EMRP SIB05 NewKILO WP 4

Deliverable 4.2.1: Report detailing the cleaning and post clean storage procedures investigated and outlining an optimised technique for each material

Content

1 Scope

This document highlights the results of task 4.2: Comparison, selection, validation and optimisation of cleaning techniques for primary mass standards. The measurements leading to these results were conducted at NPL, CNAM, MIKES and METAS. Detailed reports can be found in [1-8].

2 Introduction

The aim of this task was to compare, select, validate and optimise the most appropriate techniques for effective and repeatable cleaning of primary mass standards and to identify optimum post-clean storage methods for materials which may be used as primary mass standards. For the evaluation of the mass stability of artefacts the influence of the applied cleaning method and the subsequent storage conditions were studied by different NMIs.

3 Experimental

Alternative cleaning techniques to the nettoyage-lavage procedure, such as UV/ozone, hydrogen/oxygen plasma and ethanol, were investigated. The cleaning techniques were applied to different materials to study the subsequent surface recontamination caused by cyclic venting and/or by storing the samples under different environmental conditions. The recontamination and the effectiveness of the cleaning techniques were verified using surface analysis techniques such as XPS, AFM and TDS as well as gravimetric measurements.

4 Results

4.1 Surface analysis using XPS

NPL analysed the surface of five potential materials (Ni-alloy U720, single crystal tungsten, PtIr, Ir and Si) using XPS. The samples were measured after cleaning with UV/ozone, H-plasma and nettoyage-lavage, and again after storage for one month using the three different storage methods air, vacuum and nitrogen. The results showed that UV/ozone and H-plasma cleaning exhibit similar effectiveness in removing hydrocarbon contamination from the surfaces of Ni-alloy and Si as well as from the surfaces of PtIr, Ir, and W (Figure 1). Nettoyage-lavage was applied to the Ni-alloy and Si samples only and showed to be less effective than UV/ozone and H-plasma, leaving a surface contamination with a layer of about 1 nm thick [2].

The air stored Ni-alloy and Si samples showed an increase in hydrocarbon overlayer thickness. The nitrogen stored samples showed a slight decrease in hydrocarbon thickness after storage apart from the UV/ozone cleaned Ni-alloy sample. The vacuum stored samples appeared to gain the most amount of hydrocarbon contamination. The PtIr, Ir and W samples were stored in air and nitrogen and all showed an increase in hydrocarbon thickness after storage (Figure 2).

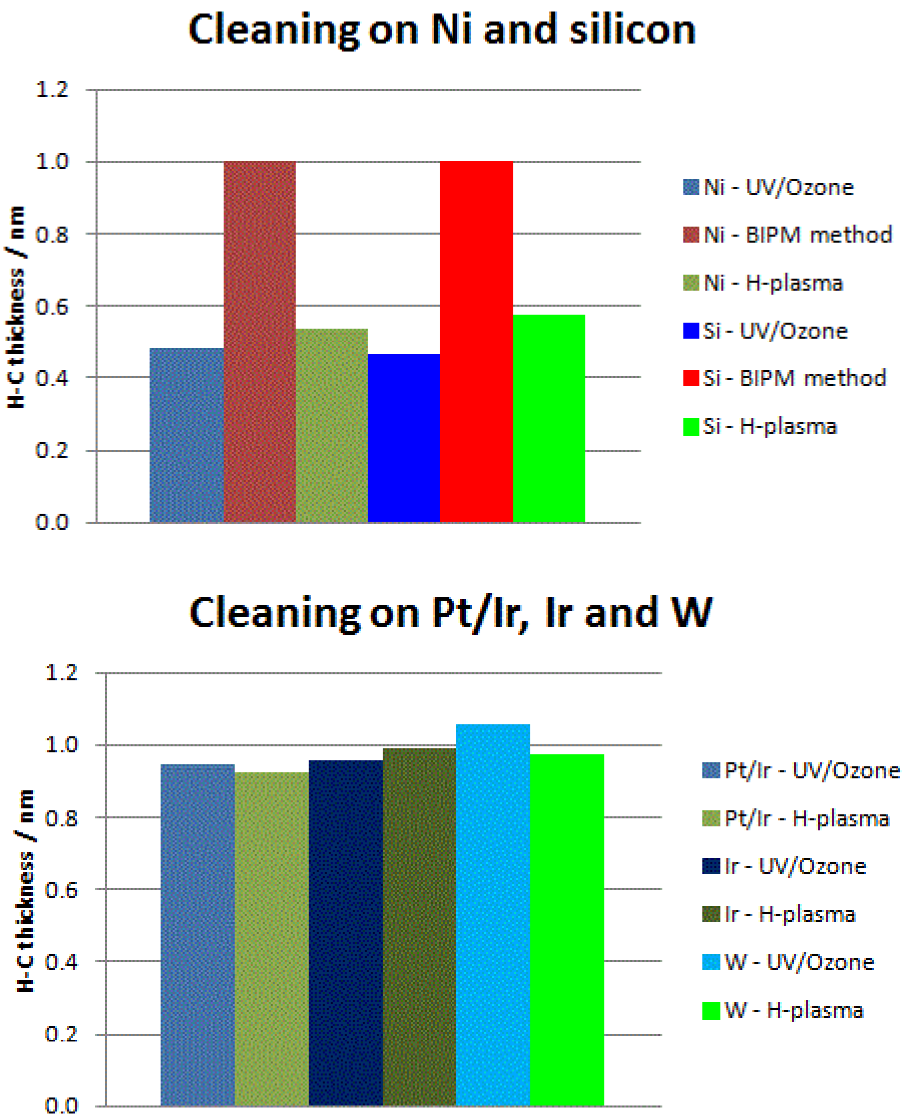


Figure 1: Hydrocarbon overlayer thickness after cleaning (NPL) [2].

