Guide on permeation method for the dynamic generation of NO$_2$ and SO$_2$ standard gas mixtures at limit values

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1. CONTEXT

Historically, the main air pollution problem in both developed and rapidly industrialising countries has typically been high levels of smoke and sulphur dioxide (SO_2) emitted from the combustion of sulphur-containing fossil fuels such as coal and heavy-oil, used for domestic and industrial purposes. These days, the major threat to clean air is posed by traffic emissions. Petrol and diesel-engined motor vehicles emit a wide variety of pollutants, principally carbon monoxide (CO), nitrogen oxides (NO_x), volatile organic compounds (VOCs) and particulate matter (PM10), which have an increasing impact on urban air quality.

Photochemical reactions resulting from the action of sunlight on nitrogen dioxide (NO_2) and VOCs, typically emitted from road vehicles, lead to the formation of ozone (O_3) which often impacts rural areas far from the original emission site as a result of long-range transport.

Because of their potential impacts on human health, welfare and the natural environment, ambient concentrations for numerous pollutants are measured with different sampling and analytical methods at a wide range of rural and urban monitoring sites throughout the world.

In the framework of a European Joint Research Programme (JRP) of EURAMET named Metrology for Chemical Pollutants in Air (MACPoll), one task aims to provide harmonized preparative dilution methods of air pollutant gases for calibration and quality control purposes in air quality monitoring with a need for improved methodologies.

2. OBJECTIVES

This guide focuses on the description of the permeation method used for the generation of SO_2 and NO_2 standard gas mixtures at concentration levels corresponding to the limit values given in the European Directive on "Ambient air quality and cleaner air for Europe" (2008/50/EC) for the measurement of ambient air pollutants" [1]. Nitrogen oxide (NO) is studied as well because it is normally measured in combination with nitrogen dioxide for the measurement of NO_x. The methods for generating NO standards at limit values are described in a separate guide [2].

The document gives some guidance on how to generate SO_2 and NO_2 standard gas mixtures in concentration ranges and with associated uncertainties in accordance with the specifications given in the European Directive 2008/50/EC and relevant EN standards [3][4] (cf. Table 1).

Component	Limit values (LV) from the European Directive 2008/50/EC	Scope of the guide	
		Concentration range (nmol/mol)	Expanded uncertainty (%)
NO_2	One hour: 105 nmol/mol* Calendar year: 21 nmol/mol*	20 to 100	3
SO_2	One hour: 132 nmol/mol* One day: 47 nmol/mol* Calendar year: 8 nmol/mol**	40 to 150	3

Table 1: Limit values and scope of the guide for SO_2 and NO_2 standard gas mixtures
generated with dynamic methods
air quality directive (2008/50/EC) Annex XI and art. 13
** air quality directive (2008/50/EC) Annex XIII and art. 14

This guide is originally based on the international standard 6145-10 [5] and is completed with newer references, the knowledge and the experience of the participating laboratories in the framework of the MACPoll project.

3. PRINCIPLE OF PERMEATION METHOD

Permeation of a gas through a membrane is a widely-used method for the preparation of gas mixtures for various applications, especially in air quality measurements. It comprises the preparation of standard gas mixtures for calibration and testing of analyzers for air quality measurements and for inter-laboratory comparisons.

The permeation method is based on the fact that gases dissolve and migrate under a concentration gradient in the molecular structures of polymers.

The permeation device consists of a tube in which the analyte is in its liquid phase. The tube is tightly closed on both ends, but a semi-permeable membrane in the tube wall allows the gas to permeate through. The permeation device is put in a temperature and pressure controlled chamber (a water bath or oven) with adjustable and controlled temperature in order to maintain constant conditions (temperature, pressure) for the permeation device and a defined flow of an ultra pure gas (carrier) followed by a further dilution for generating standard gas mixtures of known composition. The mass flow of analyte gas passing the semi-permeable membrane is determined by the temperature, the area and the type of the (mostly proprietary) membrane material and the ambient pressure. It is coarsely selected in the range between 100 to 1000 ng/min by various types of permeation devices. Owing to the stationary conditions, the permeation rate of the gas through the membrane remains rather constant over extended time periods (up to several months).

The permeation rate (mass per unit time) of the gas is defined by weighing the mass loss as a function of time. It is realised with either of two methods:
- Weighing the permeation tube with an accurate electronic balance at regular intervals and calculating the loss of mass of the contents during the period between two consecutive weighings (this conventional method is described in ISO 6145 Part 10 [5]);
- Weighing the permeation tube continuously on line with a magnetic suspension balance (MSB). This method largely eliminates perturbations caused by manipulating the permeation device and by environmental influences [5][6]. It has been described in more details by Knopf [7].

The permeation method has the potential to fulfil the criteria of a primary method of measurement [8][9] implicating that all relevant quantities are traceable to the SI. There are a number of issues that need to be taken care of as the purity of the source gas in the permeation tube (relating the mass loss of the analyte to the amount of substance), that no chemical reaction can take place with the carrier or dilution gas (e.g. with moisture), that all parameters of the measurement equipment associated with the method are calibrated to SI units and that the uncertainty of the measurement method can be calculated at least for the major sources of uncertainties according to the Guide to the expression of uncertainty in measurement (GUM) [10].

