EMRP SIB05 NewKILO WP4
Deliverable 4.2.4

Report on application of the cleaning procedures to mass standards including gravimetric results

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Contents

1. Introduction

This document summarizes the part of the results of Task 4.2: Comparison, selection, validation and optimisation of cleaning techniques for primary mass standards, which leads to Deliverable D4.2.4: Report describing the application of the cleaning procedures to kilogram mass standards including gravimetric results. Measurements leading to these results were conducted at the MGRT. Results of other partners (NPL, CNAM, MIKES and METAS), which also studied aspects of application of the cleaning procedures to mass standards including gravimetric analyses of the results are summarized in the report for Deliverable D4.2.1 [1]. The aim of this activity was to compare and validate various techniques for effective and repeatable cleaning of primary mass standards in order to select the most optimal and appropriate one. MGRT undertook the validation of BIPM nettoyage-lavage, ultrasonic bath in solvent, UV/ozone and hydrogen plasma cleaning procedures using stainless steel and platinum-iridium mass standards and gravimetric measurements on a mass comparator.

2. Experimental procedure

The experimental procedure was designed and executed according to Procedures for cleaning primary mass standards [2]. Four different cleaning techniques were used for cleaning of stainless steel and platinum-iridium standards. Besides two contact cleaning techniques, the nettoyage-lavage procedure and ultrasonic bath in ethanol, two new non-contact cleaning techniques were used, UV/ozone and low pressure hydrogen plasma. Gravimetric measurements were performed on a mass comparator before and several times after the cleaning in order to study the effectiveness of the cleaning procedures and the stability of mass of the standards after the cleaning. Initial cleaning trials were performed on naturally contaminated standards and afterwards, the standards were artificially contaminated in order to be able to perform further study of the cleaning procedures.

2.1 Cleaning procedures

2.1.1 BIPM nettoyage-lavage

The BIPM nettoyage-lavage cleaning procedure was carried our according to [3]. The first cleaning stage of the process, which is shown on Figure 1 (left), consisted of rubbing the standard with a natural chamois leather cloth soaked in the mixture of equal parts of diethyl ether (Sigma-Aldrich, purity ≥ 99,8 %) and ethanol (Sigma-Aldrich, purity ≥ 99,8 %). The second stage of the process, shown on Figure 1 (right), consisted of washing the standard with bidistilled water steam jet.

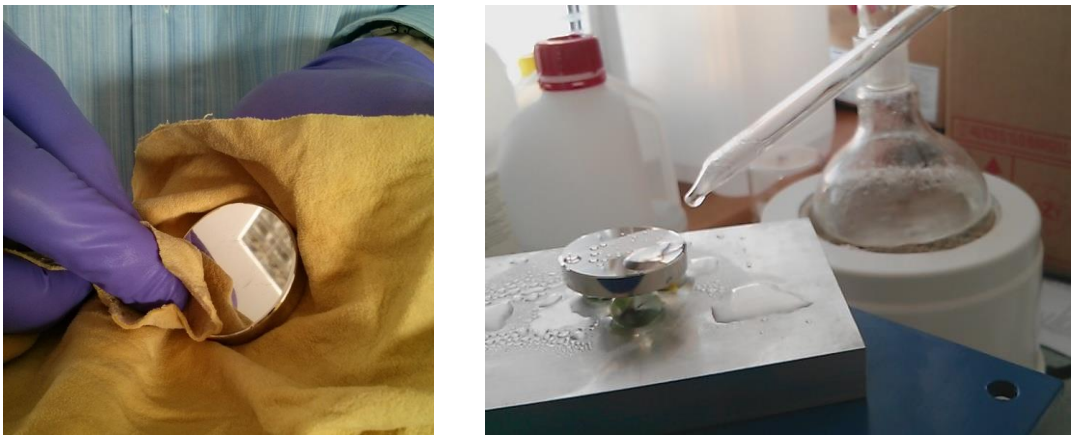

Figure 1: Cleaning with chamois leather cloth soaked in ether-ethanol mixture (left) and washing with bidistilled water steam jet (right).

2.1.2 Ultrasonic bath in ethanol

The first cleaning stage consisted of washing the standard in solvent in an ultrasonic bath. The ultrasonic bath used was 250 W Iskra PIO model 2 GT. The solvent used was ethanol (Sigma-Aldrich, purity ≥ 99,8 %). The platinum-iridium disc standards were placed horizontally inside an ethanol filled glass beaker which was then placed in the bath. The stainless steel standards were suspended into the beaker using a thin nylon filament as show on Figure 2 (left). The bath was operated for a period of 5 minutes. The second stage of cleaning process involved rinsing the standard with bidistilled water. Bidistilled water was poured over each surface of the standard in copious amounts for about 5 minutes as shown on Figure 2 (right). The remaining water droplets were wiped off with a lint free tissue. Then the weight was left to dry for at least 48 hours.

