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1 Overview

Realisations of the pascal relied on piston gauges (also known as pressure balances) and liquid manometers containing toxic mercury, both of which measure force per area. Their performance however had remained essentially unchanged over the past few decades, and they suffer from practical and environmental limitations. This project developed photon-based standards, which determine the pressure via gas density using the gas law. Following the implementation of the redefined SI in May 2019, the uncertainty of the Boltzmann constant has been eliminated, so at a given temperature, photon-based standards promised primary measurements limited only by the accuracy of the quantum calculations. By improving these calculations for relevant gas parameters for helium and argon and by realising, further developing, and evaluating six different density-based methods to assess and realise gas pressures in the 1 Pa to 3 MPa range, this project paved the way for quantum-based realisations of the pascal in the EU. In the longer term, such primary standards could be miniaturised, providing faster and calibration-free pressure measurements for industry at a fraction of the present cost.

2 Need

Accurate and fast gas pressure measurements were needed to ensure control and safety in a variety of critical industrial processes. In addition, manufacturers of pressure sensors required reliable, fast and automated calibration, preferably for a wide pressure range depending on the particular application. Conventional methods for the realisation of the pascal were based on force per area with relative uncertainties of a few parts in 10^6 at 100 kPa and a few parts in 10^4 at 1 Pa and had remained basically unchanged over recent decades. Piston gauges started to replace mercury manometers due to their superior accuracy and lack of environmental hazards. However, the fact that weights need to be exchanged on the piston gauge during a calibration leads to drawbacks such as slowness, bulkiness, fragility and complexity of operation. For pressure measurements below 3 kPa, other methods involving static or continuous expansion of gases had to be used which significantly increased the effort required for operation.

The importance of overcoming these limitations had been identified as a strategic goal by the CIPM (Comité international des poids et mesures) the Consultative Committee for Mass and related quantities (CCM) and the EURAMET Technical Committees for Mass and related quantities (TC-M), and in several publications where optical quantum-based methods were proposed for calibration-free sensors. The drawbacks can be overcome by photon-based devices, that could become inherent primary pressure standards significantly outperforming conventional standards, and which can potentially be implemented as desktop or even as on-chip versions.

Two national metrology institutes, NIST (USA) and NIM (China), had invested significant resources in developing quantum-based pressure standards utilising Fabry-Pérot (FP) cavities. Further research and development were however required to address limiting effects such as outgassing, cavity deformation, gas permeation as well as thermal and temporal instabilities.

Due to the very wide range of pressures that needed to be addressed, it was not feasible for this to be covered by one technique alone. The potential of other quantum-based techniques to act as pressure standards such as superconductive microwave resonators, Rayleigh scattering, multi reflection interferometry, gas thermometry methods and absorption spectroscopy therefore also needed to be investigated and evaluated.

In addition, a prerequisite for developing quantum-based primary pressure standards was accurate knowledge of the thermodynamic and electromagnetic properties of the gas used, however the available information was often limited or insufficiently accurate.

3 Objectives

The overall aim was to develop novel quantum-based pressure standards based on optical, microwave and dielectric methods and to assess their potential with the aim of replacing existing mechanical based pressure standards. Therefore, the specific objectives of this project were:

1. To improve the accuracy and extend the working range of Fabry-Pérot refractometry quantum-based methods that have the potential to become primary standards of the SI unit of pressure, the pascal. The target uncertainties (k=1) and pressure ranges are 500 ppm in the range 1 Pa - 1 kPa and 10 ppm in the range 1 kPa - 100 kPa.

2. To improve the accuracy and evaluate the potential of alternative pioneering (non Fabry-Pérot based) quantum-based approaches and detection methodologies for the realisation of absolute and partial pressure standards, including superconductive microwave resonators, Rayleigh scattering, multi-reflection interferometry, gas thermometry methods, absorption spectroscopy of selected molecular species with very long optical pathways and modulation techniques, with target uncertainties (*k*=1) less than 500 ppm between 1 Pa and 10 Pa, less than 50 ppm between 1 kPa and 100 kPa, less than 500 ppm between 100 kPa and 1 MPa and less than 5 ppm between 1 MPa and 3 MPa, depending on the measurement technique.
3. To develop improved ab-initio calculations of the thermodynamic and electromagnetic properties (static and dynamic polarisability, diamagnetic susceptibility along with dielectric- and density virial coefficients) of He, Ne, and Ar and the electromagnetic properties (intensities of specific absorption lines) for CO and CO_2 of gases as needed to meet objectives 1 and 2. For gases other than He, the accuracy of the calculations (targeted uncertainty contributions of 1 ppm to 5 ppm at 100 kPa, equivalent to an improvement of at least a factor of 5) to be validated by comparisons with the results from experiments using He as a calibrating reference substance.
4. To demonstrate the performance of the methods (FP-based refractometers, Rayleigh scattering, multi-reflection interferometry, gas thermometry, superconductive microwave cavity) developed in objectives 1 and 2 by comparison with conventional primary absolute pressure standards such as pressure balances.
5. To facilitate the take-up of the technology developed in the project by end users, i.e. the scientific, metrological, and industrial communities and standards developing organisations.

4 Results

Refractivity or permittivity Fabry-Pérot cavity-based techniques for the realisation of the pascal (Obj. 1)

To develop primary pressure standards for the range 1 Pa to 100 kPa and to address the need for overcoming some of the limitations of piston gauges for the realisation of the pascal, especially slowness, bulkiness, fragility and complexity of operation, novel types of quantum-based pressure standards, in particular those utilising Fabry-Pérot (FP) cavities (FPCs), have been proposed, and, in this project, further developed. In view of this, and in particular as a means to address objective 1 of the project, which reads "*To improve the accuracy and extend the working range of Fabry Pérot refractometry quantum-based methods that have the potential to become primary standards of the SI unit of pressure, the pascal. The target uncertainties (k=1) and pressure ranges are 500 ppm in the range 1 Pa - 1 kPa and 10 ppm in the range 1 kPa - 100 kPa*", the work has been addressing potentially limiting effects of FPC-based techniques, predominantly cavity deformation, gas permeation and outgassing, and thermal and temporal instabilities.

As is described in some detail in the report D1 of the project, *"Fabry-Pérot-cavity-based refractometry — A guide to its realisation and implementation*"[1] and as is exemplified in Fig. 1, a variety of FPC-based refractometers have, in this project, been realised and scrutinised: single and double cavity systems, constructed using various types of spacer materials (glasses and metals), addressed by light of different wavelengths (ranging from 532 nm to 1.55 µm).

[1] QuantumPascal design guide D1 (FP-based refractometry) https://doi.org/10.5281/zenodo.7786489

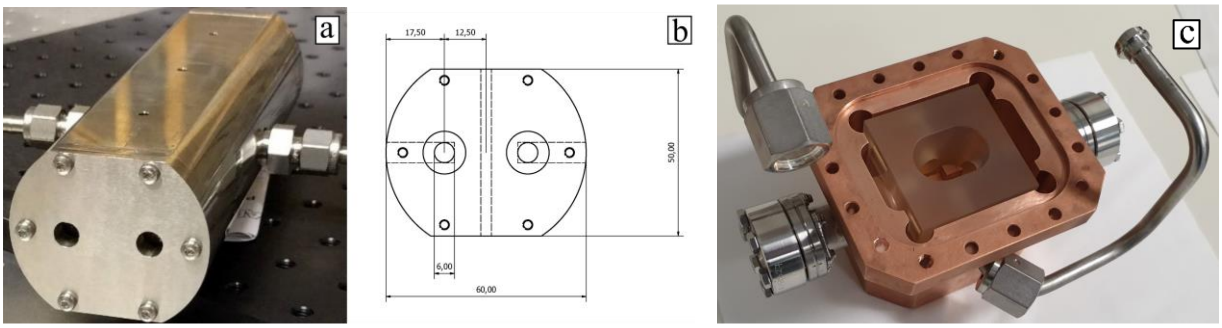

Figure 1. Panel (a): An Invar cavity assembly developed by UmU and RISE before being equipped with temperature probes and mounted inside an Al oven. The plates screwed into the spacer at its short ends press the mirrors, via O-rings, onto the spacer. Panel (b): A schematic drawing of the cavity assembly. Units in mm. Panels (a) and (b) are reproduced with permission from Rubin et al. [21]. Panel (c): Picture of the open refractometer at CNAM comprising a 50 mm-squared single FP resonator (with its two silica mirrors and a spacer made in Zerodur) residing inside the copper enclosure[1].

To improve on the performance of FPC-based techniques and instrumentation, the three aforementioned limiting effects, viz. (i) changes in the length of the cavity that are induced by the gas (i.e., cavity distortion); (ii) gas permeation; and (iii) control and assessment of the temperature of the gas, have been addressed in some detail. It was first concluded that to be able to assess pressure with the targeted relative uncertainty of 10 ppm, cavity distortion has to be assessed, when N_2 is addressed, with a relative uncertainty of at least 3×10^{-14} Pa^{-1} and the temperature of the gas has to be known with an uncertainty of at least 3 mK. In addition, the gases used must remain without impurities (which implies that only minor amounts of gas permeation from the cavity walls are allowed). The FPC-systems also need to be well stabilised so as to reduce the influence of drifts and fluctuations. (iv) To alleviate the influence of remaining disturbances, also a novel modulation-based detection methodology, termed Gas Modulation Refractometry (GAMOR), that has the ability to mitigate the influence of disturbances, has been further developed and scrutinised in some detail.

Fabry-Pérot cavity distortion

As is described in detail in the guide "*Pressure-induced cavity deformation in Fabry-Perot refractometry assessed by the use of simulations and experimental characterizations*",[2] by a combination of simulations, developmental work, and experimental assessments, the consortium has made significant progress regarding assessment of pressure-induced cavity deformation in FP-based refractometers.