One of the most difficult tasks in the operation of the method relates to the environmental conditions (temperature, pressure and carrier flow) in the permeation chamber. This method needs to be kept constant during the period between consecutive weighing of the tube. The time between two consecutive weighings can vary from some weeks to some months depending on the size of the tube, the tube material and the sensitivity of the balance. In addition, the amount of impurities in the gas can be problematic if not known. With the magnetic suspension method where weighing of the permeation tube is continuous, a change in environmental conditions directly manifests in a change of the permeation rate. A very detailed study including the uncertainty budget associated with the method is given in [7].

Concerning permeation apparatus, conventional method and magnetic suspension balance can be implemented.

3.1. CONVENTIONAL PERMEATION METHOD

The permeation tubes can be put in a temperature and pressure controlled chamber (a water bath or oven) with adjustable and controlled temperature in which circulates a permanent carrier gas flow (air or nitrogen). This permeation tube is removed from the chamber at regular intervals to measure its mass: the permeation rate is calculated by combining the mass loss and the time. To generate standard gas mixtures the carrier gas is diluted with a dilution gas (air or nitrogen).

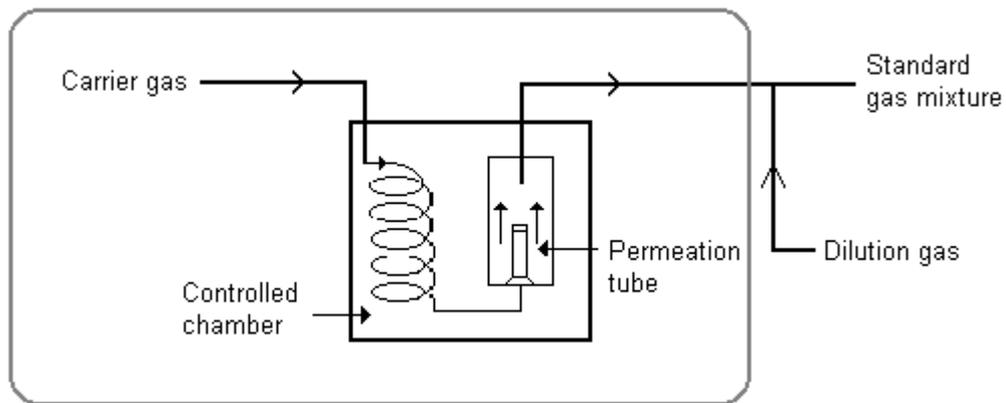A schematic layout of the conventional permeation apparatus is shown in Figure 1.

Figure 1: Principle of the conventional permeation apparatus

3.2. MAGNETIC SUSPENSION BALANCE

The central part of the system is the magnetic suspension balance from Rubotherm with a mass range of 10 to 30 g and a resolution of 1 μg [11]. It continuously records the mass change of the permeation process with a sampling interval of 3 min. The permeation device is suspended by means of a magnetic suspension system without mechanical contact to the micro balance. The temperature controlled permeation chamber is entirely made of glass. The two volume flows of the carrier and dilution gas are regulated by thermal mass flow controllers. The gas pressure in the permeation chamber is kept constant with a pressure controller at 1013.25 hPa.

If the produced gas mixture is directly used for measurements (e.g. for calibrating gas analysers) the total dilution gas volume flow is additionally measured with a laminar flow element (for example Molbox/Molbloc system from DHI Instruments).

A schematic layout of the magnetic suspension balance is shown in Figure 2.
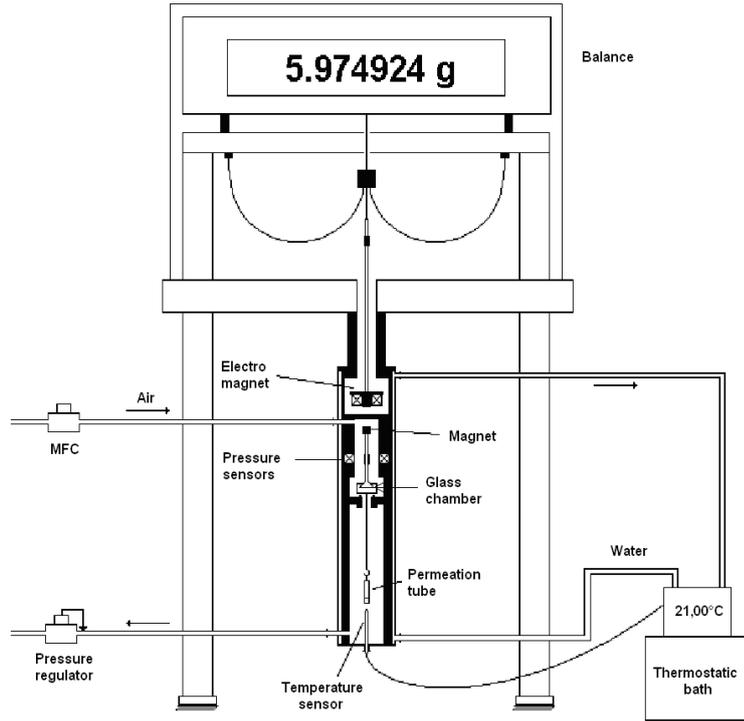
Figure 2: Principle of the magnetic suspension balance