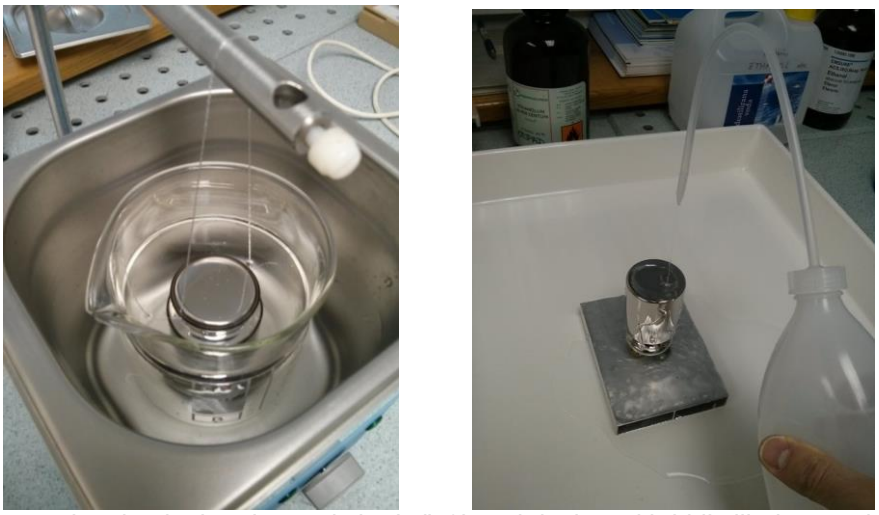

Figure 2: Cleaning in the ultrasonic bath (left) and rinsing with bidistilled water (right).

2.1.3 UV/Ozone

The apparatus for UV/ozone cleaning (Figure 3) was designed and manufactured for MGRT based on the design introduced in [4]. The apparatus consisted of a 115 L cylindrical steel chamber equipped with a valve to control the gas flow of air. Compressed air was supplied from a gas cylinder into the chamber at the flowrate 1 L/min. A charcoal filter was included in the exhaust line from the chamber to absorb and neutralize the ozone before exhausting to the environment. One pen ray and one grid low-pressure mercury UV lamp (Ultra Violet Products) emitting radiation at 254 nm and the ozone-generating 185 nm were used. The UV intensity at the position of the standard was 20 mW/cm^2 for pen ray lamp and 43 mW/cm^2 for grid lamp [5]. The distance between the standard and the lamps was kept at around 1 cm. The average concentration of ozone was 80 ± 5 ppm, measured by an ozone analyser (Thermo SCIENTIFIC, Model 49i). The exposure time for each section of the surface, if the standard was rotated (for 30 °), was 30 min, altogether 6 hours for full cleaning cycle.

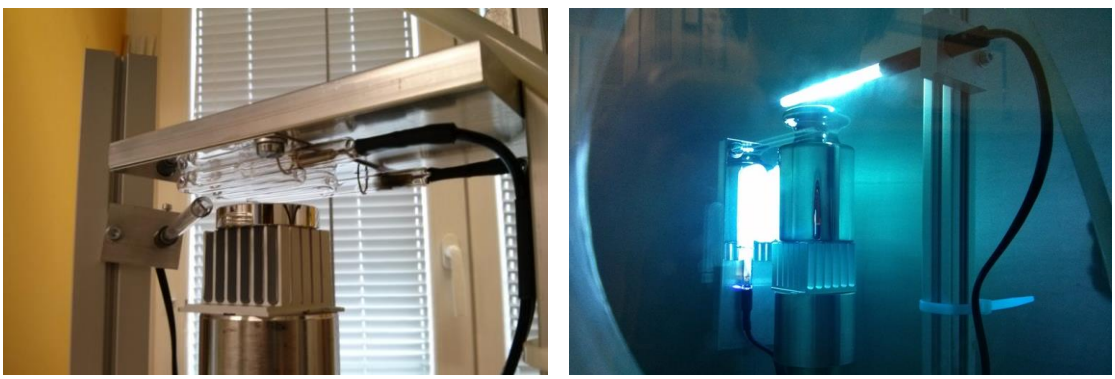

Figure 3: Platinum - iridium disc standard (left) and stainless steel standard (right) in the UV/ozone apparatus

2.1.4 Hydrogen plasma

The low pressure plasma cleaning experiments were performed using a commercial Diener Pico plasma system (Figure 4) with 40 kHz, 200 W plasma generator. During the cleaning process the pressure in the 5 L plasma chamber was kept at 0,7 mbar. High-purity hydrogen gas (Messer, 99,999 %) was supplied from a gas cylinder. Applied exposure time for the plasma cleaning cycle was 30 minutes.

Figure 4: Diener Pico plasma system (left) and cleaning of stainless steel standard with hydrogen plasma (right).

2.2 Mass standards

Three 1 kg stainless steel standards and two 200 g platinum-iridium standards were used as standards to be cleaned. Detailed information about their properties is given in Table 1.

Table 1: Data about the standards

Nominal mass	Identification	Material	Density	Shape
1 kg	LM-041	Stainless steel	8009,7 kg/cm^3	Cylinder with knob
1 kg	LM-044	Stainless steel	8050,6 kg/cm^3	Cylinder with knob
1 kg	LM-006 *	Stainless steel	7963,4 kg/cm^3	Cylinder with knob
200 g	D 1	Platinum-iridium	21543,02 kg/cm3	Disc
200 g	D 4	Platinum-iridium	21542,54 kg/cm3	Disc

The 1 kg standards have been moderately used in the MGRT mass laboratory as working standards for more than 15 years. The 200 g standards were used at NPL. The standards have never undergone any cleaning except removal of visible dust particles from the standards using a soft brush. Cleaning procedures were also performed on a tungsten and two silicon standards but due to standard deviation of mass measurements above 10 µg further cleaning cycles were terminated.

2.3 Gravimetric measurements

Sartorius CC1000 S-L mass comparator (resolution 1 µg, typical pooled standard deviation 2 µg at 1 kg) was used for gravimetric comparison of the standards against stable reference standards. Standards and reference standards were always placed on the same position of weight exchange mechanism to avoid any eccentric loading error. Mass of the standards was determined by at least three series of five ABBA comparisons with two reference standards. Mass difference between the two reference standards was also monitored during each series of measurements to account for any deviations of reference standards. Standard uncertainty of all relative mass measurements of stainless steel standards was approximately 4 µg.