To gain a basic understanding of this concept, PTB performed simulations of a single closed cavity with particular regard to the dependence on three parameters, viz. (i) the radius r of the bore of the cavity; (ii) the thickness d of the mirror substrate (which is also the sealing plate of the cavity); and (iii) the length L of the cavity. As has been described in detail in the guide regarding the pressure-induced cavity deformation,[2] it was found that the deformation mainly has (i) a quadratic dependence on the radius of the measurement cavity, (ii) a strong dependence on the thickness of the mirrors for mirror thickness smaller than the diameter of the cavity but a weak one for thickness larger than the bore, and, (iii) for all but the shortest cavity lengths, a proportional dependence on the length of the cavity. For the case with mirrors pressed into the spacer material, which so far has been the case for the Invar-based system at UmU and at RISE [2], it was found that the deformation is virtually independent of the cavity diameter. In this case, it was the width of the interaction area between the rim of the mirror and the spacer that had the strongest influence on the deformation.

To assess the influence of various macroscopic properties of the cavity spacer and the mirrors on cavity deformation, simulations of deformations of a handful of FP-systems with a variety of geometries and spacers materials (Zerodur, Sapphire, Invar, and NEXCERA, where the latter is an ultra-low thermal expansion ceramic) were performed by UmU, PTB, CNAM, and CEM. It was found that the relative deformation varies over a wide range; from 0.20×10^{-12} Pa^{-1} to 7.8×10^{-12} Pa^{-1}, the former for a multi-cavity system based on sapphire components[2] and the latter for a FP cavity system realised in an Invar spacer [2]. This implies that, if

[2] QuantumPascal guide A114 (pressure-induced deformation in FPCs) https://doi.org/10.5281/zenodo.7501925

not corrected for, cavity deformation can contribute to the assessment of pressure on a level ranging from 75 ppm to 3 ‰. This implies that deformation needs to be assessed with high accuracy.

Unfortunately, it was found, in a joint work performed by UmU, CNAM, INRiM, and PTB, that the simulations often were limited by the uncertainty in the material parameters used, e.g., the Young's modulus and the Poisson ratio [8]. Out of a handful of simulations, only two could provide deformations with uncertainties below, and one close to, the 3×10^{-14} Pa^{-1} benchmark for the 10 ppm targeted uncertainty in pressure.[2] It was therefore concluded that it is advisory to assess cavity deformation by experimental means.

As a means to address this, CNAM has assessed the relative cavity deformation of their Zerodur-based FPC refractometer to a value of $-6.70(2) \times 10^{-12}$ Pa^{-1}, with an uncertainty of 2×10^{-14} Pa^{-1}. Although this is slightly smaller than the targeted 3×10^{-14} Pa^{-1} benchmark, the experimentally assessed value differs from the simulated value by 2 %, which is significantly (four times) larger than the targeted 3×10^{-14} Pa^{-1} benchmark,[2] making it impossible to assess the deformation by simulations to such a level that the targeted benchmark can be reached.

To achieve low uncertainty assessments of cavity deformation, UmU, in collaboration with RISE, have developed a novel methodology that can assess cavity deformation with high accuracy [4]. By utilising two gases with dissimilar refractivity (e.g., N_2 and He) at a series of pressures in combination with the gas modulation refractometry (GAMOR) methodology, it can provide assessments of cavity deformation that are independent of systematic (constant) errors in the reference pressure and the assessment of gas temperature, immune to linear drifts of the length of the cavity, and have a significantly reduced sensitivity to gas leakages and outgassing [12]. It has been used to assess deformation in two Invar-based FPC systems with such low uncertainties that they contribute to the assessment of pressure of N_2 solely to a level of 1 to 2 ppm [4]. This implies, in practice, that, if gas purity can be guaranteed, cavity deformation is not a limiting factor in FP-based refractometer assessments of pressure of N_2. This has provided users and developers of FPC-based refractometry instrumentation with a means to perform low uncertainty assessments of cavity deformation.

Methods for control and assessment of the temperature of the gas in Fabry-Pérot cavities

As is described in detail in the report "*Development of methods for control and assessment of the temperature of the gas in Fabry-Pérot cavities*", the consortium has developed and characterised a variety of means to control and assess gas as well as the cavity spacer temperature.

The various FPC-based refractometers that have been realised during the project have in common that they, in combination with a temperature regulation system, provide stable temperature conditions for the assessments using a series of enclosures. For example, a system comprising a Zerodur based FPC, developed by CNAM, has been realised with a set of four enclosures (made of polystyrene, steel, Cu, and Cu, respectively) in combination with a temperature regulation system comprising thermofoil heaters [9]. A characterisation has revealed that this system provides a stability of the temperature in the innermost enclosure under constant gas conditions, where the FPC resides, that is well within ± 1 mK. A second system, comprising an Invar-based FPC developed by UmU and RISE, has demonstrated a temperature stability (k=2) of ± 220 µK [5]. Both these systems provided an accuracy well within the required 3 mK (10 ppm) temperature uncertainty benchmark.

A concern regarding the stabilisation of the temperature in FPC-based refractometry is that the filling of gas in the cavity can, by thermodynamic processes (referred to as pV-work), affect the temperature of the cavity. Since the GAMOR methodology utilises the shortest filling times (with typical periods of 100 s), a specific study was dedicated to the influence of pV-work on the Invar-based FPC utilising GAMOR. In a joint study by PTB, UmU, and RISE, it was found that for pressures up to 100 kPa, as is shown by Fig. 2, this system is not significantly affected by thermodynamic processes that are associated with the exchange of gas (i.e., pV-work) on the time scale of 100 s [21]. This is mainly caused by the fact that the system has a small volume (< 5 cm^3), which implies that only a small amount of energy is carried by the gas exchange process (< 5 J), no heat islands, and that the spacer material has large thermal conductivity and heat capacity. It was found that the dynamic pressure and temperature processes in the gas equilibrate on a time scale of ms and 2 s, respectively, while heat dissipation in the spacer takes place on a time scale of tens of seconds, which is roughly two orders of magnitude faster than previously characterised systems. Additionally, it was shown by improved temperature assessments that the real temperature alterations were solely approximately a third of the upper limits predicted by simulations in the first work [21]. This implies that pV-work is currently not a limiting factor in the Invar-based system and is not an obstacle for reaching the targeted 10 ppm uncertainty benchmark it is not an obstacle, provided that the system has a sufficiently small gas volume and its relevant components in contact with the gas have a sufficiently high thermal conductivity (considering thermal capacity).

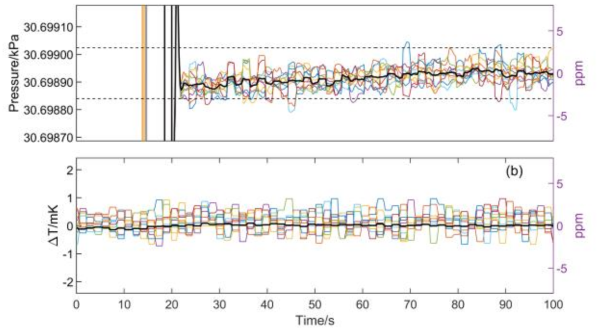

Figure 2. The upper panel displays, by the coloured curves, the gas filling part (0 - 100 s) of 10 individual consecutive gas modulation cycles (each with a total modulation time of 200 s) for a pressure of 30.7 kPa. The black curve shows the mean of the ten individual, coloured curves. The dashed black curves represent ± 3 ppm deviations from the measured pressure. The lower panel illustrates, by the coloured curves, the mean temperature of the three Pt-100 sensors in the cavity spacer during the same 10 cycles in terms of the average temperature of 100 consecutive temperature assessments of the three Pt-100 sensors. The black curve depicts the mean of 100 consecutive temperature assessments normalised to their individual averages. Reproduced with permission from Rubin et al. [21].

A multitude of approaches were used by PTB, CEM, CNAM, RISE, and UmU to assess gas temperature, primarily Pt-100 thermistors, thermocouples (TC), 4-wire measurements of SPRTs, and AC thermometry bridges. To achieve the best temperature stabilities, some systems, primarily developed by CNAM, UmU, and RISE, were run close to, and referenced to, the temperature of a Ga fixed point cell (29.76 °C). The thermistor measurements were in general limited by their drifts, while the TC measurements were mainly limited by the stability of the nano voltmeter and wiring. SPRT measurements have yearly drifts in the order of 1 mK and AC thermometry bridges can have an accuracy better than 0.1 mK. Several of the systems have demonstrated uncertainties well below the targeted uncertainty of 10 ppm. All this implies that the control and assessment of the temperature of the gas in FP-cavities should not be an obstacle to reaching the targeted 10 ppm uncertainty benchmark in pressure.

Gas permeation

Permeation of He gas in the spacer material can adversely affect both the purity and the pressure of the gas (as well as the physical length of the cavity). This implies for example that, if a FP cavity that is made of a material into which He can permeate is exposed to He for a certain period of time, the He will diffuse into the walls of the cavity. After subsequent evacuation and filling with another measurement gas, He will diffuse out of the cavity walls (outgassing) which will contaminate the measurement gas.

As is presented in some detail in the report "*Guide: Information about permeation of gas into various cavity spacer materials*", PTB and IMT have jointly established that the temperature dependent permeability, diffusivity, and solubility of He gas in ULE glass is significant. It is significantly less (3 to 4 orders of magnitude) in Zerodur, and virtually non-existent in sapphire or metals. Hence, to minimise the effect of gas permeation, the use of either of the latter two materials is recommended.

