92) and 200TD(92) were used to evaluate the vacuum gauge method and information on them is given in Table 2. 200 g masses were used instead of kilogram masses as there were no suitable kilograms available. 200D(92) and 200TD(92) are cylindrical discs and were used to test the vacuum gauge contamination method whilst 200(82) was used as a reference mass to monitor mass changes in the contaminated artefacts.

Table 2. Mass artefacts used to test the vacuum gauge method.

Identification	Nominal mass / g	Material	Volume at 20 °C / cm^3	Surface area / cm^2	Alpha / 10^{-6} °C^{-1}	Beta / 10^{-9} °C^{-2}
200(82)	200	Stainless steel	25.4556		45	0
200D(92)	200	Stainless steel	24.9672	70.15	43.9	0
200TD(92)	200	Stainless steel	24.951 0	70.15	43.9	0

2.3.3 Surface samples used to test the vacuum gauge method

Surface samples with a diameter of about 1 cm manufactured from Pt-Ir alloy and silicon were used to test the vacuum gauge method. The Pt-Ir samples were supplied by the Bureau International des Poids et Mesures (BIPM) and manufactured from the same type of Pt-Ir (90:10) alloy as kilogram prototypes [2]. The silicon samples were square samples with dimensions of 1 cm by 1 cm and were cut from boron doped silicon wafers supplied by University Wafer. Three Pt-Ir samples identified as Pt_B2, Pt_B3 and Pt_B4 and three silicon samples identified as Si4, Si5 and Si6 were used in the tests. The surface samples were used in X-ray Photoelectron Spectroscopy (XPS) measurements of the chemical composition of the applied contamination. XPS was carried out using a Kratos Axis Ultra machine and survey spectra in the range 1400 to –10 eV binding energy were taken at an emission angle of 0° to the surface normal from an area of each sample using an Al monochromated x-ray source operated at 15kV, 5mA emission. Analysis conditions used were 160 eV pass energy, 1 eV steps, 0.2 sec dwell per step and 1 scan.

3 EXPERIMENTAL PROCEDURE

3.1 HEATED OIL METHOD

Initially the mass differences between the test artefacts (62D and 62TD) and the reference artefacts (62 and 62DD) were measured on a C1000S mass comparator before measuring the surface temperature of 62D and 62TD using the contact thermocouple probe. Then the thermocouple temperature control of the hot plate was set to control the temperature of the S60 oil within the glass desiccator to about 75 °C. Once the oil had reached 75 °C the small fan was switched on and the two test artefacts 62D and 62TD were placed on the metal grating inside the desiccator. 62D and 62TD were then left to contaminate within the desiccator for a period of 18 hours before they were removed and their temperature measured again using the contact thermocouple probe. 62D and 62TD were then compared again with the reference artefacts on the C1000S comparator once they had been left for 24 hours to reach thermal equilibrium with the environment of the C1000S.
The test artefacts were then cleaned using the following two-stage cleaning process:

1. Lens cleaning tissue soaked with 50:50 ethanol:ether solution was rubbed on all surfaces of each artefact to remove the contamination.
2. The artefacts were immersed in distilled boiling water for a period of ten minutes to remove any remaining ethanol:ether solution from the surface.

After cleaning the test artefacts, the contamination and cleaning processes were repeated a further four times.

3.2 VACUUM GAUGE METHOD

3.2.1 Stainless steel mass artefacts

Initially the mass differences between the test artefacts and the reference artefacts were made on the C1000S. Then the test artefacts were placed on the stand as shown in Figure 3 and a small quantity of S60 oil was spread around the circumference of the entry port to the inverted magnetron gauge in the vacuum chamber. The vacuum chamber was sealed and pumped down to a vacuum of about 5×10^{-2} mbar. Once the pressure had reached about $5 \text{ x } 10^{-2}$ mbar the inverted magnetron vacuum gauge was switched on for a period of about 72 hours. Then the vacuum pump was switched off and the test artefacts were removed from the contamination chamber. The mass measurements were then repeated on the C1000S comparator after allowing the artefacts to stabilise for a period of 24 hours post removal from the vacuum chamber.

3.2.2 Pt-Ir and silicon surface samples

The Pt-Ir sample Pt_B2 and the silicon sample Si4 were used as control samples and were measured in the XPS apparatus in the condition on arrival from the BIPM in the case of Pt-Ir sample Pt_B2 or in the condition after cutting from the main wafer in the case of silicon sample Si4. Pt-Ir samples Pt_B3 and Pt_B4 and silicon samples Si5 and Si6 were exposed to hydrocarbon contamination using the same vacuum gauge method as for the artefacts (§ 3.2.1) but with an exposure time of just 24 hours. A shorter exposure time was selected for the surface samples so that the thickness of the overlaying material on the substrate was kept less than the XPS instruments penetrating range of 10 nm. After contamination in the vacuum chamber Pt-Ir samples Pt_B3 and Pt_B4 and silicon samples Si5 and Si6 were measured in the XPS apparatus.

4 RESULTS AND DISCUSSION

4.1 HEATED OIL METHOD RESULTS

The results of the contamination trials on the stainless steel kilograms 62D and 62TD are shown in Table 3. The average mass increase of 62D and 62TD due to exposure to the heated oil in the desiccator was equal to 80 µg and 79 µg respectively with standard deviations of 24 µg and 26 µg. An increase in surface temperature of both 62D and 62TD was found after each trial with the average temperature of 62D increasing by 10.3 °C and 62TD increasing by 10.8 °C.

This method successfully met the aim of applying a repeatable controlled amount of hydrocarbon contamination within the desired 30 µg to 105 µg range. However, the method was also found to increase the surface temperature of the test artefacts which may have an effect on their surface properties such as increasing the thickness of the oxide layer.

Table 3. Results of the heated oil contamination method.