3.3. MODEL EQUATION FOR PERMEATION

The substance mass flow of analyte B through the membrane of the permeation device (q_{mB}) is calculated from the mass m of the permeation device and the time t:

$$q_{mB} = \frac{\Delta m.P_{B,c} + (\rho_1 - \rho_2).V_{rf}}{\Delta t} = \frac{(m_1 - m_2).P_{B,c} + (\rho_1 - \rho_2).V_{rf}}{\Delta t} \tag{1}$$

$$q_{mB} = \frac{\Delta m \cdot P_{B,c} + (\rho_1 - \rho_2) \cdot V_{rf}}{\Delta t} = \frac{(m_1 - m_2) \cdot P_{B,c} + (\rho_1 - \rho_2) \cdot V_{rf}}{\Delta t}$$

With:

q_{mB}	mass flow of analyte B out of permeation device at a given temperature T
Δm	mass difference
$P_{B,c}$	mass related chemical purity of substance B
ρ_1, ρ_2	respective air densities in the weighing room during the consecutive weighings
V_{rf}	volume of the permeation tube
Δt	time interval: $t_2 - t_1$
m_1	mass of permeation device at time t_1
m_2	mass of permeation device at time t_2

In the case the permeation tube is weighed with a magnetic suspension balance the permeation tube is not influenced by the variation of the air density. The *equation 1* is simplified as follows:

$$q_{mB} = \frac{\Delta m . P_{B,c}}{\Delta t} = \frac{(m_1 - m_2).P_{B,c}}{\Delta t} \qquad (2)$$

The amount of substance fraction of analyte B in the gas mixture C_B is calculated by taking into account its molar mass (M_B), the dilution gas flow qv_{null}, its molar volume VM_{null} and the residual amount of analyte C_{Bnull} in the dilution gas:

$$C_B = \frac{n_B}{n_{null}} + C_{Bnull} = \frac{q_{mB}(T).VM_{null}}{M_B.qv_{null}} + C_{Bnull} \qquad (3)$$

With:

n_B and n_{null}	amount of substances of analyte B and dilution gas (null), respectively
VM_{null}	molar volume of substance B at standard temperature and pressure
M_B	molar mass of substance B
qv_{null}	the sum of the dilution and carrier gas flows at standard temperature and pressure

4. IMPLEMENTATION OF THE PERMEATION METHOD

The implementation of the permeation method to generate low concentrations of NO_2 (below 100 nmol/mol) and SO_2 (below 150 nmol/mol) requires some precautions to achieve the target uncertainty of 3%.

The various criteria to consider are listed below:

- Requirements for used materials
  - Nature of the materials in contact with the different gases used to avoid reactions between materials and the different gases
  - Leak detection
- Permeation device
  - Determination of mass loss
  - Purity of the analyte substance inside the permeation tube
  - Long-term stability of the permeation rate
- Requirements for environmental conditions in the chamber
  - Temperature control
  - Inside surfaces
  - Carrier gas flow
  - Pressure controller
- Regulation and measurement of the gas flows (carrier and dilution flow rates)
  - Calibration of gas flowmeter
- Quality (purity) of the dilution gas
- Homogeneity of the generated standard gas mixture
- Stabilization time to obtain a reference gas mixture with a stable amount of substance fraction

4.1. NATURE OF THE MATERIALS AND MATERIALS COMPATIBILITY

Before generating standard gas mixtures by dynamic dilution, it is advised to further check better used components and the transfer system against the possible chemical reactions of mixture components. Special consideration shall be given to the attack by corrosive gases such as SO_2 and NO_2 on metals and possible reactions with elastomers and greases used, for example, in valve seats and seals. Such reactions can be prevented by using only materials that are inert to all components of the mixture. If this is not possible, measures shall be taken to minimize corrosive attack on the materials with which the gases are in contact so as to prevent any significant effect on mixture composition and any danger in storage and use. Information on the compatibility of gases with container materials is given in gas sampling guidelines, corrosion tables of materials and gas supplier handbooks.

Information on NO_2 and SO_2 mixtures and their level of compatibility with a range of materials is outlined in Table 2. When using polymeric transfer lines, it is also important to consider their permeability by certain gases and water vapour. For example, PTFE is very inert and suitable for a large range of gases; however, the permeability of this material makes it unsuitable for use with water-soluble gases, as water vapour can easily permeate into the transfer line.

Gas	Material					
	Stainless steel		Teflon			Glass/quartz
	316L[1]	Silica-lined stainless steel[2]	Polytetra-fluoroethylene (PTFE)	Perfluoroalkoxy copolymer resin (PFA)	Fluorinated-ethene-propene (FEP)	
NO_2	Possible[c]	S	S[a] Possible[c]	S[a]	N[b]	S
SO_2	N	S	S[a]	S[a]	N	S

Table 2: Material compatibility, S: Satisfactory for use with the intended gas with suitable conditions at room temperature, N: Not satisfactory for use with the intended gas, [a] use is possible but the concentration of the reference gas mixture may be influenced by permeation of analyte, [b] possible use with high flow rates, [c] satisfactory but corrosive in presence of water except for high quality stainless steel.

In general it is advised to:
- use short transfer lines in order to:minimize permeation and to decrease the stabilization time for obtaining a stable concentration.
- limit the leaks in the transfer system between the cylinder and the analyser,
- take care of the connections,

It is recommended to use all metal sealed connections.

4.2. PERMEATION DEVICE

4.2.1 Description

The tubular device, a sealed permeable tube containing the desired permeate reference material is the most widely used type of the various permeation devices. Release of the substance occurs by its permeation through the tube for the entire length between the impermeable plugs. A wide range

of rates can be achieved by varying the length and thickness of the tube with typical rates ranging from 50 ng/min to 3000 ng/min.