Further development of gas modulated refractometry (GAMOR) for mitigation of the influence of drifts and fluctuations

As is described in detail in the report "*Gas modulated Fabry-Perot cavity-based refractometry (GAMOR) — Guide to its basic features, performance, and implementation*",[1] although it is simple in theory to realise FPC-based instrumentation, it is not trivial in practice to perform low uncertainty refractivity assessments. One reason for this is that FPCs often (knowingly or unknowingly) are exposed to a variety of disturbances, primarily drifts, fluctuation, and noise, on different time scales. The high sensitivity of refractometry to disturbances was early recognised as a practical limitation of FPC-based interferometry for high-accuracy assessment of pressure and realisation of the pascal. For example, a disturbance that causes a change in the length the cavity of 1 pm, a percent-sized fraction of the "size" of an individual atom, gives rise to, for a 15 cm long cavity, a change in the frequency of the cavity mode addressed that corresponds to an alteration in the assessed pressure of nitrogen of 2 mPa. It was therefore widely recognised that the realisation of refractometry systems requires an exceptional mechanical and thermal stability. This implies, for example, that it is far from trivial to assess refractivity with low uncertainty by assessing the length of the cavity in the absence and presence of gas, i.e., L_0 and L, in two separate assessments. A number of procedures to reduce the influence of disturbances and thereby alleviate some of the above-mentioned limitations, have therefore been developed and implemented in various instrumentations over the years.

Of particular importance is the gas modulation refractometry (GAMOR) methodology, developed jointly by UmU and RISE, which has the ability to significantly reduce the influence of disturbances on the assessment of refractivity. As is described in some detail in the guide "*Gas modulated Fabry-Perot-cavity based refractometry (GAMOR) — Guide to its basic features, performance, and implementation*",[3] this methodology is built upon two principles (often referred to as two cornerstones); viz.,

(i) the refractivity of the gas in the measurement cavity is assessed by a frequent referencing of filled measurement cavity beat frequencies to evacuated cavity beat frequencies; and

(ii) the evacuated measurement cavity beat frequency at the time of the assessment of the filled measurement cavity beat frequency is estimated by use of an interpolation between two evacuated measurement cavity beat frequency assessments, one performed directly before and one directly after the filled cavity assessments.

Molar density and pressure are then assessed by conventional means, i.e., by the use of the Lorentz-Lorenz expression and an equation of state, respectively.

In addition to further developing and scrutinising the GAMOR methodology UmU and RISE have summarised its properties and present achievements. It has been shown that it has the ability to assess refractivity while mitigating the influence of various types of disturbances in refractometry systems, not only those from changes in length of the cavity spacer (e.g., caused by drifts in its temperature), but also several of those that have other origins (e.g., those from gas leakages and outgassing) [12], resulting in such an excellent precision that it, for the instrumentation utilised, solely plays a minor (under optimal conditions, virtually no) role in the total uncertainty budget of the pressure assessment. This has allowed for the realisation of systems with a sub-ppm precision (using an Invar-based FPC system, for an for assessment of 4303 Pa, a minimum (Allan) deviation of 0.34 mPa, which corresponds to relative deviation (or 1σ precision) of 0.08 ppm [14] and an uncertainty (k=2) in the assessment of pressure down to the targeted 10 ppm (mainly limited by the uncertainty in the molar polarisability of nitrogen, 8 ppm) [13].

Thanks to its extraordinary precision, this methodology has made possible the development of novel methodologies for assessments of important characterisation parameters with low uncertainty. For example, as was alluded to above, it has been shown that the methodology can significantly improve on the ability to assess cavity deformation using a novel methodology that performs assessments of refractivity of two gases with dissimilar refractivity at a series of pressures [4].

UmU, RISE, and PTB have jointly shown that it also has allowed for the development of a methodology for accurate in-situ assessment of the penetration depth of mirrors to such an extent that its uncertainty presently does not have any significant impact on the assessment of pressure [23].

It has similarly allowed for the construction of a transportable system (denoted the transportable optical pascal, TOP) [13], shown in Fig. 3, that has been used to reach other objectives in this project, most importantly a circular comparison of conventional pressure standards.[4]

Moreover, by use of two GAMOR utilising refractometers coupled to a common pressure reference (Ruska), it has been shown that the refractometers can provide short-term precision on the 1 s time scale of 3×10^{-8}, which is an order of magnitude better than the corresponding stability of the pressure reference (DWPG) [14]. This is an important result, indicating that the precision of the Invar-based GAMOR utilising dual FPC-based refractometers is significantly better than that of many types of standard pressure reference devices.

[3] QuantumPascal guide A143 (GAMOR: performance & implementation) https://doi.org/10.5281/zenodo.7786349

[4] QuantumPascal report D8 (circ. comparison with transport. refractometer) https://doi.org/10.5281/zenodo.7786697

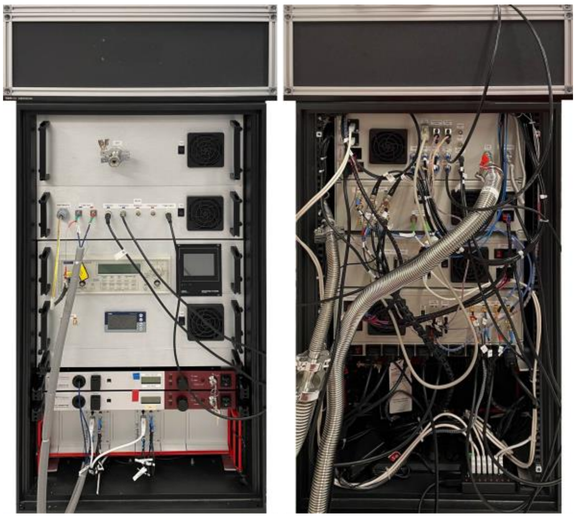

Figure 3. Picture of the TOP from the front (left) and back (right). On top of the rack there is a temperature regulated Al breadboard with an attached isolating enclosure, within which the dual FPC sits. Below this, within the rack, are five modules containing the gas handling system, fibre optics, and electronics, lasers, and locking electronics. The various modules are connected to each other by the use of standard detachable electric-, fibre-, and gas connectors, which implies that each individual module easily can be removed from the system for easy reparation or replacement. Reproduced with permission from Forssén et al. [14].

All this clearly indicates that FPC-based refractometry has a great potential to be developed into a powerful methodology for assessment of refractivity, molar density, and pressure, as well as for future realisation of the pascal.

To disseminate the use of the GAMOR methodology as widely as possible, its performance has, as a part of the project, been summarised and mediated in the literature [6, 11, 20, 23]. In addition, the "*Gas modulated Fabry-Perot cavity-based refractometry (GAMOR) — Guide to its basic features, performance, and implementation*",[3] presents, for the first time, a recipe, in terms of 29 points, for how to construct a GAMOR-based FPC refractometry system suitable for high precision and low uncertainty assessments. It also presents recommendations for how to realise and implement state-of-the-art FPC based refractometers.

State-of-the-art performance of FPC-based refractometry systems developed as a part of this project

As is described in some detail in the report D2, "*Report evaluating the performance of the different types of FP-based refractometers developed with respect to their precision, accuracy, working range and target relative uncertainties of 500 ppm in the range 1 Pa – 1 kPa and 10 ppm in the range 1 kPa – 100 kPa*",[5] several instruments have been developed within the project in order to reach the target uncertainties. While only a couple of systems have undergone proper uncertainty evaluation in terms of their ability to assess pressure, the joint efforts and achievements clearly shows that the target uncertainties not only can be reached, but also exceeded, if the individual realisations are combined.

As is shown by Fig. 4, at least one system (denoted the stationary system) has been developed that, in the 10 Pa to 25 kPa pressure range, has an uncertainty below the targeted benchmark (500 ppm for 1 Pa to 1 kPa and 10 ppm for 1 kPa to 100 kPa). Below 10 Pa, the system exhibited, at the time of the characterisation, limitations due to its empty cavity repeatability, outgassing and leaks, and ability to estimate the residual gas pressure. Regarding pressures above 25 kPa, the system was not, at the time of the characterisation, explicitly characterised due to limitations in the vacuum system.

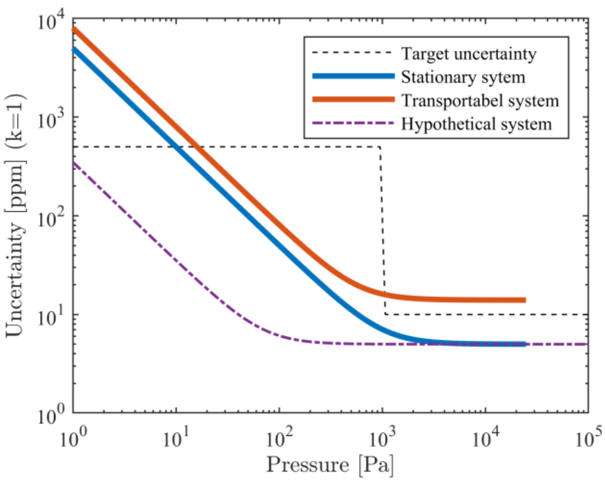

Figure 4. Performance of some FP-based refractometers developed within this project. The black dashed lines correspond to the target uncertainties of the project. The blue and red curves represent the performance of the SOP and TOP systems that were evaluated in Silander et al. [13]. The purple dashed-dotted line represents the performance of a hypothetical, but not yet realised system, which is based on the combined best findings of various systems within the project.

[5] QuantumPascal report D2 (performance of FP refractometers) https://doi.org/10.5281/zenodo.7786658

To facilitate the uptake by end users of the technology developed in the project, in addition to the D1 and D2 reports,[1,5] a number of guides related to cavity deformation,[2] temperature control and assessment, gas permeation, and the GAMOR methodology have been produced. Based on the above description, the project successfully achieved the objective.

