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JRP-Coordinator	
Name, title, organisation	Dr. Karl Jousten, PTB
Tel:	0049-30-3481 7262
Email:	karl.jousten@ptb.de
JRP website address	http://www.ptb.de/emrp/ind12-home.html
Other JRP-Partners	
Short name, country	PTB, Germany CEM, Spain CMI, Czech Republic IMT, Slovenia INRIM, Italy LNE, France TUBITAK UME, Turkey Danfoss, Denmark INFICON AG, Liechtenstein INFICON GmbH, Germany Lazzero, Italy VACOM, Germany

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REG1-Researcher
(associated Home Organisation)

Researcher name, title	Vincenzo Ierardi	Start date: 1 September 2011
(Home organisation Short name, country)	UNIGE, Italy	Duration: 30 months

REG2-Researcher
(associated Home Organisation)

Researcher name, title	Stergios Naris	Start date: 01 April 2013
(Home organisation Short name, country)	UTH, Greece	Duration: 12 months

REG3-Researcher
(associated Home Organisation)

Researcher name, title	Christian Day	Start date: 1 December 2012
(Home organisation Short name, country)	KIT, Germany	Duration: 19 months

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1 Executive Summary

Introduction
This project has established the basis for improved efficiency, control and economy of industrial processes performed in a vacuum environment. It has done this by developing new and more reliable and accurate reference standards, vacuum gauges, techniques and methods for the measurement of vacuum related parameters that are better suited to industrial environments.

The Problems
The manufacture of computer chips, mobile phones, solar cells, semiconductor and pharmaceutical products all rely on production steps carried out in a vacuum environment. The processing of products in a vacuum is more economical the faster the process proceeds providing that the quality of the end product can be ensured. Vacuum gauges are used to control some of these processes however historically end users have had little or no information about how quickly or reliably the gauges can follow and measure sudden pressure changes during the process.

Some vacuum processes (e.g. glass coating) require particular gas species with well-known partial pressures. Quadrupole mass spectrometers (QMS) are commonly used to measure partial pressures, however before the project it was not possible to reliably calibrate them and neither was it possible to characterise their metrological quality and performance.

For most vacuum systems it is important to monitor and control not only those gas species that used in the process but also the gas species (e.g. water vapour) that evolve from the components of the vacuum system as they can adversely affect the process and final product. Outgassing rates are therefore a vital quality-assurance parameter in vacuum technology, but historically there has been no established way to measure outgassing rates, no traceability for the values obtained and no comparability between different methods.

The leak tightness of vacuum systems and containers is very important for safety, environmental and economic reasons. The most sensitive, widespread, versatile and accurate method for leak measurement is to measure the helium throughput through the leak into the vacuum. Leaks, however, usually occur under different conditions (e.g. gas species, temperature) from those used for calibration. If the leak rate cannot be predicted from the “standard” leak’s metrological properties then the “standard” leak needs to be calibrated for each gas species used which is a time-consuming and hence costly process.

The Solution
The project has developed new and more reliable and accurate reference standards, vacuum gauges, techniques and methods for the measurement of vacuum related parameters that are better suited to industrial environments, including:

- An SI traceable calibration facility for measurement of the time response of vacuum gauges and the fastest vacuum gauges in the world, with a validated response time of around 1 ms.
- A primary standard for partial pressures for characterisation and calibration of quadrupole mass spectrometers, assessment of their performance and a draft Technical Specification for their calibration and characterisation.
- Two SI traceable outgassing rate reference systems, three types of reference outgassing artefacts/samples for some important industrially relevant gas species such as water vapour and a draft Technical Specification for the measurement of outgassing rates.
- New types of standard leaks which can be calibrated for helium, but whose flow rates can be predicted for any other gas species.

Impact
This project had delivered impact through new products, new measurement capabilities, new draft written standards and new scientific knowledge, which will improve efficiency, economy and reliable of manufacturing processes performed in a vacuum environment.

The fastest capacitance diaphragm gauges in the world with a response time around 1 ms developed within the project are now available as a commercial product (the "Stripe" series by INFICON AG) and are also

subject to patent applications. This will enable end-users to more reliably monitor and control fast changing pressures, and in the longer term this will lead to more efficient and economical vacuum processes. One of the reference outgassing samples developed during the project is subject to a patent application and will also lead to a new product, which will be pursued by VACOM together with the inventors.

The calibration standards for dynamic vacuum, partial pressures and outgassing rates established in the project will for the first time provide SI traceable capability for parameters and ranges applicable for industrial applications where this was not previously available and will enable the vacuum industry to test and improve their developments and products in terms of speed and reliability. The methods developed will be applicable to improving the performance of vacuum systems and pumps and reduce their energy consumption.

The results of the project were taken up by the ISO Technical Committee 112 "Vacuum Technology" in the form of draft Technical Specifications developed by the project for the characterisation of quadrupole mass spectrometers and the measurement and reporting of outgassing rates, and the two proposals have been accepted as new work items.

The scientific impact is evidenced by the two invitations received by project members to present at the key conferences 19th International Vacuum Congress and the 60th AVS Symposium.

2 Project context, rationale and objectives

2.1 Context

Computer chips, flat-panel displays, mobile phones, solar cells and semiconductor manufacture all rely on production steps carried out in a vacuum environment, with the semiconductor industry alone making up about 40% of the market for vacuum equipment. A vacuum processing environment is also an important and indispensable tool for many other industrial processes such as pharmaceuticals, lighting, coatings and food packaging industries, where it is necessary to ensure a sterile environment, the correct operation of products or the longevity of products.

Vacuum technology has developed and matured a lot over the last 50 years, but there are still important challenges to overcome for industrial applications in order to ensure the reliability and quality of vacuum processed products and to improve the cost efficiency of vacuum processes which are becoming ever more complex. Existing vacuum measurement standards provide traceability from 10^{-9} Pa to 10^{5} Pa for pure gases under equilibrium conditions. Industrial processes, however very rarely work with pure gases (e.g. physical and chemical vapour deposition for electronics manufacture or coatings for hardening tools etc.) and often take place in non-equilibrium environments where the pressure is changing dynamically (e.g. physical and chemical deposition for optical disc manufacture). The lack of industrially relevant standards and traceability means that it is often difficult for manufacturers and end users to obtain reliable and representative measurements of their process parameters.

Contaminants and poorly controlled processes reduce the consistency and reliability of the manufactured products leading to poorer quality products, a higher number of rejects and also result in reduced process efficiency, wasted raw material and higher energy usage. Industry therefore often requires a complete reliable characterisation of the vacuum including the total pressure, fast changing vacuum pressures, the partial pressures of either desired or unwanted (outgassing) gas species, and also needs to be able to make reliable measurements of leak rates to ensure the leak tightness of process and containment equipment.

2.2 Rationale

2.2.1 "Time is money" in vacuum processes – reliable measurement and control of fast changing pressures

As with many industrial processes, the processing of products in a vacuum is more economical the faster the process proceeds providing that the quality of the end product can be ensured. The production of any part in a vacuum process requires the part to be introduced from atmosphere into the vacuum, which is often done via a load lock. The load lock is opened under atmospheric pressure, the part (typically a wafer or an optical disc) introduced, and the load lock closed and evacuated using a vacuum pump. Once the pressure is sufficiently low, the load lock is opened to a medium or high vacuum process chamber, the part transported into the chamber and the load lock closed again. When the vacuum process has finished, the part is returned

to the load lock which is then closed again, nitrogen, air or another suitable gas is fed into the load lock until atmospheric pressure is reached, the load lock is opened and the part is taken out of the system.

Such load lock operations are automated and need to occur within seconds otherwise the vacuum process would not be economically viable. Vacuum gauges of various types are used to control these processes by determining when the pressure has reached the desired level and hence when the valves to the pumps, to the process chamber and to atmosphere can be opened or need to be closed. These vacuum gauges obviously need to follow the pressure changes as quickly and reliably over a pressure range from 100 kPa (atmospheric pressure) to about 100 Pa, at which pressure the valve of the load lock can be opened to the process chamber.

A key issue for vacuum gauge manufacturers and end users is how quickly and reliably their gauges can follow sudden pressure changes. If a chamber or a load lock is evacuated to a lower pressure than required then the process will be slower than optimum, if the load lock is not filled with gas to at least atmospheric pressure then contamination of the environment or the process chamber may occur and if the process pressures are not reliably controlled then sub-standard products may be produced and processing material and gases wasted. Whilst the time response of the vacuum gauge's electronics can be tested electronically, the vacuum gauge sensor has to be subjected to a known changing pressure in order to be tested and historically this has not been possible for fast pressure changes. The time response of a vacuum gauge sensor will depend on its principle of operation, so for example the response of a sensor which relies on measuring thermal conductivity is expected to be slower than one which relies on the deflection of a thin membrane to measure the pressure. It is not possible to predict these time responses from first principles.

In order to verify the ability of a vacuum gauge to follow pressure changes or to measure the time response of a vacuum gauge, that is the 1/e decay of a sudden pressure reduction, a reference system is required which can both generate a sudden pressure change and generate pressures that are well known at any time during the change. The first is a technical challenge that requires a very fast opening valve with a large conductance to generate the sudden pressure change; the second is a theoretical challenge that requires utilising fluid and rarefied gas dynamics to be able to predict the pressure at any point in time using simulations.

2.2.2 Accurate and reliable control of vacuum process gas species constituents

Some vacuum processes (e.g. glass coating or the manufacture of electronic circuitry) require particular gas species with well-known partial pressures. Lack of control of the partial pressures of certain gas species (for example water) may result in unwanted oxidisation of surfaces and the creation of inappropriate insulating layers. Quadrupole mass spectrometers (QMS) are commonly used to measure partial pressures as they are relatively inexpensive. There are, however, a number of issues related to the metrological performance of QMS that had already been identified prior to the project:

a. The settings of QMS (emission current, electron energy, ion energy, field axis potential, m/e resolution, scan speed, multiplier gain) affect the sensitivity, transmission probability, fragmentation patterns, space charge in ion source, stability etc.
b. The settings of each type of QMS have different effects on their metrological characteristics, even for individual QMS of the same type the settings will often have different consequences
c. The relative sensitivity for single gas species (with respect to nitrogen) cannot be predicted
d. The QMS sensitivity depends on the total pressure
e. The QMS sensitivity depends on the gas mixture
f. QMS produce new artificial mass peaks that are not related to the gas under investigation

Historically the only primary standard worldwide suitable for the calibration of QMS was in Japan, with none available in Europe. It has also not been not possible to reliably characterise the metrological quality of QMS. From earlier publications and the problems described above, it was recognised that a QMS cannot be calibrated in a general sense, but only for special applications with known gas mixtures and total pressures.

In order to investigate these problems and to provide traceability for partial pressures for some applications, a primary standard for partial pressures is required in Europe, which is able to generate two or three well known partial pressures independently at the same time. The range of interest for the total pressure is from 10^{-6} Pa where the effects of the total pressure and non-linearity are not expected to be significant up to the upper measuring range of a typical QMS, i.e. 10^{-2} Pa. In order to be able to calibrate QMS and disseminate

the partial pressure scale using the QMS it is also necessary to have information about their metrological parameters and the stability of these parameters.

Although QMS are routinely used for the measurement of partial pressures, optical spectroscopic methods have several advantages in terms of metrological quality compared to QMS, however their applicability in vacuum metrology requires further investigation.

2.2.3 Quantifying undesired gas species in vacuum chambers and components

For most vacuum systems it is important to understand and control not only those gas species that have intentionally been introduced into the system but also the gas species that evolve from the components of the vacuum system (e.g. water vapour). Any surface that is exposed to vacuum will release gas that is absorbed on the surface or gas that originates from the bulk of the material. Gas release or ("outgassing") from the vacuum chamber walls and surfaces of other components needs to be reduced to an acceptable level for a given vacuum process. Only materials which have low outgassing rates can be used for the construction of vacuum chambers and tools for technologies which require high vacuum (pressures lower than 0.1 Pa) and ultrahigh vacuum (< 10^{-5} Pa) environments. Moreover, even in medium vacuum (0.1 Pa to 100 Pa) some processes require the absence of certain "contaminant" gas species which would be detrimental for the process itself or the final product. Although oil-free vacuum pumps and other components have improved in recent years, in terms of cleanliness, components in particular can still be a source of unwanted gases that get released or “outgassed” into the vacuum. Outgassing rates are therefore a vital quality-assurance parameter in vacuum technology, but historically there has been no established way to measure outgassing rates, no traceability for the values obtained and no comparability between different methods.

In the past it has only been possible to quantify outgassing rate of vacuum materials and components in a traceable way by loss of mass measurements, which are very slow due to the time taken for measurable mass changes to occur and which cannot be used to determine very low outgassing rates. This approach also only provides information on the total outgassing rate and not the outgassing rates for specific unwanted species. Mass spectrometry is sometimes used to measure outgassed gas species but the results are not traceable to the SI system of units. This has therefore resulted in a wide spread in the values published in the literature for different vacuum materials and an unacceptably high uncertainty in the reported outgassing rates.

The uncertainty of outgassing rate measurements is influenced by a number of factors including the design of outgassing measurement apparatus, the vacuum gauges selected, the measurement procedure used and the sample preparation. To ensure traceability of outgassing measurements in industry and to establish a uniform set of procedures for sample handling and evaluation of results a standardised approach is necessary.

2.2.4 Leak tight vacuum systems and secure containers – reliable measurement of leak rates

Leak detection is crucial to ensure the safety and reliability of vacuum systems and products. For example vacuum leak detection prevents refrigerants in air-conditioning systems or toxic, radioactive and environment polluting substances in containment systems from escaping. In an industrial or safety critical environment time is also important and so the leak tests need to be performed quickly. The leak tightness of vacuum systems and containers is tested using mass spectrometer leak detectors, which measure small flows of a test gas, e.g. helium or a refrigerant, which either flow out of the container or penetrate into it. In order to meet legal environmental or safety regulations where maximum limits for leak rates are specified, these detectors need to be calibrated in a traceable manner.

Mass spectrometer leak detectors are usually calibrated against known gas flow-rates (generally in the range 10^{-7} Pa m^3/s to 10^{-3} Pa m^3/s) generated by “standard leaks”. Detailed and traceable knowledge of the gas species, gas flow and gas dynamics and geometry of the leak element (the part of the leak that the gas flows through) enable a simple duct to be converted into a reference leak.

Standard leaks, often of the crimped capillary type, have historically been used to accurately tune the detectors within industrial leak detectors. These leaks exhibit a good metrological behaviour, are stable, robust and cheap but their metrological properties, i.e. their leak-rate, cannot be determined from the geometry of the actual leak element as this is unknown. In industrial applications leaks usually occur under different pressures, temperatures and temperature gradients, gas species and mixtures or can even involve liquid flows through the leak instead of gas. Consequently, if the leak rate cannot be predicted from the

leak's metrological properties then the leak needs to be calibrated for each gas species used which is a time-consuming process and challenging for some industrial gases.

There was therefore a need to improve knowledge of the gas flow through the ducts of standard leaks in terms of predictability for different gas species and environmental conditions used in industry. Three aspects needed to be addressed; firstly to produce ducts for standard leaks with stable metrological properties and a well-defined geometry which can be accurately measured (e.g. diameter, thickness and profile), secondly to develop theoretical models for the flow through the ducts which are applicable for industrial service (e.g. models that do not require extensive simulation for each standard leak) and thirdly to compare the developed theoretical models to measurements performed using industrially relevant gas species.

Limited information on appropriate procedures for leak testing is available. End users would therefore benefit from guidelines on aspects such as the metrological characteristics of helium commercial leak detectors and industrial analysers for the detection of refrigerants, procedures to quantify the leaks, and the influence of industrial environments (changing atmospheric pressures and temperatures) on leak calibration.

2.3 Objectives

The overall aim of the project was to develop improved techniques and capabilities applicable for industrial production environments for the measurement of (a) fast changing vacuum pressures, (b) partial pressures of industrially relevant gas species, (c) outgassing rates (d) leak rates.

The specific objectives were to:

Develop a novel vacuum calibration facility for dynamically changing pressures including
- Development of a vacuum system capable of producing very fast pressure changes over three orders of magnitude from 100 kPa to 100 Pa and vice versa within a second or less.
- Development of vacuum gauges with very fast response times of a few ms.
- Development of an "ab initio" simulation method to predict pressure changes with respect to time for pressures <100 kPa and with an accuracy of 50 % or lower.
- Evaluation of the feasibility of optical methods for the detection of fast pressure changes
- Provision of validated data on the relaxation time of vacuum gauges for fast pressure changes

Provide traceability for partial pressure measurement in industry by
- Identification of the key parameters needed for the calibration of quadrupole mass spectrometers (QMS)
- Establishment of a measurement standard to calibrate QMS from 10^{-8} Pa to 10^{-2} Pa
- Provision of information on the metrological characteristics of industrial QMS
- Evaluation of the feasibility of using optical methods as an alternative for partial pressure measurement
- Provision of methods to compare results obtained with QMS from different manufacturers
- Development of a draft for a technical specification for the calibration of QMS (for consideration by ISO TC 112 Vacuum Technology)

Provide traceability for industrial outgassing rate measurements and material characterisation by
- Development and testing of an industrially applicable method for outgassing rate measurement from 10^{-8} Pa L/s to 10^{-1} Pa L/s, with target uncertainties between 10 % and 20 %
- Provision of reference materials for the validation of outgassing rate measurements in industrial environments
- Provision of information on the comparability of different outgassing methods in terms of reliability, accuracy, and practicability for industry
- Development of a draft for a technical specification for a traceable outgassing rate method (for consideration by ISO TC 112 Vacuum Technology)

Improve capabilities for leak measurement and testing in industrial environments by:
- Development of methods better suited to leak measurements under realistic industrial conditions e.g. with regard to the actual gas species and pressure conditions
- Specification of alternative methods to mass spectrometer leak detectors in order to detect leaks within a second or less (dynamic measurements)
- Production of a practical guide for industry on the metrological performance of commercial leak detectors

3 Research results

3.1 "Time is money" in vacuum processes: Development of the new dynamic vacuum standard, fast response vacuum gauges and measurement of the time response of vacuum gauges

3.1.1 Introduction

The overall aim of this work was to develop SI traceable capability to measure and calibrate fast changing pressures such as those that occur during vacuum based industrial processes. To do this the work focussed on

- Development of a vacuum calibration facility for dynamically changing pressures capable of producing very fast pressure changes over three orders of magnitude from 100 kPa to 100 Pa and vice versa within a second or less.
- Development of vacuum gauges with very fast response times of a few ms.
- Provision of data on the relaxation time of vacuum gauges for fast pressure changes

In addition the possibility to compare and independently verify different types of reference standards is an important quality control aspect for metrology. An experimental feasibility study of a reference standard based on an optical interferometric technique was therefore also undertaken with the aim of demonstrating agreement between the optical method and the dynamic expansion method to within 50 % at any time during a fast pressure change.