	Mass added to 62D / µg	Mass added to 62TD / µg	Increase in surface temperature of 62D / °C	Increase in surface temperature of 62TD / °C
Contamination 1	98	46	11.4	11.7
Contamination 2	56	83	10.1	10.5
Contamination 3	109	96	10.4	10.7
Contamination4	58	59	10.4	11.0
Contamination 5	80	101	9.2	10.0
Average	**80**	**77**	**10.3**	**10.8**
Standard Deviation	**24**	**24**	**0.8**	**0.6**

4.2 VACUUM GAUGE METHOD RESULTS

4.2.1 Weighing results from the stainless steel artefacts

The results of the contamination trials on the stainless steel 200 g artefacts are shown in Table 4. The average mass increase of 200D and 200TD due to exposure to contamination in the vacuum chamber was equal to 61 µg and 46 µg respectively. This equated to a mass gain of 122 µg and 92 µg respectively on an equivalent cylindrical steel kilogram with a surface area of 140.02 cm^2.
This method successfully met the aim of applying a controlled amount of hydrocarbon contamination to the surface of stainless steel artefacts. An additional advantage of the vacuum gauge contamination method was that the temperature of the artefacts was not increased as a result of the contamination process.

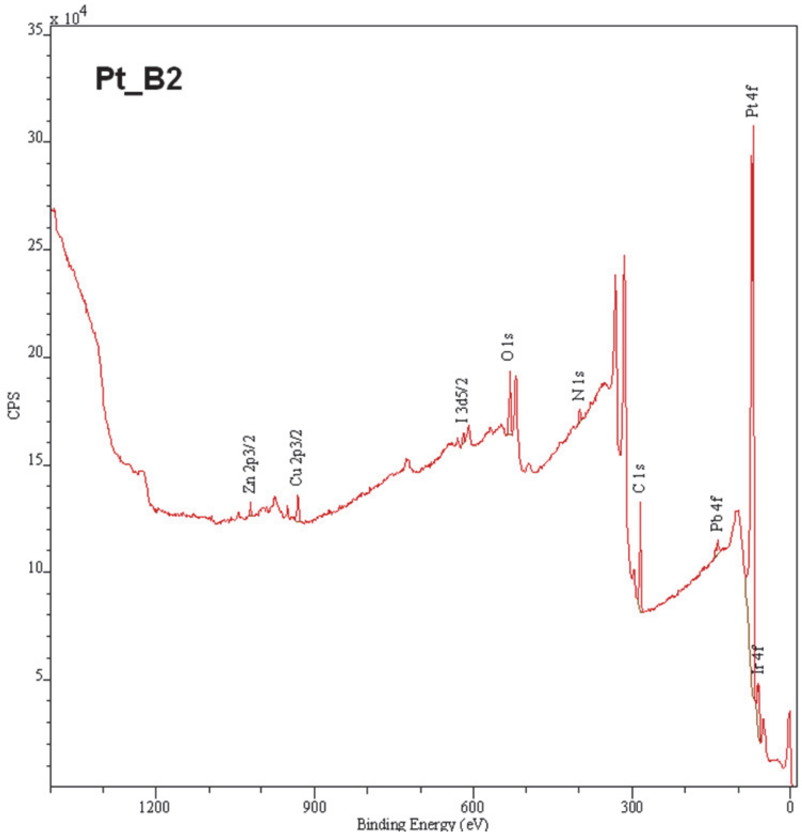
Table 4. Results of the vacuum gauge contamination method.

	Mass added to 200D / µg	Equivalent mass added to a cylindrical steel kilogram / µg	Mass added to 200TD / µg	Equivalent mass added to a cylindrical steel kilogram / µg
Contamination 1	58	117	50	100
Contamination 2	73	145	16	32
Contamination 3	51	103	72	144
Average	**61**	**122**	**46**	**92**
Standard Deviation	**11**	**21**	**28**	**56**

4.3 SURFACE ANALYSIS RESULTS

4.3.1 XPS Survey scan spectra

The atomic percentages of the elements identified in the survey scan of the samples are shown in Table 5 and Table 6 for the Pt-Ir and silicon samples respectively.



Survey scan spectra for samples Pt B2 and Si4 with natural overlayers are shown in Figure 4 and Figure 5 respectively and spectra for the vacuum gauge contaminated samples Pt_B3, Pt_B4, Si5 and Si6 are shown in Figure 6, Figure 7, Figure 8 and Figure 9 respectively.

The elements identified in the survey scans of the Pt-Ir and silicon samples were expected as they made up either the substrate or the carbonaceous contamination layer or oxide layer above the substrate. Trace elements such as iodine, copper, lead, zinc and sodium were also identified in the Pt-Ir and/or silicon samples and were probably a result of contamination from the environment in which the samples were stored or arose as a result of the procedure used to polish the samples.

The Pt-Ir samples Pt_B3 and Pt_B4 showed an increase in the percentage of carbon peak (C 1s) on the surface and a decrease in the percentage of the substrate peaks (Ir 4f and Pt 4f) compared with sample Pt_B2 demonstrating that the vacuum gauge method was successfully applying carbonaceous contamination to the surface of the samples. Interestingly the percentage of the O 1s peak also increased for samples Pt_B3 and Pt_B4 which showed that the vacuum gauge method was either increasing the oxide on the surface of the samples or the carbonaceous contamination forming on the surface was comprised of a significant number of oxygen containing compounds. Similar patterns for the percentage differences of the C 1s and O 1s peaks were found with the silicon samples which were presumably due to the same reasons identified above for the Pt-Ir samples.

Table 5. Survey scan quantifications for the Pt-Ir samples.

Name	Pt_B2 / %	Pt_B3 / %	Pt_B4 / %
C 1s	48.5	61.0	64.9
Cu 2p	1.1	0.1	0.1
I 3d	0.2	0.0	0.0
Ir 4f	2.6	0.7	0.5
N 1s	3.3	2.9	2.8
O 1s	10.4	27.1	26.3
Pb 4f	0.5	0.2	0.1
Pt 4f	33.0	8.0	5.4
Zn 2p1/2	0.3	0.1	0.0

Table 6. Survey scan quantifications for the silicon samples.