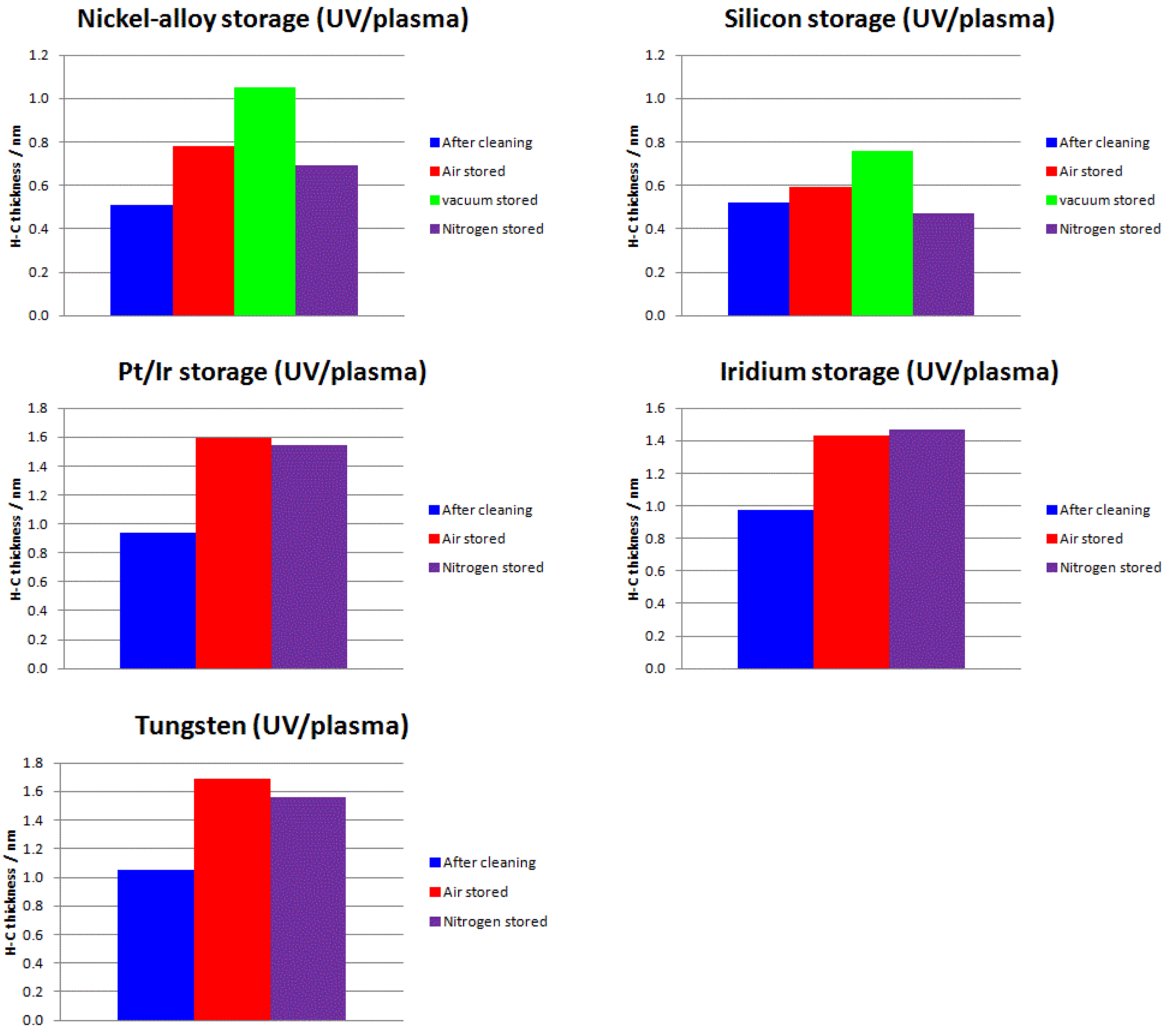


Figure 2: Hydrocarbon overlayer thickness after cleaning and after storage for 1 month in air, vacuum, and nitrogen (NPL) [2].

At METAS AuPt, Ni-alloy and tungsten samples were analysed using XPS after UV/ozone and H-plasma cleaning and after storage for 1 month in vacuum, air and argon.

The samples were initially cleaned with UV/ozone before storage. With UV/ozone cleaning the hydrocarbon contamination could not be removed completely. After storage in vacuum, air and argon, all samples showed an increased overlayer of hydrocarbon contamination of between 0.2 nm and 0.4 nm thick. Subsequently, the samples were cleaned with H-plasma and the hydrocarbon contamination could be removed to a great extent. After storage in air or vacuum, the increased amount of hydrocarbons was much larger than after storage in argon. In general, the contamination rate after H-plasma cleaning is higher than after UV/ozone cleaning. Nonetheless, the amount of accumulated hydrocarbons during vacuum, air and argon storage was lower when the samples had previously been cleaned with H-plasma. The results are shown in Figure 3 and Figure 4.

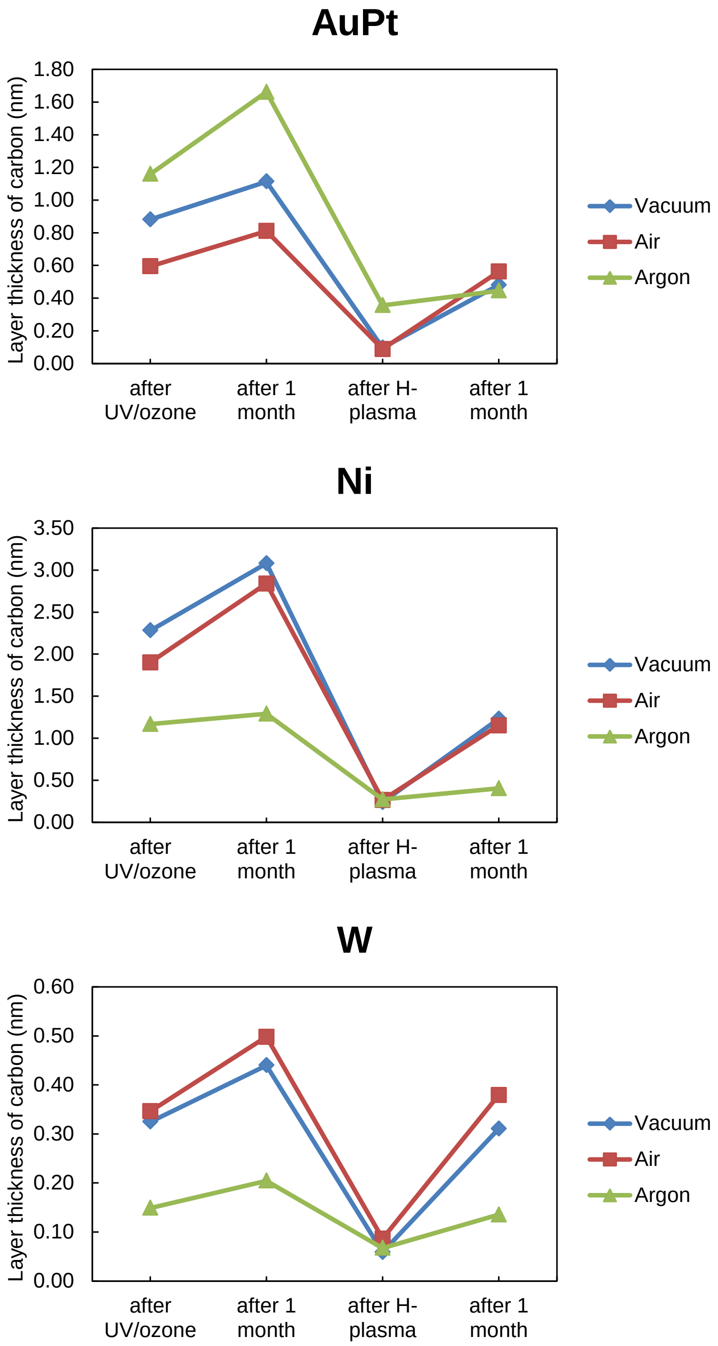


Figure 3: Layer thickness of hydrocarbon on AuPt, Ni-alloy and W samples after cleaning with UV/ozone and H-plasma and after storage for 1 month in vacuum, air and Argon (METAS).