3.1.2 Overview and principle of the standard for dynamic measurement of fast changing pressures

A dynamic pressure standard based on the expansion of gas from a very small volume via a calculable conductance (orifice or duct) and a very fast opening gate valve into a much larger volume was developed by PTB in collaboration with the industrial project partner VACOM GmbH. The conductance was chosen such that the pressure decrease in the small volume V_1 (see Figure 1) is fast enough to reduce the pressure from 100 kPa to 100 Pa within 1 second. The conductance is highest if no orifice or duct is installed and the full opening of the fast opening valve is used, in which case a pressure reduction step can be generated within about 20 ms. By changing the orientation of the fast opening valve, it is also possible to produce very fast pressure rises from high vacuum to 100 kPa.

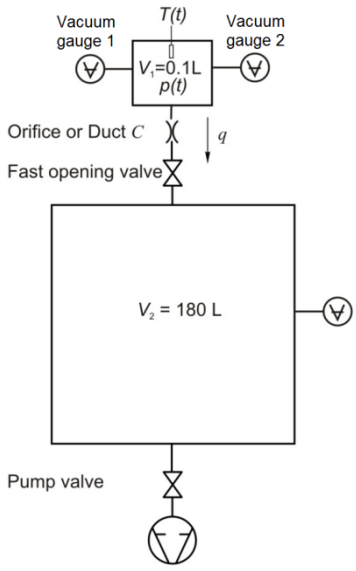

Figure 1 Scheme of the new dynamic vacuum standard of PTB

The small volume V_1 is 0.09472 L, whilst the larger volume V_2 is 185.4 L. During the expansion the valve to the pump is closed. Either volume, V_1 or V_2, may be evacuated or filled independently with gas to a desired pressure of up to 100 kPa. The expansion is initiated by a fast opening DN40 gate valve which opens the full

diameter within 4.6 ms. The dead volume V_1' (0.03309 L) between the duct and the valve plate contributes to an offset p_{offs} in pressure in V_2 after the valve has opened.

Once the expansion is complete and the gas has returned to room temperature, the final pressure is determined by the expansion ratio f_2 and the final pressure in both chambers will be

$$p_f = f_2 p_{01} = \frac{V_1 + V_1'}{V_1 + V_1' + V_2} p_{01} = 6.889 \cdot 10^{-4} p_{01}. \quad (1)$$

The vacuum gauges to be investigated were mounted on the upper chamber V_1. When volume V_2 is filled to 100 kPa and the gas expanded into V_1, an upwards pressure step is generated in V_1.The original plan was that the gauge readings during the expansion would be compared to the pressures obtained using simulations. Once the system had been validated it was however found that lower uncertainties could be achieved when very fast capacitance diaphragm gauges developed by the industrial project partner INFICON AG are installed as secondary standards in the small chamber.

The fast opening valve

In order to initiate the expansion process, a fast-opening valve with an opening time of less than 10 ms and a conductance much larger than the conductance of the orifice or duct was required. A very fast-opening DN40CF gate valve with a conductance in the molecular flow regime of 67 L/s (for nitrogen at 20 °C) was developed by the vacuum equipment manufacturer VAT. The opening time of the valve was then tested by PTB. The low pressure side of the valve was mounted onto a large vacuum chamber which could be pumped down to high vacuum, the high pressure side was blind flanged by a DN40CF viewport to observe the movement of the valve plate and a high speed camera installed at a suitable angle to observe the opening of the sealing valve plate (see Figure 2).

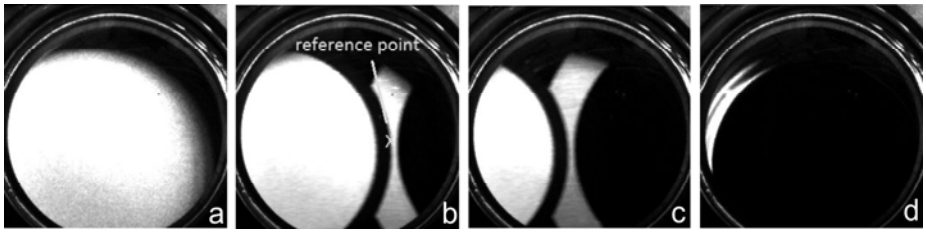

Figure 2 Pictures of the opening phase of the valve taken with a high-speed camera at 0.6 ms, 2.6 ms, 3.6 ms and 5.5 ms (start time of the opening phase was at 0 ms). The reference point used to characterise the opening process is indicated. The ring segment shown to the right of the valve plate belongs to the holder of the valve plate.

Two time periods were defined: Firstly the 'valve opening time' which is the period when movement of the valve gate is detectable and secondly the 'area opening time' which is the period between the time when the reference point appears at the inner diameter of the valve body and the time when the holder ring has just disappeared from the inner diameter of the valve body. The area opening time characterises the period when the conductance of the valve is changing.

It turned out that the two time periods were independent of both the differential pressure across the valve plate and the total pressure. The valve opening time was (5.8 ± 0.1) ms, where the uncertainty was due to the scatter of the actual opening times and the resolution in time. The area opening time, which was the time that was most relevant for this application, was (4.6 ± 0.1) ms.

The fastest pressure reduction possible in the facility is a decrease in pressure from 100 kPa to 100 Pa within 23 ms, when the full opening between the two expansion volumes is used, and this exceeds the most demanding current requirements of industry. The valve is the fastest opening valve ever developed worldwide, therefore suitable for studying fast vacuum processes.

The orifice or ducts

The pressure reduction can be made to occur over a longer period if nozzles or ducts are installed between the small volume and the fast opening valve. A conical orifice and two Laval nozzles were manufactured. If the orifice is used, the reduction is reached within 600 ms, and if two different Laval nozzles are used the corresponding times are 450 ms and 900 ms.

Orifice: The orifice comprised a 2.5 mm thick conical section with a maximum diameter of 8 mm and a minimum diameter of 3 mm, followed by a 0.1 mm thick cylindrical section of 3 mm diameter. The narrow part of the cone was installed facing the low pressure chamber (V_2). The orifice dimensions were calibrated and the orifice's conductance was about 1 L/s in the molecular regime.

Laval nozzles: A de Laval nozzle is a tube that is pinched in the middle, making a carefully balanced, asymmetric hourglass-shape. The standardised geometry (based on ISO 9300) was used for the de Laval nozzles. The measured "neck" (minimum) diameters of the nozzles were confirmed by calibration as 2.651(5) mm and 3.739(5) mm respectively. It was estimated that these values would be sufficient for the expansion of the gas within 1 s or less. The nominal flow rate achieved with these dimensions was 1.07 L/s and 2.14 L/s under viscous flow conditions.

The advantage of this type of nozzle is that choked flow conditions (a limiting condition where the mass flow will not change when the ratio of the downstream to the upstream pressure is changed) can be maintained for higher pressures and longer time intervals, leading to more accurate theoretical predictions of the flow rate than for the orifice.

3.1.3 Calculation of pressure with time

Numerical simulations for steady state configurations are increasingly used in vacuum applications, however simulations of non-steady state conditions have received much less attention.

Simulation of non-steady expansion of a gas into a vacuum has a wide range of applications but is not straightforward because the combination of several flow regimes (rarefied/non-rarefied, compressible/incompressible, choked/non-choked) poses significant challenges in the choice of the appropriate methodology. Moreover, the accumulation of errors with time and a pressure range which covers several orders of magnitude requires a method that offers good accuracy in a reasonable computational time. Finally, the possibility of three-dimensional flow and non-trivial geometrical features poses significant difficulties to current codes based on kinetic theory.

To tackle these problems a hybrid continuum-particle solver was developed. The flow domain was decomposed into two parts: a rarefied domain where the direct simulation Monte Carlo (DSMC) method was applied, and a continuum domain where typical compressible flow numerical schemes were used. The decomposition criterion was the gradient of the local Knudsen number that changed in time. The two computational regions overlap at the buffer cells. Particles were generated in the so-called buffer cells at the interface between the two methods according to the local Maxwellian distribution. Moreover, macroscopic properties obtained at the same cells through sampling of the particle properties are imposed for the continuum part. The dynamic characteristics of the algorithm, the ability to handle unstructured meshes for arbitrary geometries and the parallelisation scheme enable non-trivial, practical applications to be considered. The solver was then validated for benchmark problems.

By considering symmetry and by incorporating model approximations (choked flow, simulation of only those regions that were truly needed, ignoring the opening time of the valve) the effort to produce the mesh (up to 300 000 cells) and the simulations could be reduced. This was possible because only the pressure and its uniformity in the small vessel was of interest. The validity of these model assumptions were tested before both by other simulations with different software (ANSYS CFX module) and also by experiments.

Forty processor cores were used for the simulations. The computational time for the complex case was around 3 weeks for the first stage of the flow where only the hydrodynamic solver was used, and about a further 3-5 weeks for every 100 ms after that, so several months in total.

The pressure curves may be approximated by a simplified model,

$$p_1(t) = p_{20} + (p_{10} - p_{20})\exp(-t/\tau_1) \quad \textbf{(2)}$$

where p_{10}, p_{20} are the initial pressures of the small and large volume respectively and τ_1 is the flow time constant

$$\tau_1 = V_1 / C\,. \quad \textbf{(3)}$$

C is the conductance which is assumed constant as just a rough estimate (it varied by about a factor of 2 during the time of the expansion). This expression is valid for both flow directions, that is, for gas flow from the small vessel to the large vessel and vice versa.

3.1.4 Determination of the temperature during expansion

The temperature of the gas changes drastically (more than 100 K) during the expansion of the gas hence knowledge of the gas temperature during expansion is important. Some vacuum gauges are sensitive to temperature and therefore information of the gas temperature distribution within chamber V_1 is important. In addition, a comparison of the temperature values obtained by simulation and experimentally is one part of the validation process.

Thermocouples (Type K) with 13 µm and 25 µm diameter wires were used for temperature measurements in V_1, but due to their small heat capacity compared to the solid body of the wires their response time had to be investigated using conjugate heat transfer simulations.

The evolution of the temperature during the gas expansion was indicatively examined for the case of flow through the conical orifice. Figure 3 shows both the calculated temperature and the thermocouple measurements. In addition the temperature evolution calculated using the hybrid solver is also included as the curve labelled “Ambient conditions”. This temperature is set as a boundary condition at the six sides of the nitrogen domain. The agreement is satisfactory overall, with a 16 K deviation at the minimum temperature point and 9 K average deviation. It is worth noting that the minimum values for both the conjugate heat transfer and thermocouple measurement curves appear at the same time, thus confirming the time scale characteristics. It can therefore be concluded that the measurement lag caused by the thermocouple’s physical principle has been satisfactorily taken into account. The deviations from the experiment may be caused by other warm gas emanating from parts with small conductances (“virtual” leaks), which are difficult to locate and eliminate.

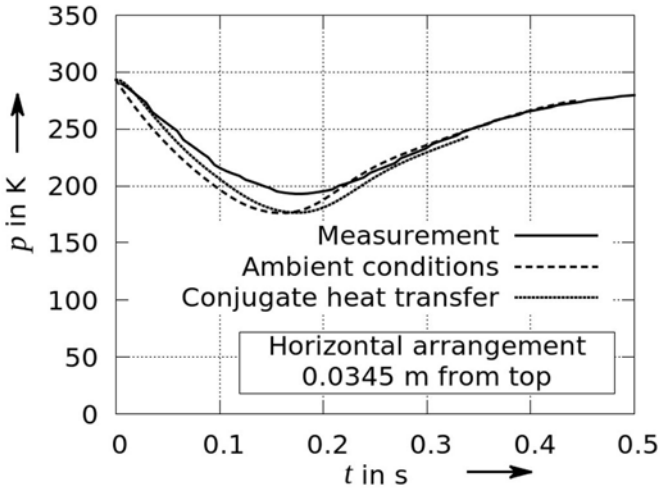

Figure 3 Comparison of the temperature of the gas during expansion estimated by modelling and measurement

3.1.5 Validation of the standard for dynamic measurement of pressure

A number of approaches were taken to validate the standard for dynamic measurement of pressure described in 3.1.2. Two capacitance diaphragm gauges (CDGs) with full-scale of 1.3 kPa and 133 kPa respectively, which provided measurement values every 0.7 ms with output at 21 bits resolution and integration times of 0.3 ms, were developed by the industrial partner INFICON AG for the fast measurement of vacuum pressures. The two CDGs were initially calibrated using the static expansion method. Experiments (see Section 3.1.6) verified that the response time of the new CDGs was less than 1.3 ms.

Measurements and other procedures were undertaken to ensure the correct function of the new dynamic vacuum pressure facility:

- Confirmation was obtained that the flow was choked by changing the downstream pressure and observing the upstream pressure both experimentally and by simulation (ANSYS CFX).
- Expansion experiments were performed for several different gases, namely helium, nitrogen, argon, krypton and xenon using the conical orifice (Figure 4) and the Laval nozzles (Figure 5**Error! Reference source not found.**). The consistency between the different curves was checked by comparing the time constant obtained from the measurements fitted with the model (Eq 2) for a drop

in pressure of one order of magnitude, with the corresponding value predicted by the choked flow closed form expression. The factor by which the time constants differ can be directly derived from the molar masses and the heat capacity ratios of the two gas species. The results are given in Table 1, normalised by the time constant calculated for nitrogen and the value of the time constant obtained from the measurements is 78.14 ms, which is in good agreement with the theory of choked flow, differing only in the third significant figure in all cases except for helium.

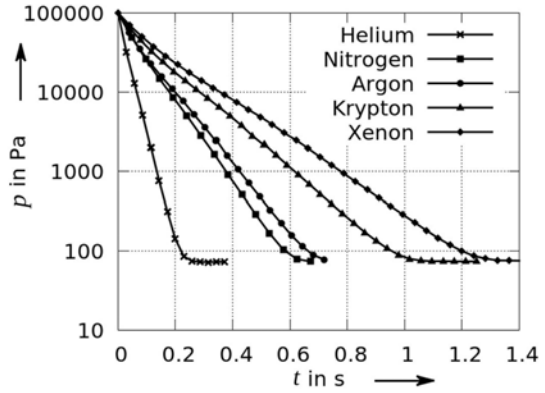

Figure 4 Measured upstream pressures versus time for the expansion of several different test gases through the conical orifice

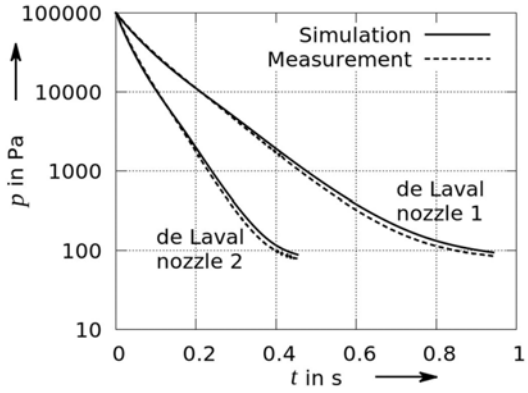

Figure 5 Comparison between measurements and simulations of the pressure evolution for expansion of nitrogen through the Laval nozzles

Gas	τ/τ_{N2} (meas.)	τ/τ_{N2} (choked)
Helium	0.368	0.356
Nitrogen	1.000	1.000
Air	1.023	1.018
Argon	1.127	1.127
Krypton	1.616	1.631
Xenon	2.020	2.042

Table 1 Normalised time constant ratios obtained from measurements and the choked flow approximation.

- Any significance of desorption effects were excluded by desorption rate measurements.
- Since the possibility could be excluded that the time responses of the newly developed CDGs were not sufficiently fast (see Section 3.1.6), the simulated and measured pressures during expansion were compared for all three orifices or ducts using nitrogen. The typical difference was 10 % with a maximum deviation 27 %. The total expanded relative uncertainties of the measured pressures within the small volume during the expansion are estimated to be between 1 % and 2.5 % (depending on the pressure). Uncertainties in the simulated pressures were not determined as it would have been too time consuming computationally and taken a number of months to change the model assumptions and repeat the simulations.
- The contour results for pressure and temperature and velocity in Figure 6 show that the pressure remains uniform in the small upstream vessel and up to the “neck” of the de Laval nozzle. The temperature exhibited a significant drop after the de Laval nozzle and also a smaller but considerable drop in the upstream volume. The temperature at the position of the vacuum gauge, however, hardly changed during the expansion.
- Similar experiments comparing the measured *p(t)* data with simulation results were also performed for the reversed flow (sudden pressure increase) and showed good agreement between the simulations and experimental data.