Research in Piezo-electric Materials in Pressure Measurements (RMG01)

Literature review and simulations of piezo-electric and elasto-optic effects in FP-based interferometers using different materials

Potential cavity spacer materials with promising optical and electronic properties were selected for this feasibility study: α-Quartz, B_2O_3, $LiTaO_3$, $LiNbO_3$, Al_2O_3 (Sapphire), PVDF (Plyvinylidene fluoride), Lead Zirconite Titanate (PZT4, PZT5A, PZT5H, PZT8), $PbTiO_3$, $BaTiO_3$, $BiFeO_3$, $KNbO_3$, NaCl, KCl, and Fused Silica. For these 17 materials, the important properties (refractive index, elasto-optic tensor, piezo-electric tensor, density, Young's modulus and compliance tensor, Poisson ratio, coefficient of thermal expansion, thermo-optic coefficient, pyro-electric coefficient, thermal conductivity, specific heat, transmittivity, electrical resistivity and total dielectric permittivity for frequencies < 1 GHz) were researched from the literature to simulate the pressure-induced voltage generated for piezo-electric materials and pressure-induced changes in optical path length for elasto-optic materials. The three materials with the strongest measurement effects were: α-Quartz, Al_2O_3 (Sapphire), and PVDF (Plyvinylidene fluoride). The α-Quartz is a piezo-electric, non-pyro-electric, elasto-optic and thermo-optic material. Sapphire is an elasto-optic and thermo-optic material, it is potentially piezo-electric due to its structure, however no literature was found about it. Both materials are birefringent, so the refractive index depends on the direction, which can be useful for specific measurements. Finally, PVDF was selected due to its piezo-electric and pyro-electric properties.

Simulations of temperature- and pressure-induced changes of the optical path length in sapphire

As shown in Figure 5 a slightly simplified design (panel a) was used to simulate temperature- and pressure-induced changes of the optical path length in PTB's sapphire-based FPC.

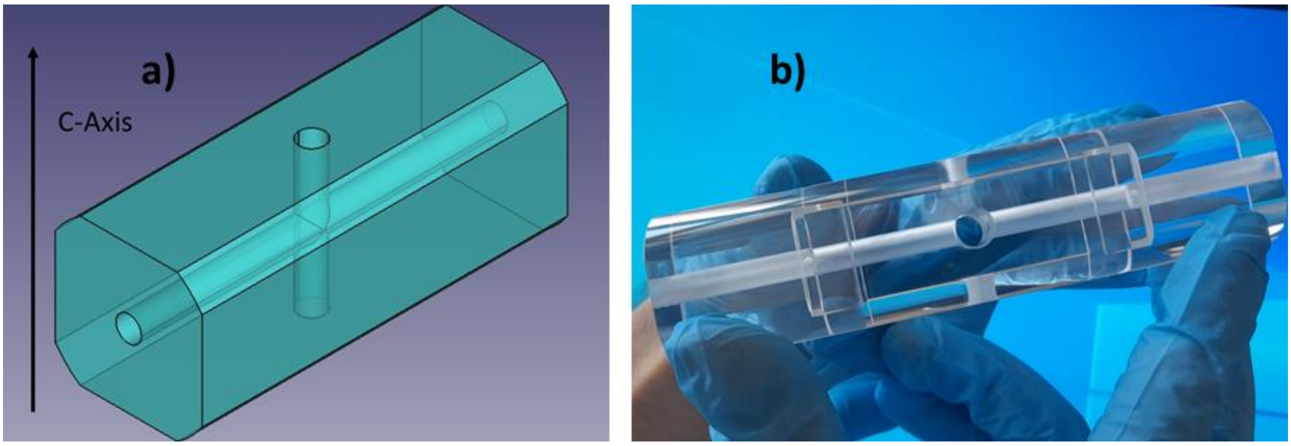

Figure 5. Left: Design of the simulate cavity – Right: PTB's sapphire spacer, here directly used as FPC

Two diode lasers with different polarisation were each locked to FSR of the sapphire spacer. The cavity here is given by the front and back of the spacer with respect to the long direction. The beat between an iodine-stabilised HeNe-laser and the horizontal polarised beam from one diode laser was measured and as simulated more sensitive to temperature changes compared to the beat between both diode lasers (horizontally and vertically polarised), which was more sensitive to the pressure changes. The simulated effects were compared to the experimentally achieved results, showing an excellent agreement in the ultra-high temperature sensitivity as well as the high pressure sensitivity. The feasibility was confirmed and therefore the task completely fulfilled.

Alternative non Fabry-Pérot based techniques for the realisation of the pascal (Obj. 2)

The feasibility of using alternative non FP-based techniques to assess absolute and partial pressure was investigated: various systems based on different methods and techniques have been realised and their metrological performances evaluated by the consortium, as it is described in the report D4 of the project.[6] The realised systems are specifically based on the following methods: Rayleigh scattering (**RAY**), multi-reflection interferometry (**UINT**), Dielectric Constant Gas Thermometry (**DCGT**), Refractive index Gas Thermometry (**RIGT**), superconductive RIGT (**S-RIGT**) and absorption spectroscopy (**TDLAS**). Jointly, the developed techniques cover the wide pressure range from 1 Pa to 3 MPa.

RAY: To implement the method based on Rayleigh scattering, a simple and compact device has been designed and realised at INRiM, that is capable of working in an extended pressure range up to 1 MPa. Both the principle and the experimental setup of RAY are extremely simple, and this aspect represents one of the strengths of its realisation: a short wave (blue) CW laser beam interacts with the gas in a vacuum/pressure chamber. Each gas atom or molecule immersed in the electromagnetic field acts as a dipole oscillating at the EM frequency and irradiating energy proportionally to the gas polarisability. A photon collecting system allows to accurately measure the strength of the interaction, which depends on the gas pressure. As the most important factor influencing the performance of a scattering-based system is the stray light, which can dramatically influence the accuracy of such kind of system, a multi-step stray light analysis has been carried out with the support of UmU and RISE. After a predictive estimate of stray light of the system, the optomechanical components, designed to reduce stray light, have been introduced in the model, obtaining a reduction factor of 10^{-5}, which fully meets our requirements. The optical layout has been consequently designed and realise to minimise the stray light effects. The associated vacuum/pressure apparatus was designed to work up to 1 MPa, including the custom viewports able to work up to a “conservative” over-pressure of 2.5 MPa (Fig. 6).

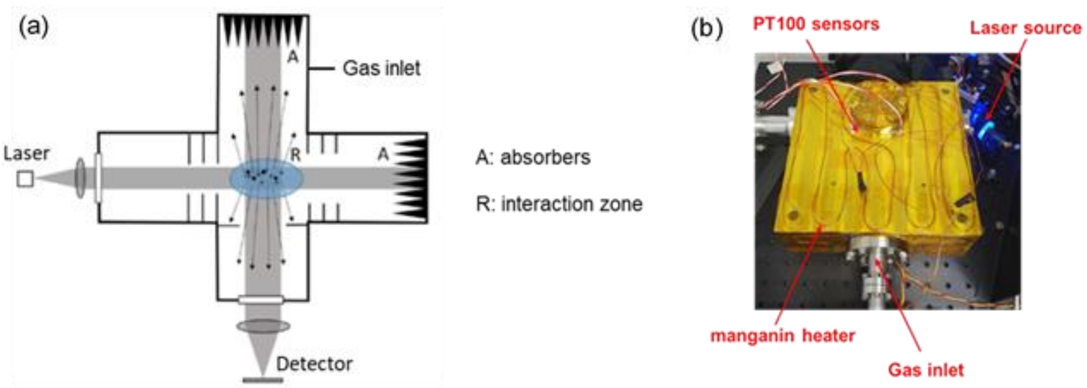

Figure 6. Rayleigh scattering for pressure measurement (RAY): (a) scheme of the experimental setup; (b) aluminum vacuum chamber equipped with heater for thermal control.

The adopted solution consists in an all-metal chamber in which the gas is forced to distribute itself along an asymmetrical cross-shaped volume and the temperature is maintained constant by means of a custom temperature control.

A custom software in python™ ambient has been developed to analyse the acquired images from the camera detector, with the double aim of detecting and correcting the effect due to eventual spurious scattering centres and calculating the light intensity The software allows to easily process all the images of a dataset in one shot, checks each image for possible acquisition issues, calculates the light intensity at each pressure value and shows the resulting curve of the scattered light intensity vs. pressure value. The realised software and the design of RAY system have been presented in [15]. The RAY system has been extensively characterised in terms of resulting intensity of scattered light as a function of gas pressure for three different gases: helium, argon, and nitrogen: the results evidenced a strong linear dependence between scattered light intensity and pressure with residuals within 400 ppm for all the considered gases. The obtained results demonstrated that RAY can be realised through a simple experimental setup (in principle at low cost), and it is able to provide

[6] https://www.ptb.de/empir2019/fileadmin/documents/empir/QuantumPascal/reports/QP_D4_update_08_Dec_2022.pdf

fast measurement at least up to 1 MPa with an accuracy better 500 ppm, paving the way for the realisation of a transfer standard based on this technique.

UINT: A novel version of an optical pressure standard based on a multi-reflection interferometric technique was realised at INRIM and it will be extensively described in a forthcoming publication. Such realisation of the pascal is achieved by the measurement of the refractive index of a gas through an unbalanced homodyne interferometer (UINT) and aims to propose an alternative route to current Fabry-Perot cavity-based techniques. The UINT methodology has been used for assessment of pressure in the 100 Pa – 120 kPa range, with a target relative uncertainty of 10 ppm at 100 kPa. The realised system was designed by INRIM, in collaboration with PTB and RISE, to be equipped with a custom pressure/vacuum apparatus, with a double-step temperature control and suitable to contain the optical system, i.e. the novel interferometer, whose measurement arm is formed by two high-reflective mirrors and a spacer made of Zerodur (Fig.7).