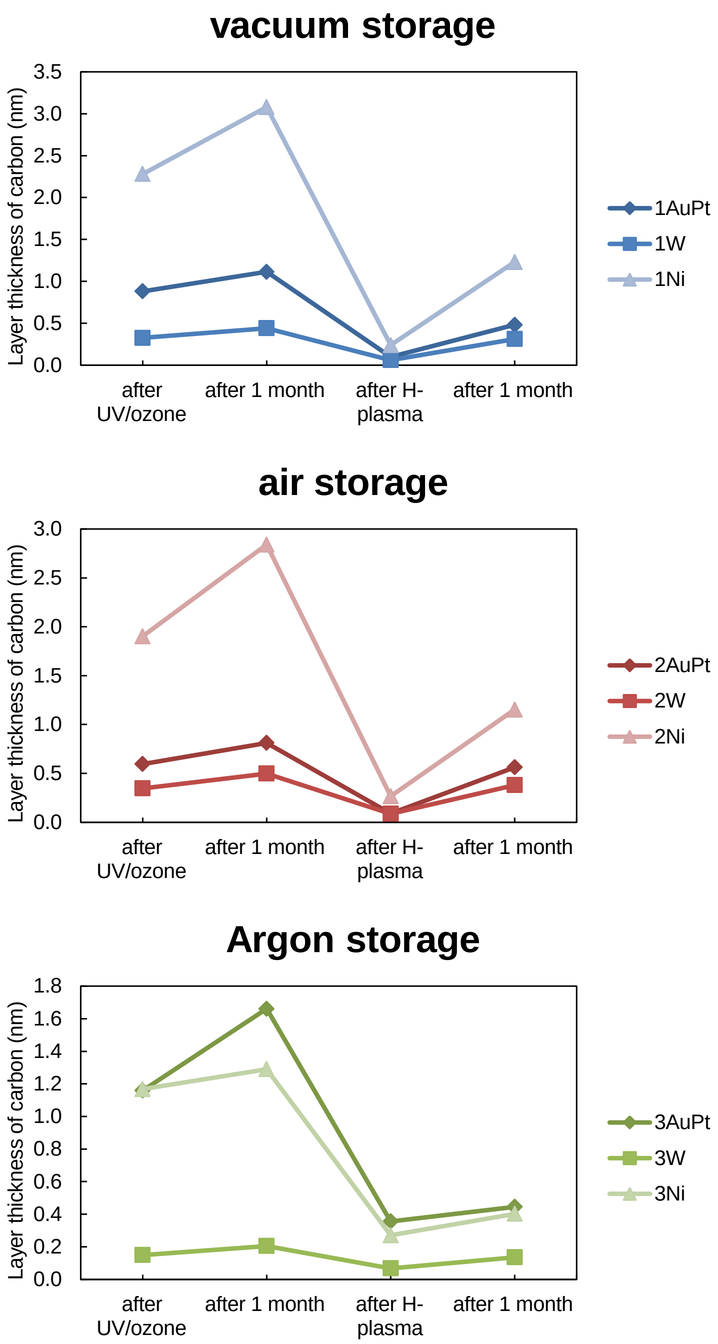


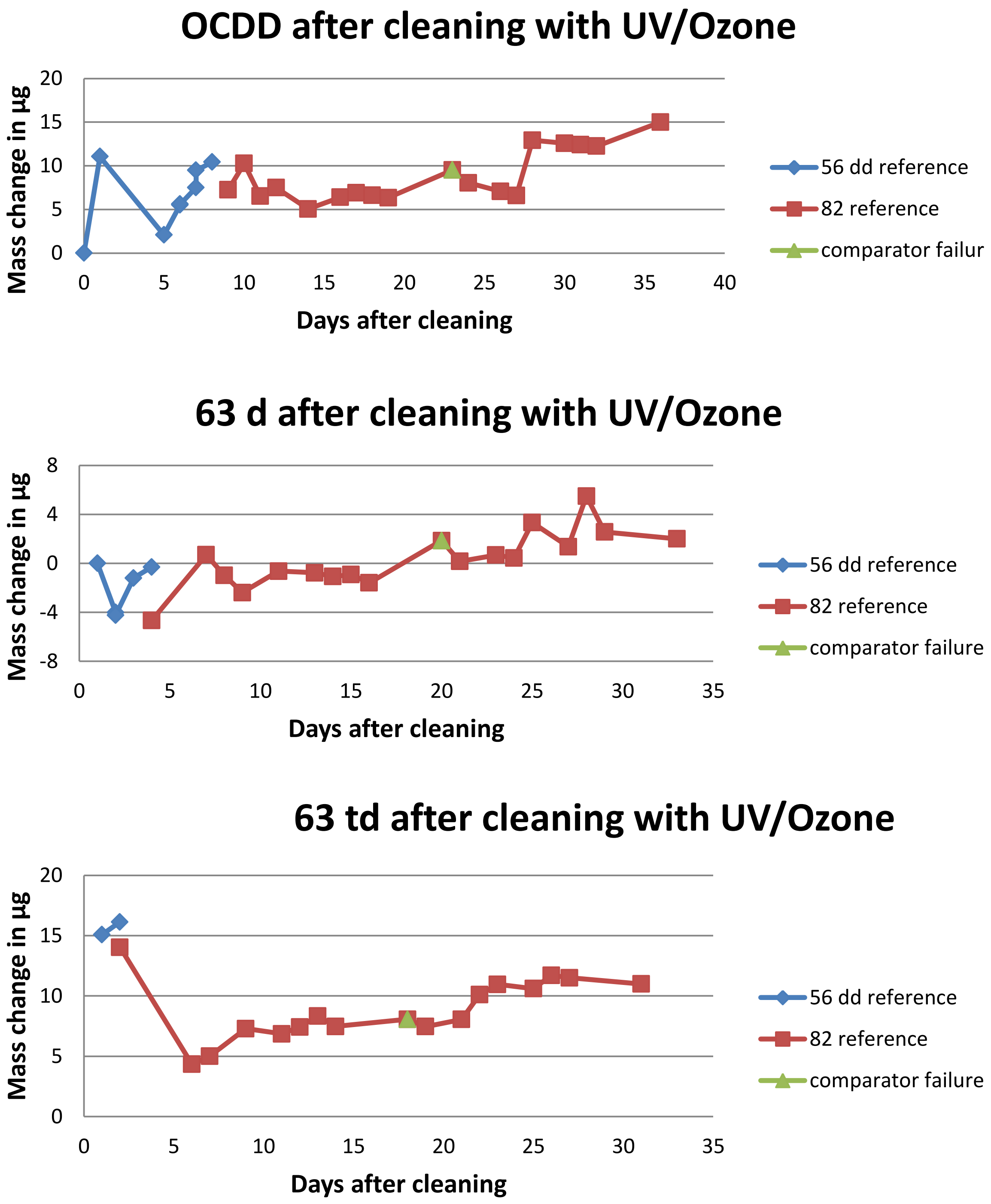
Figure 4: Layer thickness of hydrocarbon on AuPt, Ni-alloy and W samples after cleaning with UV/ozone and H-plasma and after storage for 1 month in vacuum, air and Argon (METAS).