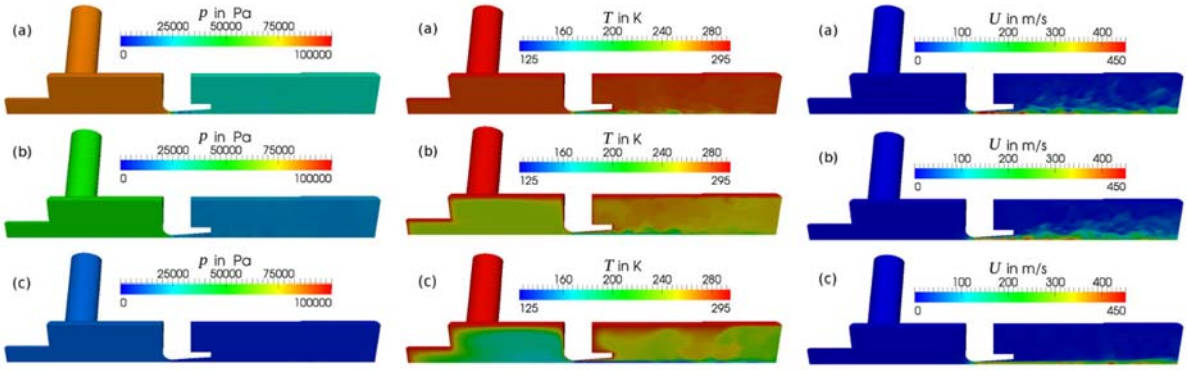

Figure 6 Contour lines for pressure (left), temperature (middle) and velocity magnitude (right) contours for Laval nozzle 1 flow at (a) *t*=10 ms, (b) *t*=50 ms and (c) *t*=200 ms

The most accurate determination of the pressure decrease is achieved when the fast response vacuum gauges developed by the project partner INFICON AG are used rather than determining the pressures by simulations, and using these gauges the pressure during the pressure reduction can be determined with an uncertainty of 5 %. For this reason, the new fast CDGs will be used as secondary standards and the dynamic expansion system will be used as dynamic pressure generator and the vacuum gauges to be tested will be compared to the secondary standards.

3.1.6 Response time of vacuum gauges

The response time τ (see also Eq. (3)) was defined as the time taken for the vacuum gauge to indicate the fraction 1/*e* of a downwards pressure change Δp or the fraction (1-1/*e*) of an upwards change Δp. The response times of the very fast gauges (CDGs) developed for the project were tested with the full opening of the valve (orifice removed). In this case, the response time of the dynamic standard provided the upper limit of the response time. Since the valve opens fully within 4.6 ms and is too time-consuming to calculate the conductance of the valve over this interval, the response time of the dynamic expansion standard can only be estimated to range between about 1 ms and 2 ms.

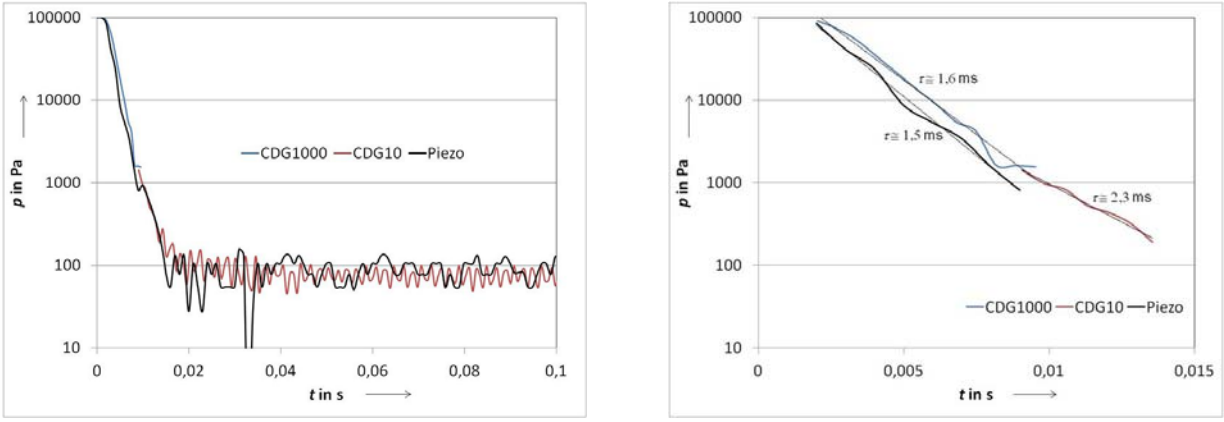

Figure 7 Pressure indications (smoothed values used as the line for better visibility) versus time for 3 different vacuum gauges during a pressure change from 100 kPa to about 73 Pa (nitrogen) in the dynamic vacuum standard. Left: linear time scale; Right: logarithmic time scale, readings before the noise becomes significant. CDG 1000: capacitance diaphragm gauge with 133 kPa full scale; CDG 10: capacitance diaphragm gauge with 1.3 kPa full scale; Piezo: vacuum gauge based on piezoelectric effect. τ is the response time.

Figure 7 shows the result for three gauges and it can be seen that the gauges have reached the final pressure of about 73 Pa within 20 ms. At this stage, a significant signal noise can be seen which is due to the mechanical vibrational shock of the valve opening.

In the first phase of an expansion, the pressure decay could be fitted by an exponential function, and the fastest exponential function that matched the CDG response was 1.3 ms for the 133 kPa full scale CDG. This was therefore taken as the upper estimate of response time for both the dynamic pressure system and the CDG.

Pressure increases could be realised faster than pressure decreases, because the large volume is filled to 100 kPa while the small volume is evacuated to high vacuum (<0.1 Pa). By expanding the gas into the small volume, the pressure in the large volume is reduced by only 0.1 %, so that the large volume acts as an "infinite" reservoir with almost constant pressure. This greatly increases the gas flow rate through the full opening compared to the pressure decrease.

The 133 kPa full scale CDG reached around 100 kPa from high vacuum within less than 3 ms (τ = 1 ms) with similar damped oscillations caused by the mechanical shock from the valve opening (Figure 8, left) as for the downwards pressure step for the 1.3 kPa full scale CDG.

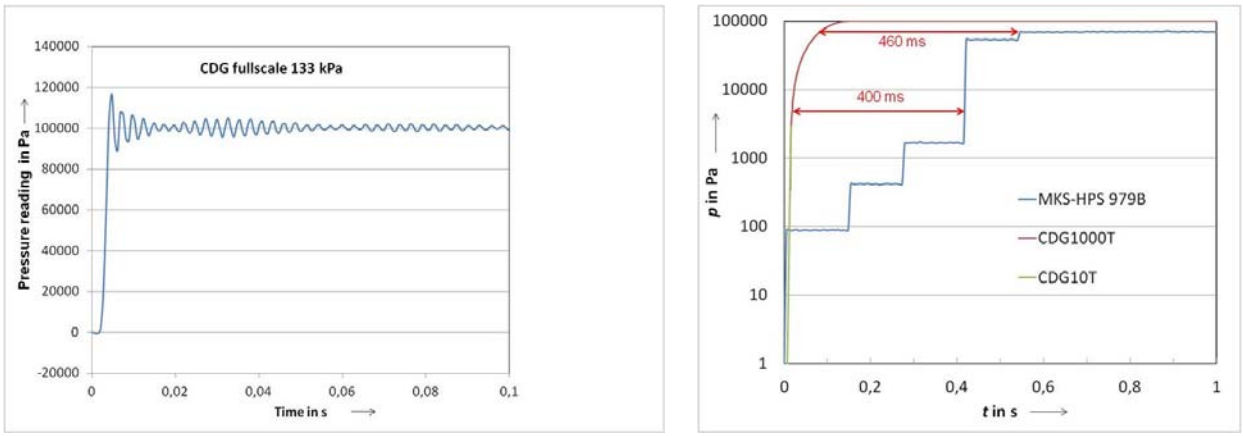

Figure 8 Pressure indications (smoothed values used as the line for better visibility) versus time for 3 different vacuum gauges during a pressure change (nitrogen) from high vacuum to about 100 kPa in the dynamic vacuum standard. CDG 1000: capacitance diaphragm gauge with 133 kPa full scale; CDG 10: capacitance diaphragm gauge with 1.3 kPa full scale; MKS-HPS 979B: vacuum gauge (micro-Pirani) based on thermal conductivity effect.

A significant delay in the indicated pressure rise was noticeable when a Pirani gauge was used (see Figure 8 right) and it could take up to 490 ms compared to a fast CDG, before this gauge indicated that the pressure was at atmospheric pressure. Similarly, the Pirani gauge also showed a significantly larger time constant (τ = 153 ms) than the dynamic vacuum standard, even when the Laval nozzle 1 with the largest time constant (τ = 109 ms) was used. It was therefore clear that whilst the new fast capacitance diaphragm gauges developed by the project have a time response around 1.3 ms and are ideally suited to measuring fast pressure changes, the Pirani vacuum gauge is not suitable for fast processes.

3.1.7 Feasibility of dynamic vacuum measurement using an interferometric technique

An experimental feasibility study for a reference standard based on an optical interferometric technique for measurements of dynamically changing pressures was undertaken by INRIM. The prototype optical device developed was a homodyne Michelson interferometer which measures the variation of the optical path due to changes in the refractive index of air related to a fast decrease in air pressure during a gas expansion process. In order to achieve high sensitivity, the layout was based on a folded optical path and composed by two quasi parallel mirrors, which allowed a 1.5 m long path in a measurement volume of about 1 litre.

A primary method, based on the Lorentz-Lorenz equation, was used to measure the pressure during a gas (air) expansion from 100 kPa to 100 Pa in less than 3 s. The first results obtained using this new optical dynamic vacuum standard were compared with two new fast CDGs which were used as reference standards (see Section 3.1.6) and showed a maximum relative difference of 12 % during the whole fast evacuation process. This demonstrated the potential of this technique, however further research is required and there are still sources of uncertainties that need to be analysed.

3.1.8 Conclusions

Techniques, instrumentation and facilities were developed for the measurement of fast changing pressures. A novel vacuum system capable of producing very fast pressure changes over three orders of magnitude from 100 kPa to 100 Pa and vice versa within a second or less was developed. Capacitance diaphragm vacuum gauges with full scale ranges of 1.3 kPa and 133 kPa with very fast response times were developed by INFICON AG and their response times confirmed to be 1.3 ms or less using the new dynamic pressure facility. These gauges are now available as a commercial product. A simulation method based on a hybrid

continuum-particle solver was developed to predict pressure changes with respect to time for pressures <100 kPa and with an accuracy of 50 % or lower. The performance of the new fast CDGs was however so good that the most accurate measurements of the changing pressures (around 5 %) can be obtained if the dynamic expansion system is used as dynamic pressure generator and the new fast CDGs are used as secondary standards against which the vacuum gauges to be tested are compared. Using this facility, the relaxation or response time of vacuum gauges was tested for fast increases or decreases of pressure, which was not previously possible. Using the new fast gauges as secondary standards it was also possible to verify that optical methods measuring refractive index changes are suitable to measure fast pressure changes.

3.2 Accurate and reliable control of vacuum process constituents: Traceability, characterisation and guidance for partial pressure measurements

3.2.1 Introduction

The overall aim of this work was to develop SI traceable capability to characterise and calibrate partial pressure measuring instruments such as those used in vacuum based industrial processes. To do this the work focussed on

- Identification of the key parameters needed for the calibration of quadrupole mass spectrometers (QMS)
- Establishment of a measurement standard to calibrate QMS from 10^{-8} Pa to 10^{-2} Pa
- Provision of information on the metrological characteristics of industrial QMS
- Evaluation of the feasibility of using optical methods as an alternative for partial pressure measurement
- Provision of methods to compare results obtained with QMS from different manufacturers
- Development of a draft for a technical specification for the calibration of QMS (for consideration by ISO TC 112 Vacuum Technology)

3.2.2 Survey on the industrial use of quadrupole mass spectrometers

Quadrupole mass spectrometers (QMS) are commonly used to measure partial pressures as they are relatively inexpensive, there are however a number of issues related to the metrological performance of QMS. Although basic information concerning the use of quadrupole mass spectrometers for partial pressure measurement in industrial applications was available to the project partners at the start of the project, one of the initial tasks was to supplement this general overview with more detailed information from end-users, in particular identification of the key parameters of interest to end-users.

A questionnaire was therefore developed and distributed to manufacturers, distributers and users of quadrupole mass spectrometers (QMS). 24 questionnaires from 21 parties were returned and evaluated. The number of responses was such that the results of the questionnaire could be considered as significant and whilst the cross section may have not been completely representative, it did represent a broad range of the QMS user community.

The main applications of quadrupole mass spectrometers identified from the responses were leak monitoring, outgassing rate measurement and residual gas analysis. Fortunately these applications were not too diverse in terms of operational range and the gas mixtures to be analysed. Common to them was the similarity of gases to air and the importance of quantifying water vapour partial pressure. The quantification of hydrocarbon partial pressures was also identified as important, but more in the sense of “its partial pressure must be reliably below the level of …” and not the need to provide accurate measurement of the partial pressure below this level. The vast majority of users (75 %) indicated that (at least moderate) accuracy and reproducibility were needed in their application. The pressure range of interest to most users ends in the upper part of the 10^{-4} Pa decade. It was therefore concluded that a calibration procedure for partial pressures for the applications mentioned above is required by users. Rather surprisingly in addition to accuracy and reproducibility of the partial pressure indication, the minimum detectable partial pressure was the most important parameter of the QMS for the users, and was identified as far more important than for example linearity or mass resolution. Any calibration procedure should therefore include the reliable determination of this parameter.

The questionnaire responses indicated a clear need for calibration of QMS for a significant and important minority of users. The approximately 30 calibration requests/year received by the 5 manufacturers and 3 distributors already make it reasonable that a few NMIs provide traceability.

One approach that was considered within the project was to use air (ideally humid air, if possible) enriched with Kr and Xe as a calibration gas mixture since air is easily and cheaply available everywhere for on-site testing and this mixture was very similar to the major applications requiring accuracy.

3.2.3 Primary standard for partial pressures and outgassing rate measurement

A primary standard for partial pressures was established by PTB (the "partial pressure calibration system", PPC) capable of generating well-known pressures of three different gases at the same time with the option of generating mixtures of more than three gases with somewhat higher uncertainties.

Primary systems for high and ultrahigh vacuum, such as required for this application, are based on the principle of continuous flow. A known gas flow q_{pV} is injected into a vacuum chamber (calibration chamber) and then pumped out of the chamber through an orifice or duct with well--known conductance C. The ratio

$$p = \frac{q_{pV}}{C} \qquad (4)$$

gives the pressure in the calibration chamber (ignoring some minor necessary corrections).

The flow q_{pV} is normally generated and measured using a flow meter which is often a rather complex device. In order to independently establish well-known partial pressures of three gases in a high or ultrahigh vacuum chamber, three flow meters of this type would be required which would be too expensive and not justified by the accuracy of the partial pressures needed for the calibration and characterisation of quadrupole mass spectrometers (QMS). For this reason, the following more simple design was chosen:

Three reservoirs can each be filled with a known pressure of a different pure gas species. The gas from a reservoir can flow out under molecular flow conditions into the calibration chamber through a leak element with a conductance which is known for nitrogen and helium. Under molecular flow conditions this conductance is independent of the upstream pressure and it scales with the square root of the inverse molecular mass of the gas. So, by knowing the conductance of the leak element for one gas species it is possible to calculate the conductance under molecular flow conditions for any other gas species provided that its molecular mass is known, thus avoiding the need to calibrate the conductance for each gas used. Ideally, the conductances should be such that molecular flow conditions exist up to about atmospheric pressure.

The leak elements developed and manufactured by the project went beyond the state of the art. Two different approaches with glass capillaries and small holes drilled by focused ion beam into a silicon nitride membrane (thickness 100 nm and 200 nm) provided predictable gas flows. Leak elements manufactured from a sintered material did not provide stable results.

Finally, the primary standard was designed with an additional module such that it could also be used for traceable outgassing measurements. The module comprises a probe chamber that houses the outgassing sample and a load lock that enables the outgassing sample to be introduced from atmosphere without significantly disturbing the quality of the vacuum in the probe chamber.

The schematic of the primary standard is shown in Figure 9. One of the reservoirs has a volume of 10 litres, the other two are 1 litre. All reservoirs are equipped with two capacitance diaphragm gauges (CDGs) enabling accurate measurement over 4 decades of pressure, the large reservoir from 10 Pa to 100 kPa, the smaller reservoirs from 0.1 Pa to 1 kPa. The conductances were designed such that both mixtures of species of about equal pressure and of trace gas concentrations in the ppm regime could be generated.

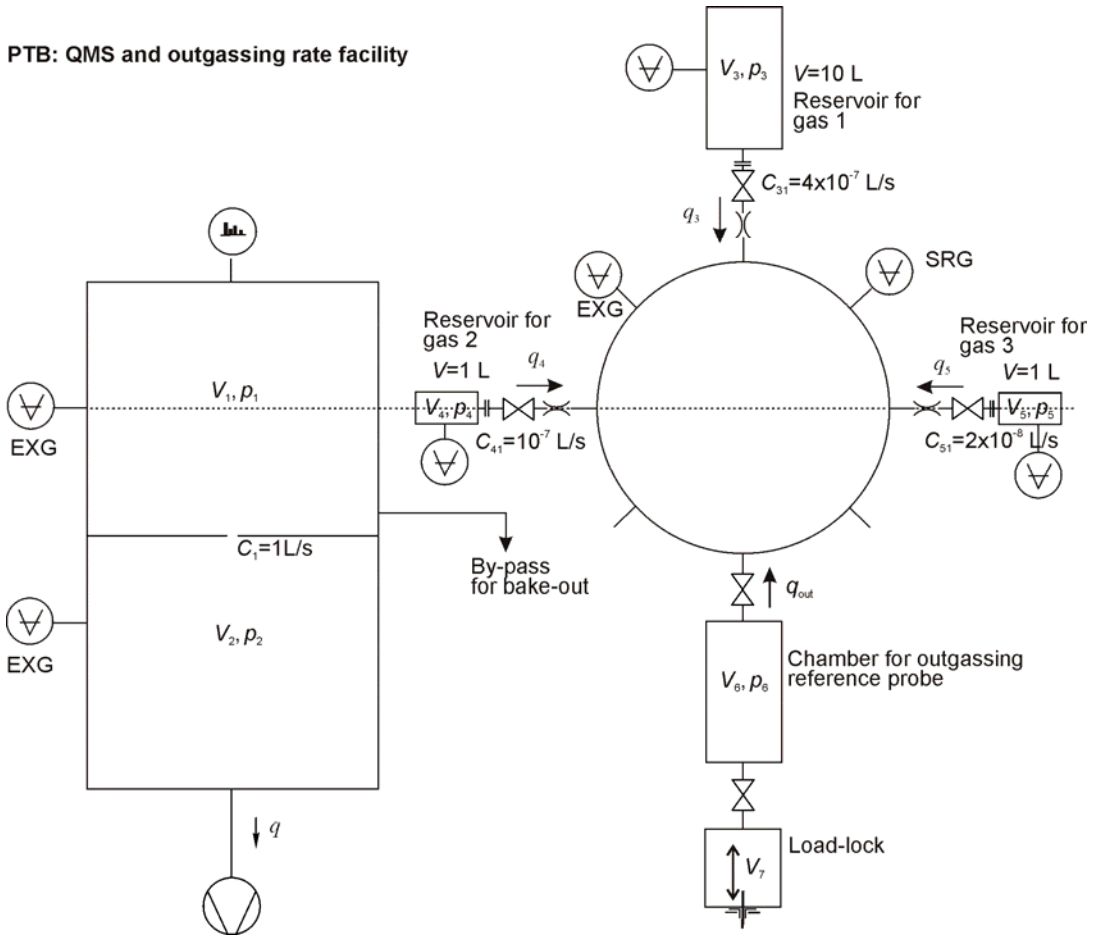

Figure 9 Scheme of the PTB's primary standard for partial pressures and outgassing rate measurement (PPC). Left: side view of the standard; right: top view of the standard. Conductance values are nominal and for nitrogen. EXG = extractor vacuum gauge; SRG = spinning-rotor gauge

With the highest possible conductance C_{31} of 4.5x10^{-7} L/s (nitrogen) and a pressure in V_3 of about 25 kPa, a flow of about 1x10^{-2} Pa L/s could be achieved, which according to (Eq. 5) results in a pressure of 1x10^{-2} Pa. This is desired upper pressure limit. With the smallest conductance C_{31} of 2x10^{-8} L/s (nitrogen) and a pressure in V_5 of 0.1 Pa, a flow of about 2x10^{-9} Pa L/s could be generated corresponding to a pressure of 2x10^{-9} Pa in the calibration chamber, which is below the desired lower pressure limit. When mixed with the highest possible partial pressure this corresponds to a concentration of 0.2 ppm. The uncertainties in the generated pressures were typically a few percent.