2.4 Contamination

Initial measurements on platinum-iridium standards were performed with natural contamination which originated from regular use of the standards in NPL for the last 10 years. Afterwards, artificial contamination was applied to the standards. The artificial contamination was applied by rubbing the standard with a new chamois leather cloth, impregnated with a small quantity of hydrocarbon mineral oil (Pfeiffer, P3) commonly used in the rotary vane vacuum pumps. The target was to apply a suitable layer of contamination, e.g. 50 µg to 100 µg for the stainless steel standards and 20 µg to 40 µg to the surfaces of the platinum-iridium standards. Only a single surface of the standard was contaminated, i.e. the upper disc surface of the platinum-iridium standards and the side of cylinder of the stainless steel standards, for practical reasons which is handling of the weights and avoiding the contamination of the load receptor and weight handler on the comparator.

2.5 Measurement procedure

Initially, the mass of the standard to be cleaned was measured against the stable reference standards. Then the standard was cleaned using one of the selected procedures and parameters described above (§ 2.1). After leaving the standard for a period of 48 hours to stabilize, the mass of the standard relative to the stable reference standards was measured again and the mass change due to cleaning was calculated. The entire cleaning and measurement process was repeated again to confirm that all the contamination has been cleaned from the standard and to assess the repeatability of the cleaning processes. Gravimetric measurements of the cleaned standard against the reference standards were repeated several times in the period of one month after the last cleaning.

3. Measurement results

The results of gravimetric measurements for each evaluated cleaning procedure are summarized on Figures Figure **5** to Figure 13. The figures present the mass change of the standards in relation to the evaluated cleaning procedure. Each data point on the chart represents the change in mass of the standard relative to the mass of the standard before applying the contamination to it. The change in mass after the contamination is not presented on the charts in order not to lose the readability of the charts. The additional mass applied to the standard by artificial contamination is noted in brackets in the legend of the charts. Chart data points with solid fill present measurements after the cleaning cycle and data points with no fill present repeated measurements. The measurement results are not presented as “mass per surface” (µg/cm^2) because the standards were not contaminated over the whole surface for reasons mentioned above (§ 2.4). The measurement results were evaluated according to two criteria. The first was the effectiveness of each individual cleaning procedure in removing the contamination and the second was the stability of mass of the standard after the last cleaning cycle.

3.1.1 BIPM nettoyage-lavage

Gravimetric measurements on the stainless steel standard with 95 µg of applied contamination, cleaned twice with BIPM nettoyage-lavage procedure, are presented on Figure 5. The second cleaning cycle removed additional mass compared to the first cleaning cycle, but it still did not return to the initial mass value, i.e. the mass value before contamination. In the span of 76 days after the second cleaning cycle three mass measurements results were within 0,5 µg. This shows very stable mass of the standard after the cleaning cycle procedure.

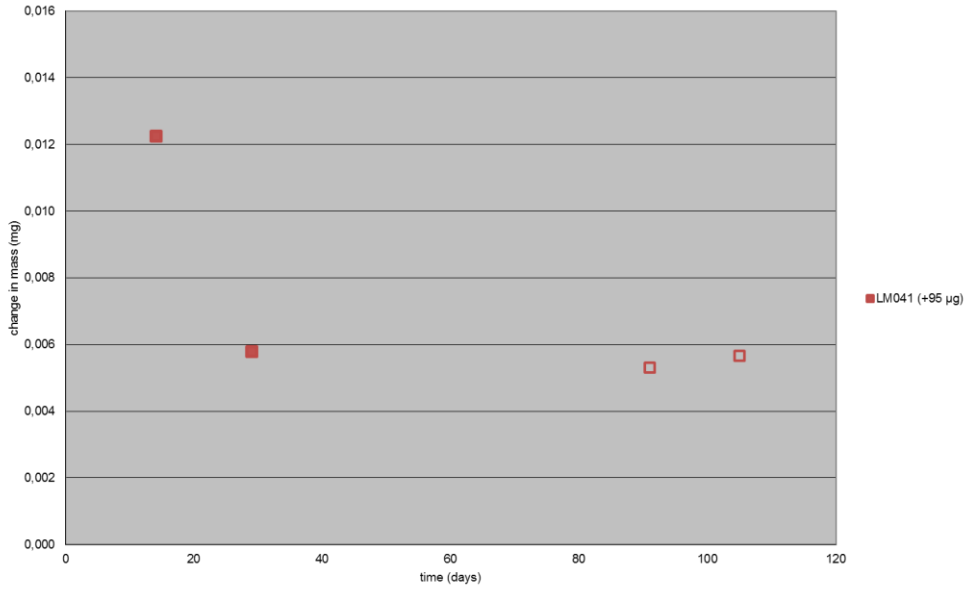

Figure 5: Change in mass of stainless steel standard during the BIPM nettoyage - lavage cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

Gravimetric measurements on the platinum-iridium standard with 27 µg of applied contamination, cleaned twice with BIPM nettoyage-lavage procedure, are presented on Figure 6. The second cleaning cycle didn't not make any significant difference in mass of the standard compared to the first cleaning cycle. The negative change in mass is attributed to the additional removal of contamination, which was not removed by previous cleaning procedure before applying the contamination. Similarly to the stainless steel standard, a good stability of platinum-iridium standard was obtained after the cleaning cycle. All the mass measurements in the span of 50 days were within 2,3 µg, which is well within standard uncertainty of the measurements.

