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TABLE OF CONTENTS

1 Executive Summary

Introduction

In 2018 the kilogram will be redefined in terms of a fundamental constant of nature rather than being defined by a physical object. The redefinition will be realised in a vacuum, but will have to be transferred and disseminated under in-air conditions. The unit of mass, the kilogram, is currently defined as the mass of the International Prototype Kilogram, which makes the maintenance and dissipation of the unit, undertaken in air, relatively straightforward. This project developed next generation mass standards, new methods to store, clean and monitor mass artefacts, and procedures and equipment for the transfer of mass artefacts between vacuum and other media, and identified and evaluated the uncertainty components inherent in the *mise-en-pratique* for the kilogram, in order to minimise any uncertainties introduced into the dissemination of mass following the redefinition. The results of this project will help ensure the redefinition is successful, and that the kilogram can be disseminated to National Measurement Institutes and end users with the highest degrees of accuracy achievable.

The Problem

The kilogram, the SI base unit of mass upon which all mass measurements made globally are ultimately based, is currently defined by a platinum-iridium cylinder kept in Sèvres near Paris, known as the International Prototype Kilogram (IPK). In 2018 the definition will change, and the kilogram will be redefined in terms of a fundamental constant of nature, rather than a physical artefact. The redefinition will fix the value of the Planck constant and either the Kibble (watt) balance approach can be used to realise the unit of mass in terms of the fixed Plank constant, or the X-ray crystal density approach can be used to realise the unit of mass via the Avogadro constant (and thus with relation to the fixed Planck constant).

Although the definition will no longer be based on a physical artefact, artefacts will still be used as transfer standards, to transfer the definition from the location in which it is realised to National Measurement Institutes (NMIs) around the world and eventually to end users. To ensure the continuity of the global mass scale following the redefinition, the redefined value must also be based on the IPK, i.e. the exact proportion of the Planck and/or Avogadro constant must be chosen that results in the same mass value as the IPK.

The IPK and its copies are currently stored under in-air conditions and most mass measurements are performed in air, however the redefinition will be realised in a vacuum (both the Kibble balance and X-ray crystal density approaches are performed in a vacuum). This means that the IPK must be transferred between in-air and vacuum conditions in order to fix the redefinition to the IPK, and that mass standards must be moved from vacuum to in-air conditions to disseminate the redefinition to NMIs. These different environmental conditions will influence the value of the standards, and will introduce a degree of inaccuracy and uncertainty into the process by which the kilogram is disseminated via physical standards. In addition, Kibble balances produce strong magnetic fields, so mass standards to be used with Kibble balances must be non-magnetic.

The Solution

The project aimed to develop and provide the practical infrastructure, procedures and technologies necessary to fix the Planck constant with relation to the current definition (IPK) and to disseminate the mass unit following redefinition. This was addressed by the following objectives;

- Develop and evaluate artefacts suitable for the determination of the Planck and the Avogadro constants to provide traceability to the IPK and to maintain and disseminate of a redefined kilogram
- Provide appropriate procedures and apparatus for the mass transfer between in-vacuum experiments (Kibble balance apparatus and vacuum mass comparators) and to in-air experiments (comparison with the IPK and dissemination of the unit to end-users)
- Develop and adapt surface analysis techniques (e.g. X-Ray Photoelectron Spectroscopy, (XPS), Ellipsometry, Contact Angle Spectrometry, (CAS)) and overlayer models for the accretion of contamination on mass standards (including silicon spheres), including the use of complimentary surface analysis techniques to evaluate transfer, storage and cleaning techniques

- Evaluate the mass stability of suitably stored mass artefacts and develop the metrological infrastructure for the (medium term) maintenance of the mass unit and its dissemination based on different realisations (via a pool of artefacts which may be held at a number of NMIs and key comparisons)
- Develop and validate methods to allow reproducible cleaning (to less than 5 µg) of primary mass artefacts, including optimisation and comparison of non-contact cleaning techniques (such as the use of UV activated ozone and gas plasma) with traditional solvent and nettoyage-lavage method
- Identify and evaluate the uncertainty components inherent in the *mise-en-pratique* and their propagation through the dissemination chain for the kilogram and its multiples and sub-multiples

Impact

This project has developed the practical infrastructure and procedures to successfully implement the kilogram redefinition and the subsequent maintenance and dissemination of the unit of mass. Next generation mass standards with high-quality surfaces, low magnetic susceptibility, and good stability have been manufactured and evaluated. Major weight manufacturers have been engaged in the process in preparation for the provision of new mass standards compatible with the dissemination of the mass unit from primary realisation experiments. Protocols for the transfer of weights from vacuum to air have been developed and optimum operating pressure ranges for Kibble balances and vacuum mass comparisons have been published. The design of vacuum/inner gas storage/transfer vessels and a report on compatible vacuum mass comparators and equipment has formed the basis of a new generation of “weighing in vacuum” equipment being developed by the major balance manufacturers. The stability of mass standards stored in various media has been evaluated and this will assist future developments necessary to maintain traceability to the mass scale after redefinition (e.g. via the BIPM *ensemble of mass standards*). The complimentary use of a wide range of surface analysis techniques has improved the characterisation of the surfaces of mass standards to a level where they can be used to deterministically predict changes in their mass values. Rigorous uncertainty analysis has been carried out on the processes that will be involved in the dissemination of the redefined kilogram, most notably the additional vacuum to air transfer step. Results have also informed the development of the written *mise-en-pratique* for the redefined kilogram by the Consultative Committee for Mass (CCM), the instructions that will allow the redefinition to be realised in practice in NMIs. The way in which surface sorption corrections are measured and applied to this stage has been evaluated and guidance, including 2 Good Practice Guides, has been provided on issues affecting the calculation of the associated uncertainty.

Guidance, papers and reports regarding the technical aspects of the project has been produced and disseminated and in addition more general details of the redefinition of the kilogram has been made available to the mass measurement community. The project’s results and outputs were presented in detail at a workshop attended by over 60 participants from NMIs, industry and academia, ensuring wide dissemination to the scientific community and good take up of best practice among EURAMET members. 20 peer reviewed publications have been produced, some covering the technical aspects of the project but some also addressing the dissemination of information to a wider audience, together with 4 articles published in trade journals or popular media and a further 3 articles published on non-project external websites.

2 Project context, rationale and objectives

2.1 Context

The unit of mass, the kilogram, is the last of the seven base units of the International System of Units (SI) to be defined in terms of a material artefact rather than by relation to an invariant of nature. Progress has been made towards a redefinition of the kilogram in terms of the Planck constant (h), realised via the Kibble balance and Avogadro experiments, and the International Committee for Weights and Measures (CIPM) has targeted the 2018 meeting of the General Conference on Weights and Measures (CGPM) for the ratification of the redefinition. In order for this to be feasible, a practical means of linking the new definition to the current mass scale must be in place. Procedures necessary to provide this link at the required uncertainty (<1 in 10^8) and to ensure the continuity of the worldwide mass scale are therefore required, as without them the uncertainty with which the Planck constant can be fixed (target 2 parts in 10^8) will be compromised and furthermore it will not be possible to disseminate the benefits of a redefined kilogram to the worldwide mass user community. The preparation of the redefinition of the kilogram based on the Planck constant, its practical realisation, maintenance and dissemination are probably the most challenging tasks for mass metrology since the implementation of the present system of prototypes of the kilogram at the end of the 19th century.

In order to ensure the continuity of the worldwide mass scale the Consultative Committee for Mass and Related Quantities (CCM) developed recommendation G1(2010) that the following *mise-en-pratique* conditions (relevant to this project) be met before the kilogram is redefined:

- To be able to fix the Planck constant with relation to the International Prototype Kilogram (IPK) with minimum uncertainty and thus redefine the way in which the unit of mass is realised. The target uncertainty for fixing the value of the Planck constant is 2 parts in 10^8, (due to the uncertainty in the realisation from the Kibble balance and Avogadro (X-ray crystal density based) experiments). The uncertainty contribution due to the provision of traceability to the IPK should not contribute significantly to this uncertainty and therefore needs to be less than 1 in 10^8 (10 µg for a 1 kg standard).
- To provide a means of disseminating a redefined kilogram realised in vacuum, to the mass user community operating under ambient conditions at the uncertainty levels required. As the IPK currently has an uncertainty of zero and dissemination takes place entirely in air, the current best level of uncertainty provided to the mass user community is about 15 µg on a 1 kg stainless steel mass standard ($k=1$). It is necessary to ensure that the dissemination of the mass scale from the redefinition experiment(s) does not significantly increase the uncertainty with which the unit is realised (2 in 10^8) and that provides a level of uncertainty commensurate with that required by the mass community (~25 µg at $k=1$).
- To deliver a means of providing continuous access to the mass scale following the redefinition without the need to refer to the (group of) primary realisation experiments. This may be achieved with a pool of mass standards, of different materials and stored under different conditions, which continuously maintain the scale and provide ad-hoc access for top-level calibrations.

To achieve an uncertainty for traceability to the IPK of less than 10 µg (1 in 10^8) in order to fix the value of the Planck constant with relation to the current mass scale, to provide a means of disseminating a redefined kilogram to the mass user community and to deliver a means of providing continuous access to the mass scale following redefinition, the (presently unknown) uncertainty components for air/vacuum transfer and for transportation of mass standards under vacuum or inert gas (including nitrogen) conditions must be investigated and minimised and the most appropriate materials and finishing techniques for new more stable mass standards identified and quantified. Techniques and procedures to clean and store primary mass standards must be optimised and complimentary methods to monitor surface cleanliness and relate it to changes in the mass of the standards must be developed and well understood.

2.2 Rationale

This project addressed the new requirements that will result from the redefinition of the unit of mass in order to ensure the continuity of the global mass scale before and after the redefinition of the kilogram and to allow the effective dissemination of the mass unit to end users. The dissemination of the new realisation of the kilogram at NMI level must be achieved with uncertainties smaller than the required relative uncertainty of the realisation (2×10^{-8}) in order to ensure that existing uncertainties can be maintained or improved for end users. The project also addressed the fundamental limitations in the maintenance and dissemination of the unit of mass, i.e. the stability of the artefact mass standards. The output of this project will help to ensure that the full impact of the redefinition of the SI unit of mass can be realised in practice by facilitating access to the mass scale.

Mass standards

The current state-of-the-art for mass standards is represented by the construction of the International Prototype Kilogram which is a cylinder of platinum-iridium alloy. The use of platinum weights dates back to the end of the 18th century and the IPK and original national copies were manufactured in the 1880s. More recent national copies have been diamond turned rather than polished, which results in a slightly improved surface roughness ($R_z \approx 10$ nm compared with 20 nm for polished surfaces) but the construction remains largely unchanged. To provide traceability to Kibble balance and Avogadro experiments and to maintain the mass scale, next generation mass standards should have the following properties:

- Low magnetic permeability (<0.0002) to allow use on the Kibble balance experiment
- Good surface hardness (HV>200) to minimise surface wear during handling
- Easily machineable to allow a good surface finish ($R_z < 0.01$ µm)
- Low (and repeatable) surface sorption coefficient (<0.1 µg/cm^3)
- High density is also beneficial as the surface area (for sorption) is minimised and the air buoyancy correction is small.

One or more of these parameters can be met using current mass standards of platinum-iridium or stainless steel (and also silicon) but it is desirable to identify a material and finishing process which fulfils all parameters. The next generation mass standards not only need to be compatible with use on Kibble balance experiments and but also need to be optimised for transfer between air and vacuum and for stability when stored in vacuum or inert gas.

Vacuum-air transfer of mass standards

As the new definition of the kilogram will be realised under vacuum conditions, there will be at least one additional step in the dissemination chain, where a mass standard has to be transferred from vacuum to ambient air (with an optional intermediate storage under inert gas). To achieve this transfer without causing unpredictable changes in the masses of the transfer standards and unacceptable additional uncertainties, requires research and improved knowledge in the areas of materials, surface studies, surface behaviour in vacuum and inert gas.

Some previous experiments investigated the effect on mass standards of transfer between air and vacuum, however the results showed a wide variation in measured sorption effects (0.05 µg/cm^2 to 0.5 µg/cm^2) even when taking into account variations in materials and vacuum pressures. Furthermore, the underlying surface physics relating to these sorption effects (between 10 µg and 75 µg on a kilogram) is not understood and has not yet been investigated.

A protocol therefore needs to be developed and evaluated for the transfer of mass standards between air and vacuum which will minimise the effects of surface sorption and maximise repeatability. A typical sorption coefficient of 0.1 µg/cm^2 with an uncertainty of ±0.02 µg/cm^2 would result in a mass change of 8 µg and an associated uncertainty of 1.6 µg on a platinum-iridium cylinder and 20 µg ± 4 µg for stainless steel. The surface sorption phenomena requires investigation to characterise the accreted overlayers on mass standards (or surface samples) in order to obtain improved knowledge of the underlying physics and enable identification of the optimum transfer process..

Surface analysis techniques applicable to mass standards

In order to develop a better understanding of the factors affecting the mass of weights such as contamination, accreted overlayers and surface properties including surface sorption phenomena, to obtain knowledge of the underlying physics and to quantify and characterise the state of mass standards, complementary surface analysis techniques (such as XPS, XRR, XRF, Ellipsometry, CA, TDS, Mirage effect) are required. Further knowledge is needed about the information that these techniques can provide with regard to the characterisation of mass standards and which are the most applicable for particular applications.

Stability of mass standards

The availability of stable mass standards is key to enabling the comparison of the new realisations of the kilogram with uncertainties better that 1 in 10^8, to ensure that the benefits of the new realisation are achieved and for dissemination of the mass scale. In the short to medium term it will also be necessary to rely on artefact based mass standards to ensure continual access to the SI unit of mass due to the limited number and complexity of the primary realisation experiments. This will be achieved, for example, via the BIPM Ensemble of Reference Mass Standards. Mass standards are vulnerable to damage and surface contamination and wear due to exposure to the environment, handling, storage and transportation. Better knowledge of the mass changes that occur and their causes, together with the ability to predict them and techniques to improve the stability of mass standards are all required.

Storage of mass standards

Mass standards are currently almost exclusively stored in filtered laboratory air. To date there has been limited investigation of the storage of weights under vacuum conditions. Up until now, it has not been possible to perform mass comparisons with artefacts permanently stored and transferred under vacuum or inert gas at different NMIs. In addition, a metrological infrastructure for the maintenance and dissemination of a redefined kilogram based on primary and/or secondary mass standards stored under different environmental conditions (vacuum, inert gas) and made of different materials with different surface properties does not exist. Such an infrastructure is required for the implementation of the redefined kilogram and for the future advancement of mass metrology.

Equipment necessary to store and transfer weights under inert gas therefore needs to be developed and the storage and transfer of mass standards under inert gas conditions investigated both gravimetrically and by surface analysis, with a view to improving the medium-term stability of primary mass standards (to better than 10 μg for periods of up to 10 years).

Cleaning of primary mass standards

Regardless of how carefully mass standards are stored and handled, contamination inevitably builds up on the surface over time. The cleaning of primary mass standards is essential to return them to a reference value and is routinely performed by the BIPM using the nettoyage-lavage process when national standard (platinum-iridium) kilograms are calibrated. Additionally the transfer of mass standards between air and vacuum and the additional handing required by a comparison of primary realisation experiments will increase the rate (and variability) of the accretion of surface contamination and necessitate more regular cleaning of the transfer standards than is normal practice. It is essential that the techniques used to clean these mass standards are repeatable both temporally and between institutes.

The kilogram is currently explicitly defined as the value of the IPK after cleaning. The currently accepted method for this cleaning is the nettoyage-lavage technique, the origins of which date back to 1882. The manual cleaning stage has been demonstrated to be extremely user dependant, which limits its application to the cleaning of platinum-iridium (PtIr) standards only at the BIPM. The technique is also likely to be, at least in part, responsible for the relative drift of the “cleaned” prototype kilograms (changes of tens of μg have been observed between nominally similar prototype kilograms). Current mechanical cleaning techniques such as nettoyage-lavage and solvent cleaning do not appear to offer the level of repeatability required (less than 5 μg) and new non-contact techniques using UV activated ozone and plasma must be optimised and evaluated to provide the level of repeatability required.