4.2 Gravimetric measurements combined with XPS analysis

The effects of the cleaning methods UV/ozone and H-plasma on the artefact surface were investigate not only by surface analysis techniques but also by gravimetric measurements. Some of these studies were conducted within the framework of the EMRP Researcher Mobility Grants [1, 3].

4.2.1 Stainless steel

Stainless steel weights were treated with UV/ozone followed by gravimetric and XPS measurements. The gravimetric measurements revealed an initial increase in mass right after UV/ozone cleaning by about 15 µg, followed by a mass decrease after 5 days. Subsequent measurements showed again an increase in mass (Figure 5). XPS measurements were conducted on small stainless steel samples before and after exposure to UV/ozone. The results showed a significant decrease of carbon and an increase of oxide compounds upon cleaning. Within the next two weeks a growth of carbon compounds and magnesium compounds could be observed [3].



OCDD after cleaning with UV/Ozone

63 d after cleaning with UV/Ozone

63 td after cleaning with UV/Ozone

Figure 5: Changes in mass of stainless steel weights after an initial UV/ozone cleaning (NPL) [3].

The effect of UV/ozone was also studied on 1 kg stainless steel cylinder and stack of discs [1]. The artefacts were exposed to four cycles of UV/ozone. The first two cycles were followed by gravimetric measurements, XPS analysis and gravimetric measurements again. The last two cycles were followed directly by XPS analysis and gravimetric measurements afterwards. The first cleaning strongly reduced the amount of hydrocarbon contamination (Figure 6). Subsequent UV/ozone treatments did not further diminish the surface contamination but instead caused a growth of metal oxides (Figure 7). The change in the surface chemical composition affected the mass of the artefact which could be measured gravimetrically. An initial loss in mass of approximately 22 µg after the first cleaning cycle was observed for the steel cylinder (Figure 8). Subsequent measurements showed a linear increase in mass. The stack of discs, however, showed a consecutive decrease in mass with every cleaning cycle (Figure 9).

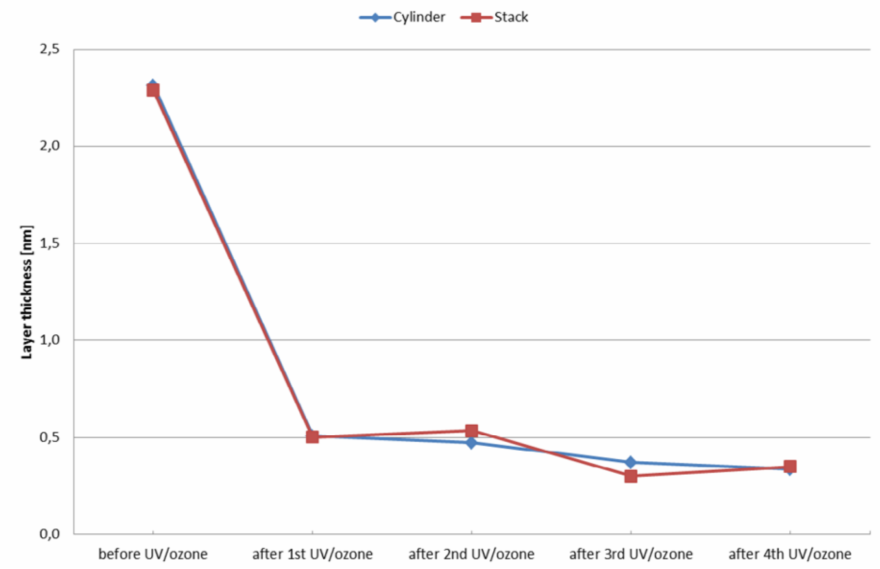


Figure 6: Change in layer thickness of hydrocarbon on the steel artefacts upon several steps of UV/ozone cleaning (METAS) [1].

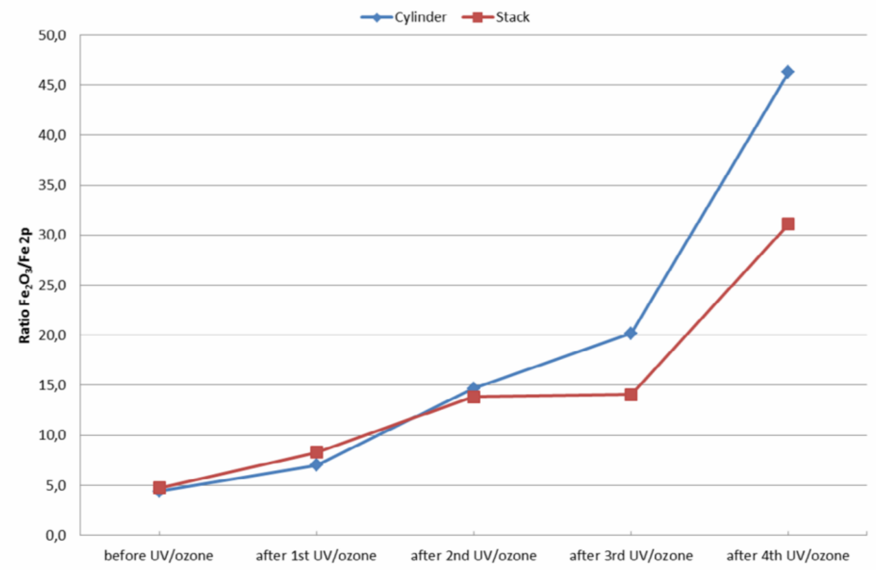


Figure 7: Growth of metal oxides on the steel artefacts upon several steps of UV/ozone cleaning (METAS) [1].