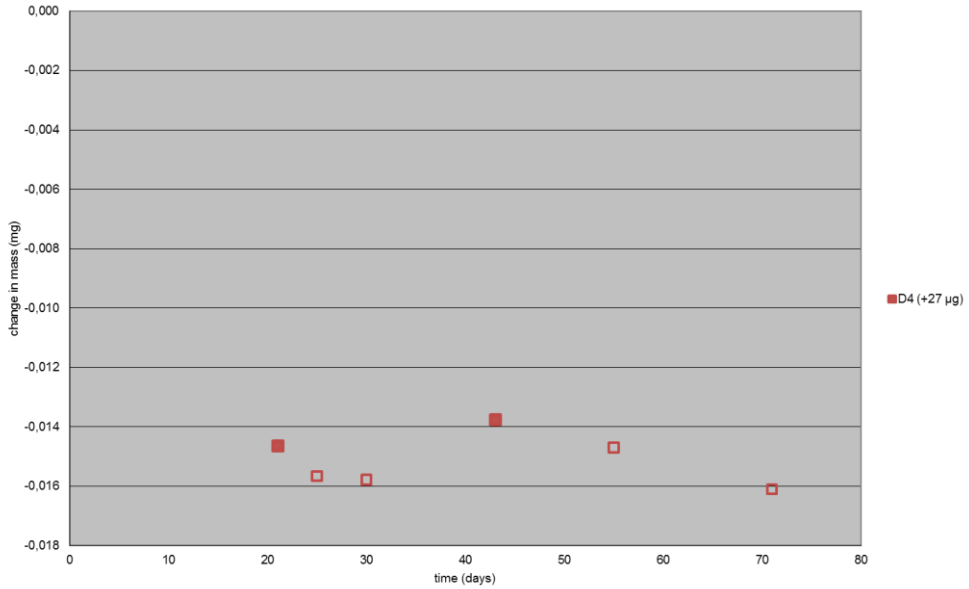

Figure 6: Change in mass of platinum-iridium standard during the BIPM nettoyage - lavage cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

3.1.2 Ultrasonic bath

Gravimetric measurements on two stainless steel standards with 41 µg and 71 µg of applied contamination, cleaned twice with the ultrasonic bath in ethanol, are presented on Figure 7. It can be observed that for heavier contamination two cleaning cycles were necessary, as for lighter contamination only one cleaning cycle was sufficient. Concerning the stability of the mass, after the second cleaning cycle good stability of the mass was observed. The measurement results were in the range of 2 µg in the span of 100 days, and in the range of 6 µg in the span of 40 days.

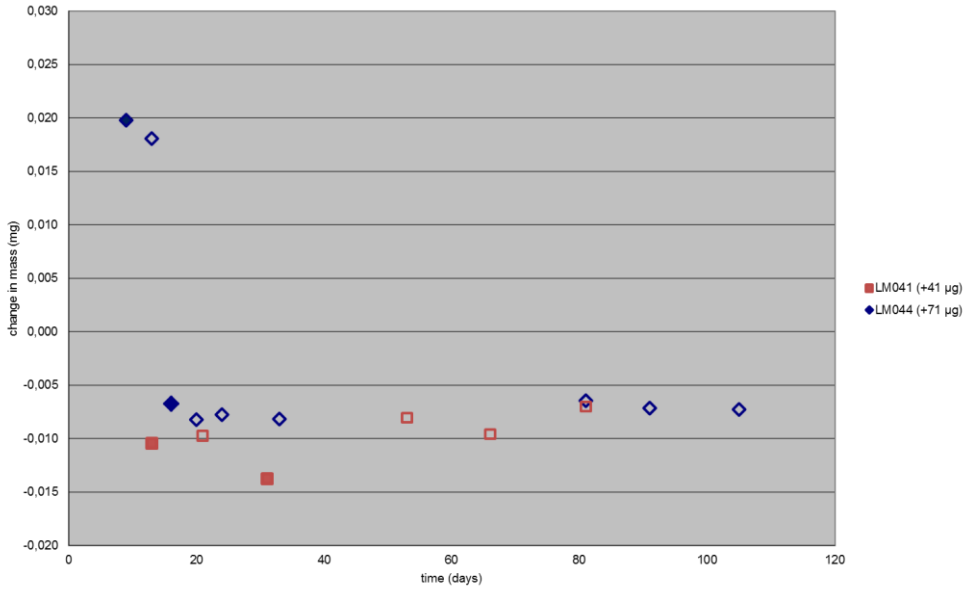

Figure 7: Change in mass of stainless steel standard during the ultrasonic bath cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

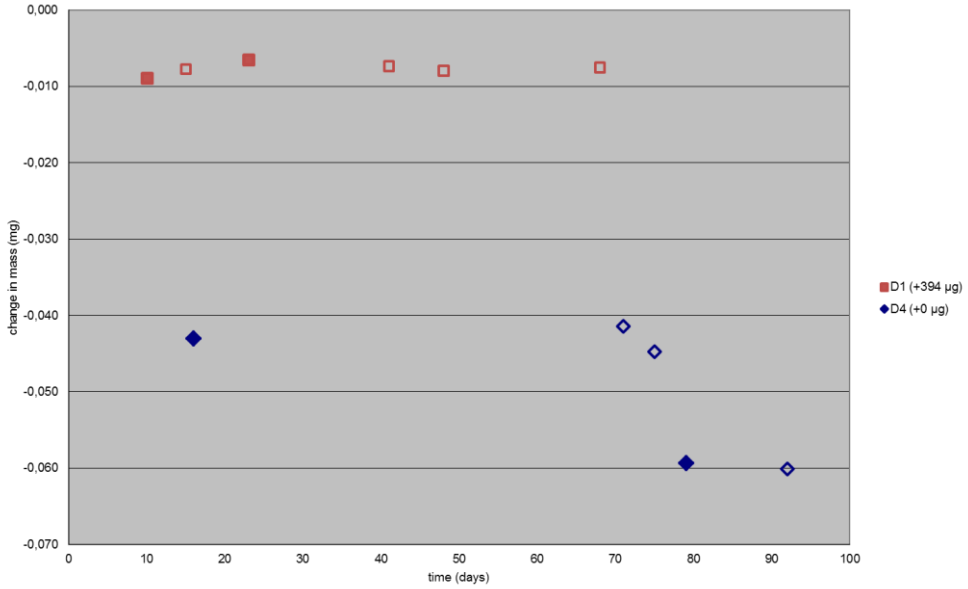

Figure 8: Change in mass of platinum-iridium standards during the ultrasonic bath cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