Other permeation devices are available like so called wafers which have only a small permeable window (wafer), so permeation rates are typically lower than for tubular devices. Since permeation occurs only through the polymeric wafer, the permeation rate is controlled by varying the wafer material, its thickness and the surface area of the permeation opening. Gases whose high vapour pressure at normal permeation temperatures prevent their containment in a tubular device can be contained in a wafer device. Wafer devices are available in different styles to allow their use in calibrators of various manufacturers.

For example for producing NO_2 mixtures with amount of substance fractions corresponding to ambient levels between 20 and 100 nmol/mol wafer permeation devices are used with mass flows in the range between 100 and 1000 ng/min. They allow to generate gas mixtures in the above substance range with total gas flows between 1 and 5 L/min, according to the necessary minimal flows for the analyser and the devices under test.

For wafers the ratio of the permeation surface and the reservoir volume is ideal for long term use and storage. The accuracy of the specified target permeation mass flow for individual permeation devices at a given temperature is however only within 15 to 25 %. Thus the permeation rate of each permeation device needs to be measured and determined (as function of temperature in the used range).

4.2.2 Handling the tube

All weighings shall be performed with extreme cleanliness and avoid any direct contact with the operator's hands. It is recommended to use gloves, clean tweezers and paper breathing masks.

4.2.3 First use

When first using the permeation tube, system shall reach a state of equilibrium before carrying out the first weighing so as to ensure that the permeation rate is well stabilized at the constant value. The time needed to reach equilibrium is dependent on the component contained within the permeation tube (several days to several months).

4.2.4 Determination of mass loss using discontinuous weighing

When removing permeation tubes from their storage containers for weighing, some precautions shall be taken.

The temperature and relative humidity of the air in the weighing room must be controlled and kept constant during successive weighings.

Recommendations are given for weighing:
- The time that the permeation tube spends outside the temperature controlled environment for obtaining stable weighings shall be determined. Before being weighed the temperature of the permeation tube must be returned to room temperature (for example in the case the use temperature is at 30°C and the weighing temperature is at 20°C a stabilization time of 30 min is recommended).
- In a given time interval, the permeation device will decrease in mass; the measurement of this change in mass will have an associated measurement uncertainty; therefore, the choice of the time interval over which weighings are made depends on the required accuracy.

4.2.5 Determination of mass loss using continuous weighing

Short stabilisation periods are achieved by using fresh absorbing media and dry air in the storage container. Generally it is observed, that the shorter the storage period, the shorter is the necessary stabilisation time.

Recommendations are given for weighing:

- The necessary stabilisation time for a permeation device at its operating temperature (for NO_2 typically 30°C) is estimated as a function of the mass differences between the measured and the linearly fitted values. If the differences are getting below 20 µg (on a balance with a resolution of 1 µg), the permeator is considered stable. The total sampling time depends on the sampling interval and the targeted uncertainty of the mass loss. It is typically 3 days for sampling intervals of 3 min and to achieve an uncertainty for the permeation rate of 1.5 %. This holds for a typical permeation rate of 200 ng/min used for generating mixtures with amount of substance fractions in the range 20 to 100 nmol/mol.

4.2.6 Determination of the stabilisation time from the analyser response signal

For a permeation device put in an oven, stabilisation is estimated being achieved if the initial temporal drift decreases below the noise level of the analyser of typically 0.5 nmol/mol.

4.2.7 Increasing the shelf life

When not being used NO_2 permeator devices are preferably stored in one-sided sealed glass tubes closed with threaded turning caps containing a desiccator and activated charcoal bag in a refrigerator at a temperature of (7 ± 1) °C. By this measure the shelf-time of the permeators can be considerably increased due to the much lower vapour pressure of the substance.
Prior to their use the cooled permeator devices need to be thermalised within the glass tube during at least 12 h in ambient air at (20 ± 1) °C.

4.2.8 Purity of the analyte substance

Since for calculating the substance flow the mass flow is measured, the purity is a factor of conversion and should be as close to 1 as possible. The purity of the analyte substance declared by the manufacturers is typically between 99.5 and 99.8 % for NO_2 and 99.9% for SO_2, respectively.

It's important to distinguish the purity of the analyte substance inside the tube and the purity of the substance passing the membrane. To determine the permeation rate accurately it is necessary to know the purity of the analyte substance passing the membrane rather than its purity inside the tube since after passing the membrane it may contain fewer impurities. As it is laborous to determine and quantify the concentrations of impurities it is recommended to take a purity equal to 100% with its associated uncertainty and taking into account, for example, the deviation between this ideal purity and the purity given by the manufacturer.

On the other hand, the purity of the compound can evolute over the time because the impurities and the analyte substance are likely to have different permeation rates.

4.2.9 Long-term stability of the permeation rate

The stability of the permeation rate during the life cycle of the non-refillable permeation devices should stay ideally within 1 % relative, otherwise the temporal drift needs to be corrected.
The long-term stability of the permeation rate depends on the component. In present case the SO_2 permeation rate is more stable over the time than the NO_2 permeation rate.

4.3. REQUIREMENTS FOR ENVIRONMENTAL CONDITIONS IN THE CHAMBER

The permeation device shall be stored in a well characterized chamber because the permeation rate depends on the environmental conditions: changes in environmental conditions can induce significant variations of the permeation rate.