Name	Si4 / %	Si5 / %	Si6 / %
C 1s	19.5	51.6	45.0
Ca 2p	0.0	0.0	0.0
N 1s	0.5	2.1	0.8
Na 1s	0.3	0.0	0.9
O 1s	28.0	30.2	30.4
Si 2p	51.7	16.2	22.9
Zn 2p1/2	0.0	0.0	0.0

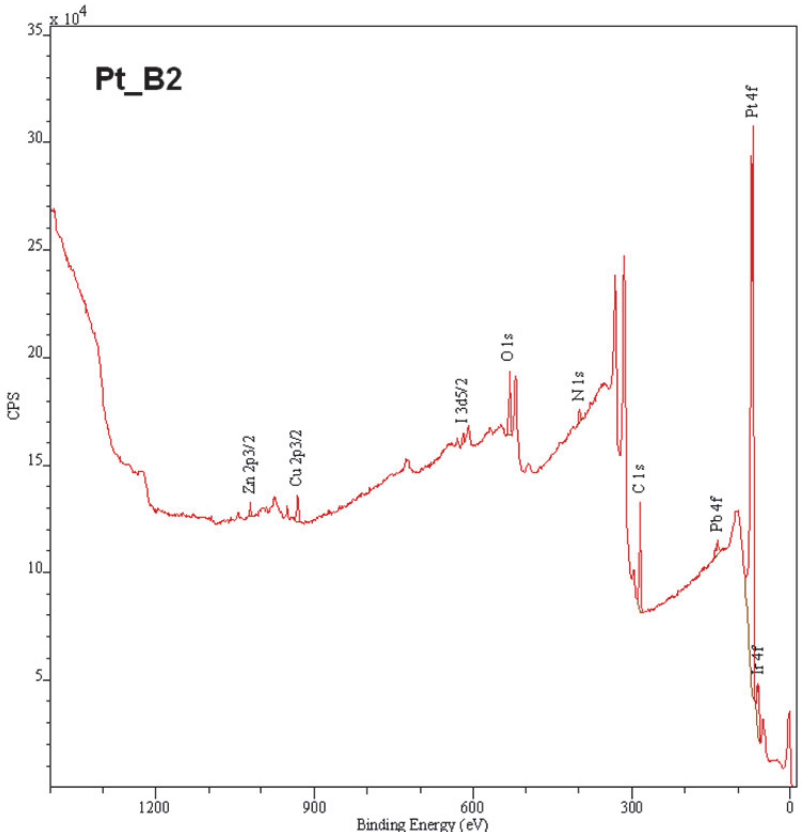


Figure 4. Survey scan of Pt-Ir sample Pt_B2.

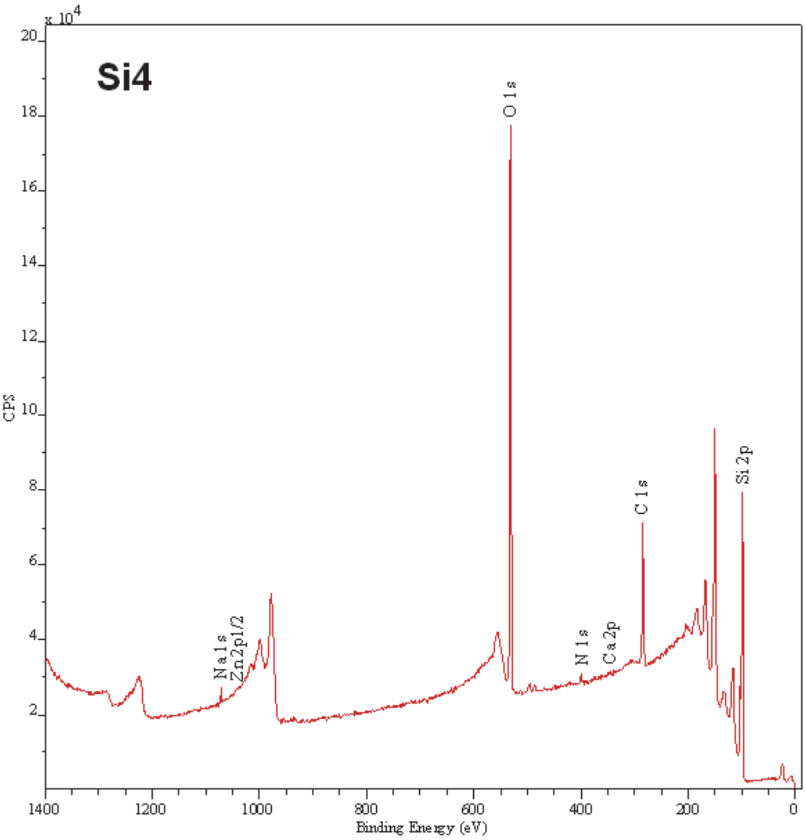


Figure 5. Survey scan of silicon sample Si4.