Gravimetric measurements on two platinum-iridium standards, one with a very heavy artificial contamination of 394 µg and the second one with natural contamination, cleaned with the ultrasonic bath in ethanol, are presented on Figure 8. It can be observed that for heavier contamination one cleaning cycle was necessary to remove the majority of contamination, whereas for the naturally

contaminated standard two cleaning cycles were necessary. Similarly to the stainless steel standard, we also got good stability of mass after the cleaning cycle. In the span of around 50 days we got measurement results in the range of 1,4 µg for first standard and 3,3 µg for the second one.

3.1.3 UV/ozone

Gravimetric measurements on the stainless steel standard with 50 µg of applied contamination, cleaned twice with UV/ozone, are presented on Figure 9. It was observed that second cleaning cycle did not remove any more contamination than the first one and that mass of the standard gradually increased after the cleaning, roughly 8 µg in 50 days. Observation confirms previous findings in [6,[7], where increase of mass could be attributed to growth of oxides on the surface of the standards. The measurements results from MIKES [8] and NPL [9] show similar rate of increase in mass after the cleaning.

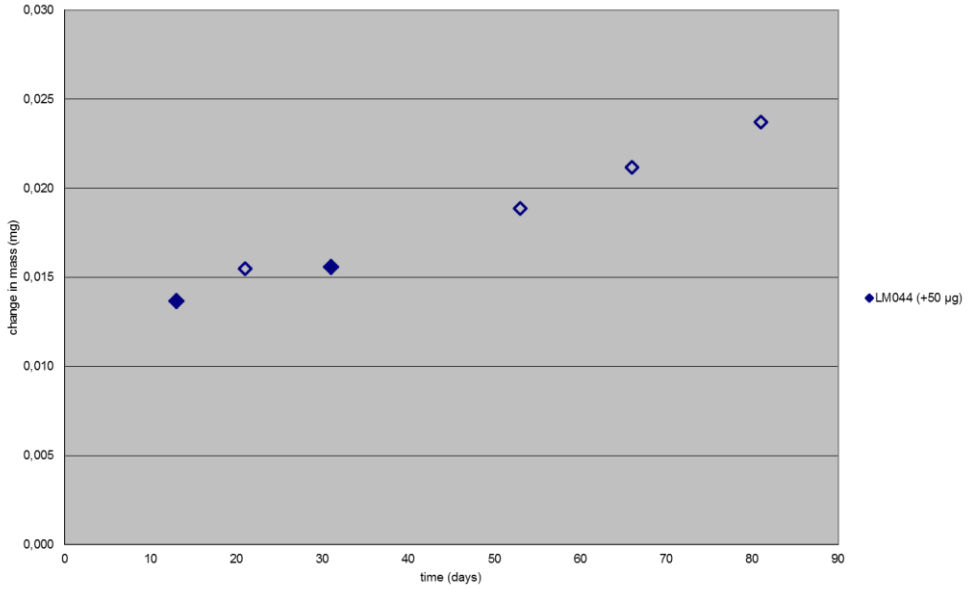

Figure 9: Change in mass of stainless steel standard during the UV/ozone cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

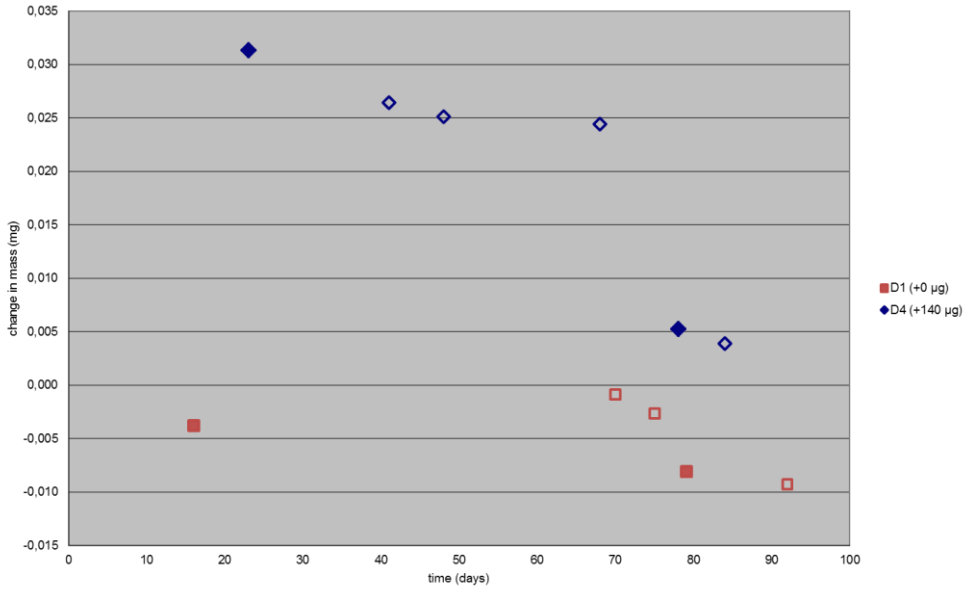

Figure 10: Change in mass of platinum-iridium standard during the UV/ozone cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

Gravimetric measurements on two platinum-iridium standards, one with very heavy artificial contamination of 140 µg and the second with natural contamination, cleaned with UV/ozone, are presented on Figure 10. It was observed that for the heavier artificial contamination two cleaning cycle were necessary to remove majority of contamination, whereas for the natural contamination one was enough. After the cleaning, no increase in the mass of the standards was detected. The mass values stayed stable, or even a small initial decrease in the mass was noticed.