Besides the basic input quantities there are a number of control quantities and parameters:

- The temperature of the chamber, of the carrier and dilution gas (it is recommended to have a regulation of 0.01°C for obtaining a long-term stability below 0.1°C);

- The ambient air (variations lower than ± 2°C) and the humidity (variations lower than ± 20%) of the laboratory;

- The pressure of the carrier and dilution gas regulated at a constant value with variations below $\pm$ 2hPa, its chemical purity and humidity;

- The thermal isolation of the chamber and the isolation of the balance from building vibrations;

- The electrical supply of the socket-outlets for the appliances is stabilised and interruption-less.

4.3.1 Temperature control

The local and temporal temperature variations near or at the permeation device should be minimised.

A change in the chamber temperature will induce variations of the permeation rate. The change of temperature should be within $\pm$ 0.1ºC in order to keep the changes in permeation rate acceptable [12]. Larger temperature fluctuations change the permeation rate by an order of several percents.

In the case an oven is used which allows only heating, it is recommended to set the temperature of the chamber well above room temperature, to control it thermostatically and to measure it continuously for avoiding changes of the permeation rate. To record the temperature of the permeation device, a calibrated temperature sensor can be added and located within the chamber at the location of the permeation device.

In the case the permeation chamber is equipped with a temperature regulation for heating and cooling, it is possible to work at a temperature close to the ambient; this type of device allows to minimize the thermal shocks and the time outside the chamber for obtaining stable weighings.

The choice of temperature depends on the tube characteristics and the permeation rate required. Some instructions on temperature can be given by the manufacturers.

4.3.2 Inside surfaces

An important requirement for the inside surfaces of the chamber and the tubings is that they are made of the utmost inert materials towards SO_2 and NO_2 and with the lowest possible adsorption rates.
Glass largely fulfils these requirements; however the risk of breaking is a clear disadvantage for mobile applications.
Stainless steel with glass coated inner surfaces can be also used.

4.3.3 Carrier gas flow

A constant gas flow through the permeation chamber and a varying total zero gas flow for setting the desired amount of substance fraction is required. It is realised by splitting the zero gas into a

carrier and dilution gas flow. The carrier gas flow is maintained constant during the whole operation time. It results in both, a perfect thermal stabilisation of the gas and of the permeation device in the chamber and in a constant absorption/desorption rate of analyte on the dominant surface area part of the chamber.

The flow rate through the chamber shall be stable: it can be regulated with a critical orifice, MFC or similar and recorded with a flowmeter.

4.3.4   Pressure controller

The purpose of a pressure controller at the outlet of the permeation generator is to isolate the chamber from the varying atmospheric pressure.

4.4.   REGULATING AND MEASURING OF GAS FLOWS (CARRIER AND DILUTION FLOW RATES)

The regulation and the measurement of the gas flows are crucially important for the accuracy and the stability of the concentration of dynamically produced standard gas mixtures.

Moreover the dilution flowrates shall fulfil the technical specifications of the analytical systems e.g. the dilution flowrate shall be higher than the required flowrate of the analytical systems.

4.4.1   Common criteria for all flow elements

Since substance specific properties of the gas are used for controlling the flow, it depends on the nature and composition.

The dead volumes of the flow regulator elements (MFCs, sonic nozzle, valve…) should be kept as small as possible in order to minimize contamination. The inner stainless steel metal surfaces of the elements and tubings are preferably all electropolished to minimise gas adsorption.

For the use, the mounting and the operation of the flow elements, the instructions given by the manufacturers should be followed. Electronic elements dissipating heat should be placed above the gas tubings, the housing should be vented. The use of solenoid valves is discouraged, pneumatic valves are recommended.

All components and fittings (seals) should be evacuable to enable the much more efficient flushing cycles with vacuum and pressure instead of pressure only. Furthermore the construction of the dilution system should allow to calibrate the flow elements in its running configuration without the need for disassembling the hardware. This guarantees the validity of the formerly performed leak test – a crucial requirement especially for the tubing parts between the flow elements and the mixing zone.

Advises to be considered for the calibration of flow elements.

Interval: at least each year by an accredited laboratory in the operating measurement range and under defined operating conditions (temperature and pressure). It should be noted that the values of the flows usually given in certificates are at standard conditions, normally at 0°C (273.16 K) and 1013.25 hPa. The measured values need to be converted to standard conditions.

Dilution gas: use the same gas matrix as afterwards for generating the dynamic standard gas mixtures to be sure that there is no difference between the flow measured during the calibration and the flow measured for the generation of the dynamic standard gas mixtures. If laminar flow element is used as flow meter it is advised to verify that it has been calibrated with air of the same specifications than the one used for the permeation method.

Only the mass flow meter (MFM) for measuring the total gas flow is required to be calibrated. Indicative but stable values for the two MFC's are sufficient.

4.4.2 MFC's

It is recommended to use flow meters not below 10 % of the full scale. The foreline pressure set by the reducing valve is generally sufficiently stable but should be as specified during the calibration and for the use. Due to the much faster response time of MFC's with sensor based on the Complementary Metal Oxide Semiconductor (CMOS) technology and consequently better stability and reproducibility, this new type is preferred where ever possible. Flushing with inert and dry gas after each use is necessary to avoid corrosion. It is recommended to take care of the compatibility between the materials of the MFC's and the gas passing through the MFC's.

4.4.3 Laminar flow elements

The laminar flow theory is well established which serves the way to define the gas behavior accurately. An application for determining the flow rate based on laminar flow theory is made commercially available e.g. by DH Instruments, Inc., USA (Molbloc/Molbox flow measurement system). The Molbloc/Molbox system achieves unprecedented levels of stability and precision by applying today's modern pressure sensors, mathematical modeling and data processing technologies to the laminar flow principle.