Uncertainties

It is essential that the implementation of the redefined kilogram does not disturb the continuity of the mass scale in terms of the traceability and uncertainties provided to end users. Accredited calibration laboratories and legal metrology institutes in most European countries demand uncertainties at the highest level (Organisation Internationale de Métrologie Légale (OIML) Class E1 and better), which can only be provided by NMIs with direct reference to the realisation of the mass scale (currently the International Prototype Kilogram). This in turn allows these bodies to provide calibrations at a level commensurate with the requirements of their customers. Additionally research laboratories, academia and industry (e.g. pharmaceutical, power generation, aerospace) require direct traceability to NMIs to achieve the uncertainties they require for research and product development and evaluation. Uncertainties vary from sub microgram for fractional (milligram) mass standards to 15 μg at the kilogram level. Such uncertainties can only be achieved if the current level of Calibration and Measurement Capabilities (CMCs) is maintained. Existing uncertainty components must therefore be reduced and additional components minimised. Additionally, as the uncertainty with which the (redefined) kilogram is improved the uncertainty in the dissemination of the unit needs to be minimised in order to fully benefit from these improvements.

This project has developed a practical means of comparing the existing mass scale and the new realisation experiments to ensure the continuity of the mass unit. This has been achieved by providing a means of accurately fixing the Planck (and Avogadro) constant with reference to the International Prototype Kilogram (IPK). The dissemination of the new realisation of the kilogram at NMI level must be achieved with uncertainty contributions smaller than the required (relative) uncertainty of the realisation (2×10^{-8}). Additionally issues with access to the new realisations, of which there will be a small number, required research into a means of maintaining a robust mass scale without the need for continuous reference back to these few primary realisation experiments.

2.3 Objectives

The overall aim of the project was to develop the practical infrastructure and procedures to successfully implement the kilogram redefinition, in particular (i) to ensure the continuity of the mass unit between existing and new realisations of the kilogram by providing a means of accurately fixing the Planck constant with reference to the International Prototype Kilogram (IPK) (Objectives 1, 2 and 5) and (ii) to develop the metrological infrastructure to enable the dissemination of the new realisation of the kilogram at the NMI level with uncertainty contributions smaller than the required uncertainty of the realisation ($u_{rel} < 2\times10^{-8}$ at k=1) (Objectives 1-6).

The project therefore aimed to:

1. Develop and evaluate artefacts suitable for the determination of the Planck and the Avogadro constants to provide traceability to the IPK and for the maintenance and dissemination of a redefined kilogram;
2. Provide appropriate procedures and apparatus for the mass transfer between in-vacuum experiments (Kibble balance apparatus and vacuum mass comparators) and to in-air experiments (comparison with the IPK and dissemination of the unit to end-users);
3. Develop and adapt surface analysis techniques (e.g. X-Ray Photoelectron Spectroscopy, (XPS), Ellipsometry, Contact Angle Spectrometry, (CAS)) and overlayer models for the accretion of contamination on mass standards (including silicon spheres), including the use of complimentary surface analysis techniques to evaluate transfer, storage and cleaning techniques;
4. Evaluate the mass stability of suitably stored mass artefacts and develop the metrological infrastructure for the (medium term) maintenance of the mass unit and its dissemination based on different realisations (via a pool of artefacts which may be held at a number of NMIs and key comparisons), including optimisation of the design of storage containers and evaluation of the benefits of the medium term storage (6 months) of mass standards in vacuum and inert gas;
5. Develop and validate new methods to allow the reproducible cleaning (to less than 5 µg) of primary mass standards, including optimisation and comparison of non-contact cleaning techniques (such as the use of UV activated ozone and gas plasma) with traditional solvent and nettoyage-lavage method;
6. Identify and evaluate the uncertainty components inherent in the *mise-en-pratique* and their propagation through the dissemination chain for the kilogram and its multiples and sub-multiples;
7. Disseminate information to relevant parties, including the Consultative Committee for Mass (CCM) who will develop the *mise-en-pratique* for the redefined kilogram and undertake a pilot study and subsequent comparisons of primary realisation experiments, and to provide guidance to the general scientific community regarding the management of the redefinition of the kilogram and on its potential impact on end users.

3 Research results

3.1 Development and evaluation of artefacts suitable to provide maintenance and dissemination of a redefined kilogram

3.1.1 Introduction

The overall aim of this work was to evaluate potentially suitable materials and to develop next generation mass standards which are compatible with use in Kibble balance experiments and that have optimised stability (a change of less than 1 in 10^8) for transfer to vacuum and storage in vacuum and inert gas (including dry nitrogen). To do this the work focussed on

- Investigation of materials and finishing techniques for next-generation primary mass standards compatible with use in vacuum and in Kibble balance experiments
- Production of kilogram artefacts based on the evaluation of materials

Potential materials for the fabrication of next generation mass standards need to be compatible with use in vacuum and in high magnetic fields and should offer mass stability at least as good as the current primary (platinum-iridium) standards. Materials evaluated included iridium, mono- and poly- crystalline tungsten, nickel-based super-alloy Udimet720 (U720) and a tertiary alloy of predominantly gold and platinum. Samples of gold and rhodium plated copper were also evaluated to identify if there were any potential benefits of using plated materials. The three materials currently used in the mass field for standards (platinum-iridium, stainless steel and silicon) were measured alongside the new materials.

3.1.2 Surface properties and charge retention of heat treated silicon samples

The surface properties of materials used for mass standards are critical in influencing the long-term mass stability and therefore the ultimate performance of the artefact. Silicon has many of the properties required for the Kibble balance experiment and is used in the realisation of the kilogram in the Avogadro project. This material has the potential advantage that natural oxides can be grown immediately on the silicon surface, which protects the surface from the surrounding environment. Research was undertaken to determine whether any significant differences in surface hardness exist between native and thermal oxides of different thicknesses.

The growth of (native or thermal) oxides on the surface of silicon artefacts additionally raises issues with static charge accumulation and retention. Silicon dioxide is an extremely good insulator providing charge retention times of tens of years for electronic devices, which could pose problems for mass determination and effective stability, so the static properties of silicon artefacts were investigated with a view to characterising and minimising the effect on mass measurement. In particular tests were undertaken to determine whether the type or thickness of the oxide layer influenced the accumulation of charge on silicon artefacts and additionally to assess the ease with which accumulated charge could be dissipated.

Three samples of silicon were prepared, one with a natural oxide layer and two with thermally grown oxides of nominal depth 5 nm and 10 nm. Due to the thin nature of the oxide layer it was not possible to determine the hardness of the surface (oxide) layer of the silicon samples by micro-indentation measurements or by using an instrumented indenter. Surface acoustic wave measurements were therefore used to assess the hardness of the surface oxide layers based on assumptions about the thickness of the oxide layers and the Young’s modulus of the substrate. For all three samples the calculated Young’s modulus for the oxide layer was 73.1 GPa (comparable with published data for the bulk properties and for surface oxide layers), indicating that for all 3 samples (including the one with only the natural oxide) the oxide depth was sufficient for the surface acoustic wave measurement technique to measure the modulus of the oxide. The relatively low value of Young’s modulus also confirms the relative lack of robustness of the oxide surface on silicon artefacts and the need for careful handling in order to maintain a stable mass value.

The samples were charged using two different techniques and then treated using three anti-static methods (an ion source, an anti-static gun and exposure to UV light) to assess the effectiveness of removing the surface static charge. Both forms of charge accumulation successfully induced a significant level of static charge in the samples. There was a small difference between the average levels of charge induced on the three samples with the sample with 10 nm thermal oxide accumulating the highest level of static charge. However, given the repeatability of the charge induction techniques the differences in induced charge were not significant. All three charge dissipation methods proved successful in removing the majority of the induced static charge, with exposure to ultraviolet light for a period of 30 minutes being the most effective.

3.1.3 Homogeneity and resistance of metal on metal coatings and effects of thermal and vacuum to air cycling on coated surfaces

Some composite materials involve surface plating on classical metallic elements or alloys to improve corrosion inhibition, hardness and durability. The aim of coating is to combine the good surface properties of one material with the good bulk properties of another material. Primary and top level mass artefacts have not historically been coated mainly due to concerns about the integrity of the coating and the overlayer/substrate interface, however due to the additional requirements on mass standards arising from the redefinition of the kilogram coated samples were evaluated to identity any potential benefits. Rhodium plating and new methods for applying gold plating on copper (a low permeability material suitable for use with the high magnetic fields involved with Kibble balance experiments) were studied. The efficiency of the method (vapour deposition under vacuum and electroplating) used to deposit the element on surfaces, the porosity of the deposited layer and the interface between the substrate and the coating were evaluated and characterised using microscopy. In addition, the adherence of the coatings was evaluated by indentation.

The results of the tests showed that the roughness of the plated samples was approximately 5 times greater that achieved on the iridium (and other uncoated metal) samples. However, this level of roughness is still significantly better than the surface finish required for OIML Class E1 weights (weights which are intended to provide traceability between national mass standards and weights of lower class). Vacuum and humidity cycling had no measurable effect on the surface of the weights confirming the robustness of the coatings to the variations in pressure and humidity experienced on transfer between air and vacuum. After thermal cycling between 20 °C to 160 °C, the rhodium plated sample showed additional cracks, whereas the gold plated samples were unaffected in this respect. It is likely that this was caused by the difference in the linear thermal expansion coefficients of the rhodium and the copper substrate (8 ppm per °C for rhodium compared with 16.6 ppm per °C for copper). Gold and copper are much better matched in terms of their linear thermal expansion coefficients (14.2 ppm and 16.6 ppm per °C respectively). Additionally rhodium has a poorer thermal conductivity than gold or copper ($150\ \mathrm{W\cdot m^{-1}\cdot K^{-1}}$ compared with $320\ \mathrm{W\cdot m^{-1}\cdot K^{-1}}$ for gold and $390\ \mathrm{W\cdot m^{-1}\cdot K^{-1}}$ for copper). An additional effect of the thermal cycling was the desorption of contaminants from the surface of the samples which could be seen visually and by a slight increase in the surface roughness parameters due to the exposure of roughness (scratches) underlying the contaminant overlayer.

3.1.4 Properties of materials for potential use as mass transfer standards

For the redefinition of the kilogram, which aims to link the unit of mass to a fundamental constant rather than a material artefact, it is necessary to achieve a direct link between the primary realisations (the Kibble balance and Avogadro experiments) and the reference mass standards that ensure the reliable dissemination of the mass scale. To ensure the mid/short term stability (1 to 10 years) of the new definition and to realise its dissemination with the lowest uncertainties, knowledge of the behaviour (in terms of mass stability) of the materials from which mass standards are constructed is essential.

Potential materials for the fabrication of next generation mass standards were evaluated to assess their suitability for use as mass standards to disseminate the unit of mass from the new primary realisations. The materials need to be compatible with use in vacuum and in high magnetic fields and should offer mass stability at least as good as the current primary platinum-iridium standards. The materials were evaluated for the properties required when used in the primary realisation experiments and as primary standards for the medium term maintenance and the dissemination of the redefined unit of mass. The density, hardness, magnetic permeability and surface sorption characteristics of the materials (in increasing order of importance) determined which were the most suitable. The microstructure of the materials was also examined, as this affects properties such as hardness, ease of machining and therefore mass stability. The materials evaluated included pure iridium, a tertiary alloy of predominantly gold and platinum, a nickel-based superalloy Udimet720 (U720), single and poly crystal tungsten, together with the three materials currently used in the mass field for standards, namely platinum-iridium, stainless steel (SS) and silicon. Platinum-iridium is the material generally used for primary mass standards, whilst stainless steel is the metal from which most secondary kilogram standards are made.

In addition, two composite materials were manufactured and investigated, namely electroplated rhodium and gold layers on bulk copper. The aim was to combine good bulk properties such as high density and homogeneity and low magnetic susceptibility with favourable surface properties, namely hardness and chemical resistivity (for further details see 3.1.3). Silicon was also investigated as it has many of the properties required for the Kibble balance experiment (high hardness, low magnetic susceptibility and low surface sorption coefficient) and is used in the Avogadro project (see 3.1.2 for further details). The properties of all the materials tested are summarised in Table 1.

Table 1: Physical properties of the selected materials (*Hardness of coating)

Material	Density ($kg.m^{-3}$)	Hardness (Hv)	Magnetic susceptibility ($\chi_v * 10^{-5}$)	Provider	Number of samples
PtIr	21530	175	+24	BIPM	12
AuPt	15870	250	-2.8	BIPM	12
Ir	22500	380	+5.9	CNAM	12
W	19300	740	+5.5	NRC	12
Si	2300	1000	-0.3	PTB	9
Stainless steel	8000	200	+300	METAS	9
U720	8100	500	+44	LNE	9
Cu electro-plated with Au	8937	200 – 230*	-10 (bulk Cu)	METAS	12
Cu electro-plated with Rh	8937	600 – 900*	-10 (bulk Cu)	METAS	12

With respect to platinum-iridium, tungsten and iridium are comparable in density but harder and have lower magnetic susceptibilities. Udimet720 has a similar density to stainless steel but is much harder and has a lower magnetic susceptibility. However, it is not suitable to replace stainless steel for secondary and working standards due to the additional cost involved. Silicon is important because it lies at the heart of the International Avogadro Coordination. Bulk copper has a very low magnetic susceptibility, can be pure but is too soft and chemically reactive to be used for mass standards.

Surface studies using an optical roughness meter, scanning electron microscopy (SEM) and atomic force microscopy (AFM) show that all the materials studied had a relatively smooth and homogenous surface. Roughness values (R_q) of 10 nm or less were obtained for platinum-iridium, iridium, stainless steel and tungsten, which were supported by white light reflection measurements. AFM and SEM studies were performed with different samples of the same materials. The results of the two methods were qualitatively similar, except for stainless steel and tungsten. The AFM analysed samples had grooves not found on the SEM analysed samples which was probably due to the relatively poorer resolution of SEM for this application. All materials were found to be vacuum compatible as no surface damage was observed due to ultra-high vacuum exposure during SEM studies.

Impurities in the samples were also measured using X-ray photoelectron spectroscopy, thermal desorption spectroscopy (TDS) and X-ray reflectance (XRR). Measurements of surface contamination performed both by X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence (XRF) showed similar results, with copper contamination on all materials tested. The presence of copper was almost certainly due to the polishing procedure as all surfaces, except the Si samples, were mechanically prepared. Providing the copper contamination is stable then there is no issue with its minimal presence on the materials. However, further investigations into the reason behind the copper contamination is advisable, with a view to reducing or eliminating it from the future preparation of mass standard artefacts. Typical results of the surface contamination measurements are shown in Table 2.

Table 2: Trace elements on the surface of the samples identified from XRF spectra, with the most prominent fluorescence line shown in brackets. Trace elements marked in yellow exhibited high fluorescence intensities

PtIr	AuPt	Ir	Si	W
C (Kα)	-	C (Kα)	C (Kα)	-
N(Kα)	-			N (Kα)
O(Kα)	O (Kα)	-	O (Kα)	O (Kα)
-	-		F (Kα)	-
Mg (Kα)	-	-	-	Mg (Kα)
Al (Kα)	Al (Kα)	-	Al (Kα)	Al (Kα)
-	-	-	-	-
-	-	Ca (Kα)	-	-
Fe (Kα)	Fe (Kα)	Fe (Kα)	Fe (Kα)	Fe (Kα)
Ni (Kα)	-	Ni (Kα)	Ni (Kα)	Ni (Kα)
Cu (Lα & Kα)	Cu (Kα)	Cu (Kα)	Cu (Lα+Kα)	Cu (Kα)
Zn (Lα & Kα)	-	Zn (Kα)	-	Zn (Kα)
Ru (Mz & Lα)	-	Ru (Mz & Lα)	-	-
Ag (Lα)	Ag (M & Lα)	-	-	-

One of the principal aims was to identify the best candidate materials for the realisation and dissemination of the mass unit. Pure iridium samples showed a good surface finish (roughness < 5 nm, good visual appearance after polishing and low surface contamination). Given its low magnetic susceptibility compared with platinum iridium alloy, iridium appears to be a good candidate for a Kibble balance experiment, however, its hardness makes it very difficult and time consuming to polish and it is quite difficult to obtain high quality pure iridium. Similarly tungsten has good mechanical and magnetic properties and proved easier to machine and polish than iridium. Both single- and poly-crystal tungsten samples were used but obtaining good quality samples of single-crystal tungsten (without inclusions or crystal defects) proved difficult. The procedure for the preparation and polishing of poly-crystal tungsten was therefore optimised and surface samples together with 500 g and1 kg artefacts with surface roughness of less than 5 nm (R_a) were produced.