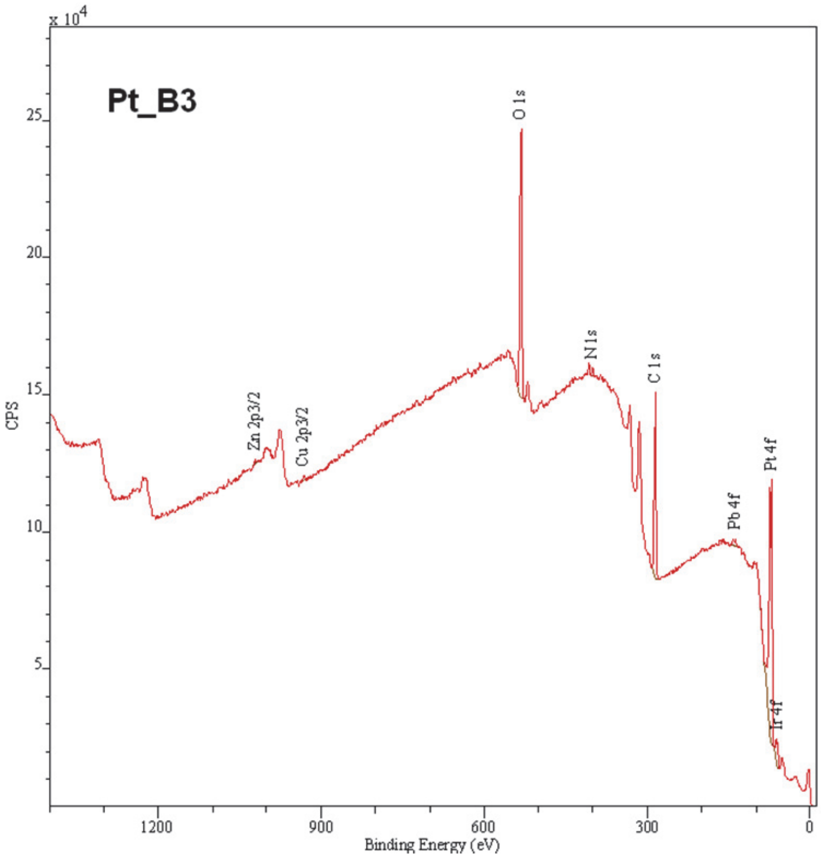


Figure 6. Survey scan of Pt-Ir sample Pt_B3 after contamination using the vacuum gauge method.

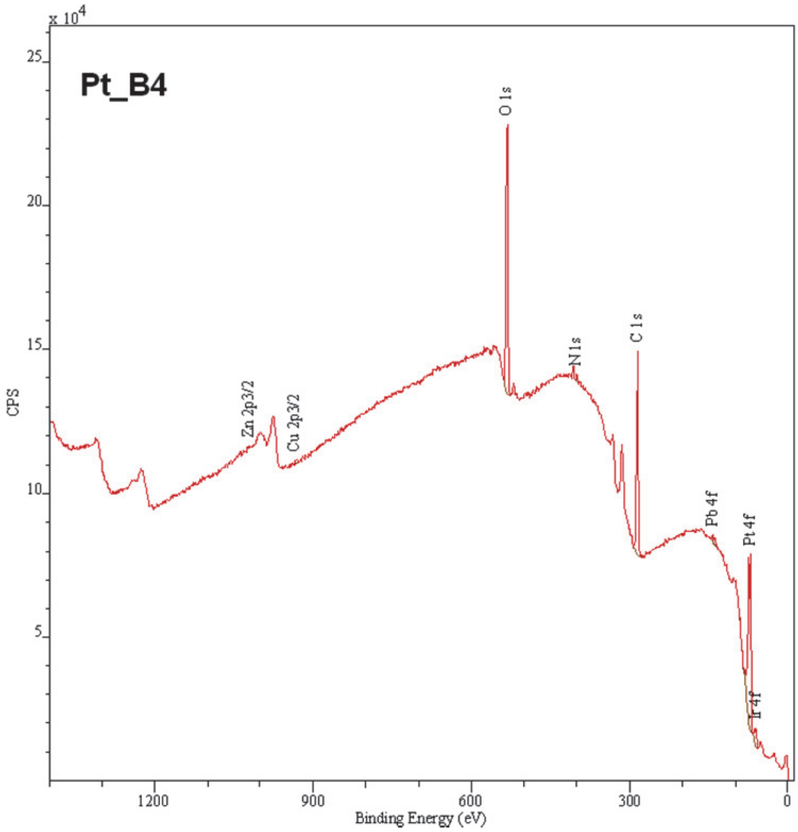


Figure 7. Survey scan of Pt-Ir sample Pt_B4 after contamination using the vacuum gauge method.

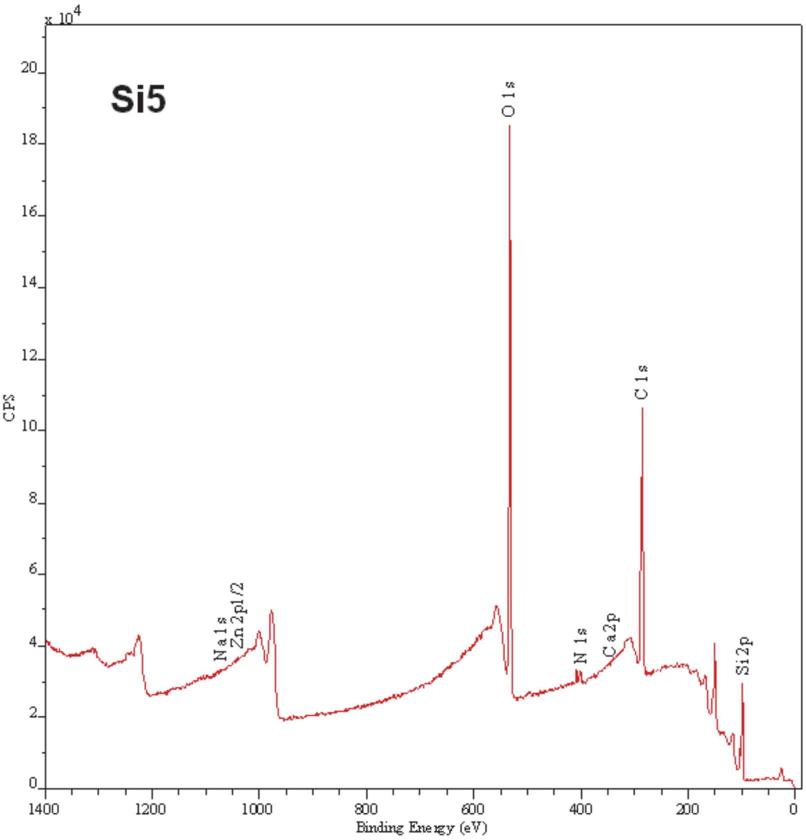


Figure 8. Survey scan of silicon sample Si5 after contamination using the vacuum gauge method.