3.1.4 Hydrogen plasma

Gravimetric measurements on the stainless steel standards with contaminations between 127 µg and 188 µg, cleaned twice with hydrogen plasma, are presented on Figure 11. We can clearly observe that in the first sequence of cleaning cycles (the data points marked as squares and circles) the first cleaning cycle removed majority of the contamination, repeated weighing and weighing after the additional cleaning cycle shows gradual increase in mass, on average 36 µg over the whole procedure. The second sequence of cleaning cycles (the data points marked as triangles and diamonds) shows less effective removal of contamination than the first cleaning sequence and also increase in mass, on average 14 µg over the whole sequence.

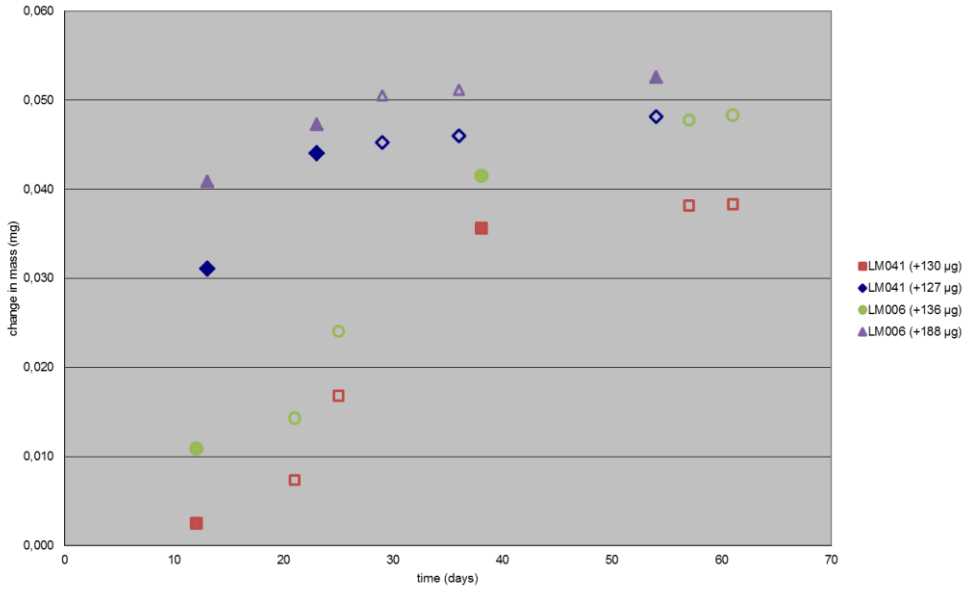

Figure 11: Change in mass of stainless steel standards during the hydrogen plasma cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

Cleaning cycles and gravimetric measurements on the stainless steel standard LM006 were also performed at METAS [10] and NPL (Figure 12). The repeated hydrogen plasma cleaning cycles for 45 minutes in METAS resulted in mass increase. Second cleaning cycle resulted in increase of 3 µg and third cleaning cycle resulted in mass increase of 11 µg relative to the mass after first cleaning cycle. XPS analysis revealed large amount of oxygen (O 1s at 531 eV). SiO_2 was found at 103 eV and 154 eV. Cu was found at 933 eV and 953. A shift of F1s at 687 eV is observed. The contamination with carbon was low. The substrate (Fe 2p at 707 eV and 720 eV) could not be detected. XPS analysis showed that multiple sets of hydrogen plasma cleaning cycle reduced the natural contamination but the oxides could not be removed.

The same standard was then sent from METAS to NPL where repeated hydrogen plasma cleaning cycles resulted in decrease in mass of the same standard. Change in mass of the standard during the hydrogen plasma cleaning cycles is presented on Figure 12. After the first hydrogen plasma cleaning cycle the mass measured in vacuum decreased for around 23 µg and further two cleaning cycles made no significant difference, mass decreased only a few µg. Mass measured in the air was roughly the same as in the vacuum. Additional plasma cleaning cycle further decreased mass for 25 µg and next one increased for 9 µg. The last, 6^{th} cleaning cycle made no difference.

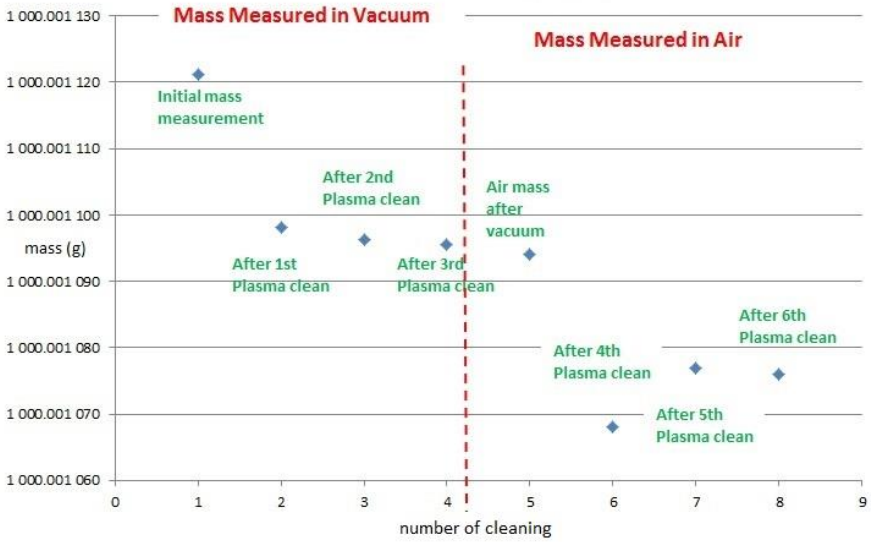

Figure 12: Change in mass of stainless steel standard LM006 during the hydrogen plasma cleaning cycles at NPL