Silicon samples had the smoothest of all surfaces (roughness < 2 nm) and silicon has already been used in the NPL/NRC Kibble balance and, of course in the International Avogadro Coordination (IAC). Due to the brittle nature of silicon, it is easier to produce spherical artefacts than cylindrical ones. Extensive ongoing work on silicon artefacts has been performed by the International Avogadro Coordination, however, the studies carried out by this project were on plane surfaces and so are complementary to the work of the IAC.

By contrast, some materials are clearly disfavoured. Aside from its low magnetic susceptibility, the gold-platinum-silver-copper quaternary alloy exhibited few advantages and it also turned out to be difficult to reproduce samples of identical composition. As for copper samples electroplated with gold or rhodium, the surface was inhomogeneous with relation to the surface structure, but this could be related to the condition of the underlying substrate, and in addition cracks occurred in the coating following heat cycling. It is recommended that substrates be characterised prior to coating if future samples are produced.

3.1.5 Prototype new kilogram artefacts

Based on the outcomes of the research in 3.1.2-3.1.4, prototype kilogram artefacts were produced from a range of materials. METAS in collaboration with Häfner/Degussa manufactured cylindrical 1 kg Rh and Au coated mass and surface artefacts. The artefacts proved reasonably stable in vacuum but showed large mass changes on transfer between vacuum and air. The analysis of the surface samples of the same (plated) materials showed some issues with the robustness of the coating due to low surface hardness and changes in the overlayer after thermal cycling. LNE produced mass standards of pure iridium which exhibited good air/vacuum transfer and vacuum storage repeatability and stability. The artefacts will be used as primary mass standards at LNE but the expense of the material and the difficulty in machining and polishing mean they are unlikely to be more widely used. NRC produced single crystal tungsten kilogram standards but it proved difficult to achieve a good surface finish, partly due to the number of dislocations and voids in the source crystal. Both NRC and NPL, in association with Häfner, therefore produced cylindrical 1 kg, 500 g and 100 g mass standards of poly-crystal tungsten. The polishing process was difficult to optimise but a method for achieving a surface roughness of less than 5 µm has been developed. The artefacts produced show excellent air/vacuum transfer characteristics and have been shown to be stable in vacuum over a period of a few weeks. One issue identified with tungsten artefacts is the fact that they lose mass on immersion in water (for hydrostatic weighing) due to the formation and subsequent dissolution of surface oxide layers. It is recommended that the density of tungsten mass standards is carried out by weighing in another liquid (such as FC40). Additionally, exposure to high humidity environments (greater that 60% RH) should be avoided. The tungsten kilogram mass standards produced at NRC and NPL will be used as primary mass standards at these laboratories and can be recommended to other NMIs particularly for use in Kibble balance experiments. Poly-crystal tungsten artefacts of 500 g and 100 g have already been provided to the BIPM for their Kibble balance experiment.

3.1.6 Conclusions

Potential materials for the fabrication of next generation mass standards were evaluated. Reports were produced comparing materials and manufacturing processes, which will provide a useful source of information for NMIs and weight manufacturers when producing the next generation of primary mass standards.

Of the materials evaluated, tungsten proved to have good mechanical and magnetic properties and good surface finishes of the order of 1 nm – 2 nm (R_a) could be achieved, an improvement on the best current (platinum-iridium) metallic mass standards. It proved difficult to manufacture larger (kilogram) artefacts from proven monocrystalline tungsten as surface defects were present due to inclusions and voids in the crystals used, so polycrystalline tungsten was therefore used to produce kilogram mass standards. New tungsten mass standards of 100 g, 500 g and 1 kg have been produced by Häfner, NPL and NRC for use as primary standards, weights have also been provided to the BIPM for use on their Kibble balance experiment. Tungsten can be recommended as a suitable material for primary mass standards and it is likely that its use will become more prevalent in the future. Pure iridium samples showed a good surface finish (roughness < 5 nm and low surface contamination) and had low magnetic susceptibility compared with platinum iridium alloy, however, its hardness makes it very difficult and time consuming to polish and it is quite difficult to obtain high quality pure iridium. LNE have produced pure Iridium mass standards which will be used in the future dissemination of the mass scale in France. Silicon samples had the smoothest of all surfaces (roughness < 2 nm), however due to the brittle nature of silicon, it is easier to produce spherical artefacts than cylindrical ones. Aside from its low magnetic susceptibility, the gold-platinum-silver-copper quaternary alloy exhibited few advantages and it was also difficult to reproduce samples of identical composition, however, artefacts produced from this alloy had good sorption properties and proved stable in vacuum. Of the plated copper samples the gold overlayer proved more robust than the rhodium under both pressure and thermal cycling, but the surface hardness is quite low so care needs to be taken in the handling of such weights. The use of low permeability weights of solid un-plated construction, such as tungsten, is therefore recommended in preference to the use of plated weights.

3.2 Development and evaluation of procedures and techniques for the mass transfer between vacuum and air

3.2.1 Introduction

Since the new definition of the kilogram will be realised under vacuum using the Avogadro (X-ray crystal density (XRCD)) or Kibble balance primary realisation experiments, there will be at least one step in the dissemination chain where mass standards have to be transferred from vacuum (typically $<10^{-2}$ Pa) to ambient air. The transfer of artefacts from vacuum to air is known to bear the risk of increased surface contamination. The pressure and quality of the vacuum and the air/inert gas environment into which the weights is transferred, as well as the transfer procedure itself, affects the stability of mass standards. Optimised procedures and techniques for the transfer of mass artefacts between vacuum and air are therefore required to ensure repeatable results and minimised uncertainties.

The overall aim of this work was to investigate vacuum/air transfer phenomena and to develop a procedure, which minimises the uncertainty in the process of transferring masses between vacuum and air (target uncertainty of less than 10 µg). To do this the work focussed on

- Investigation of the dependence of “weighing in vacuum” results on the mass comparator and vacuum equipment used
- Optimisation of the protocol for the transfer of mass standards between air and vacuum in order to minimise the uncertainty due to the repeatability of air-vacuum sorption effects
- Recommendation of operating pressures for Kibble balance and vacuum mass comparator operation to ensure compatibility and to minimise the uncertainty in traceability

3.2.2 Potential dependence of measured sorption effects on the mass balance used

Within the scope of the redefinition of the kilogram, which will be realised under vacuum via Kibble balance experiments or the Avogadro project, the sorption behaviour of mass standards when transferred from vacuum to air is one of the main aspects to be controlled. This sorption effect can be influenced by several parameters, and the environment in which the standards are placed must be carefully monitored to limit the surface contamination as much as possible.

Measurements were undertaken in order to assess the influence of the mass balance and vacuum chamber construction used by the partners on the measured sorption behaviour of mass standards. For the first time, such measurements of the sorption coefficients of selected mass standards were performed under similar conditions (temperature, pressure and humidity of the selected gas, vacuum pressure) in mass comparators, vacuum and load-lock apparatus and glove boxes (enclosures made of different materials and with different surface properties) in seven different vacuum balance assemblies at five different NMIs. The results for platinum-iridium artefacts weighed on four vacuum mass comparators in air and in vacuum are shown Figure 1, and similar results were obtained for silicon and stainless steel artefacts. Table 3 summarises the sorption results obtained for air-vacuum transfer on each balance. The reversible sorption behaviour of the three sets of artefacts was found to be independent, within the given uncertainties, of the weighing environment, i.e. the mass comparator itself and its vacuum enclosure.

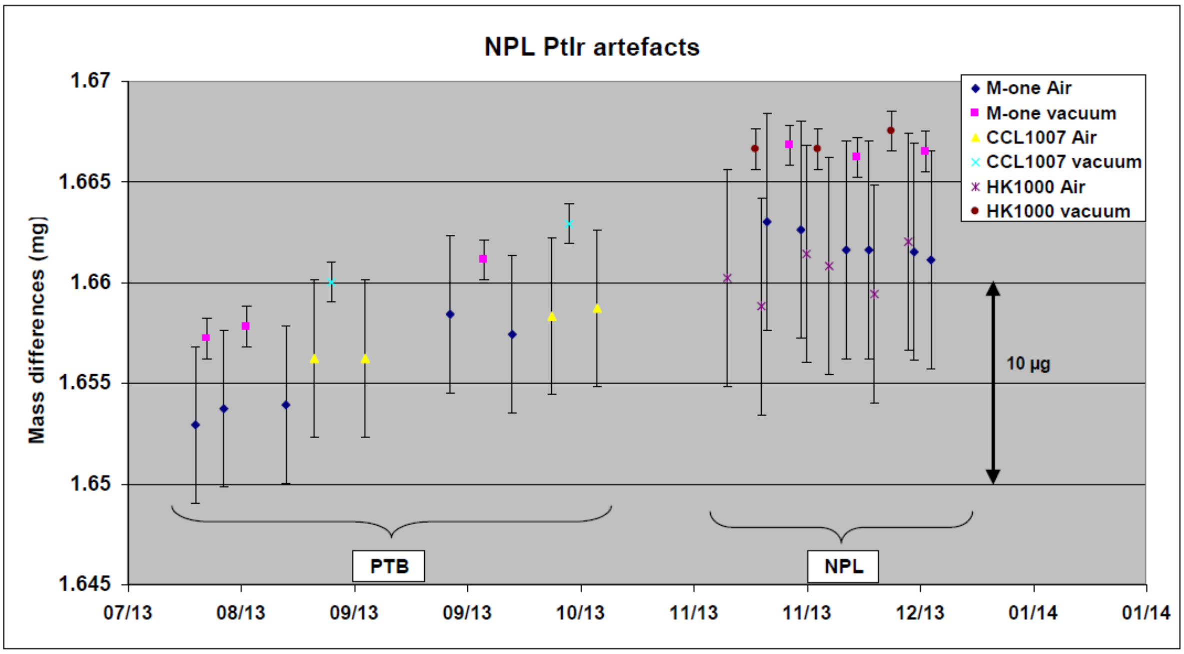

Figure 1: Mass differences between a set of PtIr sorption artefacts weighed in air and vacuum on three separate vacuum mass comparators

Table 3: Sorption values calculated for each mass balance based on three air-vacuum transfers. The uncertainty in the absolute mass change is approximately 3 µg and the uncertainty in the change per unit surface area is approximately 0.04 µg.cm^{-2}.

Institute	Mass comparator	Absolute mass change / µg	Change per unit SA / µg.cm^{-2}
PTB	M-one	-3.9	-0.050
	M-one	-4.0	-0.051
	CCL1007	-3.8	-0.049
	M-one	-3.2	-0.041
	CCL1007	-4.4	-0.056
NPL	K1000	-7.1	-0.091
	M-one	-4.0	-0.051
	HK1000	-5.5	-0.070
	M-one	-4.6	-0.059
	HK1000	-6.8	-0.087
	M-one	-5.2	-0.067

3.2.3 Recommendations on operating pressures for Kibble balance and vacuum mass comparator operation to ensure compatibility and to minimise the uncertainty in traceability

As the future definition of the kilogram based on a fundamental constant will be realised in a vacuum, it is essential that any changes in sorption coefficients due to variations in pressure during the measurement of the artefacts used to provide traceability to the new definition are well understood. Sorption coefficients are used when correcting the mass value of an artefact in air to allow for a change in humidity or when correcting the mass value of an artefact for the moisture lost/gained from its surface when it is transferred to/from vacuum.

Previous work by various researchers evaluated sorption effects on materials commonly used for primary mass standards, i.e. platinum-iridium (PtIr), silicon and stainless steel, and determined the correlation of sorption coefficients to vacuum pressure platinum-iridium, silicon and stainless steel artefacts. These published data shows significant variation in the sorption values (0.05 μg/cm^2 to 0.5 μg/cm^2) which does not appear to correlate with the material or surface roughness. Other earlier work by Berry and Davidson and others also measured sorption from atmospheric pressure to 10^{-3} Pa and found evidence of hysteresis between atmospheric pressure and 0.1 Pa, however there was no change in the mass difference between the artefacts, and hence the sorption value, over the 0.1 Pa to 10^{-3} Pa pressure range. As previous work showed that the sorption values were stable over a pressure range from 0.1 Pa to 10^{-3} Pa, this range was selected for evaluation in this project. Table 4 summarises the published data for sorption effects.

Table 4: Published sorption values of the materials used and pressure level of the measurements

Author(s)	**Material**	**Surface Roughness (Rz)**[2] **/ nm**	**Sorption value / μg cm^{-2}**	**Pressure / Pa**	**Time between cleaning and measurement**
Schwartz[1]	stainless steel	120	-0.030[1]	0.1	< 8 months
Schwartz	stainless steel (uncleaned)	120	-0.076[1]	0.1	-
Picard & Fang[2]	PtIr	10-100	-0.080	0.1	< 1 month
Picard & Fang	silicon	<10	-0.030	0.1	< 1 month
Picard & Fang	stainless steel	10	-0.040	0.1	< 1 month
Davidson[3]	PtIr	10	-0.162	10^{-4}	< 6 months
Davidson	stainless steel	60	-0.154	10^{-4}	< 6 months
Berry *et al*[4]	stainless steel	60	-0.13 to -0.25	0.05 to 10^{-4}	< 3 years
Mizushima et al[5]	PtIr	5-25	-0.013	0.1 to 10^{-3}	< 1 year
Berry & Davidson[6]	PtIr	10	-0.070	0.1 to 10^{-3}	< 5 years
Berry & Davidson	silicon	<10	-0.050	0.1 to 10^{-3}	< 5 years
Sanchez et al[7]	PtIr	10-100	-0.162	0.1 to 10^{-3}	> 20 years

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[1] Schwartz R., Precision Determination of Adsorption Layers on Stainless Steel Mass Standards by Mass Comparison and Ellipsometry. Part II: Sorption Phenomena in Vacuum, Metrologia, 1994, 31, 129-136

[2] Picard A. and Fang H., Methods to determine water vapour sorption on mass standards, Metrologia 2004, 41, 333-339

[3] Davidson S., Determination of the effect of transfer between vacuum and air on mass standards of platinum-iridium and stainless steel, Metrologia, 2010, 47, 487-497

[4] Berry J. et al, Report on the CCM WG TG1 pilot comparison to measure water vapour sorption on stainless steel mass standards, National Physical Laboratory Report ENG 46, 2013

[5] Mizushima, S., Ueda, K., Ooiwa,A., and Fujii, K., Determination of the amount of physical adsorption of water vapour on platinum-iridium surfaces, Metrologia, 2015, 52, 522–527.

[6] Berry J. and Davidson S., Effect of pressure on the sorption correction to stainless steel, platinum/iridium and silicon mass artefacts, Metrologia, 2014, 51, S107 – S113

[7] Sanchez C.A., Wood B. M., Green R. G., Liard J. O., Inglis D., A determination of Planck's constant using the NRC watt balance, Metrologia, 2014, 51, S5–S14

[1] Corrected to 50 % RH using equations (1) and (2) in NPL Report ENG50[8]

[2] Surface roughness values are indicative and may have been converted to R_z from R_a or RMS values

The measured mass differences between all of the artefacts made from platinum-iridium, silicon and stainless steel determined in this project did not vary over the 0.1 Pa to 0.001 Pa pressure range. This confirmed the previous work by Schwartz and Berry and Davidson which also did not show a variation in mass difference between artefacts of different surface areas over this pressure range. The pressure range of 0.1 Pa to 0.001 Pa is therefore recommended as suitable for the measurement in vacuum of masses used in the dissemination of the mass scale. There was however a difference between the absolute mass difference between the NPL platinum-iridium artefacts measured at NPL and the difference measured at NRC. This probably resulted from a change in the surface properties of the artefacts due to them being cleaned again at NRC and further work is required to examine the effect that surface cleanliness has on sorption values for different materials. Figure 2 shows sorption values measured by NRC and NPL on platinum-iridium artefacts as part of this project.