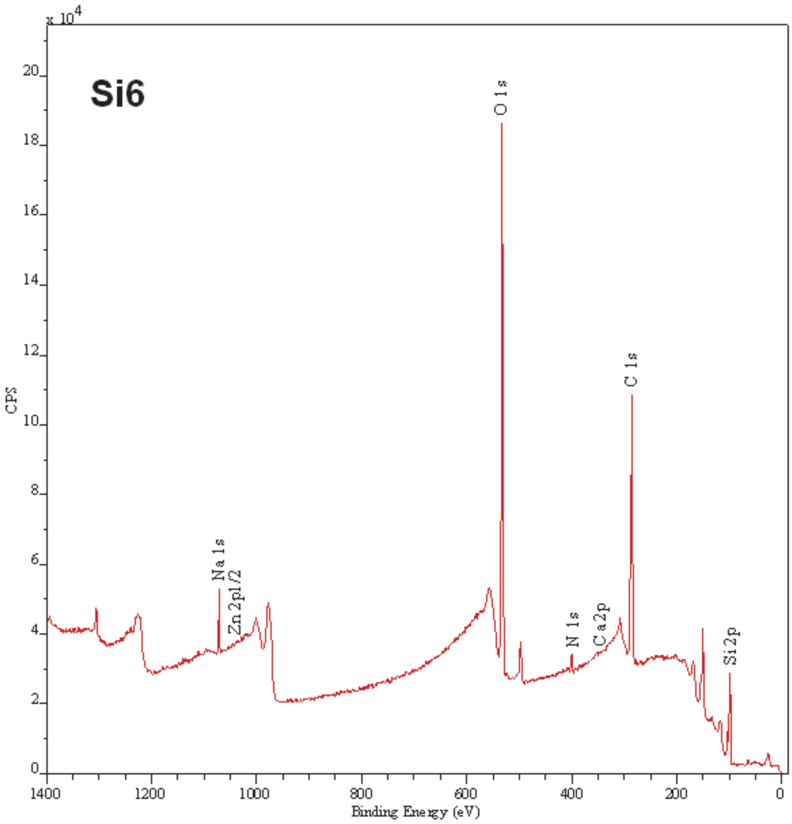


Figure 9. Survey scan of silicon sample Si6 after contamination using the vacuum gauge method.

4.3.2 Calculated thickness of the carbonaceous overlayer

The thickness of the carbonaceous contamination on the surface of the samples has been calculated using the following formula from a paper by Smith [7]:

$$d = -\lambda_{C1s,C} \cos\theta \ln\left(1 - \frac{x}{100}\right) \qquad (1)$$

Where: x = atomic %

$\lambda_{C1s,C}$ = the effective electron attenuation length for carbon 1s photoelectrons in the hydrocarbon overlayer

θ = emission angle to the surface normal

The effective electron attenuation length for carbon 1s photoelectrons in the hydrocarbon overlayer ($\lambda_{C1s,C}$) has been calculated from the following formula derived by Seah and Spencer [8] for an average organic overlayer:

$$\lambda_{C1s,C} = 0.00837E^{0.842} \qquad (2)$$

Where: E = the kinetic energy of the peak of interest

The calculated thickness of the carbonaceous overlayer for each sample is shown in Table 7. The samples that were contaminated using the vacuum gauge method (Pt_B3, Pt_B4, Si5 and Si6) have between 1 nm and 2 nm thicker overlayers of carbonaceous contamination compared with the samples with a natural overlayer (Pt_B2 and Si4). For a Pt-Ir kilogram with a surface area equal to 71.5 cm^2 this gives a mass increase of between 64 µg and 129 µg, assuming the density of the contamination is representative of a typical hydrocarbon (0.9 g cm^{-3}).

Table 7. Calculated thickness of the carbonaceous overlayer for each sample.

Name	Carbonaceous overlayer thickness / nm
Pt_B2	2.5
Pt_B3	3.5
Pt_B4	3.9
Si4	0.8
Si5	2.7
Si6	2.2

4.3.3 Carbon 1s peak fitting

The atomic percentages of the possible peaks identified in the narrow scan spectra of the samples are shown in Table 8 and Table 9 for the Pt-Ir samples and silicon samples respectively. Narrow scan spectra of the C 1s peaks for samples Pt_B2 and Si4 with natural overlayers are shown in Figure 10 and Figure 11 respectively and spectra for the vacuum gauge contaminated samples Pt_B3, Pt_B4, Si5 and Si6 are shown in Figure 12, Figure 13, Figure 14 and Figure 15 respectively. Although the overall area intensity of the C 1s region is higher for the vacuum gauge contaminated Pt-Ir and silicon samples, the atomic percentage of the hydrocarbon peak is lower for all these samples compared with the samples with natural contamination. This is due to a much higher proportion of components with higher binding energies in the contaminated samples such as alcohol/ether groups, carbonyl groups and acid/ester groups compared with the samples with natural contamination.

Table 8. C1s peak components for the Pt-Ir samples.

Name (Binding energy / eV)	Pt_B2 / %	Pt_B3 / %	Pt_B4 / %
Hydrocarbon (285.0 eV)	81.4	58.4	59.9
Alcohol/ether (286.5 eV)	10.2	21.8	22.1
Carbonyl (287.6 to 286.5 eV)	5.2	11.1	8.8
Acid/ester (289 eV)	3.2	8.7	9.2

Table 9. C1s peak components for the silicon samples.