The standard was validated as follows.

The partial pressure $p_{1,i}$ in V_1 is calculated by the following formula (compare with Eq. (4)):

$$p_{1,i} = \frac{p_i \cdot C_i}{C_{1,i,\mathrm{eff}}} \qquad i = 3,4,5 \tag{5}$$

where p_i is the pressure of the gas species in reservoir i, C_i is the conductance of the gas species flowing through the leak element of reservoir i, and $C_{1,i,\mathrm{eff}}$ is the effective conductance of the orifice between the upper and lower chamber for the gas species in reservoir i. The CDGs used to measure p_i were calibrated against the relevant primary standard at PTB. C_i was obtained from the calibrations for nitrogen and helium using PTB's reference flowmeter. C_i for other gas species was obtained by scaling the nitrogen and helium values with the square root of the inverse molecular mass of the other gas species.

The pressure $p_{1,i}$ determined according to Eq. (5) was compared with the pressure indicated by a calibrated spinning rotor gauge (SRG). Reservoir 3 was used for the comparison, since this reservoir enabled the most

suitable pressure to be generated for comparison with the SRG. A glass capillary 1 with conductance C_{31} was mounted in the exit of reservoir V_3 (10 l). V_3 was filled with nitrogen, the valve from the reservoir opened and the readings of the SRG taken. The results are shown in Table 2.

Table 2 Results for nitrogen for pressures calculated according to Eq. (5) and pressures measured with the SRG.

p_3	C_{31}	$p_{1,calc}$	$u(p_{1,calc})$	$p_{1,meas}$	$u(p_{1,meas})$	$p_{1,calc}/p_{1,meas}$	$u(p_{1,calc}/p_{1,meas})$
mbar	**L/s**	**mbar**	**%**	**mbar**	**%**		***k*=2**
9.799	4.50×10^{-7}	5.366×10^{-6}	1.22	5.426×10^{-6}	0.54	0.989	0.026
74.761	5.53×10^{-7}	5.034×10^{-5}	0.93	5.094×10^{-5}	0.28	0.988	0.019
222.909	8.01×10^{-7}	2.175×10^{-4}	0.93	2.193×10^{-4}	0.27	0.992	0.019

The calculated and measured pressures agreed to within one standard uncertainty. The results for helium indicated a ratio $p_{1,calc}/p_{1,meas}$ = (1.029±0.03). Since the results for $p_{1,calc}/p_{1,meas}$ are <1 for nitrogen and >1 for helium, any systematic error in C_1 or the measurement of p_1 can be excluded.

The primary standard was also validated by comparing the gas flow from a helium standard leak attached to the standard with the gas flow obtained from a reservoir using a QMS. The known flow from two alternative reservoirs in turn was adjusted until the helium single of the QMS was the same as the signal generated by flow from the helium standard leak. The results for the flow rates from the standard leak and the two reservoirs agreed within 1 %, with a total uncertainty of about 4 %.

3.2.4 Metrological characterisation of quadrupole mass spectrometers

Using the primary standard described in Section 3.2.3 three different types of quadrupole mass spectrometers were investigated. The following parameters (ISO 14291:2012 Vacuum gauges -- Definitions and specifications for quadrupole mass spectrometers) were included:

a. Sensitivity for pure gases and mixtures and in dependence of total pressure
b. Linear response range
c. Minimum detectable partial pressure for helium and water vapour
d. Minimum detectable concentration for helium and water vapour

The possibility of using laboratory air for calibration of the sensitivity of QMS was investigated, however whilst the mass scale could be calibrated using the constituents within air, the sensitivity was only applicable to air and as expected the sensitivities for pure gases are very different than in air. In addition water vapour from humid air did not give reproducible values due to strong absorption on the chamber walls.

A surprising result related to the dependence of the sensitivity on the total pressure, where it was found that when a specific gas is admitted to the system almost all mass peaks in the background also rise, even for mass peaks that could not be produced by fragmentation or double charging in the ion source. Whilst the details will depend on the specific instrument and settings, an example is shown in Figure 10. While from CO_2 a fragmentation pattern for 12 (C+), 16 (O+), 22 (CO_2++), 28 (CO+), 32 (O_2+) could be expected, the fact that peaks at m/z = 26, 29, 30 etc. also increase indicates significant problems related to the transmission of ions through the quadrupole of this particular QMS.

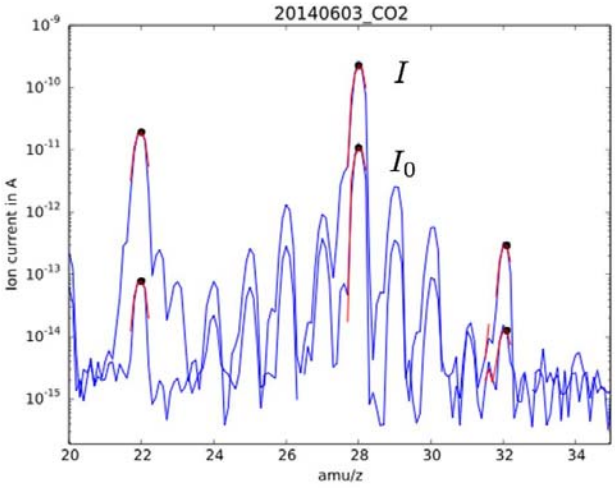

Figure 10 Ion currents for *m/z* = 20…35 when no gas is introduced (background, lower curve) and when $5x10^{-4}$ Pa of CO_2 (m/z = 44) was introduced (upper curve).

Procedures to determine the minimum detectable partial pressure and minimum detectable concentration were developed and tested to ensure that they gave reliable results provided that the QMS delivered signals of true currents (e.g. there was no suppression of negative currents).

For pure gases, it was found that the sensitivities not only become non-linear at higher pressures (>10^{-5} Pa), but also at low pressures (<10^{-7} Pa). Sensitivities for a specific gas species varied greatly with the composition of the matrix gas and also with the total pressure. Unfortunately, this even happens at low pressures (<10^{-5} Pa).

In conclusion, today's QMS cannot be characterised and calibrated without a clear and standardised procedure.

3.2.5 Investigation of the influence of operational parameters of quadrupole mass spectrometers on their signal

Some operational parameters of QMS can be adjusted by the user and usually include:

- electron emission current
- electron energy in the ioniser (ion source)
- mass resolution (or DC/RF voltage ratio)

Changing these parameters can influence the sensitivity and linearity of the instrument and also the cracking (fragmentation) patterns of different gases, therefore any change of parameters which have a significant influence on the output signal of the QMS will require recalibration of the instrument.

The sensitivity of ionisation gauges is proportional to the electron current which is used for the ionisation of gas molecules. A QMS uses the same principle for the production of ions, but instead of collecting the ions using an ion collector electrode immersed into the ion source, the ions have to be extracted from the ion source and focused into the quadrupole mass filter. The ion energy in the mass filter is quite low (of the order of 10 eV) so the extraction efficiency and focusing is very sensitive to the potential distribution inside the ion source. Changes in the electron current affect the density and space charge of electrons in the ioniser. In addition the density of ions produced (and the ion space charge in the ioniser) at a given gas pressure depends on the electron current. The electron and ion space charge can therefore both affect the sensitivity and linearity of the instrument.

6 different QMS instruments were investigated for H_2, He, N_2, Ar, and CO_2 during the study. The sensitivity was measured as a function of the pressure of hydrogen at three different electron emission currents: 2 mA (the nominal operating value of the instrument), 0.4 mA and 0.1 mA. The measured values at different emission currents were then normalised by dividing by the emission current so the sensitivities were comparable on the same scale. In an ideal case where sensitivity is proportional to the electron emission current, the normalised sensitivity would be just one curve, irrespective of the emission current. A large nonlinearity at 2 mA emission current at high pressures and also at low pressures is evident in Figure 11.

Another unexpected result of the effect of the ion current on the signal of the QMS is shown in Figure 12. One of the instruments studied exhibited a very large difference of cracking pattern for nitrogen (ratio of ion current signals at mass numbers 14 and 28, N^+/N_2^+) for different electron currents.

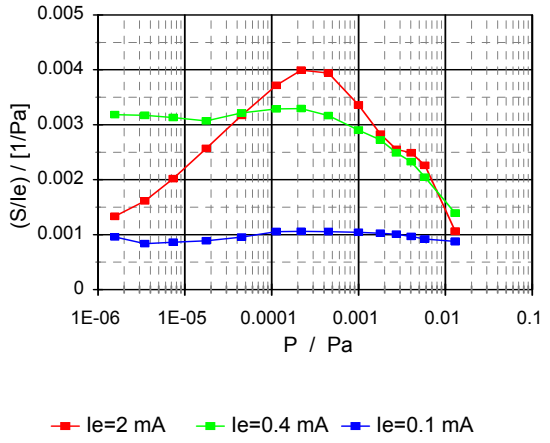

Figure 11 Measured normalised sensitivity of a QMS with an open ion source and yttrium oxide coated iridium filament as a function of gas pressure (hydrogen) at three different electron emission currents I_e, where large nonlinearities at nominal value of I_e=2 mA were evident

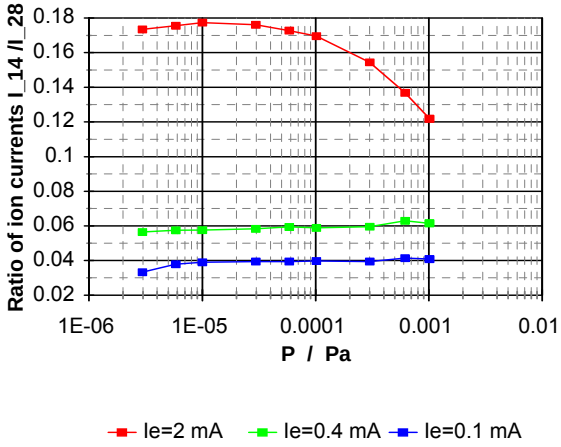

Figure 12 Measured cracking pattern of nitrogen for one of the QMS, where a very large dependence on the electron emission current was evident

Electron energy in the ioniser is determined by the potential difference between the emitting cathode and the anode grid which collects the electrons (cathode to anode voltage *Vc*). The electron energy has a significant influence on the ionisation probabilities and also on the cracking patterns of gas molecules. On the other hand changes in *Vc* also change the potential distribution inside the ion source and influence the electron and ion trajectories in the ion source. Consequently the ion extraction and focusing into the quadrupole mass filter are affected differently for different geometries of ion sources.

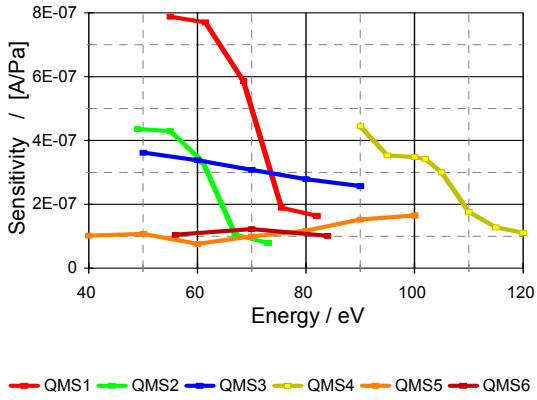

Figure 13 Sensitivity for nitrogen for 6 different QMS instruments as a function of electron energy

Figure 13 shows sensitivity for nitrogen for 6 different instruments as a function of electron energy. The curve for ionization probability of nitrogen as a function of electron energy for nitrogen has a maximum around 120 eV and at 40 eV the ionization probability is around 50 % of the maximum value. None of the curves in Figure 13 shows such dependence, so it is clear that the physical mechanism for dependence on electron energy is different from ionization probability.

Two different types of ion collector are used in QMS – single electron multiplier detectors (SEMs) and Faraday detectors. There is little published data on the dependence of the SEM gain on different ion species and different SEM gains for different ions will result in different relative sensitivities and also different cracking patterns for the Faraday detector and SEM detector. Figure 14 shows the relative SEM gain obtained for various ions with respect to the SEM gain for a N_2^+ ion at m/z=28. The SEM gain for hydrogen

ions is 1.5 time higher than for nitrogen and the gain for inert gases such as Ar and Kr is around 20 % to 30 % lower than for other gases.

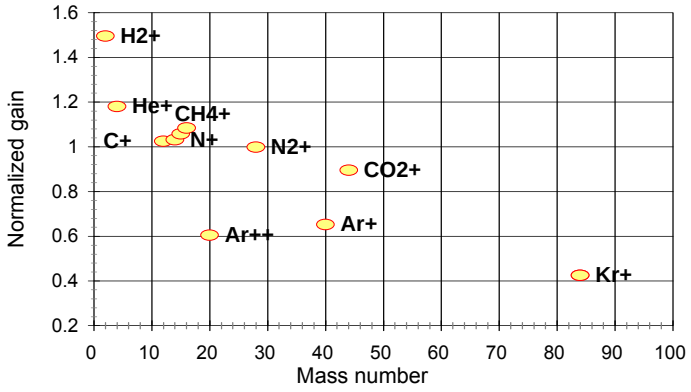

Figure 14 Relative SEM gain of different ions with respect to gain of N_2^+ ion at m/z=28

The main conclusions from the investigations were the following:

- Sensitivity is not a linear function of electron emission current unlike for ionisation gauges. When the emission current is changed the potential distribution inside the ion source also changes, which influences the ion energies, extraction efficiency and focusing of the ions into the quadrupole filter.
- Changing the electron energy in the ioniser has a different effect for different ion sources. When the electron energy is changed the ion source needs to be re-optimised for ion extraction and focusing.
- Large nonlinearities in the sensitivity as a function of gas pressure were found even for pressures below 10^{-4} Pa which indicates that QMS need to be calibrated over their entire operating range.
- Changing the mass resolution had a similar effect for all the instruments studied. To a first approximation the relative change of sensitivity was proportional to the change of resolution in the range from 0.8 u to 1.2 u.
- Cracking patterns for N2 (14/28) and Ar (20/40) in some instruments showed significant dependence on the pressure even for pressures below 10^{-4} Pa. The calibration procedure of QMS therefore needs to include the determination of the cracking pattern over the whole range of calibration.
- SEM gain depends on the type of ion detected, so the relative sensitivities for different gases for SEM and Faraday detectors are different (typically up to a factor 1.5).

3.2.6 Long term stability of quadrupole mass spectrometers

If QMS are calibrated then the long term stability of their calibrated parameters is also important. A long term 2 year study of the performance of QMS involving seven national metrology institutes (TUBITAK UME, IMT, PTB, INRIM, LNE, CMI and CEM) and the industrial partner VACOM was therefore undertaken within the project.

The stability of the sensitivities of nine different commercial quadrupole mass spectrometers (QMS) was measured at three different nominal calibration pressures of $5x10^{-6}$ Pa, $5x10^{-5}$ Pa and $5x10^{-4}$ Pa, which were selected based on the following requirements: (i) at the highest pressure all QMS instruments should be within their "linear" range, and (ii) at the lowest pressure the noise of the measured ion current of main peak using Faraday detector should be less than a few %. The stability of the mass scale, mass resolution, minimum detectable partial pressure and SEM gain were also investigated for He and N_2.

A common measurement protocol was adopted to ensure results from different participants were comparable, and stability measurements were performed at around three monthly intervals. Information about the usage of the QMS between the periodic measurements was also recorded. All participants used their own systems to generate the reference pressures, which were determined either by calibrated ionisation gauges or by primary methods. Where ionisation gauges were used, they were recalibrated against SRGs prior to calibrating the QMS. The same settings of the QMS were used for both the initial and

the periodic measurements. Prior to the periodic measurements, the QMS parameters were set to the values used for the initial measurements. Measurements were made at same emission current I_e that is used in manufacturer's specification of instrument sensitivity, which is usually the default emission current set by the QMS software.

Figure 15 and Figure 16 summarise the relative changes in the sensitivity for N_2 (m/z=28) and the minimum detectable partial pressure of He with respect to the initial measurements for all participants.