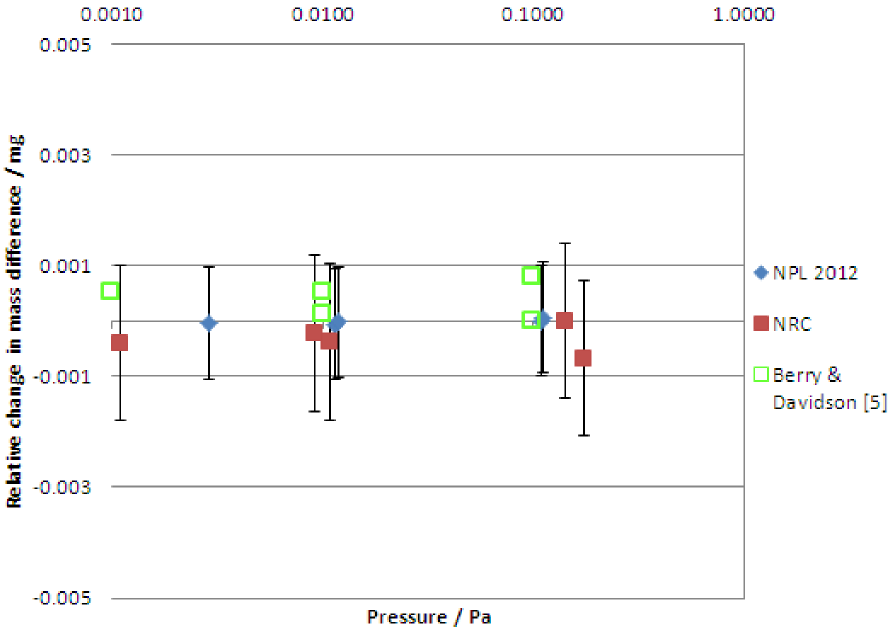

Figure 2: Measured mass differences between two sorption artefacts of different surface areas in the pressure range 0.001 Pa to 0.1 Pa

Good agreement was found between the measured silicon sorption values and the values reported by Picard and Fang, and Berry and Davidson. The stainless steel sorption values measured by PTB and INRIM agreed well with the values published by Picard and Fang and Schwartz but were much lower than the values published by Davidson and Berry et al. The stainless steel sorption values measured by CMI were much higher than the values measured at PTB and INRIM but were in broad agreement with the values reported previously by Berry et al. These differences for stainless steel could have been due to a difference in surface cleanliness of the artefacts or possibly due to differences in the surface roughness of the artefacts.

It was interesting to observe from both the previously published sorption values and the values measured in the project, that there appeared to be as much variation in sorption between artefacts manufactured from the same material as there was between artefacts made from different materials. This suggested that sorption

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[8] Berry, J.; Borys, M.; Firlus, M.; Green, R.; Malengo, A.; Mecke, M.; Meury, P.-A.; Zůda, J.: Analysis of the correlation of sorption coefficients to pressure. National Physical Laboratory Report ENG 50, 2014

values were more influenced by factors such as surface cleanliness and surface roughness rather than by the type of material from which the artefacts were made.

3.2.4 Optimised protocol for the transfer of mass standards between air and vacuum in order to minimise uncertainty due to the repeatability of air-vacuum sorption effects

Previous work by Davidson noted the accelerated accretion of hydrocarbon contamination on platinum-iridium mass standards transferred between air and vacuum when compared with similar standards stored permanently in either of the two media. Davidson's work used both XPS and gravimetric measurements to monitor the stability of mass standards. Experiments were therefore undertaken at METAS and at NPL to evaluate the effect of different venting cycles on the stability of the transfer standards. The venting cycles used were;

1. Vacuum-Air-Vacuum
2. Vacuum-Nitrogen-Vacuum
3. Vacuum-Nitrogen-Air-Vacuum

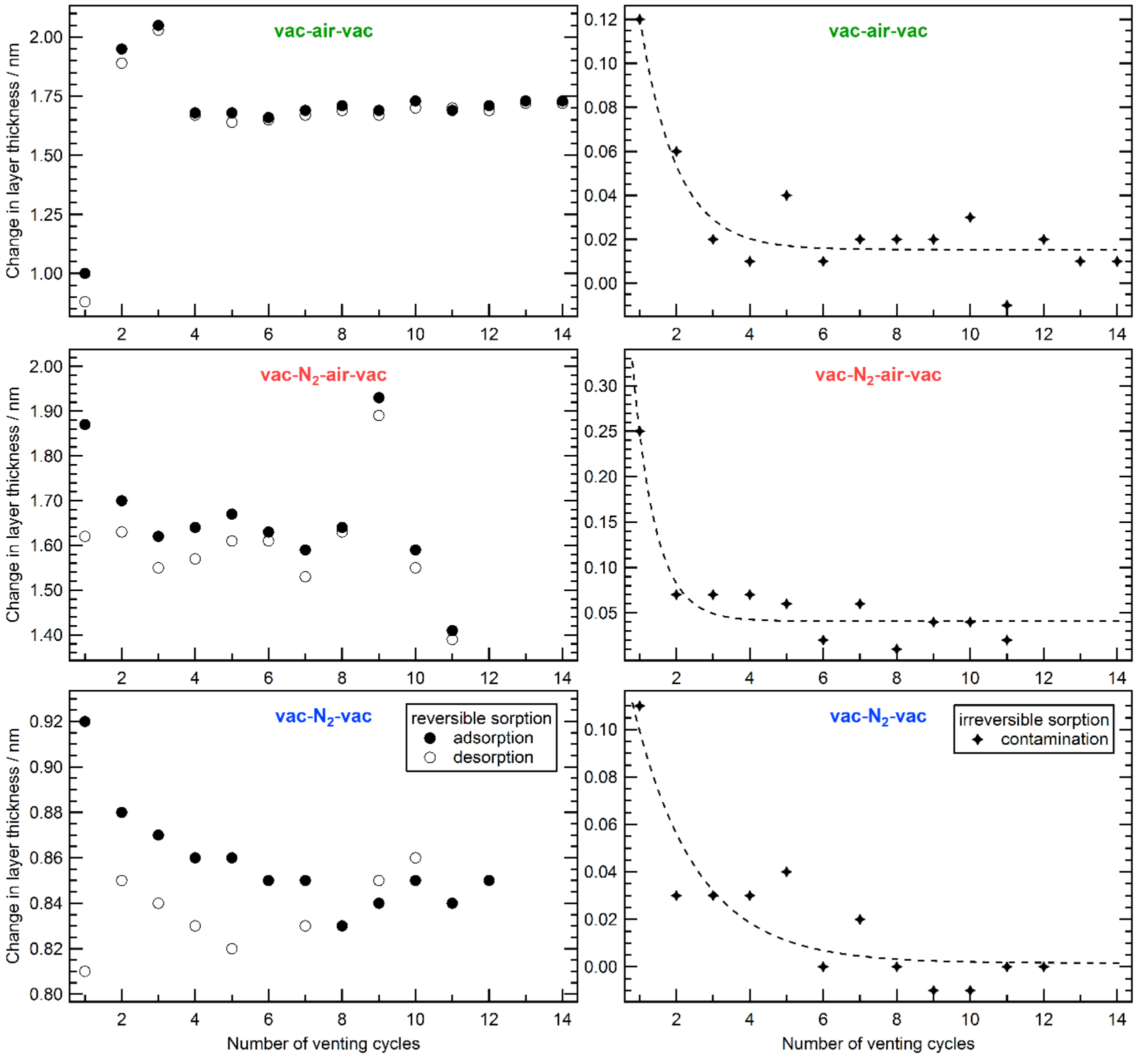


Figure 3: Sorption and desorption measurements using a gold-coated quartz crystal microbalance: The left hand graphs show reversible sorption (adsorption: dots and desorption: circle) and the right hand graphs show irreversible sorption (contamination: star) for three different venting cycles.

Nitrogen is commonly used to passivate the baked surfaces of vacuum chambers before exposure to air. The use of nitrogen as an intermediate stage in vacuum-air transfer was therefore evaluated to quantify the potential beneficial effect on maintaining the cleanliness of the surfaces of mass transfer standards. METAS studied the recontamination of surfaces following plasma cleaning for the three venting cycles using a quartz crystal microbalance (QCM) with gold plated crystals, the results are shown in Figure 3.

The results show that the cleaned surfaces accrete significant contamination (irreversible sorption) on the first venting cycle with the vac-N_2-air-vac cycled sample gaining the most. Subsequent cycles show much smaller levels of irreversible sorption. The total reversible sorption was approximately the same for the two air-vacuum cycles with the intermediate nitrogen step not affecting the amount of water sorbed onto the surface. However, the repeatability of the vac-N_2-air-vac cycled sample was much poorer than that of the sample cycled only between air and vacuum. The vacuum-nitrogen cycled sample showed much lower surface (water) sorption levels, which is to be expected since nominally dry nitrogen was used.

3.2.5 Conclusions

Optimised procedures and techniques for the transfer of mass artefacts between vacuum and air were developed with the aim of improving for the mass stability of artefacts stored under different conditions and minimising the uncertainty components inherent in the *mise-en-pratique* and their propagation through the dissemination chain. Direct transfer between air and vacuum was shown to be the most practical procedure since an intermediate nitrogen stage did not significantly improve the repeatability of the transfer or the stability of the transfer standard. Moreover, the addition of an intermediate nitrogen stage to the transfer process increased the amount of manipulation of the transfer standard increasing the risk of surface damage. Measurements showed that the reversible sorption behaviour of materials was, within the uncertainties, independent of the mass comparators used and their vacuum enclosures, indicating that measurements made by different NMIs on different systems should be comparable. In terms of the sorption values for different materials, it would appear that the sorption behaviour is more influenced by factors such as surface cleanliness and surface roughness rather than by the type of material.

The use of sorption artefacts (with different surface areas) which are transferred along with primary mass standards of the same materials, is recommended to determine in real time the sorption effects on the mass standards with the best accuracy. Transfer of weights stored in nitrogen directly to vacuum (without exposure to air, using a glove box) provided the most repeatable results in terms of sorption and the best weight stability.

The measured mass differences for artefacts made from platinum-iridium, silicon and stainless steel did not vary over the 0.1 Pa to 0.001 Pa pressure range and it is therefore recommended that this pressure range used for the measurement in vacuum of masses that are used in the dissemination of the mass scale.

3.3 Surface effects and dynamic changes on the artefact surface between vacuum, air and selected gases

3.3.1 Introduction

Artefact mass standards are used to disseminate the unit of mass and to maintain the mass scale. Therefore, high demands are placed on their material properties, surface finish and especially on their stability of mass. As the new definition of the kilogram will be realised in vacuum, the effect of vacuum-air transfers on the artefact surface needs to be well understood in order to ensure maximum accuracy for mass determination while minimising uncertainty contributions. The process of contamination and effectiveness of cleaning of old and new materials for future mass standards also needs to be better understood.

The overall aim of this work was to use complementary surface analysis techniques to underpin the work in other areas of the project to characterise the behaviour of various materials on transfer between vacuum, air and inert gas, the process of contamination and the effectiveness of various cleaning techniques. The use of small (surface) samples (instead of kilogram artefacts) allowed rapid evaluation of a wide range of materials and conditions and maximised the range of surface analysis techniques which could be used. Surface analysis was therefore used to provide additional useful information about the physical processes by which artefact mass standards gain and lose mass.

To do this the work focussed on

- Evaluation of the effect of air-vacuum venting methods on the (re-)contamination of the surface of samples.
- Evaluation of the (re-)contamination of a surface after it has been cleaned.
- Evaluation of the influence of different storage conditions combined with various cleaning techniques on the contamination of surface.

3.3.2 Surface analysis techniques

Complementary surface analysis techniques such as X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS), photo-thermal deflection spectroscopy (PDS), X-ray reflectance (XRR), atomic force microscopy (AFM) and white light interferometry (WLI) were used to characterise surface effects on various sample materials stored in and transferred between air, vacuum and inert gas. Approximately 100 small metallic samples made from platinum-iridium (PtIr), gold-platinum alloy (AuPt), iridium (Ir), tungsten (W), as well as gold plated copper and rhodium plated copper were distributed among the partners for extensive investigations, thus enabling a wider range of methods to be used and the scientific findings to be more broadly based.

3.3.3 Effect of air-vacuum venting methods

The samples were exposed to several vacuum-air, vacuum-N_2-air or vacuum-N_2 cycles to study the surface recontamination for different materials and venting methods. The amount of surface contamination was used as a weighting factor to identify appropriate venting methods for each material in order to maintain cleanliness and to achieve stable surface conditions. To substantiate the findings, a quartz crystal microbalance was used for in-situ measurements during cyclic venting. The use of a wide range of surface analysis techniques gave confidence in the interpretation of the measured contamination overlayers. Based on these results, a ranking list of best materials and best processes for handling, cleaning and storing future mass standards was generated and are available in a report.

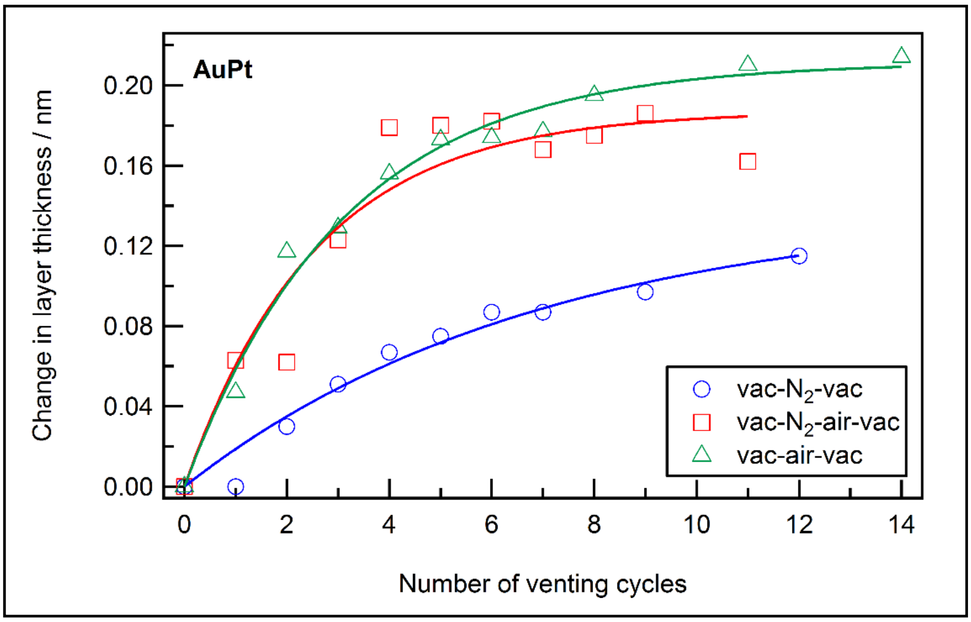


Figure 4: Overlayer thickness of hydrocarbon on gold-platinum alloy calculated from XPS measurements for cyclic venting between vacuum and air and/or nitrogen

Figure 4 shows the effect of the three venting cycles on samples of gold-platinum alloy and is typical of the results obtained for all the materials tested. It was found that cyclic venting with vacuum-air and vacuum-N_2-air showed similar levels of surface contamination. The introduction of an intermediate nitrogen stage in the vacuum-air cycle does not bring any benefit to the user with regard to stability or the amount of contamination. Cycling exclusively between vacuum and nitrogen caused the least contamination, but the handling of the samples/artefacts was more complicated. Finally, gold plated copper, gold-platinum alloy (AuPt), platinum-iridium (PtIr) and iridium (Ir) were found to be good candidates for the next generation of mass standards with relation to surface (re-) contamination.

3.3.4 Re-contamination after cleaning due to air-vacuum transfer

Additionally, the samples cleaned using different techniques (UV/O_3, H-plasma and nettoyage-lavage) were used to study differences in the subsequent recontamination caused by venting cycles.