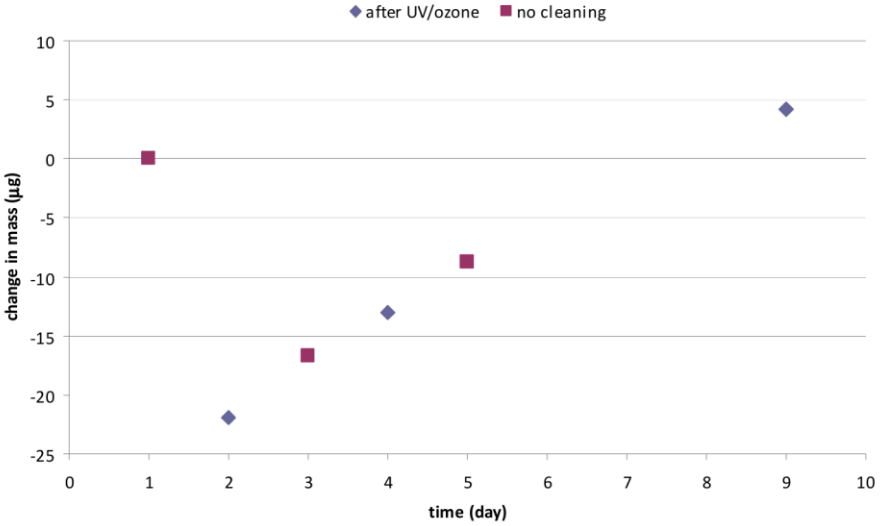


Figure 8: Change in mass of the steel cylinder during UV/ozone cleaning cycles (METAS) [1].

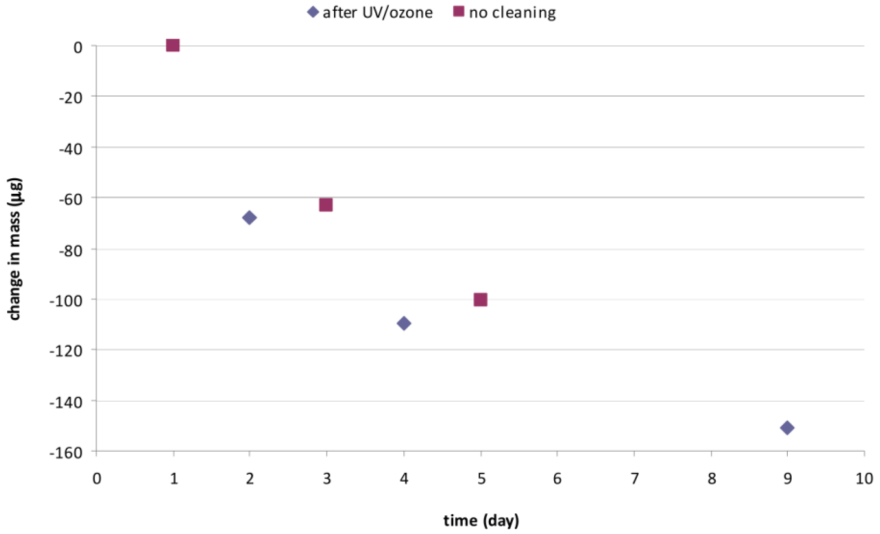


Figure 9: Change in mass of the steel stack of discs during UV/ozone cleaning cycles (METAS) [1].

4.2.2 Gold artefacts

The experiment of the 1 kg steel artefacts described above was repeated with a pair of gold artefacts consisting of a cylinder and a stack of discs. The evolution of the hydrocarbon overlayer upon UV/ozone cleaning is similar both for the gold and for the steel surface (Figure 10). But the evolution of the metal oxides on the two surface materials during UV/ozone exposure is different. On the gold surface the amount of oxides remained stable during the course of cleaning (Figure 11) whereas on the stainless steel surface the amount of oxides increased. Finally, the gold artefacts were exposed to H-plasma for 30 minutes, which caused a further decrease of hydrocarbon contamination and a reduction of the oxides.

Gravimetric measurements showed an initial loss in mass of approximately 10 µg after the first UV/ozone cleaning and a gain in mass for every additional UV/ozone exposure. The gold stack of discs, however, showed a successive loss in mass up to the third cleaning and a gain in mass after the 4th UV/ozone treatment.

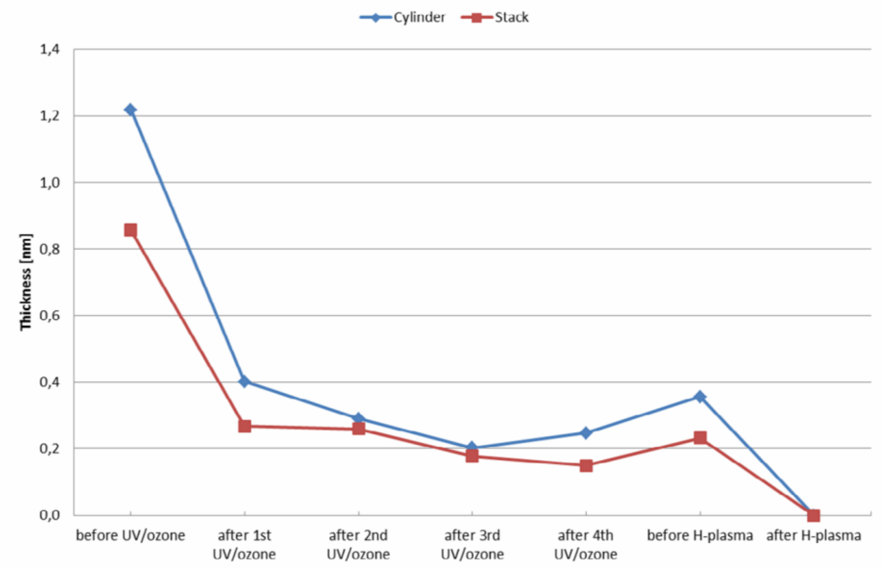


Figure 10: Change in layer thickness of hydrocarbon on the gold artefacts upon several steps of UV/ozone cleaning (METAS) [1].