Name (Binding energy / eV)	Si4 / %	Si5 / %	Si6 / %
Hydrocarbon (285.0 eV)	84.0	50.3	54.4
Alcohol/ether (286.5 eV)	8.8	23.0	23.8
Carbonyl (287.6 to 286.5 eV)	3.6	12.8	10.9
Acid/ester (289 eV)	3.6	13.9	10.9

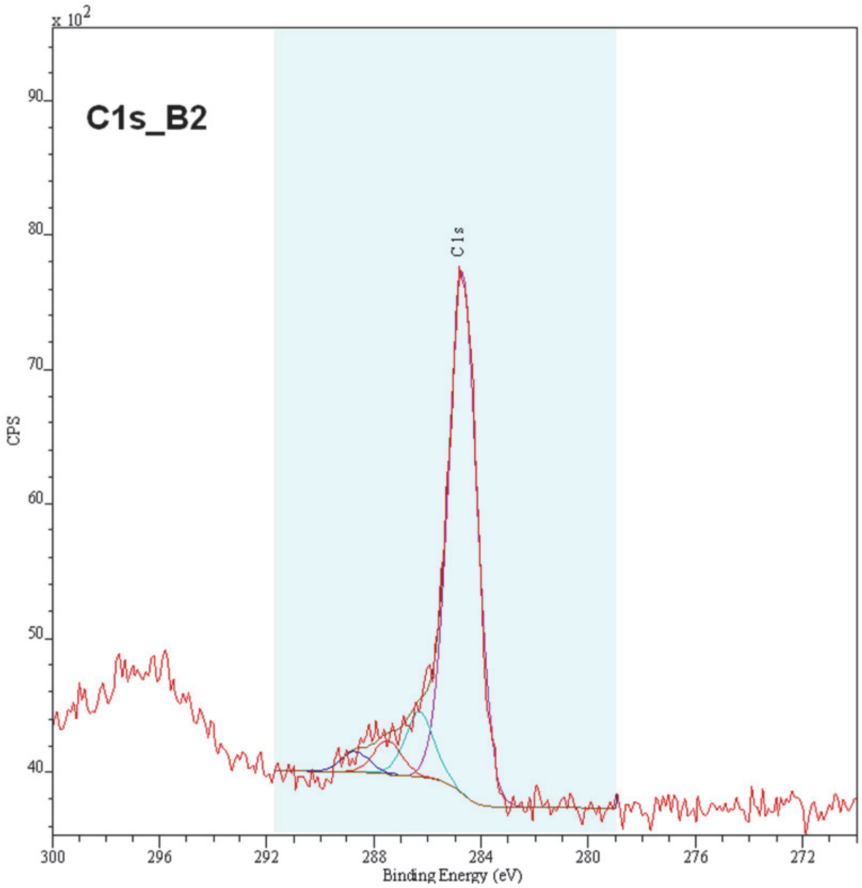


Figure 10. C 1s narrow scan of Pt-Ir sample Pt_B2.

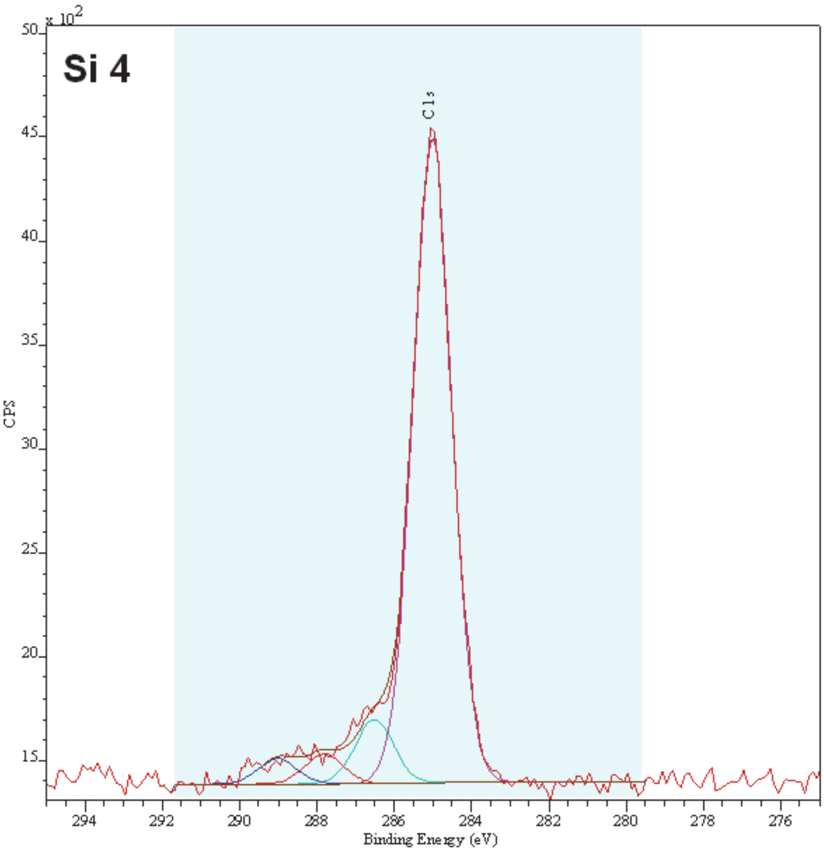


Figure 11. C1s narrow scan of silicon sample Si4.

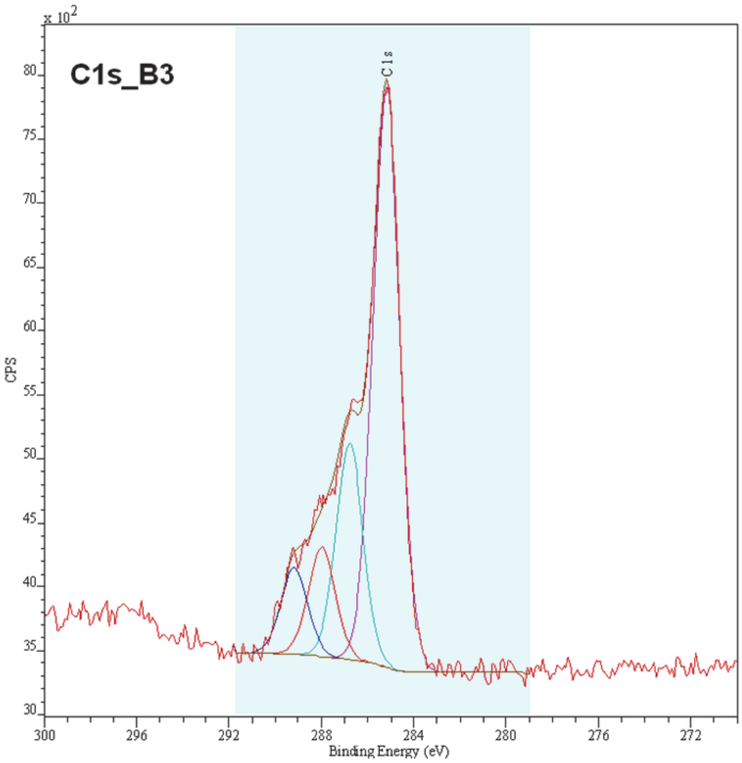


Figure 12. C1s narrow scan of Pt-Ir sample Pt_B3.