The stainless steel standard LM006 was then returned back to MGRT and comparison to the same reference standards before it was sent to METAS and NPL revealed an increased in mass of the standard for 94 µg. Differences in behaviour of mass of the same standard after hydrogen plasma cleaning procedures at different NMI's suggest that there is also influence of the used apparatus on the outcome of the cleaning procedure, therefore there is a need for more detailed description of apparatus and cleaning procedure.

Gravimetric measurements on platinum-iridium standards with contaminations between 23 µg and 50 µg, cleaned twice with hydrogen plasma, are presented on Figure 13. In contrast to the results for stainless steel standards the mass of platinum-iridium standards after hydrogen plasma cleaning is very stable. All the mass measurements in the span of 50 days are within 2 µg which is well within standard uncertainty of the measurements. Effectiveness of removal of contamination varies; only one cleaning cycle of all three removed almost all the contamination.

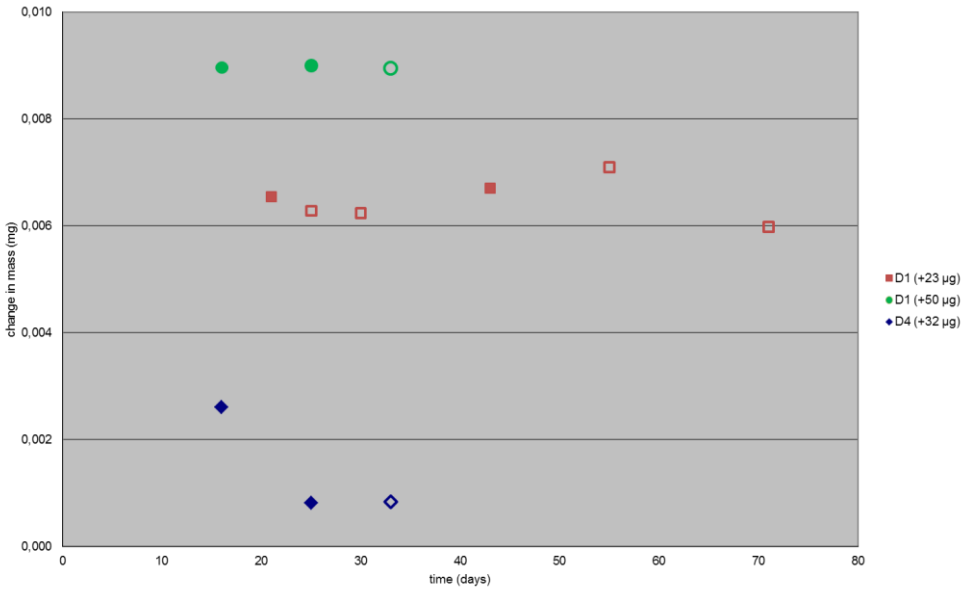

Figure 13: Change in mass of platinum-iridium standards during the hydrogen plasma cleaning cycles. Data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements.

3.1.5 Sequence of cleaning procedures

Figure 14 shows deviation from nominal mass of the platinum-iridium standard (D4) during the sequence of four different cleaning procedures: ultrasonic bath, UV/ozone, BIPM nettoyage-lavage and hydrogen plasma. Red data points present measurement results after applied contamination (data point for UV/ozone is off the chart, + 1,466 mg), data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements. Two observations could be made. The first one is that BIPM nettoyage-lavage and hydrogen plasma cleaning procedures produced similar results. Both were effective in removing contamination in the first cleaning cycle and gave good stability of mass after the cleaning. The second one is that ultrasonic bath in ethanol and UV/ozone cleaning procedures were less effective as it took two cleaning cycles to remove majority of the contamination in case of ultrasonic bath and for UV/ozone there was around 15 µg of contamination left on the surface of the standard. Probably a third cleaning cycle would be needed to remove majority of the contamination since the applied contamination was 140 µg, relatively higher contamination than for other cleaning procedures.