The main factors to be considered to reach the aforementioned target uncertainty have been carefully studied. The UINT realisation has benefitted from a series of optical simulations, fundamental for the final optimisation of its design, primarily to study the optical path inside the double mirror assembly of UINT, i.e. the measurement arm of the interferometer. The optical layout has been realised taking into account the output of suitable performed studies: a FEM analysis to estimate the deformation due to gas pressure, the ray tracing study, to estimate the value of nominal optical path, the Gaussian beam propagation study to predict the value of misalignment between the entrance and the exit laser beam. An important challenge for a primary photonic realisation of the pascal is certainly related to the measurement and control of temperature: various tests about the realised active temperature control of UINT system have been carried out demonstrating that it meets the expected requirements, i.e. proving © ability to assess the temperature with an uncertainty below 3 mK.

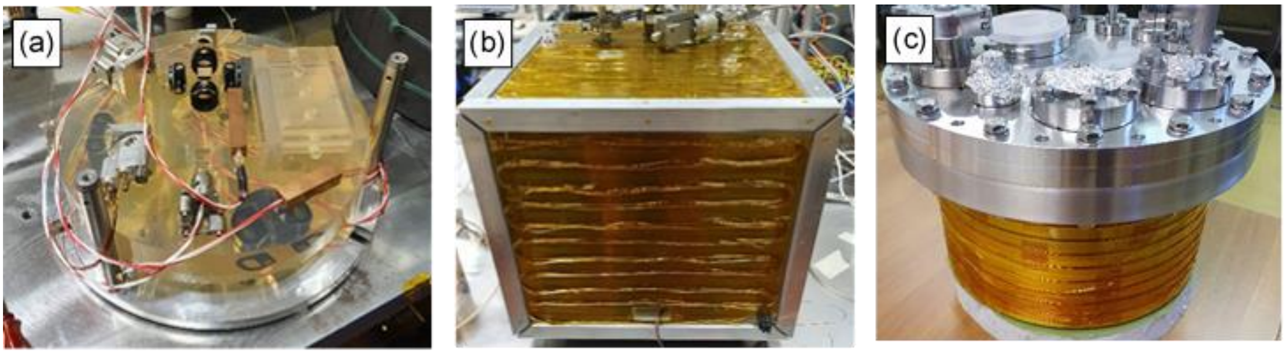

Figure 7. UINT optical pressure standard: (a) UINT interferometer; (b) Aluminum box with first stage of thermal control; (c) vacuum chamber hosting interferometer with second stage of thermal control

A fundamental further step in the development of UINT technique relied on an independent experiment to undertake an absolute measurement of the unbalance of the interferometer, which is the crucial quantity to be measured to put into operation the UINT system as primary optical pressure standard. To meet this requirement, the unbalance was determined by means of a technique based on the frequency scanning interferometry: the result agrees with the predictive estimate performed through the above-mentioned ray tracing study and allows to meet the expected target uncertainty.

The relative standard uncertainty in the range from 100 Pa to 120 kPa has been evaluated and ranges from 5.2×10^{-4} to 1.0×10^{-5} between 100 Pa and 10 kPa and it is equal to 1.0×10^{-5} above 10 kPa. Therefore, the UINT pressure standard demonstrated to fulfil the main goal to have the ability of assessing the pressure at 100 kPa with a relative uncertainty of 10 ppm, improving the uncertainty by a factor of 10, compared to previous achievements before the start of this project [28].

DCGT: A pressure standard based on the Dielectric Constant Gas Thermometry was developed and intensively characterised within the frame of a PhD thesis. It features four measuring cells equipped with cylindrical capacitors made from 1.4122 stainless steel. The capacitance was measured with a Andeen Hagerling 2500 Option E capacitance bridge. After a comprehensive check of the underlying working equation and the determination of the required order of the virials, the DCGT based pressure standard was first tested with argon at 296 K. These results have shown an agreement within 15 ppm of the reading of a traditional primary standard for pressures up to 7 MPa, using the most recent values for the virial coefficients of Ar, including Jäger re-evaluation of the second density virial coefficient. However, to reach lowest uncertainties, the highly precise DCGT virial coefficients for argon by Gaiser and Fellmuth [19] at the triple point of water had to be used. The uncertainties of calculated or other experimentally determined virial coefficients are not sufficient to reach the targeted pressure uncertainty at this point. By repeating the measurements at the tripe point of water it was shown that a DCGT pressure standard based on argon can be realised for the pressure range 1 MPa to 3 MPa with a relative standard uncertainty in the order of 10 ppm utilising commercial measuring equipment. For higher pressures, the uncertainties of the virial coefficients are dominating while for pressures below 1 MPa, the uncertainty of the commercial capacitance measurement bridge becomes the limiting factor.

RIGT: A primary pressure standard based on Refractive index Gas Thermometry was developed within the project. It is based on the accurate determination of the static refractivity of helium, neon and argon, using a microwave resonator, and on the ab-initio calculation of the electromagnetic and thermodynamic properties of the same monatomic gases. Differently from capacitance measurements of the permittivity of the gas, the microwave resonances of a cavity are sensitive to the variation of the refractive index as a function of molar density and, consequently, of the gas pressure. The refractive index n of helium and argon near T = 273.16 K were initially measured in the pressure range 200 kPa < p < 1 MPa with a 3-litre internal volume spherical copper resonator. The results of these measurements evidenced problems of contamination of the thermometric gases, leading to the design of a new apparatus comprising a 0.5-litre triaxial ellipsoidal copper resonator, a modified pressure manifold to allow measurements with a steady flow of gas through the cavity to avoid contamination. Manifold connections to a pressure balance, for the sake of comparison, were also re-designed to minimise Hagen-Poiseuille corrections.

The effective isothermal compressibility k_T of the RIGT apparatus at 273.16 K, which is the source of a relevant correction, was then determined by microwave measurements of the static refractive index of He between 100 kPa and 1 MPa, based on the ab initio calculations of the properties of He, and using the pressure balance as a reference, leading to the precise estimate $k_T = (7.395 \pm 0.004) \times 10^{-12}$ Pa^{-1}. Based on this compressibility estimate, measurements of the refractive index of Ar and ab initio calculations of the properties of Ar realise a microwave primary RIGT pressure standard with relative standard uncertainty varying between 3.7 ppm at 100 kPa and 13 ppm at 1 MPa. The results showed that an accurate RIGT pressure standard can be realised based on refractive index measurements of He, Ne or Ar, representing an interesting alternative for pressure metrology.

S-RIGT: The potential of a primary absolute pressure standard, based on a superconductive (RIGT) microwave cavity, operating between 200 Pa and 20 kPa, was investigated. After a feasibility study and an evaluation of alternative solutions, a superconductive version of a triaxial ellipsoidal microwave cavity was designed and produced. The chosen solution consists of a copper cavity with internal Nb coating. Relevant tests of its microwave, thermal and mechanical performance at ambient room temperature and atmospheric pressure were then carried out. A first cryogenic apparatus suitable for testing a superconducting microwave cavity at temperatures below 10 K was designed, realised, and installed. Subsequently, the superconducting microwave triaxial ellipsoidal microwave cavity was installed in the cryogenic apparatus at LNE/CNAM and tested (Fig. 8).

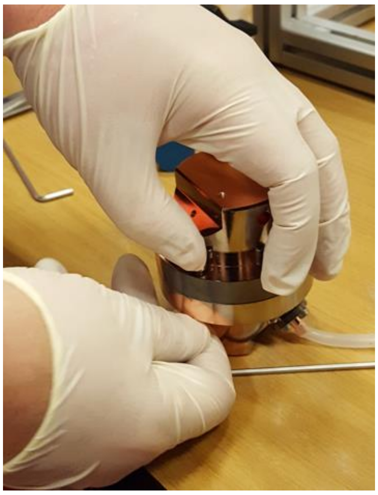

Figure 8. Left: Superconducting microwave resonator assembly. During the operation, its cavity is kept in an argon atmosphere to prevent surface oxidation. The resonator is made of copper. Its cavity has a quasi-spherical form with a niobium coating of 3 µm. Middle and Right: Figures show the cryogenic setup.

A second cryogenic apparatus was fabricated. This new version aimed to reduce the thermomolecular effect that appears at low pressure. During the manufacturing and installation of the second cryostat, the first cryostat was tested with argon. The use of argon gas implies working at temperatures higher than 87.3 K. At these temperatures, the use of nitrogen as cryogenic liquid simplifies the experiments. Argon gas pressure is measured with a microwave resonator in bare copper, thus without superconducting properties. The resonator used with helium loses its superconducting properties at temperatures above 9.2 K. Various tests have been performed, leading to: improvement of the long-term stability with GPS, use of a measuring bridge for reference temperature, thermal stabilisation of the regulation temperature measuring device, curve fitting and microwave acquisition method modifications, new amplifiers, microwave isolator.

Some relevant modifications of the apparatus, which include leak-tight sealing of the resonator and the installation of the thermometers from the temperature regulation loop, have been implemented.

Tests were performed with argon gas, the temperature of the resonator being lower than the temperature of the triple point of argon (83.8 K) which demonstrated the absence of pre-condensation. To check whether the vector network analyser used to measure the resonant frequency was not introducing distortion, it was replaced by another device. No difference was found in the measurements. Further measurement of the thermo-molecular effect is in progress. A preliminary uncertainty evaluation with helium yields a standard uncertainty of 0.2 Pa at 500 Pa and 8.2 Pa at 20 kPa, with a major contribution from thermometry, which might be substantially reduced in future work, e.g., by using a rhodium iron thermometer directly calibrated on the thermodynamic temperature scale. For more details, the description of the results of realised S-RIGT primary absolute pressure standard is reported in a PHD thesis [27] as well as in article [29].