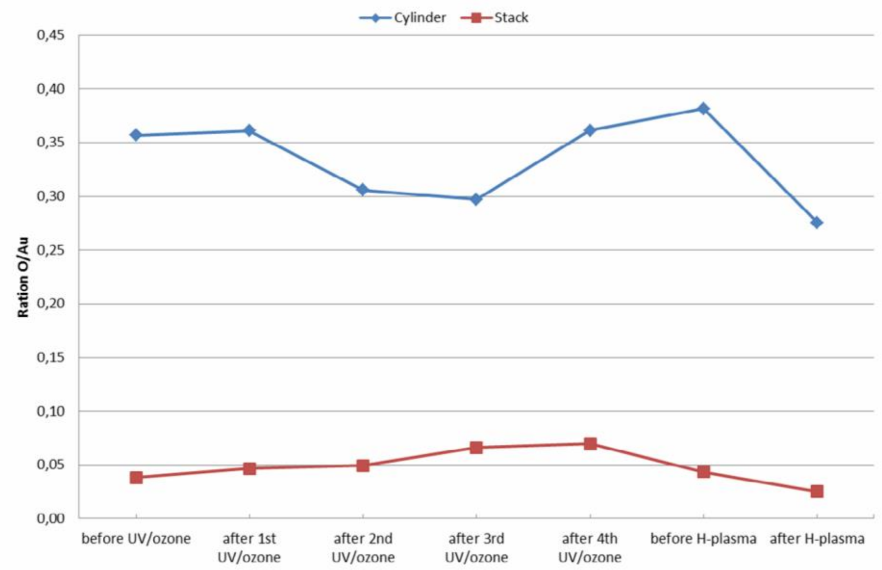


Figure 11: Change of metal oxides on the gold artefacts upon several steps of UV/ozone cleaning (METAS) [1].

The trends of the gravimetric measurements during the course of UV/ozone cleaning were similar for both the gold and steel artefacts. The first UV/ozone cleaning caused a loss in mass of approximately 10 µg for the gold cylinder and a gain in mass after subsequent cleanings. For the stack of discs are successive loss in mass was observed up to the third cleaning. The exposure of the gold artefacts to H-plasma led to a loss in mass of 39 µg and 356 µg for the cylinder and the stack of discs, respectively.

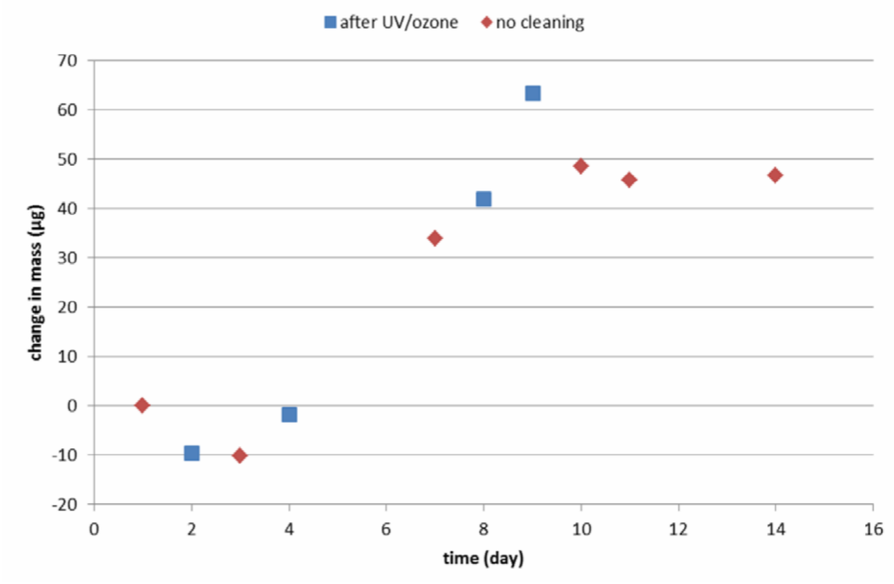


Figure 12: Change in mass of the gold cylinder during UV/ozone cleaning (METAS) [1].

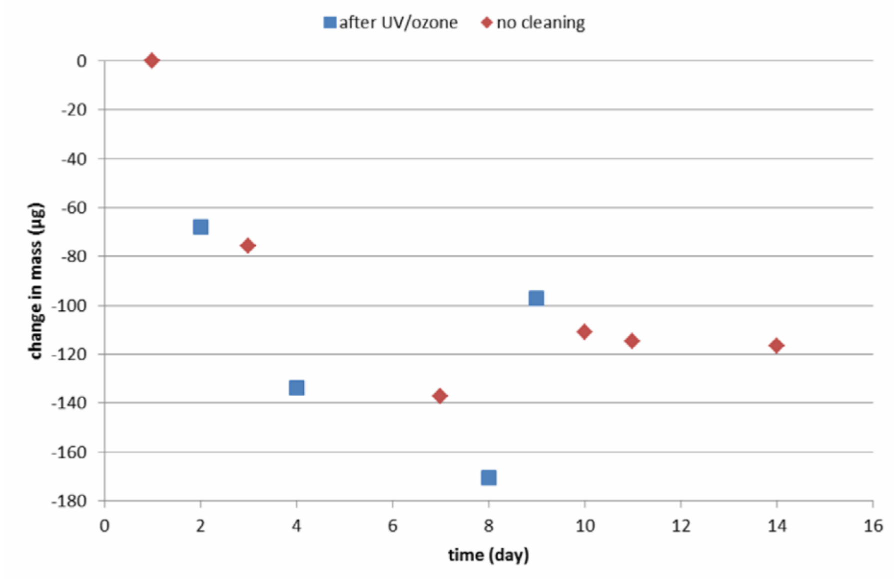


Figure 13: Change in mass of the gold stack of discs during UV/ozone cleaning (METAS) [1].

4.2.3 PtIr artefacts

CNAM performed gravimetric measurements on PtIr artefacts which were cleaned by air-plasma or according to the nettoyage-lavage procedure [5, 9]. Both cleaning methods resulted in a loss in mass right after cleaning and an exponential increase during subsequent weighings. For both cleaning methods, the mass gain reached a level of saturation which was lower than before cleaning (Figure 14).