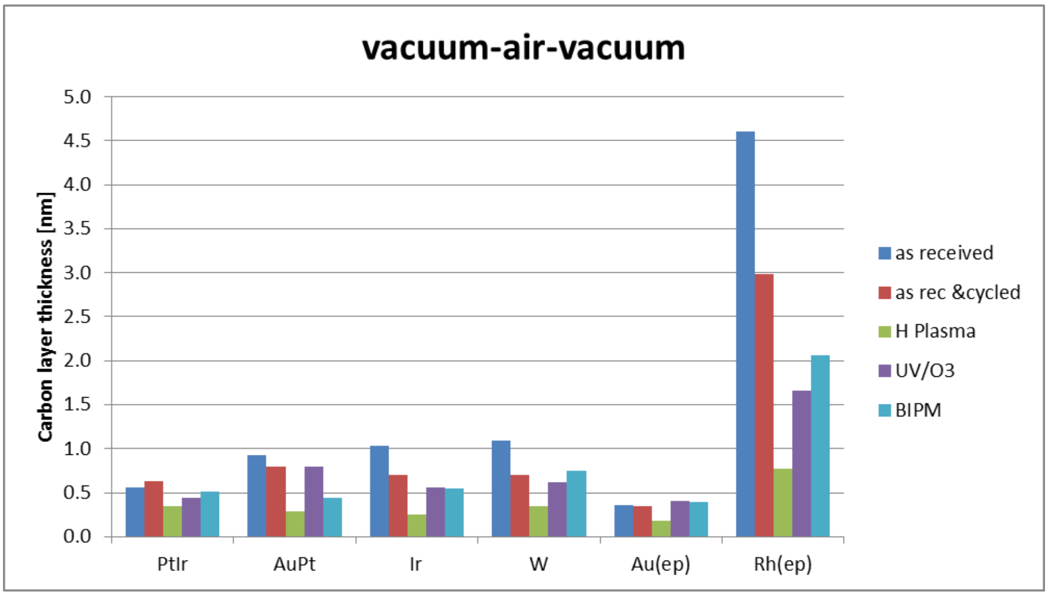


Figure 5: Carbon-layer thickness for different materials as received and after vacuum cycling and undergoing various cleaning processes

Figure 5 and Figure 6 show the effect of cleaning on the “as-delivered” samples and the subsequent recontamination due to air-vacuum cycling. Generally all cleaned samples showed an exponential increase in (carbonaceous) surface contamination. The results also show the trend of all (cleaned) surfaces to approach a self-limiting value of overlayer thickness. The results from this study indicated that a clean surface is less stable with regard to recontamination, i.e. the recontamination rate is higher immediately after cleaning. Hence, the cleaning technique not only determines the cleanliness of the surface achieved but also how quickly the surface is re-contaminated.

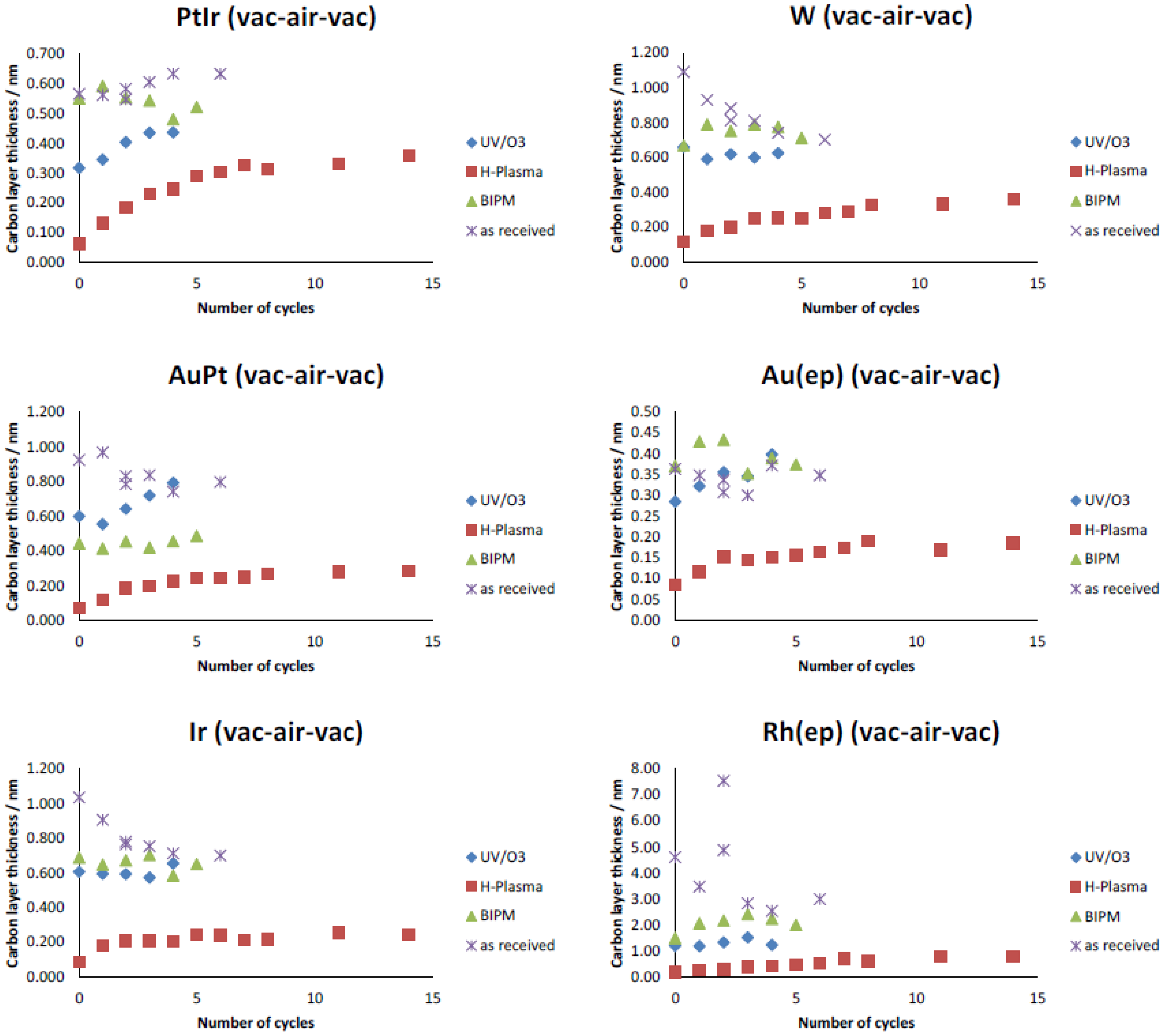


Figure 6: Effect of cleaning and subsequent venting cycles on the material samples tested (note difference in vertical scales)

3.3.5 Influence of different storage conditions combined with various cleaning techniques on the surface contamination of potential materials for future mass standards

The samples were used to study the influence of different storage conditions combined with various cleaning techniques on the contamination of surfaces. NPL analysed the surface of five 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 in air, vacuum or 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. Nettoyage-lavage was shown to be less effective than UV/ozone and H-plasma. 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 hydrocarbon contamination. The PtIr, Ir and W samples were stored in air and nitrogen and all showed an increase in hydrocarbon thickness after storage.

At METAS gold-platinum alloy, nickel-based alloy and tungsten samples were analysed using XPS after UV/ozone and H-plasma cleaning and after storage for one month in vacuum, air or argon. After storage in vacuum, air or argon, all samples showed an increased overlayer of hydrocarbon contamination. It was not possible to completely remove the hydrocarbon contamination using UV/ozone cleaning. Subsequent H-plasma cleaning removed hydrocarbon contamination to a great extent. After storage in air or vacuum, the increased amount of hydrocarbons was larger than after storage in argon. In general, the contamination rate after H-plasma cleaning was higher than after UV/ozone cleaning. Nonetheless, the amount of accumulated hydrocarbons during vacuum, air and argon storage was found to be lower when the samples had previously been cleaned by H-plasma.

CNAM used TDS to measure and compare the effectiveness of air-plasma, argon-plasma and the nettoyage-lavage method. For this reason, a platinum-iridium artefact was first cleaned with ethanol or isopropanol and then exposed to air-plasma which eliminated a large part of organic compounds, as cleaning only with isopropanol resulted in a higher TDS intensity. Air-plasma cleaning also removed water to a great extent from the surface of the platinum-iridium artefact. Studies by CNAM of the adsorption of acetone and ethanol (both in nitrogen carrier gas) on three different surfaces (Pt-10%Ir, pure iridium and Au-Pt-Ag-Cu quaternary alloys) using TDS showed that there was less adsorption on pure iridium than on platinum-iridium for both acetone and ethanol. These results are encouraging for the use of pure iridium for mass standards.

3.3.6 Conclusions

Surface analysis techniques were successfully applied to material samples and mass artefacts, which provided important insights into the (re-)contamination of surfaces and artefacts.

Cyclic venting with vacuum-air and vacuum-N_2-air resulted in similar levels of surface contamination. The introduction of an intermediate nitrogen stage in the vacuum-air cycle does not bring any benefit to the user with regard to stability or the amount of contamination. Cycling exclusively between vacuum and nitrogen caused the least contamination, but the handling of samples/artefacts was more complicated. Finally, gold plated copper, gold-platinum alloy (AuPt), platinum-iridium (PtIr) and iridium (Ir) were found to be good candidates for the next generation of mass standards with relation to surface (re-) contamination.

Generally all cleaned samples showed an exponential increase in (carbonaceous) surface contamination following cyclic vacuum-gas venting, with the trend of all cleaned surfaces to approach a self-limiting value of overlayer thickness. The results indicated that a clean surface is less stable with regard to recontamination, i.e. the recontamination rate is higher immediately after cleaning, hence, the cleaning technique not only determines the cleanliness of the surface achieved but also how quickly the surface is re-contaminated.

Regarding storage conditions, nitrogen storage showed a slight advantage over air storage post-cleaning with the self-limiting hydro-carbon overlayer taking longer to form. Vacuum storage post-cleaning showed the most rapid and least predicable accretion of the overlayer. Storage in nitrogen post-clearing is recommended if standards are to be stored for long periods (at least 6 months) but storage in air is adequate for shorter periods as it provides improved ease of access to the standards for use in air (or vacuum).

3.4 Evaluation of the mass stability of artefacts with a focus on storage and transport methods

3.4.1 Introduction

The overall aim of this work was to develop apparatus and protocols for the storage and transfer of mass standards under vacuum or inert gas, to investigate the storage of mass standards in inert media to potentially improve stability and to evaluate the transfer / storage vessels and protocols developed. To do this the work focussed on:

- Design and construction of transfer vessels, compatible with apparatus already in use, to allow the transfer of weights between NMIs under inert gas

- Development and optimisation of a protocol, based on experimental data, for the transfer between NMIs of mass standards to be used in vacuum
- Evaluation of transfer vessels and protocol for the transfer of weights under inert gas by undertaking a comparison of mass in vacuum

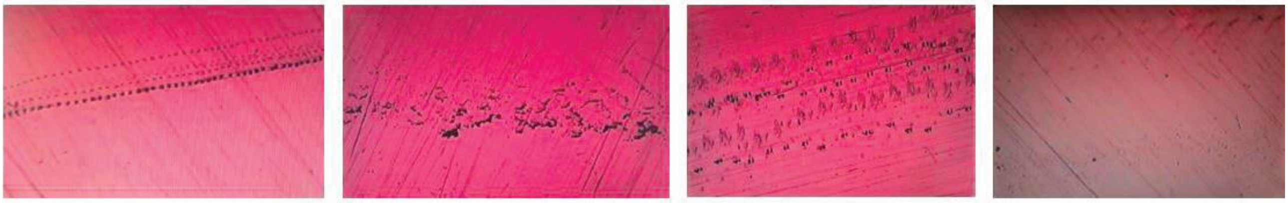
3.4.2 Apparatus for storage, transport and transfer of mass artefacts under vacuum or inert gas conditions

A survey was undertaken to determine the requirements of NMIs with regard to the storage, transport and transfer of mass standards, which identified that the majority of partners had storage vessels constructed from adapted conventional vacuum equipment and glove box type transfer apparatus. The requirements were published in a report and ensured the compatibility of equipment used for the comparisons undertaken as part of this study. The report will also be used to inform the design and build of new mass storage and transfer apparatus. The cross compatibility of these types of equipment permits a straightforward exchange of artefacts between both Kibble balance and Avogadro experiments and vacuum mass comparators, and between NMIs. Both PTB and the BIPM have propriety storage vessels and transfer apparatus which are compatible with commercial mass comparators, and which have the advantage of permitting complete transfer in vacuum which the glove box transfer method cannot achieve. They also both have glove box type transfer apparatus and their inclusion in the comparison permitted NMIs with either type of apparatus to participate and broadened the relevance of the comparisons results.

More generally there is a need for longer term storage and transfer of mass artefacts to support the redefinition of the kilogram and to facilitate traceability to a new definition once the kilogram has been redefined. Storage vessels had already been designed and manufactured by the partners which were suitable for long-term storage of mass standards as they all have valves connected to either the side or the lid which permits the vessel to be connected to either an inert gas supply or a vacuum pumping system. As part of this work NPL made modifications to the design and construction of its mass storage vessels for use as a transfer vessel for the comparisons of mass standards transferred under inert gas, ensuring compatibility with all potential participants.

NIST is currently working on an alternative method of providing traceability from mass measurements in vacuum to mass measurements in air that does not require the transfer of mass artefacts between air and vacuum. The apparatus directly links, via magnetic coupling, masses in air and vacuum. This could eliminate the need for storage vessels and transfer apparatus, though the method is still under development and would require validation with conventional sorption mass artefacts.

PEEK, aluminium, PTFE, Torlon and titanium were evaluated as potential materials for the handling and support of mass standards in vacuum/inert gas apparatus. Tests that repeatedly contacted the materials with stainless steel artefacts showed that all the materials caused marks on the surface of the artefacts. Support pegs made from PEEK, aluminium, Torlon and titanium caused damage on the surface in the form of indentations and / or grooves. Out of these four materials the titanium pegs caused the least amount of damage with smaller and shallower indentations compared with the other materials. AFM results from these tests are shown in Figure 7.



PTFE PEEK Aluminium Titanium

Figure 7: Effect of 5000 lifting cycles on a SS weight using pegs of the four materials indicated

The results for the PTFE pegs were not completely consistent. MIKES's results showed that the PTFE support pegs caused less damage than the other materials but also showed evidence of contamination forming on the surface, presumably due to transfer of PTFE material from the pegs. However, NPL's results showed that the PTFE pegs caused a similar amount of damage as the other polymer materials. It is possible that the PTFE pegs used by MIKES did not attract particulate contamination and hence did not damage the surface.

PEEK, PTFE and Torlon materials were also assessed with regard to their thermal desorption properties in vacuum. The molecular desorption rate for Torlon was much higher than PEEK and PTFE particularly with regard to water desorption (see Figure 8). Therefore with respect to desorption in vacuum PEEK and PTFE are more suitable materials to use as supports for artefacts compared with Torlon.

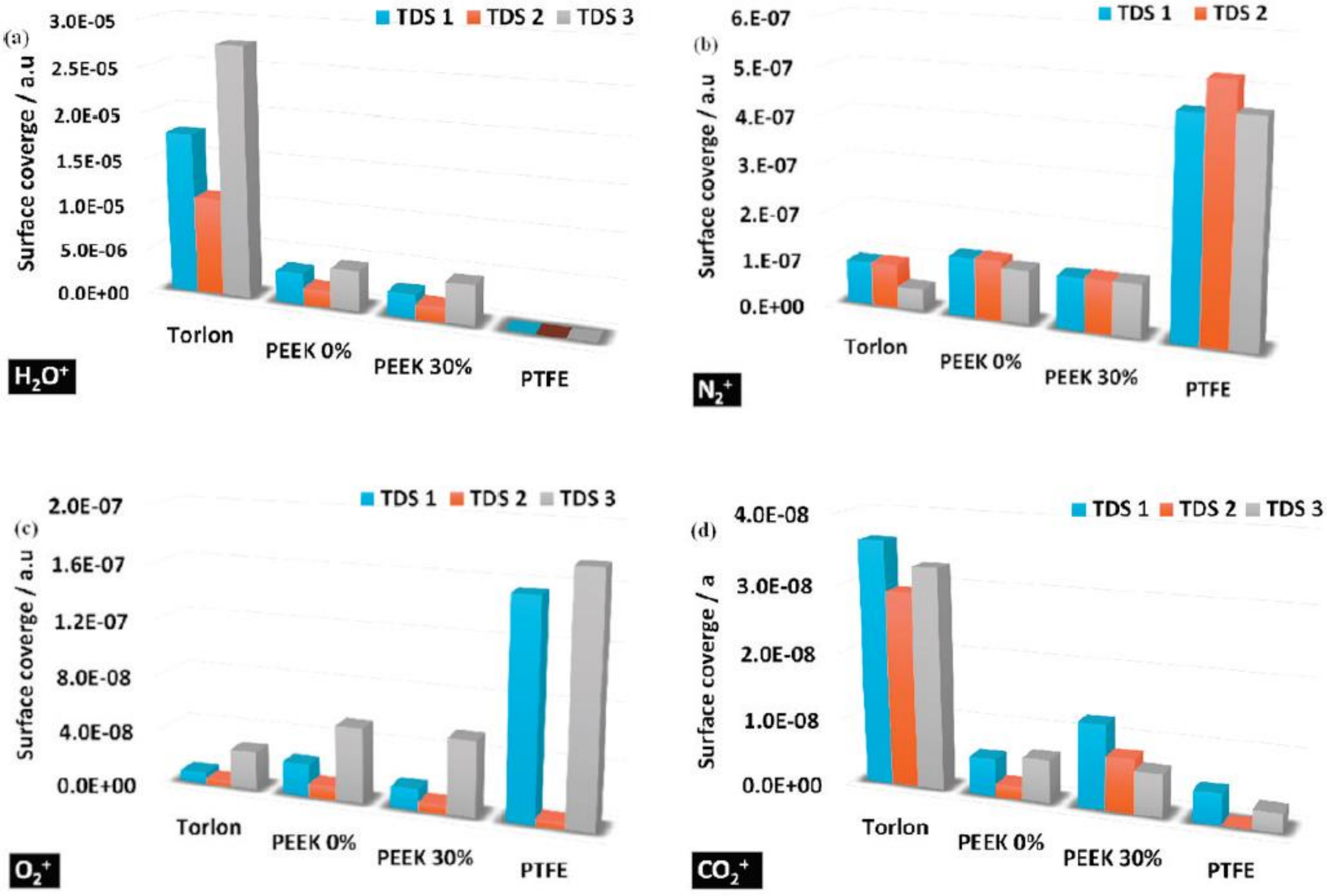


Figure 8: Thermal desorption in vacuum of water, nitrogen, oxygen and carbon dioxide for the 4 materials tested

In terms of selecting a suitable material for use in the weight handling mechanism in a mass comparator or Kibble balance, titanium appears to be the most suitable material as it caused the least damage and did not transfer significant amounts of material to the surface of the artefacts. Selecting a suitable material for use in an inert gas storage device depends on whether reducing damage to the surface of an artefact is a more critical variable, in which case PTFE or titanium would be the most suitable materials, or whether reducing the transfer of contamination to the artefact is more important in which case PEEK, aluminium or titanium were more suitable. Further research is required to determine whether surface damage or material transfer contamination is the critical component affecting the mass stability of artefacts before a decision can be made on the best material to use for supporting mass standards in vacuum / inert gas. Also, examining the topography and chemical identification of the surface of the pegs before and after the contact tests would confirm whether there is contamination present and its composition.