They need to be operated with controlled upstream pressure and with additional MFC's for setting the flow. These requirements make their use laborious and practically restricting it to laboratory applications. It is recommended to replace the initial TEFLON manufacturing tubing between the laminar flow element and the pressure sensor by a silica-lined stainless steel tubing. The different elements of laminar flow measurement system (laminar flow element and pressure sensors) should be calibrated together. It is recommended to correct the response of the pressure sensors by using the "tare function" before each measurement according to the manufacturer procedure. If necessary the pressure sensors of the elements can be calibrated and adjusted.

Following the Hagen-Poiseuille's law [13], the mass flow of a compressible medium through an annular pathway in the laminar regime can be expressed as:

$$q_m = \frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{(P,T)} \cdot \eta_{(P,T)} \cdot P_N} \cdot C_g \tag{4}$$

With
- q_m the mass flow
- p equal to $(p_1 + p_2)/2$
- p_1 the upstream absolute pressure
- p_2 the downstream absolute pressure
- ρ_N the gas density under P, T conditions
- T_N the standard temperature of gas
- Z_N the gas compressibility factor under standard conditions
- T the absolute temperature of the gas
- $Z_{(P,T)}$ the gas compressibility factor under P, T conditions
- $\eta_{(P,T)}$ the dynamic gas viscosity
- P_N the standard pressure
- C_g the geometric factor, defined experimentally
- N   Standard condition of temperature and pressure, 0 °C and 101.3 kPa

4.5. QUALITY (PURITY) OF THE DILUTION GAS

The accuracy achievable with the permeation method depends significantly on the purity of the dilution gas used for the generation of the standard gas mixtures. Impurities in the carrier and dilution gas are often one of the most critical contributors to the uncertainty of the final gas mixture composition. The uncertainty contributions depend on the amount of impurities present in the dilution gases and upon the accuracy with which these impurities have been measured. Table 3 gives an overview of the existing standards and the maximum allowed amount of substance fractions in zero air for measuring NO_2 and SO_2 in ambient air at ground level.

	Analytes with $x_{B\,max}$ values in zero air													
	SO_2	NO_2	NO	CO	Bz	To	Xy	CH_4	NH_3	Ozone	H_2S	N_2O	CO_2	H_2O
Standard	(nmol/mol)												(µmol/mol)	
EN 14211 for NO_2		1	1						1	2			4	150
EN 14212 for SO_2	1	1	1				0.05		2		100			150
Both criteria	1	1	1	-	-		0.05		1	2	100	-	4	150

Table 3: Maximum allowed amount of substance fractions $x_{B\,max}$ in zero air for ambient air measurements and the values in European standards (EN) for the specified analytes. [a] Bz: benzene, To: toluene Xy: xylene. For benzene the standard sets the criteria for zero air to be below the detection limit of the used methods, the lowest value is indicated. If the same zero air is to be used to measure all listed analytes, all criteria have to be fulfilled.

The impurities in the carrier and dilution gases can be removed/reduced using different types of filter cartridges.
The use of special regulators for ultraclean dilution gases with separate pressure, vent and evacuation ports on the high pressure side are recommended.

4.6. HOMOGENEITY OF DYNAMIC STANDARD GAS MIXTURES

It is essential that a gas mixture is homogeneous before it is analysed or used as a standard gas mixture. Homogeneity is defined in ISO 7504 [14] as the "state of a gas mixture wherein all of its components are distributed uniformly throughout the volume occupied by the gas mixture".
Inhomogeneous mixtures manifest by long and unstable readings of the measurement instrument without obvious drifts.

Precautions should therefore be taken to ensure the homogeneity of the dynamic standard gas mixtures. Since mixing by diffusion is slow, flow elements causing turbulence are necessary.
For the permeation method the homogeneity for both dilution steps have to be considered: the dilution of the permeate in the chamber and the mixing of the carrier gas with the dilution gas flow.
For the realisation in the permeation generator the homogeneity of the mixing of the carrier with the dilution flow after their unification is assured by a long meandering (or angulated) tubing. Other elements like mixing tubes containing multiple flow deviation elements might be considered.

Concerning the magnetic suspension balance care should be given for the mixing zone which does not cause a substantial pressure drop.

4.7. STABILIZATION TIME

It's important to use dynamically produced gas mixtures for calibrating analysers only when their concentrations are stable over time; otherwise the analysers will be calibrated with wrong concentrations resulting in erroneous ambient air measurements.

The necessary stabilization times for obtaining standard gas mixtures with a stable concentration are linked to:
- The nature and the implementation of gases
- The used materials
- The mixing system and the components used (materials, volumes)

5. UNCERTAINTY OF PERMEATION METHOD

The amount of substance fraction of analyte B in the gas mixture C_B is calculated as follows *(equation 3)*:

$$C_B = \frac{n_B}{n_{null}} + C_{Bnull} = \frac{q_{mB}(T).VM_{null}}{M_B.qv_{null}} + C_{Bnull}$$

With:

n_B and n_{null}	the amount of substances of analyte B and dilution gas (null), respectively
C_{Bnull}	the residual amount of analyte in the dilution gas
$q_{mB}(T)$	the substance mass flow of analyte B through the membrane of the permeation device
VM_{null}	the molar volume of substance B at standard temperature and pressure
M_B	the molar mass of substance B
qv_{null}	the sum of the dilution and carrier gas flows at standard temperature and pressure

The combined standard uncertainty, $u_c(y)$ of the permeation method is calculated from the variance of $u_c^2(y)$ according to:

$$u_c^2(y) = \sum_i \left(\frac{\partial f(x_i)}{\partial x_i} \right)^2 u(x_i)^2 \tag{5}$$

where y is the estimate of the measurand ($Y = f(x_1, x_2, …, x_n)$) and $u_c(y)$ is the combined standard uncertainty of the estimate (y). Variances ($u(x_i)^2$) of the input estimates (x_i) can be calculated or estimated from the function $f(x_1, x_2, …, x_n)$.