TDLAS: The feasibility of realising a partial pressure standard based on absorption spectroscopy was evaluated. The existing Herriott-cell based setup at PTB was further developed and improved. This includes two QCLs (Quantum Cascade Lasers) which work at the fundamental bands of CO and CO_2 at 4.6 µm and 4.3 µm respectively. To narrow the line width of these lasers as well as to provide reproducible and reliable scans of the emission frequencies of these lasers an additional lock to a commercially available FPI was realised. The maximum optical path-length inside the cell used was above 100 m. It was experimentally confirmed that the coherence length of the QCLs after applying the lock to the FPI is greater than one hundred meters, which proves the improved linewidth of the laser emission, that was estimated to be necessary to reach the targeted accuracy. It was also shown that the stability of the temperature control of the 40-litre vacuum chamber is better than 20 mK (peak-to-peak) with the temperature measurement being performed with SPRTs with an uncertainty of 350 µk (k=1). As "conventional pressure standards" for the comparison, several vacuum gauges have been prepared, which have been directly calibrated at PTB’s "Vacuum metrology laboratory" utilising the new static expansion system ‘SE3’. As a preliminary result, it can be stated that when CO was used as a measured gas, a limit of detection below 1 mPa has been achieved. Further analysis as well as the publication of the results will be part of the corresponding PHD-thesis, which is currently under preparation. Based on the above description, the project successfully achieved the objective.

Improved ab initio calculations for the thermodynamic and electromagnetic properties of gases (Ob. 3)

To fulfil objective 3, several gas parameters of He, Ne and Ar but also CO and CO_2 were calculated ab initio and experimentally verified. For the optical methods, the key property is the refractivity or dynamic molar polarisability which is the sum of the dominating static molar polarisability, the corresponding dispersion which accounts for the optical frequency dependence (influence in the low order of percent) and the magnetic susceptibility (influence in the order of some 10 ppm) since electromagnetic waves are used. For helium, these properties were known prior to the project with reasonable uncertainties particularly because of its use for the determination of the Boltzmann constant. Still, the uncertainties were lowered significantly within the frame of this project. Results for the dipole polarisability including relativity and finite mass correction with extremely low uncertainties of less than 0.1 ppm are already published by UW [1]. A paper on the relativistic treatment of the magnetic susceptibility was submitted. For neon and argon, it was clear from the beginning that the uncertainties of ab-initio calculations for the static value of the molar polarisability will not be sufficient. Instead, the highly precise experimental values [Gaiser and Fellmuth, Phys. Rev. Lett. 120, 123203, 2018] with standard uncertainties of 2 ppm are used while the limits of the theoretical calculations were pushed further. To include the frequency dependence, highly precise calculations by UW of the dispersion coefficients (published for Ne [10], submitted for Ar) were performed which correspond to an improvement by more than one order of magnitude in uncertainty. Similar improvements were reached for the magnetic susceptibility (partially published for Ne, publication on the relativistic treatment of Ne and Ar is drafted). Thanks to these ground-breaking calculations, the overall refractivity for Ne and Ar is now available for a broad temperature and frequency range with relative standard uncertainties in the order of 10 ppm for the latter.

To account for the interaction between multiple gas particles, density and dielectric virial coefficients are included in the working equations of optical and dielectric pressure standards as well. Since the density virial coefficients are part of the EMPIR project “Real-K”, in this project, only novel values of the dielectric virial coefficients were calculated and measured. The required underlying pair polarisabilities (and the three body polarisability in case of He) as well as methods for the calculations of the virials were further developed by UW and FBK. A publication on the relativistic treatment and improved values of the second dielectric virial coefficients of He^3 and He^4 is drafted by UW. Despite many efforts, it was not possible to further improve the pair polarisabilities for Ne and Ar. However, a novel path integral method was developed and used to calculate update values of the virial coefficients of the three noble gases [3] by FBK. In contrast to the previous state of the art, these values now also feature an uncertainty estimate and can be applied for a broad temperature and frequency range. The path-integral methodology was then further extended for the calculation of the third dielectric virial. The methodology and values calculated by the available literature potentials and pair polarisabilities utilising the superposition approximation were published in an impactful joint publication by FBK and UW [18]. In case of helium, fundamental work was undertaken by UW to determine the exact three-body polarisability tensor ab initio with a publication being currently drafted. A quantum mechanically rigorous value for the third dielectric virial coefficient was then calculated utilising the aforementioned path integral approach. An impactful joint publication with these results is currently drafted by FBK and UW. This is particularly important for higher pressures where the relative influence of the higher virial orders increases and becomes a dominating source of uncertainty (Fig.9).

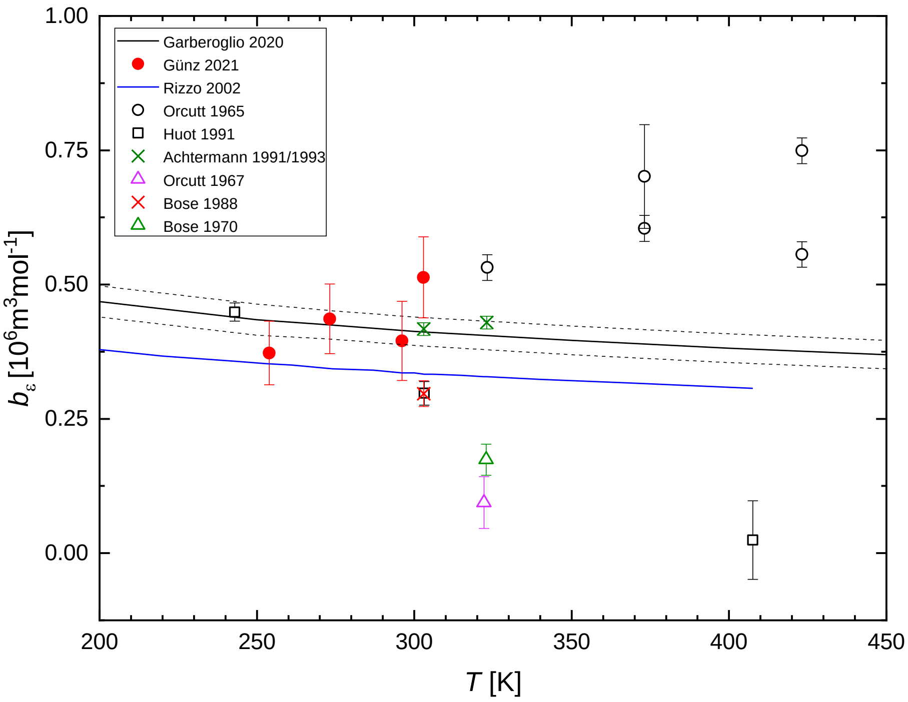

Figure 9. Comparison of values for the second dielectric virial coefficient of argon as a function of temperature obtained within the frame of the project to established literature values. The solid black line are values calculated by a path-integral approach published by Garberoglio et al. [3] utilising the pair polarisability by Vogel et al. The red points were determined by combined DCGT and expansion experiments within the frame of a PHD thesis [17]. This figure and further details on the used methods and the other literature values can be found in reference [17].

Experimentally, the dielectric virial coefficients were verified with DCGT measurements [19] for helium and by combined DCGT and expansion experiments for neon and argon by PTB. The results for argon (standard uncertainty of the second dielectric virial coefficient in the order of 15 %) are published by means of a PhD- thesis [17] and mark the first experimental determination in three decades. The results for neon were obtained in the frame of a Bachelor thesis. Additional measurements with helium were performed to constraint the apparatus constant and lower the uncertainties prior to publication in a peer reviewed journal which shall follow. RIGT measurements with argon were causing unforeseen troubles likely due to issues with impurities and other challenges. That is why the experimental determination of the magnetic susceptibility (by comparing DCGT and RIGT measurements) is not completed at this point. However, the uncertainty of the theoretical value is at least one to two orders of magnitude smaller, and the overall influence is very small which means that no knock-off effects occur. The experimental probing of the dispersion relied on simultaneous measurements at two different wavelengths. It was anticipated to use RISEs transportable refractometer (wavelength 1550 nm) in combination with the local optical pressure standards at the other institutes working at wavelengths of 633 nm (PTB) and 532 nm (CNAM) within the frame of the ring comparison of objective 4. Unfortunately, Covid 19 and the corresponding travel restrictions massively delayed this work leaving no time to perform these rather challenging and time-consuming measurements within the frame of the ring comparison. That is why the refractometer at PTB was used to perform simultaneous measurements at 1550 nm and 633 nm to probe the calculated dispersion whereas this data is still under evaluation.

Overall, two key results should be highlighted. The relevant properties of helium were calculated with unprecedented low uncertainties which, at this point, cannot be reached experimentally. This manifests the status of helium as reference fluid in highest precision gas metrology. An outstanding contribution, which will be the ultimate standard for the foreseeable future, is the development of the three body polarisability tensor, which allowed to calculate the third dielectric virial coefficient fully quantum mechanically by the developed path integral approach. Overall, the various reported improvements enable the use of helium even at higher pressures. For instance, the uncertainty contribution to a dielectric pressure standard originating from the properties of He is less than one ppm even at a pressure of 7 MPa.