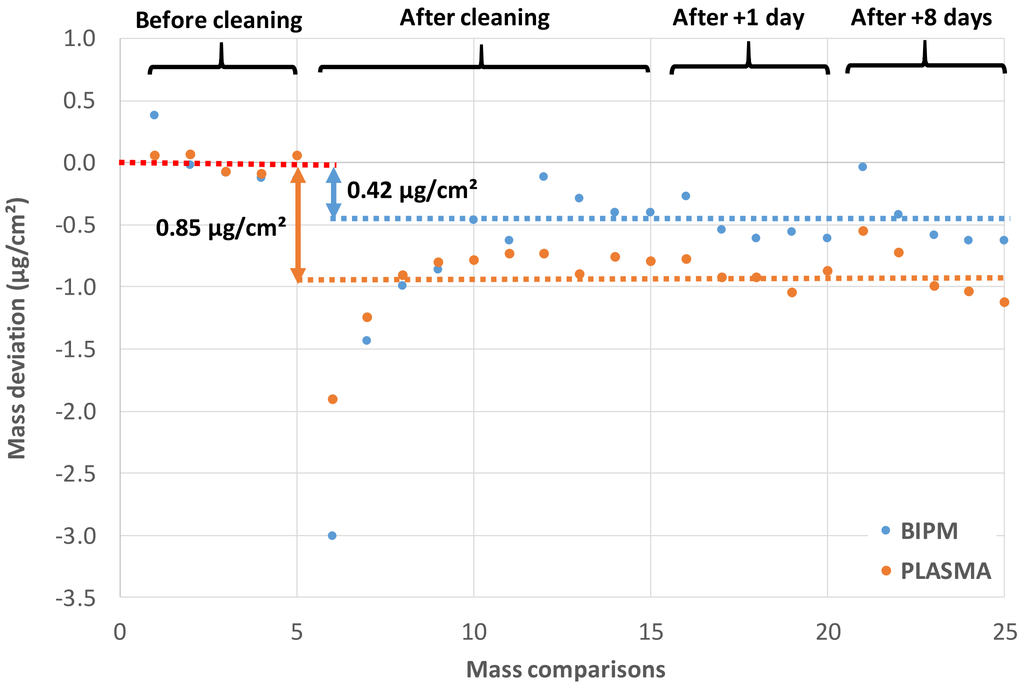


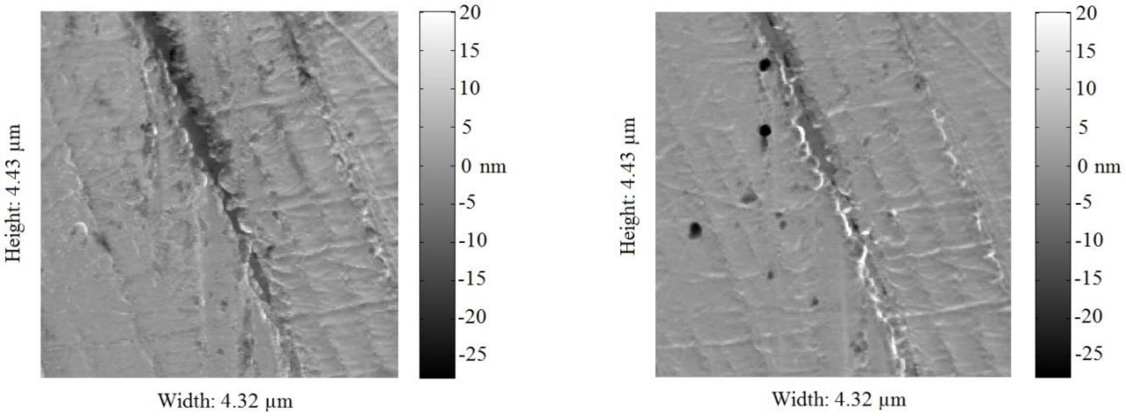
Figure 14: Mass evolution of PtIr artefacts after air-plasma and nettoyage-lavage cleaning (CNAM) [5].

4.3 Gravimetric measurements combined with AFM

MIKES studied the effect of low-pressure H-plasma cleaning on stainless steel weights using both gravimetric weighing and atomic force microscopy (AFM) [4]. For that purpose, class E_2 stainless steel sample discs were used for the cleaning studies. AFM images were used to display changes in the surface morphology of the sample discs before and after H-plasma cleaning. It was found that most of the surface contamination was removed during the first H-plasma treatment and that the majority of the removed contamination was located in the grooves (Figure 15). Ethanol cleaning removed further contamination from the grooves but caused additional protuberances on the surface [4].

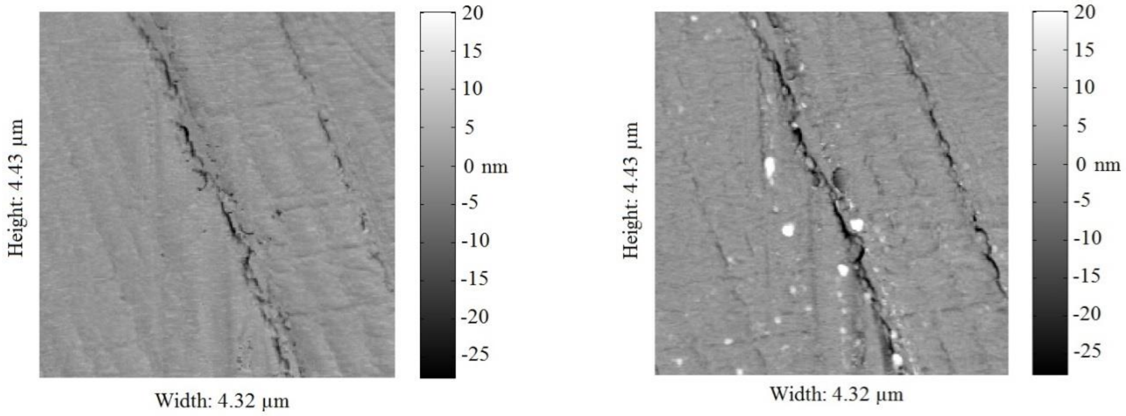
The effect of cleaning was also demonstrated by gravimetric measurements which showed a loss in mass of 3 µg after 2 minutes of H-plasma treatment. But cleaning with ethanol resulted in an increase of several micrograms in mass.

It was demonstrated that low-pressure H-plasma is an effective and non-abrasive cleaning method which is independent of the operator and thus well suited for cleaning stainless steel mass standards. Furthermore, earlier findings from Marti *et al.* [8] could be confirmed.



after 2 minutes

after 8 minutes



after 10 minutes

after additional ultrasonic cleaning in ethanol

Figure 15: Changes in surface morphology of stainless steel discs upon exposure to H-plasma for 2, 8 and 10 minutes and after an additional ultrasonic cleaning in ethanol (MIKES) [4].

MIKES extended the study by cleaning stainless steel discs with UV/ozone and a mixture of H_2/O_2-plasma. Figure 16 shows the mass changes of the sample discs as a result of different cleaning methods. An initial ethanol cleaning caused a mass loss of 5 µg to 18 µg whereas UV/ozone cleaning caused ambiguous results, a mass gain for some discs and a mass loss for some other discs. MIKES performed AFM measurements to delve into the inconsistent weighing results upon UV/ozone cleaning. AFM images revealed a granular structure typical for oxidized surfaces. It was demonstrated that the growth of oxides is strongest near the grooves of the surface and that the layer growth is uneven.