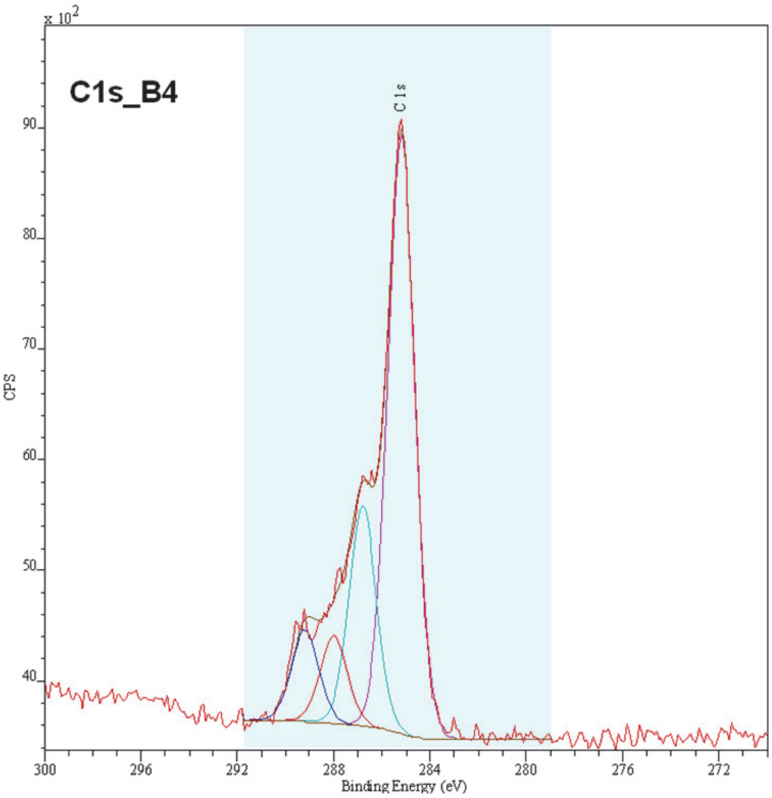


Figure 13. C 1s narrow scan of Pt-Ir sample Pt_B4.

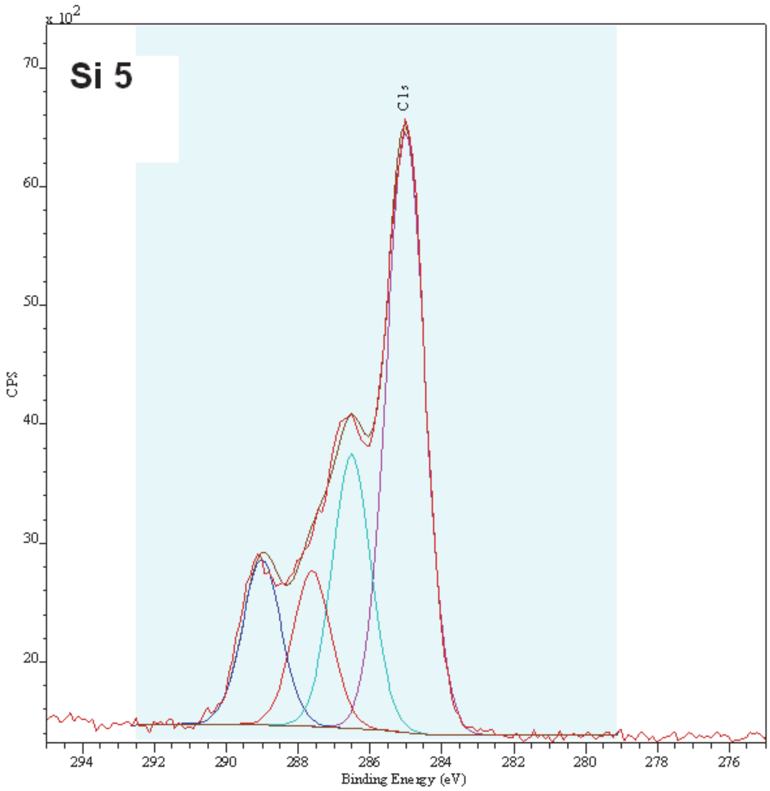


Figure 14. C 1s narrow scan of silicon sample Si5.

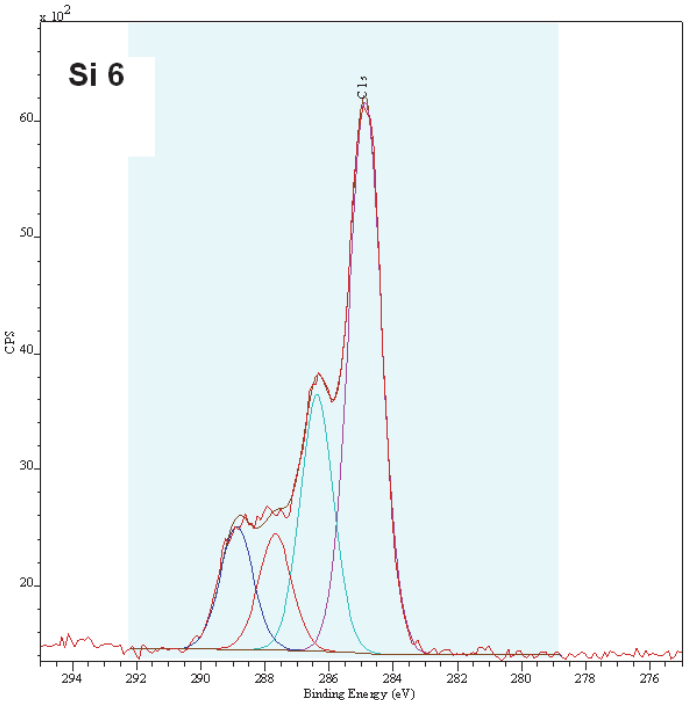


Figure 15. C 1s narrow scan of silicon sample Si6.