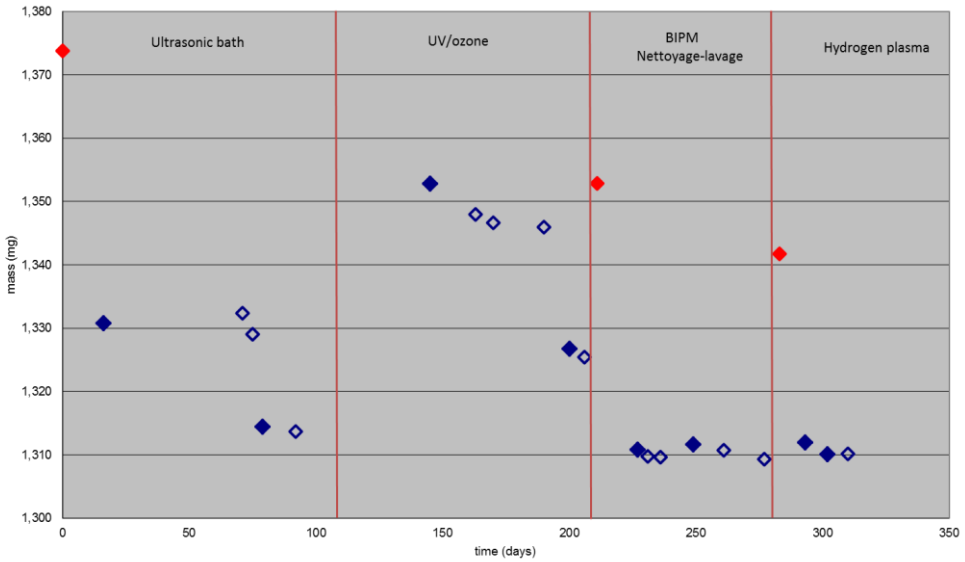

Figure 14: Deviation from nominal mass of platinum-iridium standard (D4) during the sequence of different cleaning procedures. Red data points present measurements after applied contamination (data point for UV/ozone is off the chart, + 1,466 mg), blue data points with solid fill present the measurements after the cleaning cycle and blue data points with no fill present repeated measurements.

Figure 15 shows deviation from nominal mass of the stainless steel standard (LM041) during the sequence of different cleaning procedures. Red data points present measurement results after applied contamination (data point for plasma cleaning cycles are off the chart, - 0,017 mg, + 0,019 mg), data points with solid fill present the measurements after the cleaning cycle and data points with no fill present repeated measurements. BIMP nettoyage-lavage and ultrasonic bath procedures gave good stability of mass after the cleaning. Regarding the effectiveness, it can be seen that both procedures removed majority of contamination, ultrasonic bath compared to BIPM nettoyage-lavage removed additional 8 µg. The first cleaning cycle with hydrogen plasma removed applied contamination to the same level as ultrasonic bath but subsequent cleaning cycles result in an increase of mass.

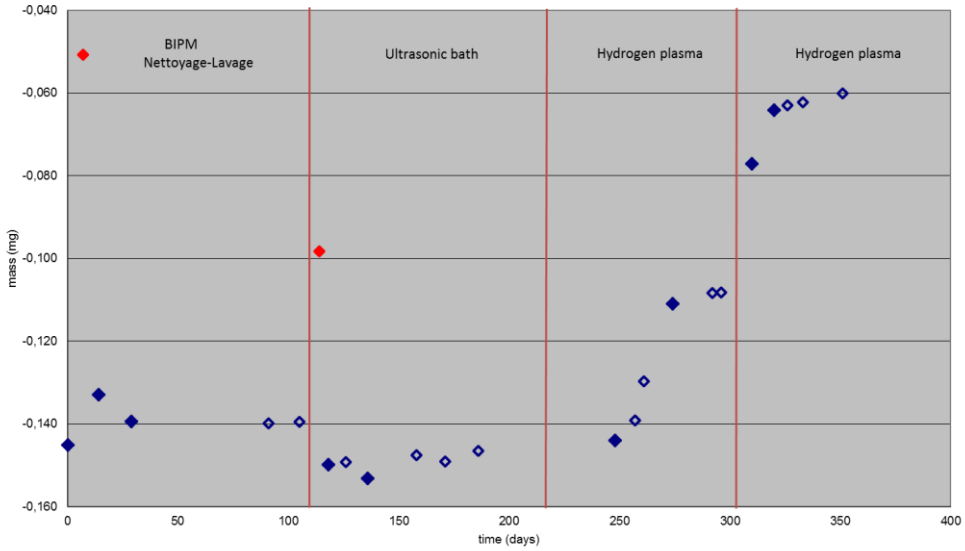

Figure 15: Deviation from nominal mass of stainless steel standard (LM-041) during the sequence of different cleaning procedures. Red data points present measurements after applied contamination (data point for plasma cleaning cycles are off the chart, - 0,017 mg, + 0,019 mg), blue data points with solid fill present the measurements after the cleaning cycle and blue data points with no fill present repeated measurements.

4. Conclusion

Overall we can conclude that the BIPM nettoyage-lavage cleaning procedure was efficient in removing contamination and gave very good stability of the mass standard after the cleaning for both stainless steel and platinum-iridium standards. With higher levels of contamination the cleaning procedure should be repeated to remove any remaining contamination.

The ultrasonic bath in ethanol cleaning procedure gave similar results. Stability after the cleaning was very good for both types of used standards. In two instances the second cleaning cycle removed additional mass which suggest that the cleaning time of 5 minutes is not sufficient to remove majority of the contamination. Based on the results we propose the cleaning time of 10-15 minutes.

The UV/ozone cleaning procedure was the most time consuming of all four procedures. Gradual increase of the mass of stainless steel standards after the cleaning proved as a main disadvantage compared to the BIPM nettoyage-lavage and the ultrasonic bath in ethanol cleaning procedures. For the platinum - iridium standards the stability and effectiveness was comparable to the other three cleaning procedures.

The hydrogen plasma cleaning procedure proved to be the least appropriate for cleaning of stainless steel standards because repeated cleaning cycles resulted in an increase of the mass. Differences in behaviour of mass of the same standard after hydrogen plasma cleaning procedures at different NMI's also suggest that there is also influence of the used apparatus on the outcome of the cleaning procedure; therefore there is a need for more detailed description of apparatus and cleaning procedure. For platinum – iridium standards the hydrogen plasma cleaning procedures produced similar results as the BIPM nettoyage-lavage and the ultrasonic bath in ethanol, i.e. efficient cleaning and very good stability of mass after the cleaning cycle.

The artificial contamination procedure based on mineral oil was used in the procedures. The results and conclusions on effectiveness of each individual cleaning procedure could be partially influenced by the fact that during the procedure of artificial contamination some components different from hydrocarbons could have been applied on the standards.

5. References

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