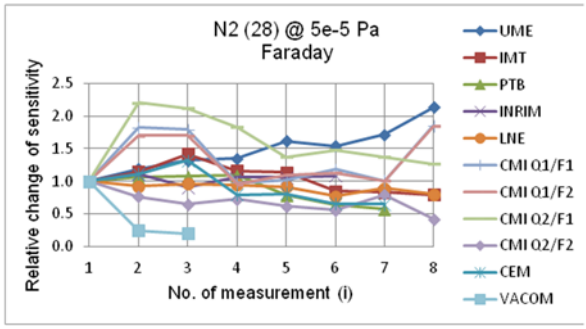

Figure 15 Sensitivity of nitrogen (N_2^+ ion at m/z=28) of QMS instruments of all participants

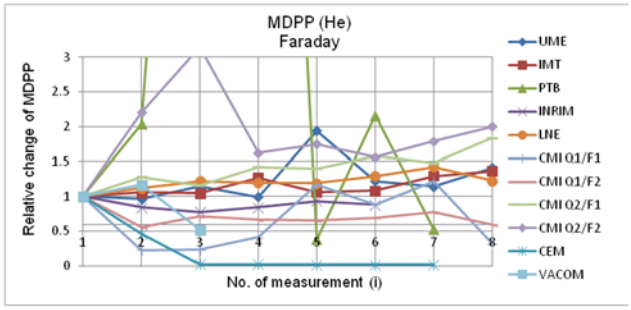

Figure 16 Minimum detectable partial pressure (MDPP) of helium (He^+ ion at *m/z*=4) of QMS instruments of all participants

The main conclusions from the study of the stability of nine QMS instruments over a 2 year period are the following:

- The stability of the sensitivity is a significant issue for QMS instruments. Typical changes of sensitivity for a Faraday detector in the range of 30 % to 60 % were observed over a three month period, with extreme changes of up to 550 %.
- Another source of sensitivity instability can be the gain of SEM detector which decreased gradually over time for most instruments. For two instruments a decrease of -70 % to -80 % was observed, with typical changes for other instruments of -30 % over a period of 2 years. For one instrument the gain unexpectedly increased by 20 %. Fortunately SEM gain can be easily measured and readjusted by the user.
- The mass scale was reasonably stable and the changes of the peak widths and peak position were generally less than 0.1 u.

3.2.7 Feasibility of optical methods as an alternative for partial pressure measurement

Finally, in terms of metrological quality, optical, spectroscopic methods have several advantages compared to QMS. For this reason, the project involved an experimental and theoretical feasibility study by PTB to investigate their applicability in vacuum metrology. Experiments using tuneable diode laser absorption spectroscopy (TDLAS) in the infrared showed that partial pressures of between 1 Pa to 1000 Pa of CO_2 can be determined with uncertainties below 1%, which is not feasible with QMS. In addition, in contrast to measurements with QMS, the results are not affected by the presence of other gas species or by the total pressure. Optical non-ionising methods do not change the gas composition by fragmentation of molecules and provide a clearer fingerprint for any gas species than obtained with QMS. Both the theoretical and experimental studies, however, showed that the effort and expense for the optical methods is much greater than with QMS. The study also highlighted that these optical methods provide more reliable results than those obtained with QMS, but are efficient only at pressures > 0.1 Pa and have the disadvantage that the gas species must be known before the measurement.

3.2.8 Guidance for end-users and steps towards standardisation for the characterisation of QMS

The responses from the questionnaire and results of the investigation clearly identified that guidance for end-users and standardised approaches to the characterisation and calibration of QMS are required if reliable measurements and comparable data are to be obtained from QMS. Since the questionnaire responses indicated that the main industrial applications are high vacuum outgassing rate measurements, leak rate monitoring and leak rate measurement, the focus was on calibration with an air mixture and also

calibration of helium and water vapour in other carrier gases. The calibration procedures also need to include determination of the minimum detectable pressure and the concentration for helium and also water vapour.

Based on the results obtained during the project, procedures for the characterisation of QMS were further evaluated experimentally by PTB and integrated into a draft Technical Specification " Vacuum gauges — Characterisation of quadrupole mass spectrometers for partial pressure measurement" developed by the project. The draft Technical Specification was circulated to ISO TC 112 "Vacuum Technology" and discussed at their meeting in April 2014. The decision at the meeting was positive and it was proposed that with some updates it should serve as a draft for a new work item proposal which was accepted early 2015.

3.2.9 Conclusions

Key applications and parameters relevant for the use and characterisation quadrupole mass spectrometers were identified. A primary standard for partial pressures capable of generating well-known pressures of three or more different gases at the same time over the range 10^{-8} Pa to 10^{-2} Pa and suitable for characterising and calibrating QMS was developed and is available. Investigations showed that the performance of QMS is affected by a wide range of operating parameters whose influence is not independent and the sensitivity and linearity are both pressure and gas matrix composition dependent, hence today's QMS cannot be characterised or calibrated without a clear and standardised procedure that describe the exact conditions required. Draft methods for the characterisation of quadrupole mass spectrometers for partial pressure measurement were developed within the project and incorporated into a draft Technical Specification which was submitted to ISO TC 112 "Vacuum Technology" which has been accepted as new work item.

3.3 Qualifying vacuum chambers and components for undesired gas species: Traceability and comparability for outgassing rate measurements

3.3.1 Introduction

The overall aim of this work was to develop SI traceable capability for industrial outgassing rate measurements and material characterisation by

- Development and testing of an industrially applicable method for outgassing rate measurement from 10^{-8} Pa L/s to 10^{-1} Pa L/s, with target uncertainties between 10 % and 20 %
- Provision of reference materials for the validation of outgassing rate measurements in industrial environments
- Provision of information on the comparability of different outgassing methods in terms of reliability, accuracy, and practicability for industry
- Development of a draft for a technical specification for a traceable outgassing rate method (for consideration by ISO TC 112 Vacuum Technology)

3.3.2 Outgassing rate measurement facilities

Three outgassing rate reference systems utilising different methods were developed and validated; two of the systems use primary techniques to determine the partial outgassing rate i.e. with independent traceability directly to SI system of units.

Outgassing rate measurement facility based on the continuous expansion method

An outgassing rate measurement facility based on the continuous expansion was developed and validated at PTB and is described in Section 3.2.3.

Outgassing rate measurement facility based on a modified throughput method

An outgassing rate measurement facility based on the throughput method where the throughput is measured by the difference across an orifice of known conductance was developed and validated at the Karlsruhe Institute for Technology. To consider the influence of the outgassing of the sample chamber itself, a second identical reference chamber without a sample was added. The outgassing rate from the sample can be derived from the net flow between sample and reference chamber. Since total pressure gauges (ionization gauges) are used for the pressure measurements, it is not possible to specify the flow of individual outgassing species. These can only be qualitatively determined by a QMS mounted on the downstream side.

Outgassing rate measurement facility based on the gas accumulation method

An outgassing rate measurement facility based on the gas accumulation method (see Figure 17) was developed and validated at IMT. In the gas accumulation method, the gases released from a sample material or component are accumulated in a closed vacuum chamber of known volume for a certain period of time. The outgassing rate of the sample is calculated from the rate of pressure rise. The rate of pressure rise in the accumulation method can only be measured using vacuum gauges which do not interact with the measured gas (i.e. they exhibit negligible self-outgassing or pumping) such as a spinning rotor gauge (SRG) or capacitance diaphragm gauge (CDG) but not an ionisation gauge.

The new measurement facility can be used for outgassing rate measurements of different materials used in industrial applications over the range from 10^{-8} Pa L/s to 10^{-3} Pa L/s. The system enables "in-situ" degassing of samples at different temperatures in the range up to 350 °C prior to the measurements, however the outgassing rate in this facility can only be measured at room temperature due to limitations of the SRG which is used for measuring the rate of pressure rise.

Figure 17 shows the schematic of IMT's outgassing rate measurement system, including a gas flow calibration attachment on the right of the figure.

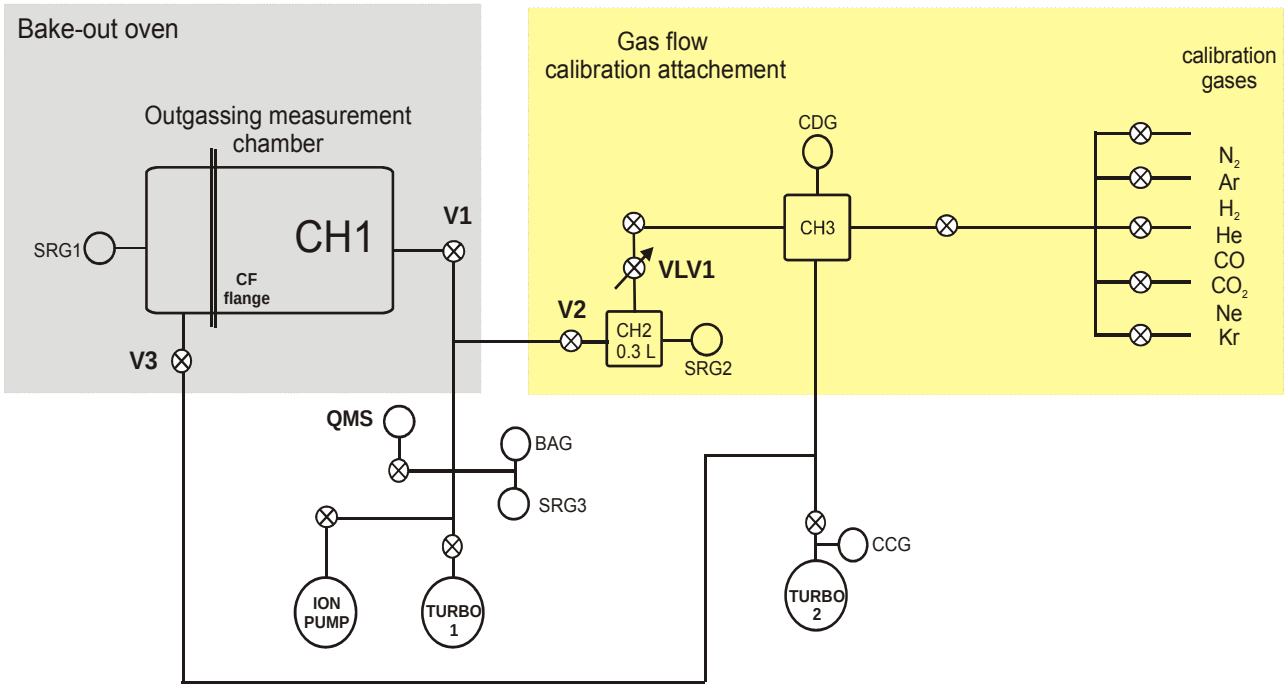

Figure 17 Schematic of outgassing rate measurement system by gas accumulation method together with a gas flow calibration attachment

The sample is placed in the outgassing measurement chamber CH1, which is then evacuated with a turbo molecular pump. Time t=0 is set when the pump is switched on, or when the pressure drops to a value defined by the measurement protocol. After initial evacuation for a specified time period, the measurement is started. Valve V1 is closed and chamber CH1 is separated from the pumping system. Due to the gases released from the sample the pressure in CH1 starts to increase. In addition to outgassing from the sample, the walls of CH1 also outgas, so this contribution has to be measured in a 'blank' measurement without a sample and subtracted from the measured values obtained with the sample.

The outgassing rate q_{pV} (in p×V units) is given by:

$$q_{pV} = V_{CH1} \frac{dp}{dt} \quad , \qquad (6)$$

where V_{CH1} is the volume of the measurement chamber and dp/dt is a rate of pressure rise measured with SRG1. When the composition of outgassed species is not known, the SRG is set to nitrogen and the

measured values are given as "nitrogen equivalent". The pressure slope dp/dt is calculated by least squares linear regression.

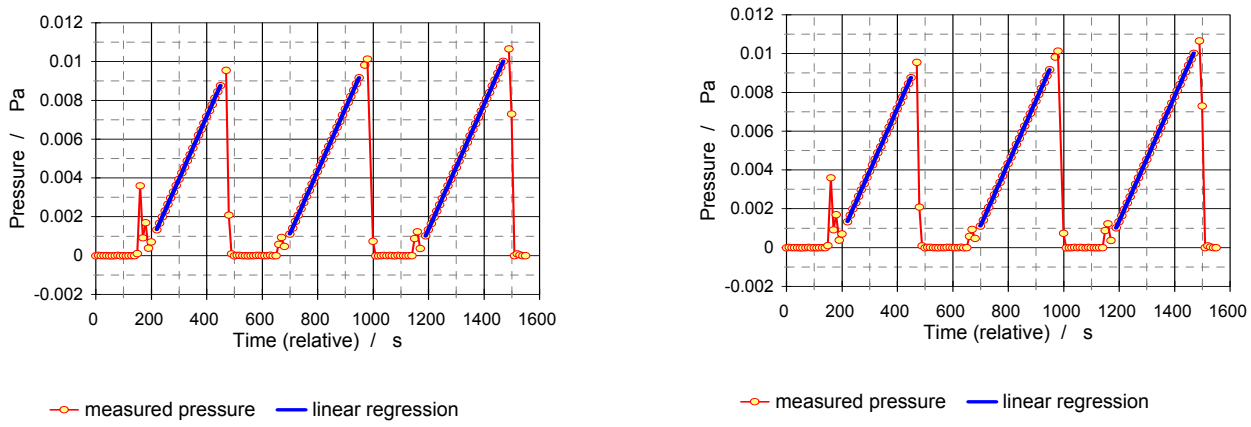

Figure 18 Examples of measured pressure increase by gas accumulation method

Figure 18 shows examples of the measured pressure increase in CH1 during the outgassing rate measurement. Three consecutive repeated measurements of the same sample are shown to demonstrate the repeatability of the method. The calculated rates of pressure rise were 3.227×10^{-5} Pa/s, 3.225×10^{-5} Pa/s and 3.221×10^{-5} Pa/s with a relative standard deviation of these three measurements of 0.08 %.

It is straightforward to establish traceability of the outgassing rate measurements for the accumulation facility as the basic quantities which require traceability are volume, pressure and time. There are several ways to determine the volume of CH1. One is a gravimetric method where the chamber is completely filled with liquid of known density (pure water) and the difference in mass between the empty and filled chamber determined with a calibrated balance. Another possibility is to precisely measure the inner dimensions of the chamber and then calculate the volume. While the gravimetric method gives more accurate results, the uncertainties with the dimensional method are sufficient for the uncertainty required for outgassing rate measurements. Therefore, this latter method was used by IMT to determine the volume of CH1. The pressure is measured with a calibrated vacuum gauge and the time measured with an internal computer clock for time stamping, which can be calibrated against a reference clock.

The typical lowest uncertainty that can be achieved using IMT's accumulation outgassing rate measurement facility under ideal conditions is 1.7 % in the middle of the measurement range. For outgassing rates below 10^{-6} Pa L/s the uncertainty increases mainly due to additional contributions from the background outgassing from the chamber walls.

In conclusion, the accumulation method is also suitable for use in an industrial environment as it is relatively easy to establish traceability and the best achievable expanded relative uncertainty can be below 5 %. However the accumulation method can be only used for outgassing measurements of gas species that do not adsorb on the chamber walls, or are not re-absorbed by the sample and the method is not applicable for strongly absorbing species such as water vapour or hydrocarbons. Adsorbing gases can be only measured using the throughput method (see Section Primary standard for partial pressures and outgassing rate measurement3.2.3).

With the accumulation method, it is only possible to analyse the gas composition after the accumulation period by using a QMS attached to the pumping line outside the measurement chamber. To do this the valve V1 is only slightly opened so that a measurable pressure pulse can be detected by a Bayard Alpert ionisation gauge and the QMS. An example of the measured ion current pulses for different mass numbers during pump down of the accumulated gas is shown in Figure 19. The area of the ion current pulse is proportional to the quantity of pumped gas and can be obtained by numerical integration. The gas composition can be calculated from the integrals of the main peaks of gases that are present if the gas flow sensitivity of the QMS is known.

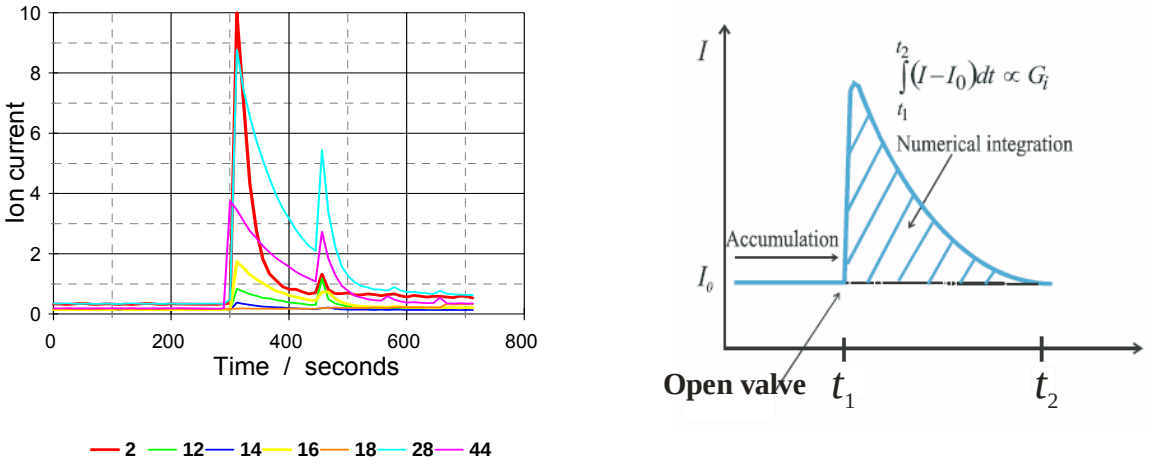

Figure 19 Examples of measured ion current impulses when valve V1 is very slowly opened after the end of accumulation (left). The area of the ion current impulse is proportional to gas quantity G_i (right).