Concerning cleaning methods, it was found that UV/ozone removes residual contaminants, but not as effectively as H_2/O_2-plasma or H-plasma. Furthermore, after repetitive cleaning with UV/ozone a gain in mass due to the formation of oxides was observed. As long as the removal of surface contaminants exceeds the growth of the oxide layer, a decrease in mass is observed. As soon as no further contaminants are removed from the surface, the mass of the artefact is increased due to oxidation [7].

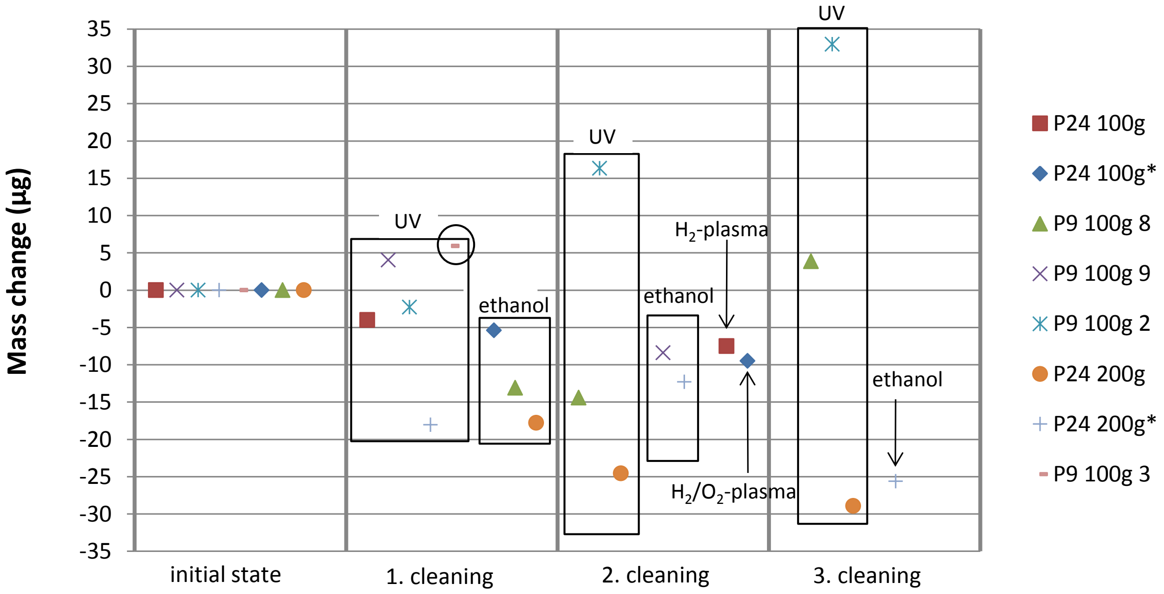
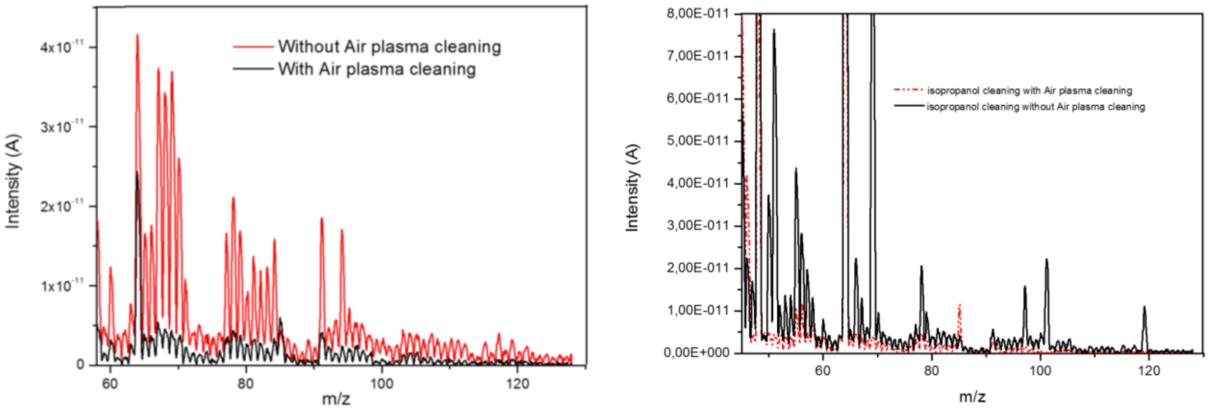


Figure 16: Change in mass of stainless steel discs upon cleaning with UV/ozone, H-plasma, H_2/O_2-plasma and ethanol (MIKES) [7].

4.4 Surface analysis by thermal desorption spectroscopy and photothermal deflection

4.4.1 Thermal desorption spectroscopy

Thermal desorption spectroscopy (TDS) observes desorbed molecules from a surface when the surface temperature is increased. It shows what molecules are adsorbed on the surface. CNAM used TDS to measure and compare the effectiveness of air- and Ar-plasma and the nettoyage-lavage method. For this reason, a PtIr artefact was first cleaned with ethanol or isopropanol and then exposed to air-plasma which eliminated a large part of organic compounds (Figure 17). When cleaned with isopropanol, the TDS intensity was higher. Air-plasma cleaning also removed water to a great extent from the surface of the PtIr artefact [5].



(a)

(b)

Figure 17: TDS spectra at 260°C of a PtIr artefact: first cleaned with ethanol (a) and isopropanol (b) and then exposed to air-plasma (CNAM) [5].

4.4.2 Photothermal deflection spectroscopy

CNAM also studied the adsorbability of solvents on three different surfaces (Pt-10%Ir, pure iridium and AuPtAgCu) by means of photothermal deflection spectroscopy (PDS) [5].

References

[1] G. Grgíc, Report on non-contact cleaning application to 1 kg surface artefacts including XPS and gravimetric results.

[2] J. Berry, S. Davidson, Summary report on NPL XPS results for WP4 deliverable 4.2.1.

[3] H. Memic, Appendix I to EMRP Researcher Grant Final Report – SIB05-RMG 2

[4] R. Högström, K. Riski, M. Ojanen and M. Heinonen, Atomic Force Microscopy study on the effect of low-pressure hydrogen plasma cleaning on stainless steel weights, 2014, IMEKO 22nd TC3.

[5] Z. Silvestri et al., Report detailing the cleaning and post clean storage procedures investigated and outlining an optimised technique for each material.

[6] P. Fuchs, Surface effects and dynamic changes on the artefact surface between vacuum, air and selected gases.

[7] R. Högström, MIKES contribution to report D4.2.1.

[8] K. Marti, P. Fuchs and S. Russi, Cleaning of mass standards II: A comparison of new techniques applied to actual and potential new materials for mass standards, Metrologia 50, 83-92, 2013.

[9] G. Girard, Le nettoyage-lavage des prototypes du kilogramme au BIPM, 1990.