3.4.3 Optimised protocols for the medium-term storage of primary mass standards

Primary mass standards are normally stored in air and are subject to hydro-carbon contamination, even when stored in filtered laboratory air. At best the mass gain on primary (platinum-iridium) kilogram standards is of the order of 1 µg a year but can be much higher. The aim here was to develop and optimise protocols for the medium-term storage of primary mass standards and for the transfer of mass standards between experiments (Kibble balance and Avogadro) operating under vacuum conditions. These protocols will be necessary for fixing the Planck constant with reference to the IPK and for the provision of ongoing access to the SI unit of mass following redefinition since continuous access to primary realisation experiments cannot be guaranteed.

An evaluation of the medium-term (6-month) storage of primary mass standards in nitrogen compared with storage in air was undertaken by NPL, PTB and CNAM. XPS results showed no significant difference in carbonaceous growth on the surface of stainless steel samples stored in nitrogen for 6 months compared with those stored in air for the same period. These results suggest that there is no advantage in storing mass artefacts in nitrogen compared with conventional air storage over timescales of 6 months or shorter.

CNAM’s gravimetric results for stainless steel artefacts showed no significant difference between storing the artefacts in dry air or in nitrogen gas. Significant differences were observed in the mass change of stainless steel artefacts following cleaning using the air-plasma method compared with the BIPM nettoyage-lavage cleaning method. CNAM’s results showed the air-plasma technique to be an effective cleaning procedure for stainless steel artefacts in contrast to the nettoyage-lavage BIPM method which resulted in contamination being added to the artefacts. The artefacts cleaned using the BIPM method subsequently lost between 30 µg and 38 µg of the 60 µg to 86 µg of contamination that had formed as a result of the cleaning process. This mass loss was attributed to the contamination formed during the nettoyage-lavage BIPM method cleaning being volatile in nature and thus it desorbed from the surface of the artefacts during the 7 month storage period.

Both NPL’s and PTB’s gravimetric results for stainless steel artefacts stored in air for 6 months did not show any significant gain in mass. This contrasted with the nitrogen stored artefact at NPL and the nitrogen and vacuum stored artefacts at PTB all of which showed significant mass gains of around 20 µg over this period. It is unlikely that this contamination was due to the nitrogen gas environment as the stainless steel samples used in the NPL XPS measurements did not show any significant evidence of carbonaceous contamination and the percentage of hydrocarbons found on the surface was similar to the air stored samples. A possible explanation for the mass gain could be due to contact with the clamps used to secure the artefacts within the storage vessels, with contamination on the surface of the clamps or material from the clamps themselves transferred onto the surface of the artefacts. Alternatively the contamination might have been introduced during the procedure used to evacuate the vessels or fill them with gas. Therefore further investigations are required in order to reduce or eliminate this potential source of contamination. Alternatively if the artefacts are not required to be transported between measurements then storing them under bell jars in nitrogen or another inert gas may offer the same excellent stability observed in the air stored artefacts at PTB.

3.4.4 Protocols for the transfer of mass standards between experiments running under vacuum conditions

The aim of this work was to develop and optimise protocols for the transfer of mass standards between laboratories with the kilogram realisation experiments operating under vacuum conditions or with vacuum mass comparators. Earlier research in the project identified air-vacuum-air cycling as the recommended transfer method.

A comparison was undertaken between seven national metrology institutes (NPL, LNE, PTB, TUBITAK, INRIM, METAS, and CMI) firstly to evaluate the benefit on weight stability of transporting stainless steel standards between institutes in inert gas/vacuum compatible storage vessels compared with the current comparison best practice of transportation in air, and secondly to identify any additional complications in using this transfer process. Three stainless steel kilogram mass standards were used as the transfer standards in two groups, and were calibrated under vacuum conditions at the participating NMIs. The participants used their own sorption artefacts to measure the sorption correction for the transfer between air and vacuum.

In both groups, two of the masses were stored and transported conventionally in air. In order to allow comparison with current comparison best practice one of these masses was cleaned using a defined ultrasonic bath solvent cleaning method by each participant to investigate this comparison procedure as an effective protocol for future mass comparisons. The remaining masses from both groups were transported in inert gas storage vessels which had been developed and produced by NPL earlier in the project. The third Group 1 mass was transported in the inert gas storage vessel filled with dry nitrogen gas (the vessel was pressurised above atmospheric pressure to about 110 000 Pa, i.e. 10% above atmospheric pressure). The mass was transferred in dry nitrogen gas from the storage vessel to the mass comparator chamber under vacuum without exposing the surface to air (i.e. using a glove box). The third Group 2 mass was transported in the inert gas storage vessel filled with air (there was no need to over pressurise this vessel).

Table 5 summarises the comparison protocol and the results of the comparison are shown in Figure 9 and Figure 10.

Table 5: Summary of the weight transfer methods used for the comparison

Mass Standard	Storage and transport conditions evaluated by Group 1	Storage and transport conditions evaluated by Group 2
1	Transported conventionally in air.	Transported conventionally in air.
2	Stored and transported in nitrogen, inside an inert gas storage vessel.	Stored and transported in air, inside an inert gas storage vessel.
3	Transported conventionally in air. Cleaned before measurements made.	Transported conventionally in air. Cleaned before measurements made.

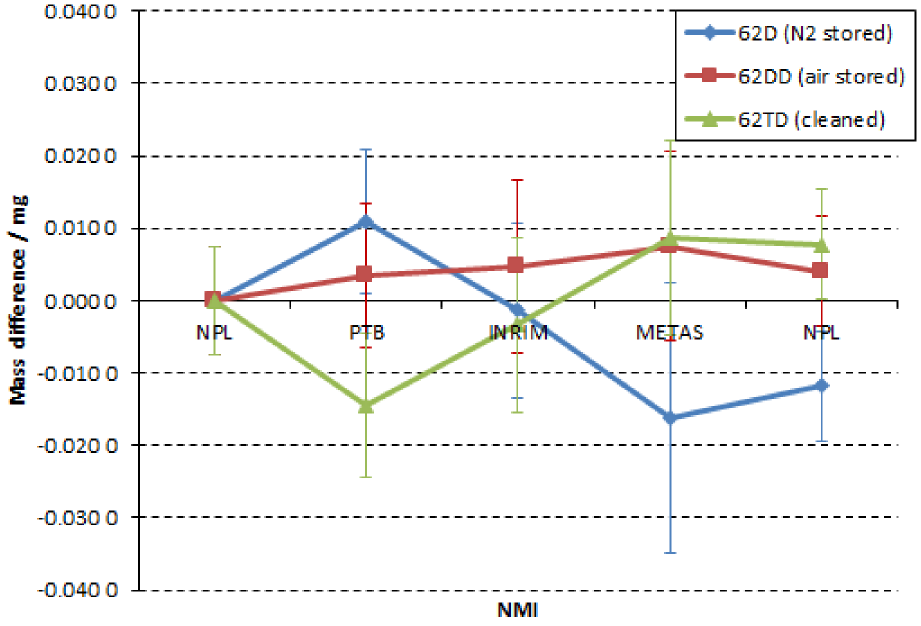


Figure 9: Mass difference in vacuum of the Group 1 transfer standards with respect to the initial mass at NPL. Error bars represent the standard uncertainty (k = 1).

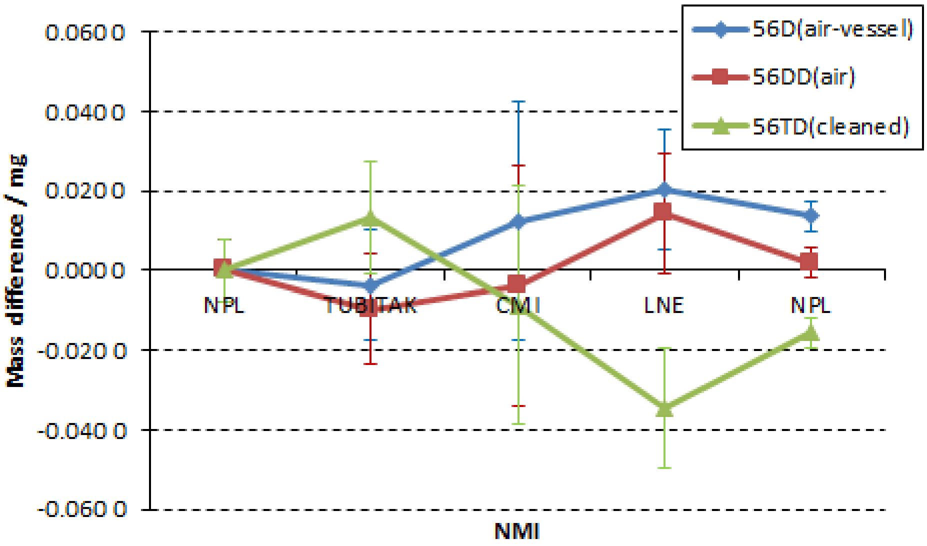


Figure 10: Mass difference in vacuum of the Group 2 transfer standards with respect to the initial mass at NPL. Error bars represent the standard uncertainty (k = 1).

The results for all three transfer standards measured by both groups showed significant correlation in the absolute mass values obtained for the standards with the institute at which they were measured. This suggested that the differences in the mass determinations of the transfer standards were mainly related to the mass scale realised at each NMI rather than any changes caused by the storage/transport techniques used or cleaning of one of the transfer standards before the measurements. After normalising the results to reduce the influence of the reference mass values no significant differences were found between the different transport methods. No significant improvement in mass stability was observed in the inert gas/vacuum vessel transferred steel standard and the standard that was cleaned before each measurement compared with the conventionally air transported standard. In fact in the Group 1 measurements the conventionally air transported mass demonstrated the best stability.

The results show that the most stable transfer standard in each case was that transferred in air (in a standard weight box). This is likely to be because the manual handling of the weight was minimised with respect to weights transferred in air or nitrogen in a sealed container. Therefore for the purpose of performing comparisons between NMIs the current best practice of transporting them in air in conventional boxes is still recommended.

3.4.5 Conclusions

Storage vessels for the transfer of primary mass artefacts, in inert gas or air, between NMIs were designed and manufactured. The vessels were used in a comparison of mass standards between the project participants and performed well, maintaining a positive pressure of inert gas or laboratory air during the transfer process. Such equipment will initially be necessary for the comparison of Kibble balance and Avogadro experiments with the International Prototype Kilogram in order to fix the Planck constant with respect to the current mass unit. Subsequently they will be required for the comparison of primary realisation experiments and for the dissemination of the unit from the primary realisations to end users via national measurement institutes. Additionally such apparatus will allow investigation of the benefits of storing mass standards in inert gas and thus improve the aggregate stability with which the global mass unit can be maintained.

For the first time a comparison was undertaken to evaluate the benefit on weight stability of transporting stainless steel standards between institutes in inert gas/vacuum compatible storage vessels compared with current comparison best practice of transportation in air, and to identify any additional complications in using this transfer process. The normalised results showed no significant differences between the different transport methods. No significant improvement in mass stability was observed for the stainless steel standard transported in a storage vessel in the inert gas/vacuum nor for the standard that was cleaned before each measurement compared with the conventionally air transported standard. The results show that the most stable transfer standard in each case was that transferred in air (in a standard weight box). This is likely to be because the manual handling of the weight was minimised with respect to weights transferred in air or nitrogen in a sealed container. Therefore for the purpose of performing comparisons between NMIs the current best practice of transporting them in air in conventional boxes is still recommended.

Guidance has been provided to NMIs/DIs in the form of a Good Practice Guide on the storage of primary mass standards.

3.5 Improvement and validation of methods for reproducible cleaning of primary mass standards

3.5.1 Introduction

The accretion of contaminants on the surface of mass standards over time is a key factor affecting their stability and it is therefore necessary to periodically remove the contaminants by cleaning. Platinum-iridium national standards sent to BIPM for calibration against the International Prototype Kilogram have historically been cleaned by BIPM using the manual nettoyage-lavage technique, however, the effectiveness of this technique has been shown to be significantly user dependent. More recently non-contact techniques have been developed such as plasma and UV/ozone cleaning, but they have not yet been fully evaluated.

The overall aim of this work was to develop and validate cleaning techniques for mass standards by;

- Development of techniques to produce controlled contamination on the surface of test samples which can be used for the evaluation of cleaning methods
- Using surface analysis techniques, evaluating the effect of manual and non-contact cleaning techniques (nettoyage-lavage, ultrasonic bath solvent cleaning, hydrogen-plasma, oxygen-plasma, UV/ozone) on the surface chemistry of materials used for mass standards
- Determining post-cleaning recontamination models for materials used for mass standards
- Directly comparing the effect of manual and non-contact cleaning techniques by gravimetric measurements on kilogram artefacts
- Making recommendations for the cleaning of mass standards of platinum-iridium, stainless steel and silicon to achieve reliable and repeatable results.

3.5.2 Provision of controlled contaminated surfaces to evaluate cleaning procedures

In order to apply controlled contamination to mass standards to enable the investigation of various cleaning techniques, two methods were devised. The first method employed a glass chamber containing oil that was heated and the vaporised oil 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 used to measure the thickness of applied contamination on vacuum gauge contaminated platinum-iridium and silicon samples. Survey scans of the samples showed that the vacuum gauge contaminated samples were contaminated with the same elements as found on the samples with natural contamination, but had higher atomic percentages of both carbon and oxygen. Calculations showed that this method successfully applied a layer of contamination to the samples between 1 nm and 2 nm thick which amounted to an equivalent additional mass on a platinum-iridium 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 contaminated using the vacuum gauge method had different C 1s compositions compared to the samples with a natural contamination overlayer, 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 showed 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.

3.5.3 Comparison, selection, validation, and optimisation of cleaning techniques for primary mass standards

Ideally a cleaning technique should remove all contamination from mass artefacts, not damage the surface and leave the surface in a condition where the weight of the mass is stable following the cleaning. In practice it is inevitable that some tightly bound carbonaceous contamination will remain on the weight surface and that a newly cleaned surface will be less stable than one with a self-limited overlayer of (hydro-carbon) contamination. Thus any cleaning method needs to optimise the repeatability of process and the stability of the post-cleaned mass.