The gas accumulation facility can also be used for dedicated in-situ calibration of QMS for gas flow and gas quantity measurement, thus providing another primary standard for the calibration of QMS in addition to the system described in Section 3.2.3. In contrast to that one, however, IMT's facility is not suitable for generating known gas mixtures. The gas accumulation facility is equipped with an additional module to generate gas flows (see Figure 17). To perform an in-situ calibration of a QMS the gas reservoir (CH3) is filled with the calibration gas and the leak valve VLV1 is set to an appropriate conductance to provide a gas flow which gives the desired ion current in the QMS (partial pressure). When the ion current has stabilised to a value I^+, the valve V2 is closed and the gas flow $q_{pv,cal}$ is measured by gas accumulation method in CH2 using SRG2 in the same way as previously described for the outgassing rate measurement. The gas flow sensitivity K_q of the QMS is equal to:

$$K_q = \frac{q_{pV\_cal}}{I^+} \quad , \qquad (7)$$

where K_q is the ratio of the effective pumping speed and the sensitivity of the QMS for different gases. As the calibration is performed in-situ, any deviations from non-equilibrium gas distribution in the pumping line are automatically compensated for. K_q is gas dependent, so it is necessary to calibrate it separately for all gases of interest. If calibration is not possible for some gases, then K_q can be estimated from knowledge of the relative sensitivity of the QMS for that gas compared to another calibrated gas (usually nitrogen) and also the dependence of the effective pumping speed on molecular mass of gas. The relative uncertainty of K_q amounts to about 3% and the system can be used for outgassing rates from 10^{-8} Pa L/s to 10^{-3} Pa L/s.

Assuming that in the accumulated gas there were n components which were detected in a pressure impulse after the accumulation period and the respective areas of peaks (integrals) A_1, A_2...A_n were calculated, then the quantity of each gas component is equal to $G_i = A_i \times K_q$. The total gas quantity G_{tot} is the sum of all components:

$$G_{tot} = \sum_{i=1}^{n} G_i = \sum_{i=1}^{n} A_i \times K_q^i \quad , \qquad (8)$$

The relative composition of the individual species i in the accumulated gas is equal to G_i/G_{tot}.

3.3.3 Investigation of suitable materials for outgassing rate measurements and the development of reference outgassing samples and artefacts

The aim of this study was to identify materials with suitable properties that could be used to produce samples with well-known outgassing rates, which could serve as a reference for calibration, validation and proficiency testing of different outgassing measurement facilities.

A literature search on permeation and absorption data for gases in different polymers and inorganic materials such as zeolite, charcoal and porous silicone, identified two materials Viton (FPM-fluoropolymer) and PDMS (poly-dimethil siloxane) as the most promising candidates for outgassing reference samples. The main criteria for selection were: (i) diffusion constants for different gases in the range from 10^{-8} cm^2/s to 10^{-4} cm^2/s, (ii) permeability in the range from 10^{-9} cm^2/s to 10^{-5} cm^2/s, and (iii) the material should be "clean" and compatible with high vacuum applications, which means that it should not release volatile organic compounds.

The physical process for gas transport in such materials is diffusion. Only materials which have sufficient repeatability and reversibility of gas absorption are suitable for use as reference samples. When gas diffuses through a membrane, any change of pressure on the upstream side will not be detected immediately as a change of gas flux on the downstream side but only after a characteristic time delay $\tau = D^2/6d$ where D is the diffusion constant and d is the thickness of the membrane. The time required to establish equilibrium, to outgas a sample or to fully load the sample with a gas is proportional to this time delay.

In order to accurately model diffusion processes such as degassing and loading of the samples with different gases extensive measurements of the diffusion constant D, permeability K and solubility S of gases (H_2, He, Ar, Kr, CH_4, N_2, O_2, CO, CO_2 and H_2O) in Viton and PDMS samples were performed. A patent application for the easy to handle permeation type outgassing artefact for water vapour, gas mixtures and dodecane has been submitted and so the results of these measurements are still confidential and will be published at a later stage.

Knowledge of D and K and S is important for sizing the reference samples in order to obtain the desired outgassing rate and released quantity of gas. Measurements showed that the transport of all the gases tested except H_2O can be accurately predicted by diffusion theory. The diffusion constant of H_2O is comparable to other gases, but the solubility and permeability are significantly larger.

Outgassing reference samples manufactured from Viton were prepared as follows. Pieces of Viton were placed in a specially designed gas loading cell and were evacuated in an ultrahigh vacuum system for sufficient time to ensure they were in a fully degassed state. The loading cell was then filled with a pure gas or gas mixture at a pressure up to 300 kPa, the cell was isolated and the samples kept in the gas for several days so that it penetrated into material to a fully saturated state. The samples were removed from the loading cell just before they were placed into the outgassing rate measurement apparatus. Atmospheric gases start to penetrate into the reference sample during handling in air so the handling time in air should be minimised to avoid contamination of the sample with atmospheric constituents.

A reference sample can be initially loaded with a certain gas or gas mixture and its outgassing rate measured using the primary outgassing measurement system (such as the system described in 3.2.3 or 3.3.2), yielding a certified reference value of the outgassing rate as a function of time. This sample can then be re-loaded with the same gas under the same conditions and sent in the loading cell to a user in industry or another laboratory for measurement in their system. By comparing their results with the certified reference value the industrial outgassing rate measurement facilities can be calibrated or validated. Certified reference samples can also be used in a round robin test for the proficiency testing of systems in different laboratories.

The typical time dependence of the outgassing rate from the Viton reference sample, which was loaded with CO at a pressure of 300 kPa, is shown in Figure 20. It can be seen that during the first few hours the outgassing rate drops quite rapidly, but after this initial phase the outgassing rate decreases at a slower rate for a long period of time (100 h). The simulation of the outgassing rate using a diffusion equation fits the entire measured curve, which indicates that the physical mechanism of the transport of molecules is solely determined by diffusion.

The distinctive feature of the newly developed reference samples based on Viton is that they can be reloaded many times with many different gases and also with mixtures of gases at arbitrary concentration ratios. Any gas which does not react chemically with Viton should produce reproducible outgassing rates. Samples can be placed in the outgassing rate measurement facility at the same location where other samples are measured, ensuring that the gas dynamics in the system are the same during measurement of the reference samples as during measurements of the ordinary samples.

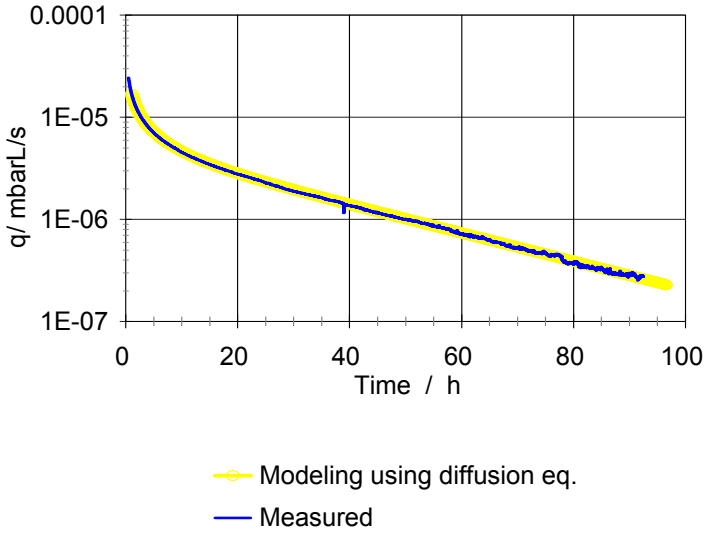

Figure 20 Measured outgassing rate of a Viton reference sample which was loaded with CO at a pressure of 300 kPa and calculated values obtained using the diffusion model

A second type of outgassing reference device based on a thin SiN membrane with the nano-holes drilled by a focused ion beam (FIB) technique was also developed with a typical throughput of 10^{-5} Pa l/s to 10^{-4} Pa l/s at room temperature. The dimensions of the nano-holes were tailored to provide an appropriate gas conductance. The membrane was attached to a small gas reservoir which was filled with a gas or gas mixture and then permanently sealed. The gas flow through nano-holes can be used to simulate outgassing. The device was constructed to be small and compact so that it can be accommodated into the usual outgassing rate measurement systems. Its outgassing rate can be also certified by a primary system. Realisation of this device would not have been possible without collaboration between the project partners and the Researcher Excellence Grant researchers from the University of Genoa, who contributed knowledge on the fabrication of nano-holes in thin membranes using FIB.

Traceable measurement of water vapour outgassing is a real challenge in vacuum metrology due to the strong adsorption of water molecules on the surfaces of vacuum systems. Two prototype compact permeation water vapour sources which produce constant outgassing rates of water around 3×10^{-3} Pa l/s and 6×10^{-5} Pa l/s respectively over a long period of time were manufactured. The prototype devices had excellent long term stability and further development of the device will bring significant advancement of the accuracy of water vapour measurements in vacuum metrology. Since this approach can also be used for other types of gases, a patent application has been submitted. The approach was also successfully tested as a reference outgassing device for other outgassing species (a mixture of rare gases, hydrogen and nitrogen). Although not originally planned in the project, the idea for the construction of such water vapour source was born from brainstorming by PTB, IMT and REG(KIT) at the workshop on outgassing, and so would probably not have happened without the project.

3.3.4 Guidance for end-users and steps towards standardisation for the measurement of outgassing rates

Guidance for end-users and standardised approaches to the measurement of outgassing rates are required if reliable measurements and comparable data are to be obtained. A Technical Specification on "Procedures to measure and report outgassing rates" was drafted by the project and submitted to the ISO TC 112 for discussion at their meeting on 9-10 April 2014 in Busan, Korea. The decision at the meeting was positive and it was proposed that it should serve as draft for a new work item proposal which was accepted in early 2015.

The Technical Specification includes five possible measurement systems, two of them as primary standards that were tested in the project (Sections 3.2.3 and 3.3.2). In other sections measurement procedures are described for the different systems, the uncertainties related to the measurements detailed, and how the results should be reported.

3.3.5 Conclusions

Three outgassing rate reference systems utilising different methods which are suitable for measurements between 10^{-8} Pa L/s to 10^{-1} Pa L/s with uncertainties between 10 % and 20 % were developed and validated.

Three types of reference outgassing artefacts for the validation of outgassing rate measurements in industrial environments were developed and assessed: reference outgassing materials (Viton (FPM-fluoropolymer) and PDMS (poly-dimethyl siloxane), a permeation reference outgassing artefact and an in-situ leak artefact based on nanoholes in a thin SiN membrane. A patent application for the easy to handle permeation type outgassing artefact for water vapour, gas mixtures and dodecane was submitted. In addition two prototype devices with nominal outgassing rates of water vapour 3×10^{-3} Pa l/s and 6×10^{-5} Pa l/s were tested and demonstrated good performance. A Technical Specification on "Procedures to measure and report outgassing rates" was drafted by the project and submitted to the ISO TC 112 for discussion. It was subsequently accepted as a new work item.

3.4 Leak tight vacuum systems and secure containers: Improved leak artefacts and guidelines

3.4.1 Introduction

The aim of this work was to improve capabilities for leak measurement and testing in industrial environments by:

- Development of methods better suited to leak measurements under realistic industrial conditions e.g. with regard to the actual gas species and pressure conditions
- Specification of alternative methods to mass spectrometer leak detectors in order to detect leaks within a second or less (dynamic measurements)
- Production of a practical guide for industry on the metrological performance of commercial leak detectors

"Time is money" is also true in leak testing services, so a feasibility study was therefore undertaken to assess whether optical measurements were a suitable alternative for improving the speed of leak testing measurements.

3.4.2 Realisation and characterisation of leak elements

As a first stage the project aimed to produce ducts with a well-defined geometry for standard leaks. The ducts were micro or nano holes manufactured using different technologies, where the geometry of each hole (diameter and thickness) could be accurately measured. Three types of leak elements were produced: short ducts in metal discs, glass capillaries, and nanometre sized holes in silicon nitride membranes.

Ducts in metal discs: 15 ducts were produced from three different metals (stainless steel, copper and aluminium), which are readily available and compatible with all vacuum ranges. For the stainless steel ducts, one side of a double knife-edged flange was reduced to 0.8 mm thickness by electro-erosion and was then polished. For the copper and aluminium ducts, discs with the same dimensions as standard CF16 flange gaskets were used. The central area on one side of each disc was reduced to 0.4 mm thickness using a mechanical process. Small holes with nominal diameters from 20 µm to 8 µm were drilled into the areas of reduced thickness metal using laser technology, which produces regular shaped holes. The conductances for helium ranged from 10^{-14} L/s to 10^{-11} L/s in the molecular regime.

Figure 21a shows the hole in a copper disc as received from the manufacturer and material can be observed deposited on the side where the laser beam pierces the disc. INRIM's nano facility Focused Ion Beam (FIB) instrument which has micromachining capabilities at the nanometre–micrometre scale was used to remove the material around the hole (see Figure 21b). The same procedure was applied to all the samples.

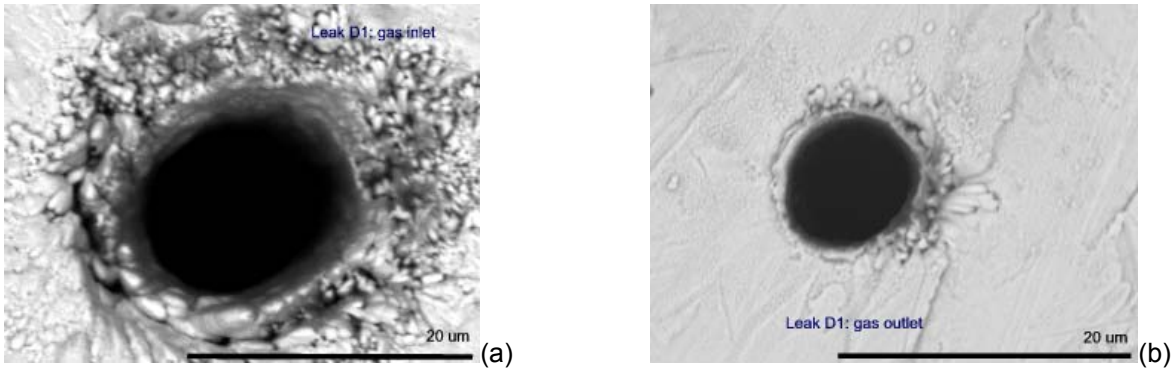

Figure 21 A leak artefact manufactured from copper. Left (a): as machined by laser; Right (b) the same leak artefact after cleaning by focused ion beam

The thickness of the disc was measured using a 1D linear comparator equipped with a laser interferometer. A mechanical probe was used to determine the starting and the ending points of the interferometric displacement measurement, and the mechanical probe diameter was determined using a calibrated gauge block. Measurements were carried out in different symmetrical positions and repeated twice (providing 3 sets of measurements) in the reduced thickness area of the flanges/discs.

A 2-D grating was used as a reference to measure the diameters of the holes in the leak elements. The grating pitch *p* was determined by measuring the angle of auto-collimation related to a laser beam with a specific wavelength. As a second step, SEM pictures of the holes, calibrated using gratings, were taken and the coordinates of the profile border were identified using image processing software. The diameter for each hole was calculated from the recorded coordinates.

The standard deviation of the diameter measurements for each side of the flange/disc obtained at the different positions, may be considered as a deviation from the ideal circle. Differences between the hole diameters of the two sides of flange/disc can also be identified from the measurements. Uncertainties associated with the diameter measurements were typically less than 3 % except for diameters below 10 µm for which relative uncertainties remained below 4 %.

Glass capillaries: Five glass capillaries (Figure 22) with nominal gas flow rates between $1x10^{-4}$ Pa L/s and $1x10^{-3}$ Pa L/s at 1 bar with reference to vacuum were supplied by the partner Danfoss.

Figure 22 (a) Schematic of the glass capillary and (b) an optical microscope picture of the restriction of the capillary

The restriction inside the glass capillary was obtained by heating using a special burner, during which helium was blown on top of the glass capillary and the leak rate measured with a leak detector (pressure difference of 1 bar) until it reached the desired value. After cooling, the capillary was cut to the final length (>1 cm) and the glass leaks observed using an optical microscope (Figure 22b). The modified glass capillaries were however found not to be fully suitable because their geometry could not be determined with sufficient accuracy.

Nanometre sizes holes in silicon nitride membranes: Nano-holes of 100 nm diameter were drilled in low stress silicon nitride (Si_3N_4) membranes (Figure 23) using a focused ion beam (FIB) at Genova University. The membranes were custom made on chips, initially with a thickness of 200 nm and later also 100 nm and are able to resist 100 kPa differential pressure. The conductances for helium ranged from $5x10^{-9}$ L/s to $5x10^{-8}$ L/s in the molecular regime.

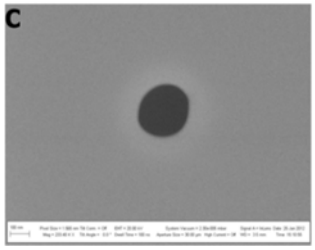

Figure 23 SEM image of a nano-hole

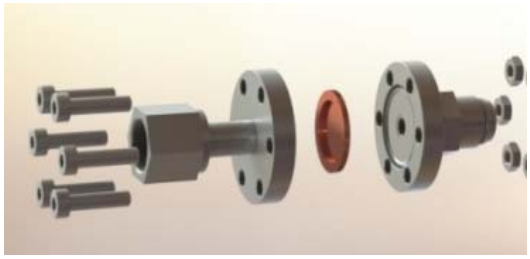

Figure 24 Example of a complete artefact, sandwiched by two DN16 CF flanges

In addition to these three types of leaks (ducts in metal discs, glass capillaries and nano-holes in silicon nitride), long capillaries (0.5 m) of polyamide material and glass, a porous body leak and a micro-device with a series of parallel rectangular micro channels etched by deep reaction ion etching (DRIE) on a silicon wafer and closed by anodic bonding with a Pyrex plate were also considered. Their characteristics and potential use as reference leak standards were investigated. The porous body leak comprised a stainless steel sintered filter capable of supplying gas flow in the molecular regime up to an inlet pressure of 10 kPa and was provided by the National Metrology Institute of Japan (NMIJ), a collaborator of the project.

In order to make the leak artefacts robust and available for measurements (i.e. easy to mount on NMI's primary flowmeters), each leak element was encased in a suitable fitting with the upstream side defined (see Figure 24). In the case of conical shapes, the larger diameter was chosen to be on the higher pressure side. The leak tightness of the seal was better than 10^{-8} Pa L/s.