A second main outcome is the possibility to use argon as a measuring gas for optical experiments over a broad temperature and frequency range now. Its eight times higher molar polarisability compared to helium and, thus, measuring effect lowers the vulnerability to impurities and the demands in experimental equipment. This is mainly enabled by the highly precise calculation of the dispersion which, in combination with the uncertainties from the static molar polarisability and the magnetic susceptibility, results in an overall uncertainty in the order of 10 ppm for the dynamic molar polarisability or refractivity. Though this corresponds to an improvement by more than one order of magnitude, the targeted uncertainty of 5 ppm could not be reached since the overall influence of the dispersion was estimated a little too low for argon.

Though not all activities were completed as planned, the overall goal of the objective was fulfilled in most parts. The properties for helium and argon are provided with uncertainties that enables their use for metrological applications. It was clear from the beginning that neon shall be used as a test fluid to learn how to best model more complex systems with a higher number of electrons in comparison to helium. It is unlikely to be used for broad gas metrological applications since the measuring effect is only a factor of two higher while it is rather expensive and not available in highest purity. That is why, though the uncertainties of several properties of neon were decreased also by on order of magnitude within the frame of the project, the available resources were focused more on argon. Also, in case of the dielectric virials further improvements were not possible for neon and argon. However, based on newly developed methods and the use of the available state of the art potentials it was possible to provide values with profound uncertainty estimates, which was not the case before.

World's most precise calculations on the 0.1 % level of the selected absorption line strengths for H_2O, CO, and CO_2 have been carried out using the MOLPRO package for the Dipole moment surface *ab-initio* points and the nuclear motion programs DUO for CO and DVR3D by UCL. The results agreed well with the experimental findings [22, 24]. One highlight was the new possibility to use infrared absorption spectroscopy and the calculated fundamental gas parameters in the sense of the redefined SI to replace the Pee Dee Belemnite standard for the $^{13}C/^{12}C$ isotope ratio [16]. Based on the above description, the project successfully achieved the objective (Fig. 10).

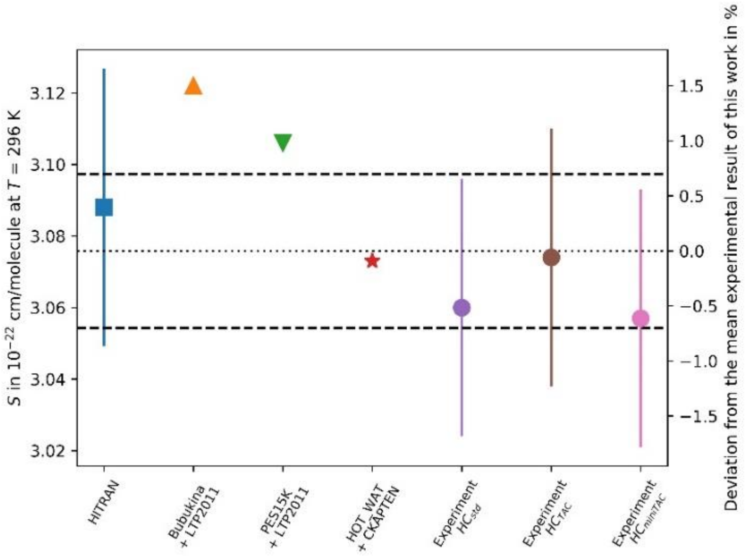

Figure 10. Comparison of theoretically calculated value (for this project represented by the red star) for the selected absorption line strength for H_2O with the values experimentally assessed by using TDLAS. (reproduced with permission from Rubin et al. [22]).

Demonstration of the performance of the novel and improved methods compared with conventional primary absolute pressure standards (Obj. 4)

Comparison with conventional pressure standards

Different intra- and inter-individual comparisons have been performed by different NMIs/DIs between conventional pressure standards and improved/developed methods in objectives 1 (Fabry-Perot based cavity (FPC) refractometer) and 2 (other quantum-based methods) in order to validate and demonstrate their performance.

Specifically, CNAM with the support of LNE (FPC refractometer and superconductive microwave resonator), CEM (FPC refractometer), PTB (FPC refractometer, DCGT and adsorption spectroscopy), INRiM (RIGT and UINT) and RISE/UmU (stationary and transportable FPC refractometers) has been involved for the different comparisons to conventional pressure standards (pressure balances (PG), Force balanced Piston Gauge

(FPG) or transfer standards). Due to Covid-19 pandemic, technical issues or longer lead times for suppliers, some comparisons did not take place or were incomplete.

In addition to establishing specific and appropriate protocols for each system, preliminary experiments or preparatory work before the comparisons were necessary. For example, the effective area piston cylinder assembly (PCA) used at INRiM for RIGT has been calibrated at PTB and the mass set was calibrated at INRiM by state-of-the-art weighings in air, vacuum and water. For summary purposes, not all comparisons carried out will be described here and here are some examples of them.

In the scope of comparisons related to objective 1 (FPC refractometers), RISE and UmU have performed comparisons in the range of 4 kPa to 90 kPa between pressure balances and their two refractometer systems: transportable system (TOP) used for circular comparison and the stationary system (SOP). Both systems [9] were characterised in terms of their uncertainty and were compared to a Ruska pressure balance in the range 4 kPa to 30 kPa. Although with an indication that both refractometer systems underestimated the pressure, it was shown that both systems mostly overlapped with the pressure balance within their respective uncertainties, At PTB, various single cavity FP-refractometers were realised in the course of the project. The performance of an Invar-based with dichroic mirrors (633 nm and 1550 nm) and a Zerodur-based with dichroic mirrors (633 nm and 1550 nm) has been evaluated by comparison to the conventional standards available at PTB (Piston gauge as well as different CDGs) and pressure sensors (type CPT9000) supplied by WIKA. It was shown that the simulated pressure induced deformation of the FPC could be confirmed.

In the scope of comparisons related to objective 2 (other methods than FPC refractometers), INRIM has evaluated the performance of the unbalanced multi-reflection homodyne interferometer (UINT) optical pressure standards by comparing it with their primary standards, namely a force balanced piston gauge (FPG) between for pressures up to 10 kPa, and a pressure balance for pressures above 10 kPa to 120 kPa. The results show the agreement of the UINT system and the INRIM conventional pressure standards FPG (400 Pa - 10 kPa) and the pressure balance DHI-FLUKE PG7601 (30 kPa - 120 kPa) within their related uncertainty (k=1). Further study will be carried out to evaluate the long-term stability of the UINT system, improve its performance at pressures below 1 kPa and extend the higher-pressure operational limit at least to 200 kPa.

PTB evaluated the performance of a novel argon-based pressure standard based on Dielectric-Constant Gas Thermometry (DCGT) for the pressure range between 1 MPa and 3 MPa by comparison to a Ruska pressure balance with two different piston cylinder assemblies. It can be clearly demonstrated that in this pressure range all values overlap very well within their standard uncertainties except for one value which is slightly outside this range. This is taken as a proof of the validity of the method.

In summary, new quantum-based instruments using various pressure measurement technologies and different ranges of pressure were developed or improved over a three-year period to meet the goals of the project (objectives 1 and 2). The results of the comparisons showed that these instruments were performed well and accurate, confirming the success of the chosen approach.

Circular comparison of the RISE/UmU transportable refractometer

Alongside these comparisons, a circular comparison of the RISE/UmU transportable refractometer (TOP) was undertaken in different NMIs across Europe. The main purpose of the circular comparison is to test and demonstrate the capability of the transportable refractometer to operate outside well-controlled laboratories, as well as to investigate whether it is suitable to be employed in future official comparisons of conventional standards.

The refractometer has been jointly constructed by RISE and Umeå University (UmU), both in Sweden, and utilises the Gas modulation refractometry (GAMOR) methodology [20]. This methodology significantly and automatically reduces the influence of various types of disturbances (primarily fluctuations and drifts) [12], which makes the system extraordinarily sturdy, and hence ideal as a transportable instrument.[4]

The refractometer is based on a dual Fabry-Pérot cavity (DFPC) made of Invar and is designed to operate between 1 Pa and 100 kPa. During the project, TOP refractometer has been upgraded to improve the performance in terms of transportability, usability, and measurement quality. Due to pandemic situations and travel restrictions, measurements in different locations were delayed roughly 18 months. The refractometer system fits on a wheels-equipped 19-inch rack with a 60 × 60 cm footprint and a height of 120 cm. It comprises, in its interior, seven modules that contain, among other things, two lasers, fibre-optics, electronics, and a gas-handling system. The DFPC is placed on top of the rack for ease of realignment. For operation, the system requires external vacuum pumps (Fig. 11).

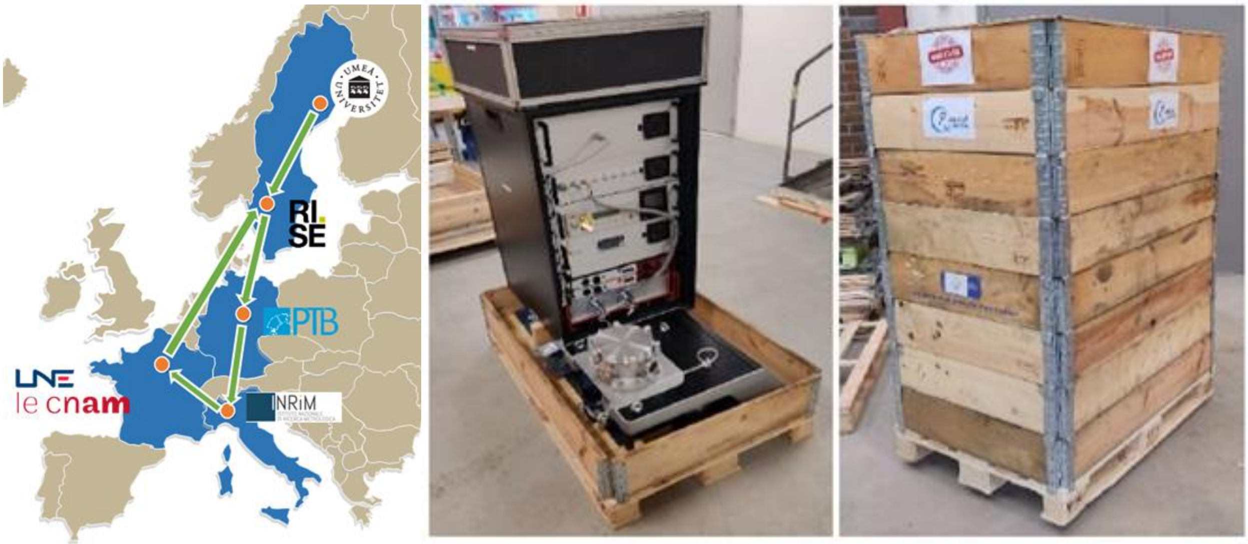

Figure 11. Left: Circular comparison tour on different NMIs – Middle: TOP set-up with its pump placed on EUR-the pallet – Right: Closed packing ready for transportation.