The new UV/Ozone and (oxygen and hydrogen) plasma cleaning techniques had already been developed by NPL and METAS and these were evaluated as part of this project by NPL, METAS, MIKES and CNAM. The materials investigated were nickel-based super-alloy, silicon, platinum-iridium, iridium and tungsten. A range of surface analysis techniques were used to evaluate the effectiveness of the techniques as implemented by the participants. Results showed significant variations between participants with only NPL (UV/Ozone) and METAS (plasma) achieving really effective and repeatable results. The results indicated that, when successfully applied, the non-contact cleaning techniques such as UV/Ozone and H-plasma were more effective and repeatable in removing hydrocarbon contamination than the manual or solvent based cleaning methods. The results of the NPL tests are shown in Figure 11 and Figure 12.

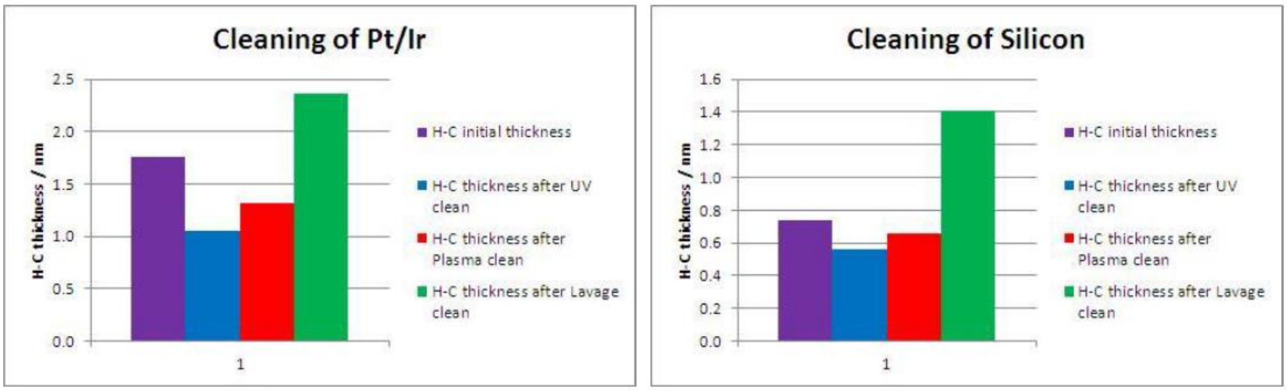


Figure 11: Hydrocarbon overlayer thickness for platinum-iridium and silicon samples before and after cleaning

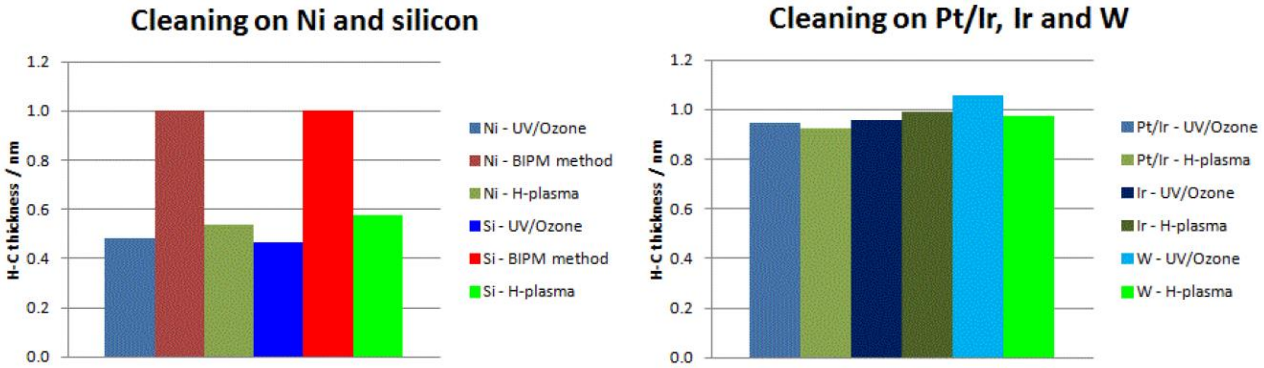


Figure 12: Residual hydrocarbon contamination following cleaning methods applied to various material samples

A direct comparison of cleaning methods, applied to kilogram artefacts, was undertaken by MGRT, who constructed apparatus to evaluate all the cleaning methods. Their results indicated that the BIPM nettoyage-lavage cleaning procedure was efficient in removing contamination and resulted in 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 ethanol cleaning in an ultrasonic bath procedure gave similar results. Stability after the cleaning was very good for both types of standards. In two instances the second cleaning cycle removed additional mass which suggest that the cleaning time of 5 minutes was not sufficient to remove the majority of the contamination. Based on the results a cleaning time of 10-15 minutes is recommended.

The UV/ozone cleaning procedure was the most time consuming of all four procedures. A gradual increase of the mass of stainless steel standards after the cleaning was observed by MGRT and this was the main disadvantage when compared with the BIPM nettoyage-lavage and the ultrasonic bath in ethanol cleaning procedures. For the platinum-iridium (PtIr) standards the stability and effectiveness of the UV/ozone cleaning procedure was comparable to that of 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 in the mass. Differences in behaviour of the mass of the same standard after hydrogen plasma cleaning procedures at different NMIs suggest that the apparatus used also influences the outcome of the cleaning procedure; hence there is a need for more detailed description of the apparatus and cleaning procedure. For platinum-iridium standards the hydrogen plasma cleaning procedures produced similar results to the BIPM nettoyage-lavage and the ethanol in ultrasonic bath, i.e. efficient cleaning and very good stability of mass after the cleaning cycle.

The artificial contamination procedure based on heated mineral oil was used for the preparation of samples and weights for the evaluation of all 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 non-hydrocarbon components could have been applied on the standards.

Two reports on the evaluations were produced and are available. In conclusion there were significant discrepancies between the results obtained by the five laboratories whom undertook the cleaning work, either on surface samples or on mass standards. This indicates that the careful implementation of the cleaning methods (particularly the UV/Ozone and H-Plasma) is necessary in order to achieve effective results. Further research in this area is recommended.

3.5.4 Conclusions

Two methods were successfully developed which apply a controlled amount of contamination to mass artefacts, enabling cleaning techniques to be evaluated. The vacuum gauge method has the advantage that unlike the heated oil method it does not increase the temperature of the artefacts and therefore is recommended as the preferred method for controlled contamination of artefacts.

New non-contact cleaning techniques for mass standards (using UV/Ozone and hydrogen plasma) were evaluated and optimised, and compared with existing manual cleaning techniques such as the nettoyage-lavage method used by the BIPM and solvent based method using ultrasonic baths. The effectiveness of the cleaning and also any effect on the surface chemistry and long term stability of the mass standards were investigated both gravimetrically and using surface analysis. When optimally implemented three UV/Ozone and H-Plasma techniques proved more effective and repeatable than traditional nettoyage--lavage or solvent techniques but it proved difficult for some laboratories to achieve a satisfactory implementation of the necessary apparatus. In particular the UV/Ozone apparatus needs careful construction to ensure all surfaces are exposed to an adequate intensity of UV light. The H-Plasma technique involves higher energy levels so again needs careful implementation to ensure only (loosely bound) carbonaceous contamination is removed and that the reactive substrate of the mass standards is not exposed resulting in short-term instability in the mass value of the standard.

3.6 Identification and evaluation of the uncertainty components inherent in the *mise-en-pratique* and in their propagation through the dissemination chain

3.6.1 Introduction

The overall aim of this work was to identify and evaluate the uncertainty components inherent in the traceability to the new definition of the kilogram and their propagation through the dissemination chain. In particular the research focussed on the uncertainty of a 1 kg mass standard, used in air, when it is calibrated with traceability to a number of primary realisations of the unit in vacuum.

When transferring the unit of mass from air to vacuum, a traditional assumption has been that only water is adsorbed and desorbed, and that the adsorption/desorption is reversible. The sorption comparison carried out in the Consultative Committee for Mass (CCM) WGM TG1 showed that adsorption/desorption is irreversible in general, so that the sorption artefacts gain mass as they are repeatedly cycled between air and vacuum. The irreversibility seems to be most pronounced if the sorption artefacts are cleaned just before the media cycling experiment. After some cycles between air and vacuum, the sorption/desorption seems to approach reversibility, and the masses of the sorption artefacts tend to stabilise in air as well as in vacuum. Simulations and modelling were therefore undertaken with the aim of improving prediction of sorption effects and their associated uncertainty.

3.6.2 Modelling and evaluation of the uncertainty components related to air-vacuum / vacuum-air transfer

The simulation experiment showed that irreversibility of the sorption/desorption is in fact useful as it enables a measurement of the relative absorption efficiencies of the surfaces of a set of sorption artefacts. The transfer functions may then be determined by performing an air-vacuum cycling experiment on freshly cleaned sorption artefacts. Once these transfer functions have been measured, their values and associated covariance matrix could be used as input to the analysis of subsequent air-vacuum cycling experiments without cleaning of the sorption artefacts, where the irreversibility of the sorption/desorption process might be less pronounced.

In the case of reversible sorption/desorption, at least three sorption artefacts are needed in order to test the hypothesis that the mass of the sorption is proportional to the geometrical area of the sorption artefacts. If a sorption artefact is made up of n discs (with spacers) having the same nominal mass, the uniformity of the sorption efficiencies among the discs could be tested in a separate air-vacuum cycling experiment in which the mass differences among the discs (with spacers) are measured in air and in vacuum.

Simulations were performed on an air-vacuum cycling experiment, in which the weight stored in air was a platinum-iridium standard, whereas the weight stored in vacuum and the sorption artefacts were made of stainless steel. This was done in order to evaluate the standard uncertainty with which the mass of a weight kept in vacuum could be measured in terms of a national prototype kept in air using the sorption standards circulated in the CCM WGM TG1 sorption comparison. This uncertainty was of the order of 0.010 mg and was actually dominated by the standard uncertainty 0.008 mg assigned to the prototype itself. The validity of this uncertainty can only be proven by performing a rather large number of air-vacuum cycling experiments (similar to the performed simulation) that leads to consistent mass values of the weight stored in vacuum, taking into account the measurement uncertainty. In such an experiment, the weight kept in air should have the same nominal volume as the sorption artefacts in order to reduce the uncertainty due to buoyancy effects when measuring in air. For the same reason the volumes (or volume differences) of the sorption artefacts and the weight kept in air should be measured with the smallest possible standard uncertainty.

The procedure defined for transferring the unit of mass between a weight kept in air and a weight kept in vacuum involves the use of sorption artefacts that are repeatedly compared to the weight kept in air and to the weight kept in vacuum in an air-vacuum cycle. A model of the measurement based on homogeneous absorption/desorption was developed, which was tested on adapted measurement data provided by participants in a sorption comparison and on simulated data. The sensitivity to modelling errors was also tested by simulation.

The model and the simulations illustrate that a mass value in air with a standard uncertainty of 0.008 mg can be transferred to a mass value in vacuum with a standard uncertainty of 0.010 mg, which means that an uncertainty contribution of 0.006 mg from the air-vacuum transfer can be achieved, at least in principle. The model is based on the crucial assumption that sorption/desorption is homogenous over the surfaces of the sorption artefacts. If this assumption is not valid in reality, the mass value calculated for the weight kept in vacuum might be significantly biased. Although the proposed method for analysing the data from an air-vacuum cycling experiment includes a tool for testing the consistency between the data and the model, there is a rather large probability, that an invalid assumption might not be detected in a single air-vacuum cycling experiment.

A report was produced on transferring the unit of mass between weights kept in air and in vacuum which describes how mass transfer may be undertaken in a way that enables the robust evaluation of the standard uncertainty associated with the mass transfer.

3.6.3 Conclusions

Rigorous uncertainty analysis has been carried out on the processes that will be involved in the dissemination of the redefined kilogram, most notably the additional vacuum to air transfer stage. The way in which surface sorption corrections are measured and applied to this stage has been evaluated and guidance given on issues affecting the calculation of the associated uncertainty.

The procedure developed for transferring the unit of mass between a weight kept in air and a weight kept in vacuum involves the use of sorption artefacts that are repeatedly compared to the weight kept in air and to the weight kept in vacuum in an air- vacuum cycle. A model of the measurement based on homogeneous absorption/desorption was developed and tested on adapted measurement data provided by participants in a sorption comparison and on simulated data. The sensitivity to modelling errors was also tested by simulation.

The results showed that a mass value in air having a standard uncertainty of 0.008 mg can be transferred to a mass value in vacuum with a standard uncertainty of 0.010 mg, which means that an uncertainty contribution of 0.006 mg from the air-vacuum transfer can be achieved, at least in principle. The model is based on the crucial assumption that sorption/desorption is homogenous over the surfaces of the sorption artefacts. If this assumption fails in reality, the mass value calculated for the weight kept in vacuum might be significantly biased. Although the proposed method for analysing the data from an air-vacuum cycling experiment includes a tool for testing the consistency among data and model, there is a rather large probability, that an invalid assumption might not be detected in a single air- vacuum cycling experiment.

3.6.4 Cooperation between the project partners and researchers

The results and outcomes of this project relied on extensive joint research with no tasks reliant on the contribution of only one or two partners, and this would not have been possible without the cooperation of all the partners and researchers. The majority of participants were involved in the production and characterisation of material samples and contributed to the reports recommending materials and fabrication techniques for next generation mass standouts. In addition a researcher excellence grant at TU-IL contributed significantly to the overall developments by the project through improved knowledge of surface properties and treatments for new mass standards. Two mobility grants from smaller NMIs outside the project (IPQ and IMBIH) enabled additional information and data to be obtained related to new cleaning methods for mass artefacts, real-time sorption measurements and the potential suitability of coated materials. NPL and NRC cooperated on the production of 3 new mass standards from tungsten. Methods for the density determination of both the raw material and completed artefacts were compared and validated and production techniques optimised as a result of this collaboration.

A comparison of weight in vacuum undertaken in the project involved nine of the partners, which allowed allow robust conclusions to be drawn regarding the stability of weights during transport between laboratories and on the transfer of weights between air and vacuum.

4 Actual and potential impact

4.1 Dissemination activities

4.1.1 Publications

16 peer reviewed papers have already been produced, including publications in Metrologia, Rev. Sci. Instrum., IEEE Transactions on Instrumentation, Measurement and Control, Vacuum and Measurement. In addition 4 peer-reviewed papers have been published in conference proceedings. 4 articles were published in trade journals or popular media and a further 3 articles have been published on non-project external websites. Some publications covered the technical aspects of the project whilst others addressed the dissemination of information to a wider audience. A diverse range of journals has been used for the latter to ensure the widest possible dissemination of this general information.

The paper “Preparations for the Forthcoming Redefinition of the Kilogram” by Stuart Davidson and Ian Robinson, published by Measurement & Control, was awarded the Worshipful Company of Scientific Instrument Makers’ Prize (the Derek Cornish Award) for the best paper published by the Institute in 2014 on the development or application of scientific instrumentation.

Two good practice guides “Good practice guide on storage of primary mass standards”, NPL GPG 139, ISSN 1368 6550 and “Good practice guide on weighing in vacuum”, NPL GPG 140, ISSN 1368 6550 have been published and are available as electronic downloads for end users in the NMI mass community and for weight and balance manufacturers. Additionally a Guide to the impact of the redefinition of the kilogram for end users has been made available on the project website.

Information related to the detailed technical aspects of the project has been disseminated via technical reports which have been made openly available on the project website.

4.1.2 Presentations at conferences

11 presentations have been given at key international conferences, including CPEM, NCSLI Workshop and Symposium, the IMEKO World Congress and the European Vacuum Conference. A further 20 presentations were made at external seminars and workshops.

4.1.3 Engagement with end-users, stakeholders and collaborators

Project results and recommendations were shared with stakeholders both directly through email and the website and via a workshop, fora and technical committee meetings. A workshop on the *mise-en-pratique*, process and redefinition of the kilogram and its impact on end users held in Sarajevo, Bosnia Herzegovina in April 2015, was attended by over 70 participants from most European NMIs and from industry and academia, including stakeholders from Mettler-Toledo, Sartorius, Häfner, the International Avogadro Coordination and Kibble balance communities. Attendees at the forum specifically for weight and balance manufacturers, held in conjunction with the workshop, included two major weight manufacturers (Häfner and Sartorius) and two major balance manufacturers (Mettler-Toledo and Sartorius). In particular, advice was given to weight manufacturers on the suitability of new materials for next generation mass standards, and to balance manufacturers on transfer and storage apparatus. Output from the forum was made available to other weight manufacturers beyond this group and collaboration will continue after the end of the project.