The 6 leak artefacts of the metal ducts type with the most regular geometry were selected and sent to the NMI partners (LNE, CMI, INRIM, PTB) for characterisation against the primary flowmeters. The gas flow rate generated by the leak artefacts with respect to vacuum and to atmosphere, at different inlet pressure values and with a number of gas species (He, N_2, Ar, H_2, SF_6 and others) were measured. Figure 25 and Figure 26 show examples of the measured normalised conductance against vacuum and atmosphere versus the inverse of the mean free path of the gas within a leak characterised using several gas species. The conductance was normalised by multiplying the measured conductance value by the molar mass of the respective gas species. By this, the mean thermal speed of the molecules does not influence the normalised conductance.

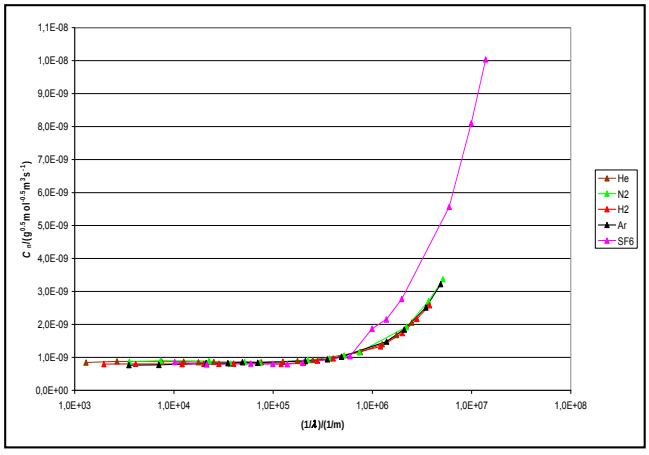

Figure 25 Measured normalised conductance of a capillary leaking against vacuum for several gas species

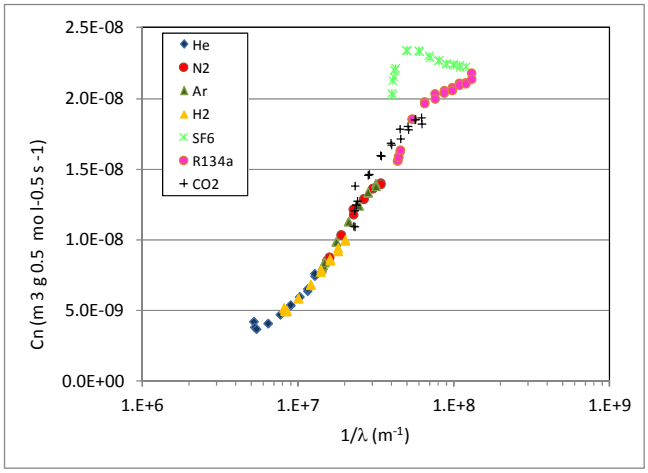

Figure 26 Measured normalised conductance of a capillary leaking against atmosphere

The porous body leak was calibrated at INRIM with reference to vacuum and atmospheric pressure with helium, nitrogen and argon and was also shown to have predicable behaviour. Longer tubes such as exist in porous bodies show a conductance, the so called Knudsen curve, which is constant in the molecular regime (lower λ^{-1} values) and increases sharply in the viscous flow regime (high λ^{-1} values) with an intermediate shallow minimum, the so called Knudsen minimum. The difference between the experimental data and the analytical Knudsen curve was less 4 % with the exception of few points and the results were consistent with results obtained with other leak elements investigated during the project.

3.4.3 Models of flow in narrow ducts

Once the geometry of the leak elements was known, theoretical models for the flow through them were developed, with the aim that the model should be applicable for industrial service (e.g. not require extensive simulation for each standard leak).

Two bridging formulas between molecular and hydrodynamic flow proposed by Gallis and Torczynski and Sharipov-Seleznev were considered. They have a simple structure and allow the computation of mass flow rates in micro channels with a very small computational effort. The formulae have two main drawbacks which can cause deviations from experimental results. The first one is related to the assumption that the cross section of the channel is constant and the second is associated with the hydrodynamic limit which affects the comparison with experimental conditions when the flow Mach number is high enough to make inertial terms important. A mathematical model was therefore developed with the help of the Polytechnical University of Milano to describe the flow inside the narrow duct from the molecular to the hydrodynamic regime using a simple bridging formula based on the Direct Simulation Monte Carlo (DSMC) method for molecular and transition regime and the hydrodynamic model for high Mach number and this model was validated using the Navier-Stokes equation.

All the micro-channels had a geometry which was roughly conical. Since both bridging formulas are only valid for constant section circular channels, a reference diameter, equal to the arithmetic mean of inlet and outlet nominal diameters, was used as a starting value. An effective value of the diameter was then found by minimising the global deviation from experimental data. Only the data in the molecular, transition and the first points in the viscous regime were considered. The theoretical model developed was then compared to measurements obtained for many industrially important gas species: He, H_2, N_2, Ar, R12, R134a, SF_6, CO_2 and a mixture of N_2/H_2 (95/5 mixture). An example of the relative differences of the normalised conductances between the measurements and the results from the theoretical model is shown in Figure 27.

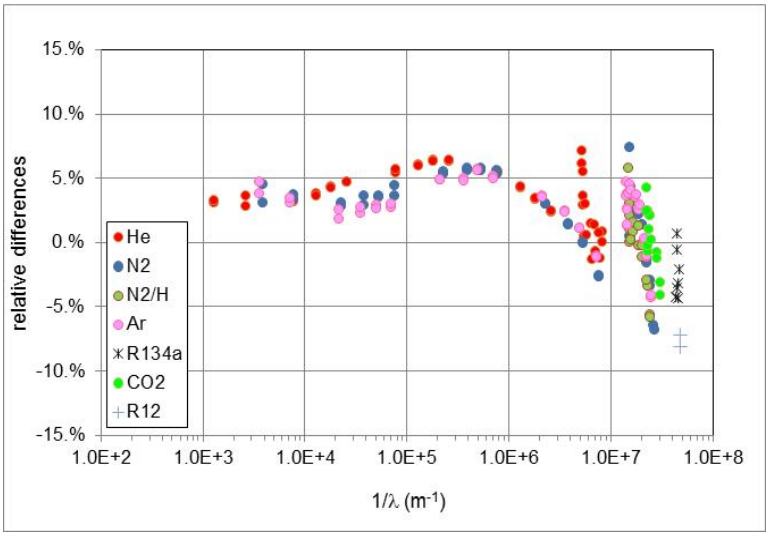

Figure 27 Example of the relative differences of normalised conductances between experimental data and calculated values using the modified Gallis and Torczynski formula versus the inverse of the mean free path for one leak

The results for the mono-atomic species and for the expansion into near vacuum showed that the bridging formulae can reproduce experimental data with an accuracy of less than 10 % provided that the effective diameter is properly determined. The hydrodynamic model appears to introduce the appropriate corrections which is more evident for heavy polyatomic species. The experimental data were also compared with numerical solutions of the compressible Navier-Stokes equation for ducts of variable section by using CFD software OpenFOAM.

From the comparison it was concluded that the hydrodynamic model for higher pressures can be used to successfully represent the experimental data when the duct has a constant section (duct geometry is regular) or a variable section (duct geometry is conical). The agreement was within 1 % to 15 % depending on the gas and the pressure.

The model that was developed in the project can be used to predict the gas flow rate of different gas species, such as a refrigerant, simply by starting from a few calibration measurements with helium in vacuum and one calibration point at atmospheric pressure with the refrigerant gas, thus avoiding the need for extensive calibration of the leak for each gas which will be used.

3.4.4 Performance of leak artefacts under industrial conditions

Some industrial applications require measurements to be performed under non-ideal conditions for example where parameters such as temperature are either changing or are at extremes of ranges and it is important for users to understand and ideally correct for the effect of these operational conditions on their measurements.

The temperature coefficients of 6 different leaks elements (3 metal ducts each from a different material, 2 glass capillaries produced in the project, and a commercial capillary made of RILSAN®) were measured in vacuum and at atmosphere with several gas species including He, N_2, Ar, CO_2 and R134a (**Error! Reference source not found.**Figure 28). The temperature coefficient was found to be in the range from -0.3 %/K to -0.5 %/K in the temperature range from 15 °C to 40 °C and so for most industrial applications between 15 °C and 25 °C the effect can be neglected. The effect should however be taken into account if measurements are performed in an industrial environment where the temperature is above 25 °C.

The effect of changes of atmospheric pressure on the measurements of the gas flow release from a capillary leak was also investigated. A capillary leak was connected to the primary flowmeter to directly measure the flow delivered at three different inlet pressures. Two pressure regulators were then connected to the flowmeter: the first regulator to ensure that the inlet pressure of the capillary remained constant during the measurements and the second one to change and to ensure that the downstream pressure of the leak (outlet pressure) remained constant. The results are shown in Figure 29.

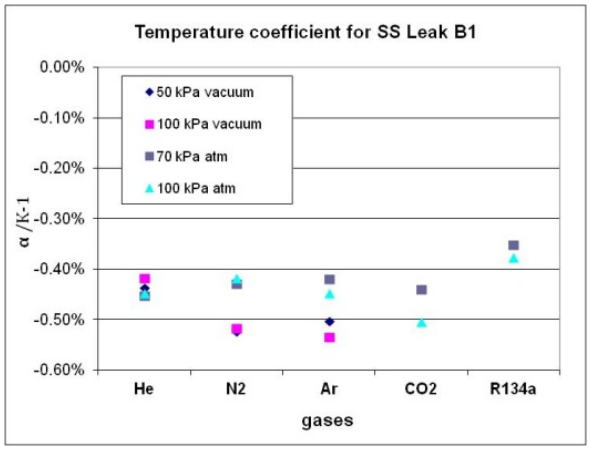

Figure 28 Example of thermal coefficients of a leak determined for different gas species at 4 pressures

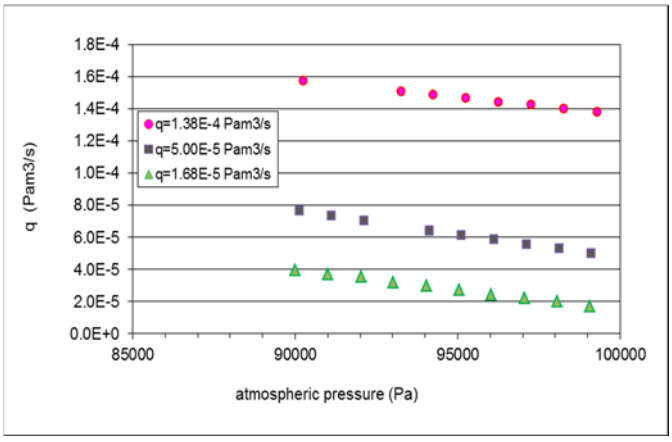

Figure 29 Dependence of the gas flows on atmospheric pressure

From the results, it can be concluded that the gas flow depends on both the inlet and atmospheric pressures and the absolute or relative inlet pressure and the atmospheric pressure should be clearly stated in the calibration certificate for a leak. Such information will enable the user to make the necessary correction if the leak is used under conditions that vary greatly from the condition under which the leak was calibrated.

3.4.5 Guidance on the metrological performance of leak detectors

In order to develop representative guidance for end-users on leak detection and the performance of leak detectors, the characteristics and performance of a number of leak detectors were investigated.

Helium leak detectors produced by 3 different manufacturers and which had been used in different environments in the past (a brand new detector, a detector that had previously been used in an industrial laboratory and a detector that had been moved and used in different places) were calibrated by INRIM, TUBITAK UME and Lazzero on several consecutive days using reference leaks. The metrological characteristics such as deviation after a self-calibration, linearity and stability were determined. It was found that the first two detectors worked efficiently and their parameters were accurate and reproducible within a few %. This was not the case for the third detector which showed a drift of greater than10%, however this was the detector that was moved to and used in different institutes and environments. In addition, to study the influence of environmental pollution of He on the leak rate measurements, the He background level inside a box, where the leak detector was located, was controlled and the signal from the detector recorded. It was found that the readings were correct and stable even in the polluted environment.

Eight commercially available refrigerant gas detectors (two detectors with infrared technology and the other ones with heated sensor technology) were selected by LNE according to their operating principle and their lower detection limit. The detectors were tested according to the standard EN 14624:2012. An adjustable crimped capillary leak was used to generate standard flow rates of the refrigerant gas R-134a in the range between 1 g/a and 10 g/a, in various setups, and four different tests were performed on the detectors. The first test determined the static detection limit: the sniffer probe was positioned stationary in front of the calibrated leak at a fixed sniffing distance of 3 cm; the second test aimed to determine the dynamic detection limit, illustrated in Figure 30: the sniffer probe travelled from one side to the other side of the calibrated leak at a speed (v = 2 ± 0.2) cm/s. The third test determined the dynamic detection limit in a chamber where the concentration of R-134a could be monitored up to 1000 µmol/mol with a tolerance of ± 10 %. The fourth test determined the recovery time: the sniffer probe was first placed in front of the largest leak specified by the manufacturer (50 g/a if not specified) for 10 s, and then placed stationary in front of the leak corresponding to the static detection limit; and the time taken by the detector to detect this leak again was then measured.

All the detectors complied with the manufacturer's specifications according to the standard EN 14624:2012 under the static conditions. Three of the detectors did not comply with the specifications under the dynamic conditions. Finally, for the dynamic conditions in the atmosphere polluted with refrigerant, none of the detectors responded according to the standard. No statement could be made about compliance of the recovery time as this specification was not included in the manual.

From the tests performed, it appears that the detectors evaluated do not strictly comply with the standard EN 14624:2012, primarily due to the fourth test.

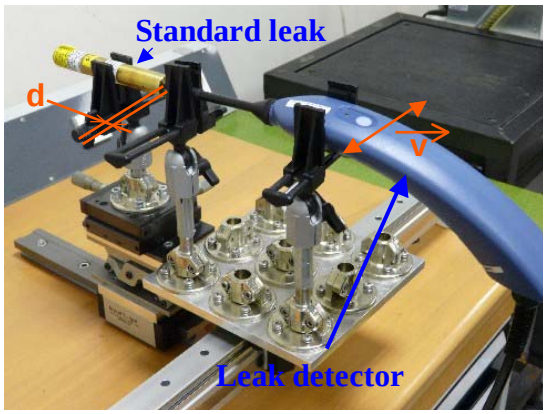

Figure 30 Dynamic test performance according to the standard EN 14624:2012. The leak detector is moved with constant speed perpendicular to the outflow direction from the standard leak.

A practical guide on leak detector calibration and uncertainty evaluation was produced and is available from the IND12 website. The first part of the guide includes general information about terms and definitions of gas flow rate and the main characteristics of different leak typologies. The second and third parts of the guide are devoted to the helium and refrigerant leak detectors used to detect leaks either in vacuum or via the 'sniffing mode'. Those chapters include a brief introduction on the operating principles of the leak detectors, followed by the results of the metrological characteristics obtained in the project. The calibration of detectors is discussed and a calibration procedure is suggested. The uncertainty evaluation of the detector is addressed starting from a calibration certificate for the reference leak and the uncertainties of the main parameters of the detector. The appendix includes an explanation of the main metrological terms as well as general consideration on the uncertainty assessment and the traceability chain. A simple Excel sheet was produced and is associated to the guide to help the user to predict the gas flow delivered by the leak starting from a few experimental flow values for helium.

3.4.6 Feasibility study of a fast optical method to detect leaks in a few seconds

A feasibility study was undertaken by INRIM to assess whether optical measurements were a suitable alternative to conventional mass spectrometer based leak detectors for those applications where the speed of leak testing measurements is an important aspect. The idea was to create a discharge in a test chamber and observe the emitted spectrum with an interferometer based instrument (see Figure 31).

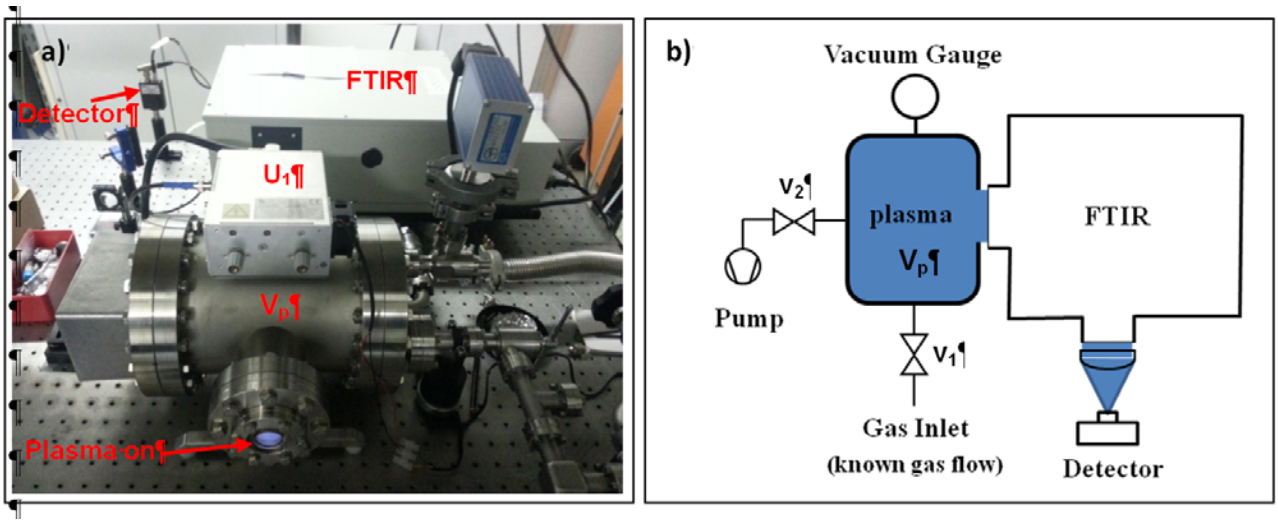

Figure 31 (a) Photograph and (B) schematic of the optical based system to detect leaks using FTIR to analyse the light emitted from the test gas plasma

The plasma was created at a residual air pressure between 2 Pa and 7 Pa in the chamber which was continuously evacuated by a dry-mechanical pump. A known flow of helium in the range between 10^{-2} Pa l/s and 1 Pa l/s was injected into the chamber, the helium gas ionised and the helium transition at 1083 nm observed and analysed using a Fourier transform infrared spectroscopy (FTIR) instrument. The feasibility of the optical based method to detect leaks was demonstrated between $7.2x10^{-2}$ Pa L/s and 1.3 Pa L/s, but further improvements are needed.