The TOP was designed to allow for easy transportation, unpacking, setting up (or initialisation), and serviceability to be able to perform measurements in a reasonably simple and fast way with a performance on par with existing standards. Hence, it was not designed to reach the highest possible performance.

The relatively small size of the system enables the use of a standard EUR-pallet for the transportation. The pallet fits both the TOP and auxiliary equipment such as vacuum pumps, oscilloscopes, and spare parts, netting a total weight of around 300 kg. Packing the system in its entirety on a standard pallet makes it easy to ship by standard shipping services. In this fashion, the system was successfully transported from RISE in Borås, Sweden, to PTB in Berlin, Germany, after which it was sent to INRiM in Turin, Italy, before it was routed to LNE in Paris, France by using commercially available service. Finally, it was transported back to RISE in Borås, Sweden. Through the support of WIKA, a CPT9000 sensor was used to accompany the TOP for simultaneous reference measurements. Despite transportation of the EUR-pallet by international carriers, only some minor technical issues that could be resolved within the time frame of the comparison of each NMI were encountered. The results from the comparison concluded that the TOP retained its performance during the comparison campaign, and that all pressure balances agree well within their respective uncertainties for pressure above 20 kPa, while some discrepancies were seen at 10 kPa. The results are at the time of the writing of this report being prepared for publication.

In summary, the TOP is a suitable system to be employed in future comparisons of conventional standards, taking into account the lessons learned from the circular comparison, such as a more robust laser locking and a rework of the cavity spacer ensemble suspension.

More details are available in the two deliverable comparison reports of the project i.e "*Report on the comparisons performed within and between different NMIs between conventional pressure standards and the new/improved methods developed including conclusions on the performance of these new methods comparison report*"[7] and "*Report on the circular comparison between a transportable Fabry-Perot refractometer and the conventional primary standards that are available at different facilities, including conclusions about how the refractometric method and the optical refractometer should be handled outside well controlled laboratories in order to enable and simplify future adaptations by end users"*.[4]

The work undertaken through extensive intra- and inter-individual comparisons has demonstrated the capabilities of quantum-based systems. Further work is required to verify their performance in terms of accuracy and stability (short and long-term) and to extend pressure range. Such comparisons are essential

[7] https://www.ptb.de/empir2019/fileadmin/documents/empir/QuantumPascal/reports/QP_D7_update_08_Dec_2022.pdf

and must be continued in order to establish the new methods and they are also important to provide benchmarks for the future development. Based on the above description, the project successfully achieved the objective.

5 Impact

The consortium published over 29 peer reviewed articles in international journals, while more have been accepted for publication as well as drafted. It came to two successful dissertations and the consortium members had 20 presentations of their results in international and national conferences (IVC-21, 26th Colloquium on High-Resolution Molecular Spectroscopy HRMS 2019, 66th AVS International Symposium and exhibition à Columbus, Warsaw Molecular Electronic Structure virtual conference 2020, and DKD annual meeting 2019). There was training to higher education students on vacuum physics and metrology and research topics in physics. The established website of the project is to make available general and detailed information and will continue to be maintained beyond the end of the project.

Impact on industrial and other user communities

Certainly, the developed and improved pressure standards will provide a major economic benefit to calibration laboratories and sensor and instrument manufacturers. The innovative approaches with the potential to perform automated calibrations between 1 Pa to 3 MPa aroused the interest of industrial stakeholder because the previous portfolio of available methods was small and calibrations in this pressure range were only covered by a combination of relatively time-consuming methods which led to higher costs for the end users.

The active dissemination of the results in the form of presentations, workshops and one-to-one meetings had led to the fact that not only the accredited laboratories are well prepared for a dissemination of the new quantum-based Pascal, but also at least the three largest European manufacturers of pressure measuring equipment and sensor instrumentation that rely on highly accurate pressure measurements have started corresponding activities in the form of feasibility studies, planning and, in some cases, production.

Impact on the metrology and scientific communities

The metrology and scientific communities have been and will be the first to benefit from the project's outputs. As a consequence of the revision of the SI in May 2019, in which the uncertainty of the Boltzmann constant k_B was eliminated, it is advantageous to realise the pascal for the given range through number density measurements to be more accurate and versatile.

The consortium liaised closely with the key metrological bodies (CIPM CCM, its working group on pressure and vacuum WGPV and the EURAMET TC-M) to present the developments within the project and get their direct feedback. This active engagement of these key stakeholders was part of the plan to ensure that the outcomes of the project will be disseminated worldwide to NMI laboratories and subsequently to any user who needs improved, traceable measurements of pressure, thus enabling broad industrial uptake. Accordingly, there were competing developments and, more importantly, synergies related to developments at other NMIs (e.g., NIST, NIM, NMIJ). Also, within Europe, other NMIs (CMI and TUBITAK) have been inspired by the results of this project and want to push the dissemination of quantum-based pressure standards. And as a bonus, the improved pressure standards and methods developed in this project also had impact on other fields of metrology, in particular primary thermometry and interferometric-based dimensional metrology.

Scientific impact is expected for the future from the application of the experimental methods developed within the project to extremely accurate, SI traceable determinations of the permittivity and the refractive index of pure gases and mixtures. The technical improvements led to advances in the field of optical cavity design. Furthermore, significant advances in the fields of atomic and molecular physics are expected by the future combination of refractometry and absorption spectroscopy, leading to highly accurate determination of absorption line strengths, for example, in the context of non-contact gas thermometry using spectroscopy. Particular benefits follow from the improved gas properties of neon and even more argon. Their higher measuring effect compared to helium can now be exploited in all kinds of gas metrology.

Impact on relevant standards

The development of photon-based measurements was still at an early stage hence no documentary standards have been affected directly. It is planned that once the novel measurement standards are established, existing documentary standards on vacuum gauges will be adapted to also account for the quantum-based methods and in the longer term, to develop standards analogous to existing standards on vacuum gauges for the quantum-based methods. In preparation for possible changes to existing standards and the development of emerging standards the ISO TC 112 “Vacuum Technology” received reports on the results achieved.

Longer-term economic, social and environmental impacts

This project further paved the way to the realisation of the vacuum scale in terms of density instead of pressure, while for most vacuum applications the density of gas molecules is the crucial quantity. The project helped to meet the growing demand from industry for high accuracy pressure and vacuum calibration services in Europe, whilst developing calibration procedures that are less time consuming. Vacuum and pressure related processes are key to many industrial applications that require very clean and well-controlled environments, such as semiconductor, photovoltaic, lighting, nanotechnology, surface engineering, pharmaceutical developments and food packaging. Better control of the vacuum and pressure processes will lead to improved cost efficiency, better overall environmental control over the complete process (higher quality products, fewer rejections), and hence increased profit margins and reduction of waste for the stakeholders.

The European vacuum and pressure industry are at the forefront worldwide, with a number of companies in Europe manufacturing pressure gauges, vacuum pumps and process tools. The introduction of optical measurement techniques led and will lead to the development of new technology of optical vacuum gauges that are less expensive than the primary ones. It is highly probable that these will be self-calibrating and require less maintenance. In the long run, this will enable manufacturers to produce a completely new generation of vacuum gauges that are more precise and in the long term more economical.

There will be advantages for aviation transport, where the height of an aircraft is measured by an altimeter that is based on an absolute pressure measurement. Further reduction in the standard vertical separation of aircraft will be needed in the future, which will increase the demands on the accuracy of pressure measurements. Not only will manufacturers of avionic measurement equipment and the aircraft industry benefit directly from the enhanced measurement capabilities at the NMI level, but the technology developed also has the potential to be directly utilised in future avionic pressure measurements, thus, supporting future transport demands.

For power plants and the storage of nuclear and toxic waste, it is crucial to reliably assess gas pressure due to strict requirements on safety and sterility. The developments achieved in this project will in the longer term provide more accurate means to monitor the operational conditions and will hence contribute to safer and more efficient conditions at power plants and critical facilities that handle toxic substances. Public agencies involved in environmental monitoring of atmospheric parameters and air pollution will profit from the improvements in absorption spectroscopy, which will lead in the longer term to the extremely accurate determination of the concentration of greenhouse gases, and hence have a significant effect on the detection of polluting sources and the improvement of climate models. Finally, the measurement of differential pressure is important for climate control in critical environments such as cleanrooms, hospitals, and biological/medical research laboratories. However, an additional 1 Pa of differential pressure in a medium-sized cleanroom requires around 3000 kWh of additional energy per year. More accurate differential pressure measurements would therefore contribute to reducing energy consumption in this environment.

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