The opportunity was also taken to update stakeholders at meetings related to the revisions of EURAMET and UKAS guides on the calibration of non-automatic weighing instruments and at annual WELMEC Committee meetings. 2 media interviews were held in Canada and the United States. In addition discussions were held directly with the public during Open House events in Denmark and the UK, and at the Royal Society Summer Exhibition. More general details of the redefinition of the kilogram have been disseminated via trade journals and via presentations to technical audiences outside the mass community. There is much interest from this type of audience and while the redefinition of the kilogram will not impact them directly, it is useful to engage with this community to be able to outline the benefits of the new SI in general and of the kilogram redefinition in particular. A guidance document “Guide to the impact of the redefinition of the kilogram for end users” has also been produced and is downloadable from the NPL website.[9]

Presentation of the project’s results and outcomes at workshops held in conjunction with the annual EURAMET Technical Committee for Mass (TC-M) meetings, attended by 50-60 participants from NMIs, industry and academia, ensured wide dissemination to the scientific community and good take up of best practice among EURAMET members. Presentations at two Consultative Committee for Mass (CCM) meetings ensured that non-European NMIs are aware of the project’s technical outputs and of the likely impact of the kilogram redefinition in general. It has also ensured that the project’s results and outcomes have informed the development by the CCM of the written *mise-en-pratique* for the redefined kilogram, the instructions that will allow the redefinition to be realised in practice in NMIs.

In addition to the 3 Researcher Mobility Grant secondments undertaken by IMBiH, IPQ and MGRT, the coordinator undertook secondments at the BIPM (3 months) and NRC (2 months). At the BIPM guidance was provided on establishing the Ensemble of Reference Mass Standards (ERMS) which will provide traceability for NMIs following the redefinition of the kilogram. Results obtained by the project on materials for storage containers, optimising storage media, weight transfer and surface analysis all helped to optimise the constitution of the ERMS and the way in which it will be maintained and monitored. At NRC advice on establishing traceability to mass in vacuum was provided and collaborations on the production of next generation mass standards and on long-term monitoring of mass stability using quartz crystal microbalances were initiated.

4.2 Early impact

This project has developed the practical infrastructure and procedures to successfully implement the kilogram redefinition and to facilitate the subsequent maintenance and dissemination of the unit of mass. A practical means of comparing the existing mass scale and the new realisation experiments now exists which will help to ensure the continuity of the mass unit by providing a means of accurately fixing the Planck (and Avogadro) constant with reference to the International Prototype Kilogram (IPK). The procedures and technologies developed in the project will facilitate the dissemination of the mass unit from the new primary realisation experiments with uncertainty contributions smaller than the required relative uncertainty of the realisation (2×10^{-8}) and enable a seamless transition (invisible to end users in industry) from the artefact based definition of the kilogram to realisations, in vacuum, based on the Planck constant.

4.2.1 Next-generation mass standards

New mass standards more suited for the dissemination of the mass unit from the new primary realisation experiments have been manufactured from novel materials, their mechanical and magnetic properties characterised, and surface and gravimetric analysis undertaken to determine their suitability with regard to cleaning and storage techniques to optimise medium- and long-term stability. These new standards have high quality surfaces, low magnetic susceptibility and good stability and will provide the template for the next generation of mass standards which will play a critical part in the maintenance and dissemination of the unit of mass following the redefinition. Major weight manufacturers (Häfner and Sartorius) have been engaged in the manufacturing process, both in the provision of material samples and the test machining of mass standards from new materials. New poly-crystalline tungsten mass standards of 100 g, 500 g and 1 kg respectively have been produced by the weight manufacturer Häfner, NPL and NRC for use as primary standards. A collaboration between NPL and NRC has been established to produce and characterise next generation tungsten mass standards, and a number of standards of various nominal values have been produced and

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[9] http://www.npl.co.uk/upload/pdf/impact-kg-redefinition-end-users.pdf

already provided to the BIPM for use on their Kibble (watt) balance experiment. LNE have produced pure iridium mass standards which will be used in the future dissemination of the mass scale in France. As a result of these studies tungsten has been recommended as a suitable material for primary mass standards and it is likely that its use will become more prevalent in the future.

Plated copper weights have been widely used in the past on Kibble balance experiments since they have very low magnetic permeability. However, investigations of the properties of copper weights plated with either gold or rhodium highlighted limitations with the robustness of the coatings and hence the use of low permeability weights of solid (un-plated) construction, such as tungsten, has therefore been recommended in preference to the use of plated weights.

Silicon is used in both the Avogadro and Kibble balance experiments, however static charge retention can be an issue. No significant correlation was found between the static charge induced and the thickness of the surface oxide layer, indicating that there are no additional benefits from thermally grown oxide overlayers and that silicon mass artefacts with natural oxide layers are suitable. Of the methods evaluated for static charge dissipation, exposure of the silicon to UV light proved to be the most reliable with just a trace level of residual static surface change remaining.

Information on the suitability of new and existing materials for mass standards, disseminated via published reports, has ensured maximum awareness among manufacturers and the end-user community. It is likely that the majority of end users will continue to use stainless steel for their reference mass standards, so the knowledge gained in this project on the behaviour of stainless steel under the new non-contact cleaning techniques (H-plasma and UV ozone) and when stored in and transferred to vacuum and inert media will help to minimise uncertainties. National measurement institutes, higher level calibration and research laboratories and weight manufacturers should consider the use of next-generation mass standards as their primary reference weights, as these will offer improved vacuum compatibility and long term stability as well as being compatible with direct comparison with the unit of mass as realised via the Kibble balance experiment.

4.2.2 Protocols for vacuum operation and the transfer of weights between air and vacuum

Recommendations on the optimum operating pressure range for Kibble balance and vacuum mass comparators based on investigations using gravimetric and surface analysis measurements have been produced. This guidance will ensure the constancy of mass measurements made on Kibble balances and reduce the uncertainty with which the Planck constant can be fixed with respect to the IPK.

Optimised protocols for the transfer of weights from vacuum to air have been developed. Essentially a direct transfer between air and vacuum is the most sensible approach because it minimises manipulation of the mass standard and an intermediate nitrogen stage was found not to be significantly beneficial in reducing the accretion of contamination.

Universally compatible mass storage and transfer enclosures developed and constructed in the project, have enabled the first comparison of ‘weighing in vacuum’ to be undertaken by 7 NMIs with mass standards transported under inert gas. The optimised design for transport enclosures has been taken on board by the major balance manufacturers (e.g. Mettler-Toledo and Sartorius) who collaborated as part of this project, to improve their design of equipment for the storage and transport of masses in vacuum and will improve and add flexibility to the design of the next generation of Kibble balances and vacuum mass comparators. The design of the enclosures and a report on vacuum mass comparators (and associated equipment) currently in use by NMIs has formed the basis of work on a new generations of weighing in vacuum equipment being developed by the balance manufacturers mentioned above. Recommendations on weighing in vacuum are now available in a Good Practice Guide.

The recommendations for an optimum operating pressure range for Kibble balances and vacuum mass standards, the research into the transfer of weights under inert gas, the universally compatible mass storage and transfer enclosures, the protocols for the transfer of weights from vacuum to air and the results of the first comparison of weighing in vacuum using various transfer methods for the travelling standards has produced findings which will inform all future mass comparisons. The methods and results are being used as the basis for the CCM pilot study being organised by the BIPM for the comparison of primary realisation experiments. In the future, they will ensure the maintenance and dissemination of the unit of mass can be undertaken, minimising the additional uncertainty which will be introduced due to the necessity

4.2.3 Improved understanding of the sorption behaviour of masses using surface analysis techniques

The use of a wide range of complementary surface analysis techniques (such as X-ray photoelectron spectroscopy, thermal desorption spectroscopy, photo-thermal deflection spectroscopy, X-ray reflectance, atomic force microscopy and white light interferometry) to characterise the surfaces of mass standards and to determine the evolution of contaminant overlayers, can be used in the future to deterministically predict drift in primary mass standards without the need for direct weighing data. Such measurements could be used, for example, to corroborate unexpected changes in the values of primary mass standards which will be beneficial in the future maintenance and dissemination of the mass scale. The importance of this development is demonstrated by the recent issues with the maintenance of the current mass scale and the significant changes in the scale seen at the 2014 *Extraordinary Calibrations* using the International Prototype Kilogram undertaken at the BIPM, where the use of corroborating evidence from surface studies gave confidence in the recalculated values for the prototypes of the project partners.

Complementary surface analysis techniques have also provided considerable insight into the mechanisms underlying the stability of mass standards and it has been possible to identify the changes in surface chemistry and overlayer thickness which lead to the increase in the mass of primary mass standards with time. This has informed the choice of new materials for mass standards and contributed to the evaluation of the merits of various cleaning techniques and inert gas and vacuum storage.

Real-time surface sorption measurements under dynamic pressure conditions are now possible using a specially developed ellipsometry cell. This has allowed the characterisation of surface during the desorption process and hence a better understanding of the changes in surface composition which take place as the pressure is reduced. This helped to validate the recommendations developed for the operating pressure for Kibble balances and vacuum mass comparators and also to decide on suitable stabilisation times for weights transferred between air and vacuum.

Quartz crystal micro-balance (QCM) technology has also been adopted to characterise surface sorption both of water sorbed during the air-vacuum transfer process and of surface contaminants resorbed after the cleaning of surfaces, with the mass standards stored in different media following cleaning. These measurements provided further insight into the mechanism which cause changes in the values of mass standards and enabled recommendations to be developed on the transfer and storage process. QCMs will also be used in future as an indicator of the long-term accretion of contaminants on the surface of mass standards stored in vacuum or inert media, thus avoiding the need for the standard to be removed from storage and weighed in order to determine their condition and likely mass change since the start of the storage process.

4.2.4 Storage of primary mass standards

Evaluation of the stability of mass standards stored vacuum and inert gas, both gravimetrically and using XPS surface analysis techniques and real time measurements with a QCM, has informed decisions on the optimum storage of mass standards in the medium and long term. This will assist future developments necessary to maintain continuous ongoing traceability to the mass scale after redefinition (e.g. via the BIPM *Ensemble of Reference Mass Standards*). QCM measurements were particularly useful in selecting media in which to store mass standards immediately after cleaning using UV/Ozone and H-plasma techniques, as immediately after cleaning and for a period of a few weeks, mass standards are particularly susceptible to recontamination. UV/ozone and H-plasma cleaning have the potential to leave the surface of mass standards in a cleaner state than traditional solvent based contact cleaning techniques (see 4.2.5). Appropriate storage of mass standards during this period is vital to minimise the magnitude of the initial mass gain and also to improve the long term stability of the mass standards. Real time QCM measurements combined with XPS data to determine the surface chemistry showed that storage in inert gas (nitrogen or argon were used for the tests) both limits the immediate recontamination of the standards and also promotes a more stable surface chemistry (oxide and carbonaceous layer), which enhances the ongoing stability of the standard. These recommendations are now available to the user community in a Good Practice Guide on the storage of primary mass standards.

4.2.5 Cleaning of primary mass standards

The cleaning of primary mass standards will continue to remain of critical importance after the redefinition as, for example, the magnitude of the effect of surface sorption on transfer between air and vacuum is correlated with the surface state of the transfer standard used. Apparatus to implement new non-contact cleaning techniques has been developed by a number of project partners. The new cleaning techniques, UV/Ozone and H-plasma, are more controllable and potentially more effective that the current (manual) cleaning methods such as nettoyage-lavage and solvent based techniques. Results from the project partners demonstrated the potential of the new non-contact techniques to improve on current methods, however the results also showed considerable variation in the effectiveness, repeatability and post cleaning stability of the weights cleaned. This suggests that the manner in which these cleaning methods are implemented is critical to the quality of the results, and hence precise guidance on constructing and commissioning UV/ozone and H-plasma cleaning apparatus has been provided. Optimisation of the use of these techniques will lead to more repeatable cleaning of primary mass standards, which will ensure the consistency of the way in which the redefined kilogram is disseminated by NMIs.

4.2.6 Uncertainty for the dissemination of the new kilogram

Rigorous uncertainty analysis has been carried out on the processes that will be involved in the dissemination of the redefined kilogram, most notably the additional vacuum to air transfer stage. The way in which surface sorption corrections are measured and applied to this stage has been evaluated and guidance provided on issues affecting the calculation of the associated uncertainty. A mathematical analysis of the air-vacuum sorption data obtained in the project showed that adsorption/desorption is irreversible in general, so that the artefacts gain mass as they are repeatedly cycled between air and vacuum with the irreversibility most pronounced if the artefacts were cleaned just before the media cycling experiment. After some cycles between air and vacuum, the sorption/desorption seems to approach reversibility, and the masses of the sorption artefacts tend to stabilise in air as well as in vacuum. This information will inform the way in which the transfer of the unit of mass between vacuum and air is achieved in future and the algorithms produced as part of this analysis will ensure that the calculation of sorption coefficients and their uncertainties are calculated in a robust way in accordance with the Guide to the expression of uncertainty in measurement (GUM).

Analysis of the uncertainties of the new traceability chain for the redefined kilogram showed that a mass value in air having a standard uncertainty of 0.008 mg can be transferred to a mass value in vacuum with a standard uncertainty of 0.010 mg. This means that an uncertainty contribution of 0.006 mg from the air-vacuum transfer can be achieved, at least in principle, which supports the overall uncertainty target for dissemination of the new realisation of the kilogram at NMI level. The results of the analysis will ensure that all NMIs are aware of potential changes to their Calibration and Measurement Capabilities (CMCs) after the redefinition and that they can inform end users of any potential changes to the calibration which they offer. It also ensures that the comparability of national metrology services, as specified in the CIPM Mutual Recognition Arrangement (CIPM MRA) is maintained directly after the redefinition, before new Key Comparisons (KCs) can be undertaken to validate the equivalence of the dissemination of the redefined unit of mass.

4.3 Longer term impact

Overall the project has ensured that a technical infrastructure has been developed to ensure the successful implementation of the kilogram redefinition via the fixing of the Planck constant with reference to the current mass unit. This includes both measurement, transfer and comparison protocols and the apparatus necessary to undertake and monitor these processes. Without these the uncertainty with which the Planck constant could be measured and the continuity of the mass scale through the redefinition process would be compromised. The uptake of this work has been focussed on laboratories with primary realisation (Kibble balance and Avogadro) experiments but will benefit the way in which all NMIs maintain and measure their primary standards. Weight and balance manufacturers have also been engaged with the construction of mass standards from new materials and with the design and production of storage and transfer apparatus for primary mass standards.

The technical challenges of the project focussed on enabling the implementation of the redefinition of the SI base unit of mass, the kilogram. The scientific outputs of the project are key to enabling the redefinition and ensuring that after redefinition the unit of mass can be disseminated robustly while minimising the increase in uncertainty disseminated to the mass end user community. The procedures and technical infrastructure developed are in the process of being adopted by the BIPM and National Measurement Institutes to ensure the full impact of the kilogram redefinition can be realised. Wider impacts will be to ensure the continuity of the worldwide mass scale without significant impact on the traceability provided to end users by NMIs. Additionally the dissemination of information regarding the redefinition and its possible impact on metrology to a wider audience is vital and is addressed with publications and guides at an appropriate technical level, in particular the guides to the redefinition of the kilogram and the background science and by the publication of articles in trade journals and general scientific magazines. Improvements to the construction of primary mass standards (materials and finishing techniques), improved cleaning and storage procedures and a better understanding of the mechanisms which lead to changes in the values of primary mass standards will have continuing benefit to the mass community as a whole.

This project has made significant contributions to facilitating the redefinition of the kilogram in 2018. It has developed a practical means of comparing the proposed realisation against the existing mass standards, ensuring continuity in mass measurements by linking the IPK to the Planck and Avogadro constants. The project has also developed methods to support the dissemination of the redefinition, and will enable a seamless transition, invisible to end users in industry. Ultimately, the redefinition of the kilogram will provide primary standards with enhanced accuracy, capable of supporting every finer mass measurements, vital to the development of new technologies in fields including quantum computing, nanotechnology and biotechnology.

5 Website address and contact details

Website address is www.newkilo.eu

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