3.4.7 Conclusions

Three different types of leaks were produced within the project and assessed: short ducts in metal discs, modified glass capillaries and nanometre sizes holes in silicon nitride membranes. In addition, two types of leaks, i.e. long micro machined channels and sintered material with porous channels for gas flow that were not developed within the project were also evaluated. All these types of leaks, with the exception of the modified glass capillaries whose geometry could not be determined with sufficient accuracy, were shown to produce predictable flow rates where the agreement between the predicted flow rate and the measured flow rate was within the combined uncertainties of about 10 %.

A theoretical model for the flow through the leaks (comprising a short tube with circular cross section) and applicable for industrial service was developed and validated. The model developed in the project can be used to predict the gas flow rate of different gas species, such as a refrigerant, simply by starting from a few calibration measurements with helium in vacuum and one calibration point at atmospheric pressure with the refrigerant gas, thus avoiding the need for extensive calibration of the leak for each gas which will be used.

The feasibility of the optical based method to detect leaks was demonstrated between $7.2x10^{-2}$ Pa L/s and 1.3 Pa L/s, but further improvements are needed.

A practical guide for leak measurements using commercial leak detectors, targeted at both for users of leak detectors and standard committees, was produced and is available from the IND12 website.

3.4.8 Cooperation between the project partners and researchers

The excellent cooperation between INFICON AG (vacuum gauge manufacturer), VACOM (gauge and components manufacturer) and PTB enabled the project to deliver a new standard for dynamic pressure along with a new commercially available vacuum gauge series. INFICON AG with its extensive experience as a vacuum gauge manufacturer was able to develop and provide the JRP with the requested fast response vacuum gauges and VACOM with its knowledge as a components manufacturer was able to optimise the geometry of the dynamic vacuum calibration standard. PTB provided expertise on rarefied gas flow and metrology. When PTB experienced technical problems with connecting very thin thermocouple wires to the vacuum feedthrough, IMT also helped to resolve a technical issue although they were not directly involved in this particular work. With the help of UTH (REG) it was possible to extend the conclusions to include binary gas mixtures.

The huge amount of data collected during the flow rate measurements through many leak elements and during the quadrupole mass spectrometers characterisation and long term stability study would have not been possible without the common effort of all of the NMIs/DIs (PTB, CEM, CMI, IMT, INRIM, LNE, TUBITAK UME) involved. Danfoss and UNIGE (REG) provided new technologies for conductance elements which were needed for several investigations within the project. Lazzero contributed equipment and measurements for the study of leak detectors. For the flow measurements alone, more than 1500 measurement points, each of them taking about 20 minutes, were generated with primary standards in order to have sufficient data to enable the development and testing of the theoretical models. This could not have been achieved within a single NMI/DI. The variety of QMS investigated and the large number of measurements provided the community of end users with a lot of data from which to attribute uncertainties to measurements made using QMS and also enables NMIs to disseminate traceability for partial pressure measurements which is badly needed in industry for outgassing rate measurements. KIT (REG) provided the consortium with a system that bridged NMI (outgassing) measurement systems to industry systems.

The workload was split between the project partners to make the overall project affordable and achievable. In addition, the project benefited from reviews, critical analyses, and suggestions by all of the project partners. Where training or knowledge transfer between project partners was necessary, it was willingly given.

The joint patent application by IMT and PTB for an outgassing reference device is another example of excellent and effective cooperation.

Each of the first 6 project meetings was organised by a different project Partner, the first and last (7th) was organised by PTB, the latter just ahead of the final public workshop.

4 Actual and potential impact

4.1 Dissemination activities

4.1.1 Publications

The project has generated 16 peer-reviewed scientific papers, a web-based Good Practice guide on a procedure for leak detector calibration and uncertainty evaluation and a conference paper published in a peer-reviewed journal (see Section 6 for the detailed list).

4.1.2 Workshops

Two 3 day workshops were organised and held during the project targeted at end users and stakeholders.

A very successful "Workshop on measurement characteristics and use of quadrupole mass spectrometers for vacuum applications" including 3 external invited speakers was organised by the project and held from on 10-13 April 2012 in Bled, Slovenia, attended by 38 delegates many of whom were collaborators, stakeholders and end-users (see: http://www.ptb.de/emrp/ws-ind12-home.html). There were some very lively and fruitful discussions, and experts from outside of the project emphasised the importance of and strongly supported the work related to QMS. As a result and at the request of the editor, a special issue of the Elsevier Journal Vacuum was dedicated to this topic, which was also open to other contributors.

The second workshop on “Vacuum Metrology for Industry” held on 25-27 June 2014 in Berlin addressed the results and outputs from the 4 key areas of the project – dynamic vacuum measurement, leak measurement and testing, partial pressure measurement and outgassing rate measurement. 54 attendees were registered and 33 presentations given. The lively discussions demonstrated the significant impact of the project on the community. Details including programme can be found on http://www.ptb.de/emrp/ws2-ind12.html.

4.1.3 Presentations at conferences

The project results and outcomes were disseminated at a number of conferences, including in particular the 12th European Vacuum Conference in Dubrovnik in June 2012 and the 19th International Vacuum Congress in Paris in September 2014. In total, 27 presentations were given by project members at these and other conferences.

The scientific impact is evidenced by the fact that in total six presentations from project members were invited by the conference / meeting organisers, two by the key 19th International Vacuum Congress and the 60th AVS Symposium 2013, 3 by specialised conferences, the European Conference on gas micro flows

(May 2012) and the RGA users group meeting (RGA11) at the Vacuum Symposium UK in 2013, and one by the annual conference of the Pakistani Vacuum Society VASSCAA-6 in 2012.

4.1.4 Engagement with end-users, stakeholders and collaborators

The results and outcomes from the project were discussed with stakeholders from industry, including the companies Singulus Technologies AG (a manufacturer of optical disc production lines) with their interest in dynamic vacuum measurements, ASML (the largest supplier in the world of photolithography systems for the semiconductor industry) and VAT vacuum valves AG (a major manufacturer of valves for vacuum applications) for outgassing rate measurements.

The working group responsible for international standardisation in vacuum technology, ISO TC 112, received a summary of the issues of the project related to standardisation from the coordinator and adopted these as new projects that started in 2015.

The industrial partner VACOM invited customers to a closed workshop on ultra clean vacuum on the occasion of its 20th anniversary in June 2012 which provided the coordinator a good opportunity to interact with those who are interested in partial pressure and outgassing measurement. The customers were eager to see the results of the project and later attended the project workshop.

4.2 Early impact

The project has provided the measurement capabilities to enable the European vacuum industry and end users to improve their products, processes and services in a number of ways.

4.2.1 "Time is money" in vacuum processes

Faster capacitance diaphragm gauges with full scale ranges from 130 Pa to 130 kPa were developed within the project by INFICON AG and their response times evaluated to be as low as 1.3 ms (the fastest in the world) by comparison with the newly developed fundamental dynamic vacuum standard. Three patents applications were submitted for these new gauges which are now available to end-users as a commercial product (the "Stripe" gauge series by INFICON AG) and INFICON AG was also awarded an R+D prize for the development of these gauges. These gauges enable end-users to reliably measure the fast changing pressures that frequently occur in industrial applications. In addition, interest in the fast vacuum gauges has already been expressed by scientists who use short pulsed gas flows for experiments.

The calibration standard for dynamic vacuum established in the project to determine the response time of vacuum gauges enables the vacuum industry to test and improve their developments and products in this respect for the first time. Companies outside of the project have already expressed interest in having their products tested.

4.2.2 Accurate and reliable control of vacuum process constituents

Different gas species present in a vacuum environment may have different effects on the technological process. For certain processes some gases may not be critical, whilst others may have detrimental effects on the final product or process. Therefore accurate determination of partial pressures of different gases in the process chamber is required and quadrupole mass spectrometers are the instruments that are most often used for this task. A two year long term study of nine different commercial quadrupole mass spectrometers by the project highlighted that the performance of QMS is affected by a wide range of operating parameters whose influence is not independent, the sensitivity and linearity are both pressure and gas matrix composition dependent and a number of parameters such as sensitivity are not stable over time. Today's quadrupole mass spectrometers therefore require clear standardised procedures for their calibration and characterisation and due to the complex interaction between parameters it is not feasible to calibrate all aspects of a QMS and calibrations must therefore focus on the key parameters and ranges that are relevant to the particular industrial application. Additional in-situ calibration of key parameters is also required to achieve the best results.

A calibration system for partial pressures to characterise and traceably calibrate quadrupole mass spectrometers for at least 3 gases at a time is now available for the first time in Europe. The system provides manufacturers of quadrupole mass spectrometers with the opportunity to improve those aspects of the metrological performance of their products that were found to be rather poor during the project. Prior to the

project, these instruments could not be calibrated in a traceable manner as required by ISO 9000 series or ISO/IEC 17025.

Draft methods, including in-situ methods, for the characterisation of quadrupole mass spectrometers for partial pressure measurement were developed within the project and incorporated into a draft Technical Specification which was discussed with ISO TC 112 "Vacuum Technology" and the relevant German standardisation committee. The draft Technical Specification has been taken up by ISO TC 112 "Vacuum Technology" and was accepted as new work item in 2015.

During the final project workshop in June 2014, users of quadrupole mass spectrometers expressed their satisfaction that the project had confirmed in a metrologically sound way their past experiences related to the performance of quadrupole mass spectrometers. These stakeholders also indicated their appreciation that, as an output of the project, a Technical Specification for the characterisation of quadrupole mass spectrometers is likely to be developed at the ISO level as this will help them to choose the instrument with suitable performance for their application, to avoid inappropriate purchases, to better characterise their vacuum process environment for the gas composition and to avoid incorrect interpretation of the measurement data obtained with the instruments.

4.2.3 Qualifying vacuum chambers and components for undesired gas species

Outgassing rates are an important quality-assurance figure in vacuum technology. The three outgassing rate reference systems utilising different methods developed and validated within the project now enable traceable measurements to be made for the first time between 10^{-8} Pa L/s to 10^{-1} Pa L/s with uncertainties between 10 % and 20 %.

Three types of reference outgassing artefacts for the validation of outgassing rate measurements in industrial environments are now available: reference outgassing materials Viton (FPM-fluoropolymer) and PDMS (poly-dimethyl siloxane), a permeation reference outgassing artefact and an in-situ leak artefact based on nanoholes in a thin SiN membrane. In addition two prototype devices with nominal outgassing rates of water vapour 3×10^{-3} Pa l/s and 6×10^{-5} Pa l/s were developed and demonstrated good performance. A patent application has been submitted for the easy to handle permeation type outgassing artefact for water vapour, gas mixtures and dodecane. The potential commercialisation of this reference outgassing artefact as a new product will be pursued by the partner VACOM together with the inventors.

The results obtained by the project and the reference systems and reference artefacts developed now make it possible to identify suitable methods for outgassing rate measurements, to make them traceable, and to validate and compare outgassing rate measurement systems, even when they utilise different methods.

Historically there has been no internationally standardised and agreed way to measure outgassing rates and to establish their traceability to the SI system of units. A draft for a Technical Specification of outgassing rate measurement procedures was therefore developed by the project and discussed with ISO TC 112 "Vacuum Technology" and the relevant German standardisation committee. The draft Technical Specification has been taken up by ISO TC 112 "Vacuum Technology" accepted as new work item.

4.2.4 Leak tight vacuum systems and secure containers

In industrial applications leaks usually occur under different pressures, temperatures and temperature gradients, gas species and mixtures. Consequently, if the leak rate for a particular gas cannot be predicted from the leak's metrological properties then the leak needs to be calibrated for each gas species used which is a time-consuming process and challenging for some industrial gases. This project addressed the need to improve knowledge of the gas flow through the ducts of standard leaks in terms of predictability for different gas species and environmental conditions used in industry by firstly producing ducts for standard leaks with stable metrological properties and a well-defined geometry which can be accurately, secondly developing theoretical models for the flow through the ducts which are applicable for industrial service and thirdly comparing the developed theoretical models with measurements performed using industrially relevant gas species.

The three different types of leaks (short ducts in metal discs, modified glass capillaries and nanometre sized holes (100 nm diameter) in silicon nitride membranes) produced by the project were shown to have flow rates that were predictable from their dimensional geometry, with agreement between the predicted flow rate and the measured flow rate within the combined uncertainties of about 10 %. The nano-holes have already been successfully introduced into the research community as leak elements with fully predictable leak rates for any gas species. When the mounting technology for the leak elements is sufficiently robust for a

commercial product - some necessary improvements were identified during the project - this will have a significant impact on the market of leak elements.

Using the theoretical model developed in the project for the flow through the leaks (comprising a short tube with circular cross section) which appropriately addresses various flow regimes and which is applicable for industrial service, it is now possible to predict the gas flow rate of different gas species, such as a refrigerant, simply by starting from dimensional knowledge of the leak (eg an SEM picture of the holes), a few calibration measurements with helium in vacuum and one calibration point at atmospheric pressure with the refrigerant gas. This avoids the need for extensive calibration of the leak for each gas which will be used and, in general, makes calibration for users cheaper and more efficient.

Users of leak detectors and standard committees will benefit from guidance on leak detection included in a practical guide for leak measurements using commercial leak detectors which was produced within the project and is available from the IND12 website. The guide includes advice on the correct use of leak detectors, uncertainty evaluation considering all the components starting from the calibrated leak through to the whole leak testing setup used in the industry to test the products, a discussion of the metrological characteristics of leaks used to calibrate the leak detectors, the metrological characteristics of the detectors (stability, repeatability, etc), the influence of atmospheric parameters (pressure, temperature) both on leak calibrations and leak detectors used to detect leaks in vacuum or sniffing mode with helium or refrigerant.

4.3 Longer term impact

The project outputs will also lead to longer term benefits.

- Implementation of the new fast capacitance diaphragm gauges into production systems will enable processes such as optical disc metallisation and plasma coating applications (e.g. SiO_2 for PET-drinking bottles) to be shortened in a reliable manner and the pumping and venting processes in applications that use load locks to be better controlled resulting in more economical processes with higher profit. The performance of vacuum pumps can also be improved as the fast capacitance diaphragm gauges will enable fast transient processes within the pump to be observed which were previously averaged out by the slow integration times of vacuum gauges.
- The methods developed for the simulation of fast pressure changes in the intermediate pressure regime will be applicable for improving the performance of vacuum systems and pumps and for reducing their energy consumption.
- The standardised procedure for the characterisation of quadrupole mass spectrometers for partial pressure measurement included within the Technical Specification should lead to performance specifications of QMS that can more readily be compared across different instruments and manufacturers, improving the quality and analysis of procurement tenders and enhancing fair competition among manufacturers.
- The availability of reference outgassing samples and the methods included in the Technical Specification for outgassing rate measurements will significantly improve the unfortunate situation for outgassing rate measurements, where due to the lack of traceability and standardised procedures, "local" solutions for testing and supporting technical specifications have been developed which were costly and not comparable to other "local" solutions. This will bring significant simplification, economical and metrological benefit for users.
- In the near future it will be possible to reliably measure the outgassing rate of vacuum components that are needed to maintain clean vacuum environments in industrial processes. Developers of new materials with lower outgassing rates will also benefit from the new traceability and reliability, as it will enable the proper characterisation of new materials with well-defined uncertainties. In this area the new standard will have indirect impact on the reduction of pumping cycle times or required pump capacity and hence the reduction of energy consumption and increased productivity.
- High energy and fusion physics research facilities are large high cost systems and among some of the most demanding users of vacuum technology with very strict requirements for vacuum properties, i.e. very low outgassing of materials and compatibility of components with ultrahigh vacuum of better than 10^{-8} Pa or even better than 10^{-10} Pa. Some industrial technologies such as EUV-lithography for future wafer illumination in microelectronics industry do not require ultrahigh

vacuum, but ultra-cleanliness (absolutely no contamination by hydrocarbons). Similarly stringent requirements for vacuum components exist in the aerospace industry, especially for components in the vicinity of very sensitive optical devices, as outgassed molecules can critically affect the lifetime of space instrumentation on the missions worth of hundreds of millions of euros. All these applications will benefit from improved outgassing rate measurements as the likely outgassing rate can be more reliably determined during the design phase, the most suitable components and the most appropriately sized pumps (including selective pumping speed for different gases) selected, potentially significantly reducing the total cost of the system.

- Over time the availability of reference outgassing samples and reference methods should improve the comparability and uncertainty of measurements and hence reduce the spread in the outgassing rates of different materials published in the literature, which have been unacceptably high over the past 50 years
- The leaks developed with predictable leak rates for many gas species and suitable for industrial environments will make it easier to reliably identify and measure leaks within vacuum systems. This will reduce the costs associated with leak testing and also the potential risks to the environment and associated costs due to leaks of toxic or polluting gases. The mathematical model developed will allow the gas flow rate delivered by the standard leaks with defined geometry developed during the project to be predicted for several typical gas species based on knowledge of the gas flow rate for one gas species. Knowledge of the performance of the leak artefacts under industrial conditions as well as the metrological characteristics of helium and refrigerant detectors will enable a critical view of the European standards devoted to the calibration of detectors.
- The improved gas flow metrology and the knowledge of the performance of leak detectors will enable industry to better meet the requirements of the European regulation 842/2006 relating to refrigerant greenhouses gases.
- The feasibility of two optical based techniques for the measurement of fast changing total pressures and the measurement of partial pressures respectively was demonstrated in the project and these innovative approaches may be applied by companies and other organisations in the future.

5 Website address and contact details

Public project website: http://www.ptb.de/emrp/vacuum.html

Contact details: karl.jousten@ptb.de

Dr. Karl Jousten
Physikalisch-Technische Bundesanstalt
Abbestrasse 2-12
10587 Berlin
Germany
Phone: +49 30 3481 7262

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