The expanded uncertainty is obtained from the combined standard uncertainty according to:

$$U = k \cdot u_c(y) \tag{6}$$

where $u_c(y)$ is the combined standard uncertainty of the measurand (Y) and k is the coverage factor. In this connection $k = 2$ for all uncertainty calculations corresponding to a confidence level of 95 % for the measurements that follow normal distribution.

The combined standard uncertainty of amount of substance fraction of analyte B in the gas mixture can be expressed applying *equation 5* to *equation 3*.

$$u_c^2(C_B) = \left(\frac{VM_{null}}{M_B.qv_{null}}\right)^2 .u^2(q_{mB}(T)) + \left(\frac{q_{mB}(T)}{M_B.qv_{null}}\right)^2 .u^2(VM_{null})$$

$$+ \left(\frac{q_{mB}(T).VM_{null}}{M_B^2.qv_{null}}\right)^2 .u^2(M_B) + \left(\frac{q_{mB}(T).VM_{null}}{M_B.qv_{null}^2}\right)^2 .u^2(qv_{null}) + u^2(C_{Bnull})$$

(7)

And the expanded uncertainty, *U*, can be calculated as following:

$$U = 2.u_c(C_B)$$

5.1. Standard uncertainty on $q_{mB}(T)$

The substance mass flow of analyte B through the membrane of the permeation device (q_{mB}) is calculated from the mass *m* of the permeation device and the time *t (equation 1)*:

$$q_{mB} = \frac{\Delta m.P_{B,c} + (\rho_1 - \rho_2).V_{rf}}{\Delta t} = \frac{(m_1 - m_2).P_{B,c} + (\rho_1 - \rho_2).V_{rf}}{\Delta t}$$

With:

q_{mB}	mass flow of analyte B out of permeation device at a given temperature *T*
Δm	mass difference
m_1	mass of permeation device at time t_1
m_2	mass of permeation device at time t_2
ρ_1, ρ_2	respective air densities in the weighing room during the consecutive weighings
V_{rf}	volume of the permeation tube
$P_{B,c}$	mass related chemical purity of substance B
Δt	time interval

The combined standard uncertainty of the substance mass flow of analyte B through the membrane of the permeation device can be expressed applying the *equation 5* to the *equation 1*.

$$u_c^2(q_{mB}) = \left(\frac{P_{B,c}}{\Delta t}\right)^2 .u^2(m_1) + \left(\frac{P_{B,c}}{\Delta t}\right)^2 .u^2(m_2) + \left(\frac{m_1 - m_2}{\Delta t}\right)^2 .u^2(P_{B,c}) + \left(\frac{V_{rf}}{\Delta t}\right)^2 .u^2(\rho_1)$$

$$+ \left(\frac{V_{rf}}{\Delta t}\right)^2 .u^2(\rho_2) + \left(\frac{\rho_1 - \rho_2}{\Delta t}\right)^2 .u^2(V_{rf}) + \left(\frac{(m_1 - m_2).P_{B,c} + (\rho_1 - \rho_2).V_{rf}}{\Delta t^2}\right)^2 .u^2(\Delta t)$$

(8)

- Standard uncertainty on m_1 and m_2

  The standard uncertainty on the masses depends on the uncertainty of the standard masses used to calibrate the balance, given in the calibration certificate of the accredited calibration laboratory and on the uncertainty of the weighings (repeatability and reproducibility of the balance…).

- Standard uncertainty on $P_{B,c}$

  The standard uncertainty on the chemical purity of substance B can be determined by the user or taken in the certificate given by the manufacturer.

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- Standard uncertainty on buoyancy effect

  a) Standard uncertainty on ρ_1 and ρ_2
  The formula for calculating density is recommended par CIPM since 2007 and is the following:

  $$\rho = \frac{P_{atm}.Ma}{Z.R.T}\left[1 - Xv\left(1 - \frac{Mv}{Ma}\right)\right]$$ (9)

  With:
  - ✓ P_{atm} atmospheric pressure
  - ✓ Ma molar mass of air
  - ✓ Z compressibility factor of air
  - ✓ R universal gas constant, 8.3144 J/(mol K)
  - ✓ T absolute temperature
  - ✓ Xv amount of substance fraction of water (calculated with relative humidity saturation vapor pressure)
  - ✓ Mv molar mass of water

  The standard uncertainties on the densities are given by applying the *equation 5* to the *equation 9* and on estimating the standard uncertainties on each parameters.

  Nevertheless, ρ_1 and ρ_2 can be calculated with a simplified formula given in OIML R 111-1 (2004).

  b) Standard uncertainty on V_{rf}
  The standard uncertainty on the volume of the permeation tube is determined by the user because this information is not given by the manufacturer.

- Standard uncertainty on Δt
  The uncertainty on the interval time is evaluated by the user.