4.3.4 Silicon oxide thickness

The thickness of the oxide layer on the surface of the silicon samples has been calculated using the following formula taken from a paper by Seah and Spencer [9]:

$$d = L \cos\theta \ln\left(1 + \frac{R}{R_0}\right) \tag{3}$$

Where: L = attenuation length of the electrons in the oxide overlayer
R = ratio of the oxide and substrate measured intensities
R_0 = ratio of the bulk oxide and bulk substrate materials

The measured intensities were obtained by applying the 3 peak fitting method to fit peaks to narrow scans of silicon samples Si4, Si5 and Si6 as shown for sample Si4 in Figure 16. The calculated thickness of the oxide layer on each sample is shown in

Table 10. There was no difference in oxide thickness between sample Si4 and the two samples Si5 and Si6 which had been contaminated in the vacuum chamber. Therefore the increased atomic percentages seen for samples Si5 and Si6 in the survey scans (§ 4.3.1) does not appear to be due to increased silicon oxide, rather it appears to be due to an increase in oxygen containing carbon compounds as seen in the fitting of the C 1s narrow scans (§ 4.3.3).

Table 10. Calculated thickness of the silicon oxide layer.

Name	Silicon oxide thickness / nm
Si4	1.0
Si5	1.0
Si6	1.0

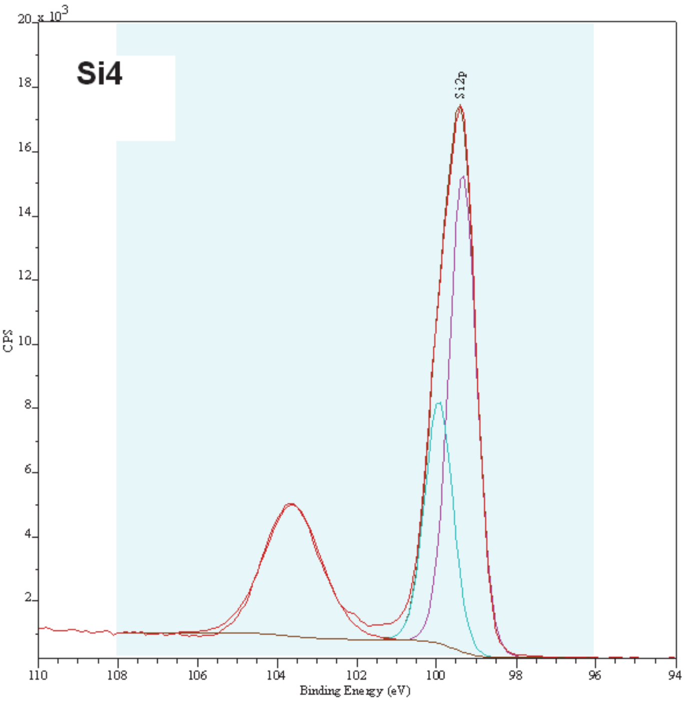


Figure 16. Si 2p narrow scan of silicon sample Si4.

5 CONCLUSIONS

Two methods of applying a controlled amount of artificial carbonaceous contamination to the surface of mass artefacts have been tested. The first method employed a glass chamber containing oil that was heated and then the vaporised oil was deposited on the surface of the artefacts. This method proved successful at applying a suitable quantity of contamination (about 80 µg) to the surface of stainless steel kilogram artefacts, although the method heated up the surface of the artefacts by between 9 °C and 12 °C which was undesirable as it could affect their surface properties.

The second method employed an inverted magnetron vacuum gauge in a chamber to contaminate the surface of artefacts in vacuum. This method was also successful at applying a controlled amount of carbonaceous contamination to the surface of stainless steel artefacts and would have added between 92 µg and 122 µg to the surface of a cylindrical stainless steel kilogram.

XPS surface analysis was also used on vacuum gauge contaminated Pt-Ir and silicon samples to measure the thickness of applied contamination. Survey scans of the samples showed that the vacuum gauge contaminated samples had the same elements as found on the samples with natural contamination, but had both higher atomic percentages of carbon and oxygen. A calculation of the thickness applied to the samples showed that this method successfully applied between 1 nm and 2 nm which amounted to an equivalent mass added to a Pt-Ir prototype of between 64 µg and 129 µg. The C 1s regions were analysed for all the samples and showed that the vacuum gauge contaminated samples had a lower ratio of hydrocarbons to carbon compounds with higher binding energies compared with the samples with natural contamination. While it is not ideal that the samples that were contaminated using the vacuum gauge method had different C 1s compositions than the samples with a natural overlayer but in terms of contaminating artefacts for cleaning trials, differences in C 1s compositions are not important providing the cleaning methods are effective at removing all the C 1s components. Analysis of the oxide thickness of the silicon samples gave an oxide thickness of 1 nm for all the samples indicating that the vacuum gauge contamination method had not affected the thickness of the oxide layer. Therefore the increase in the atomic percentage of oxygen evident in the survey scans of these samples can be attributed to oxygen bonding with carbon in the carbonaceous contamination layer a conclusion supported by the measured increase in components with higher binding energies seen in the C 1s narrow scan spectra.

In summary both methods successfully applied a controlled amount of contamination to mass artefacts. However, the advantage of the vacuum gauge method was that it did not increase the temperature of the artefacts unlike the heated oil method and therefore the vacuum gauge method is recommended as the preferred method for controlled contamination of artefacts.

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