5.2. STANDARD UNCERTAINTIES ON VM_{null} AND M_B

The uncertainties on the molar volume of substance B at standard temperature and pressure VM_{null} and on the molar mass of substance B are given in the guide EURACHEM/CITAC (April 2000) and in the IUPAC tables (1999).

5.3. STANDARD UNCERTAINTY ON qv_{null}

5.3.1 Mass flow controller

If mass flow controllers (MFC) are applied with dynamic dilution method to measure span and dilution flows, the standard uncertainties of each MFC are a combination of the uncertainty found in the calibration certificate issued by accredited laboratories or NMI's and other sources of uncertainty (influence of temperature, drift…). The uncertainty can be expressed as a relative value of the full scale or by combining the performance characteristics (e.g. linearity, repeatability, drift) of the device that give the major contributions to the uncertainty budget of the MFC. The variables and uncertainty sources that give the major contributions to the expanded uncertainty can be defined by examining the standard uncertainties of each of the variables and their respective sensitivity factors.

5.3.2 Laminar flow element

5.3.2.1 Calibration by an accredited laboratory

In case the laminar flow elements for the flows are calibrated by an accredited laboratory (according to ISO IEC 17025) the standard uncertainties of each calibration point are indicated in the certificates.

5.3.2.2 Calibration with theoretical function

The flow of a medium through a laminar flow element is analytically described by the laws of flow dynamics. The variance of the combined standard uncertainty for a single laminar flow element can be expressed in the following form, for details see Annex 1.

$$
\begin{aligned}
u^2(q_m) = & \left(\frac{q_m}{p}\right)^2 \cdot u(p)^2 + \left(\frac{q_m}{(p_1 - p_2)}\right)^2 \cdot u(p_1)^2 + \left(-\frac{q_m}{(p_1 - p_2)}\right)^2 \cdot u(p_2)^2 + \left(\frac{q_m}{\rho_N}\right)^2 \cdot u(\rho_N)^2 \\
& + \left(\frac{q_m}{T_N}\right)^2 \cdot u(T_N)^2 + \left(\frac{q_m}{Z_N}\right)^2 \cdot u(Z_N)^2 + \left(\frac{q_m}{C_g}\right)^2 \cdot u(C_g)^2 + \left(-\frac{q_m}{T}\right)^2 \cdot u(T)^2 \\
& + \left(-\frac{q_m}{Z_{p,T}}\right)^2 \cdot u(Z_{p,T})^2 + \left(-\frac{q_m}{\eta_{p,T}}\right)^2 \cdot u(\eta_{p,T})^2 + \left(-\frac{q_m}{p_N}\right)^2 \cdot u(p_N)^2
\end{aligned}
\tag{10}
$$

5.4. STANDARD UNCERTAINTY ON C_{BNULL}

The uncertainty on the amount of analyte in the dilution gas is determined or estimated by the user or - by lack of better - it is taken from the specifications or certificates of the gas producer. In case an additional gas purifier is used the specifications given by manufacturer are used.

6. CONCLUSION

Permeation is an accurate and commonly used method for preparing standard gas mixtures at amount of substance fractions in the nmol/mol range. Commonly used compounds for permeation method are reactive inorganic analyte substances like NO_2 and SO_2.

In the case of NO_2 and SO_2 it is recommended to use permeation device with permeation rates between 100 ng/min and 1000 ng/min with a relative expanded uncertainty lower than 2 %. By using dilution flows from 1 L/min to 5 L/min, this means that the amount fractions of the dynamically produced gas mixtures cover the range from 150 nmol/mol to 20 nmol/mol. Concerning the gas flows care shall be taken to the performance of the flow control and measurement systems.
The uncertainty for permeation methods depends on the permeation rate, on the impurities in the carrier and dilution gas and on the uncertainty of the flow rates measurement. The relative expanded uncertainties U_{rel} (k=2) for the permeation methods operated at the various laboratories (FMI, LNE, METAS) within the MACPoll project are expected to be lower than 3 % in the range from 150 nmol/mol to 20 nmol/mol.

The amount of substance fraction range and the associated uncertainties fulfil the requirements of the European Directive on "Ambient air quality and cleaner air for Europe" (2008/50/EC) for the measurement of ambient air pollutants" for calibrating gas analyzers.

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ANNEX 1: CALCULATION OF THE COMBINED STANDARD UNCERTAINTY FOR THE LAMINAR FLOW ELEMENT

First order derivate of *equation 1* with respect of the variables can be expressed according to:

$$\frac{\partial q_m}{\partial p} = \frac{(p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{p}$$

(A1)

$$\frac{\partial q_m}{\partial p_1} = \frac{p \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{(p_1 - p_2)}$$

(A2)

$$\frac{\partial q_m}{\partial p_2} = -\frac{p \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = -\frac{q_m}{(p_1 - p_2)}$$

(A3)

$$\frac{\partial q_m}{\partial \rho_N} = \frac{p \cdot (p_1 - p_2) \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{\rho_N}$$

(A4)

$$\frac{\partial q_m}{\partial T_N} = \frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{T_N}$$

(A5)

$$\frac{\partial q_m}{\partial Z_N} = \frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{Z_N}$$

(A6)

$$\frac{\partial q_m}{\partial C_g} = \frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} = \frac{q_m}{C_g}$$

(A7)

$$\frac{\partial q_m}{\partial T} = -\frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T^2 \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = -\frac{q_m}{T}$$

(A8)

$$\frac{\partial q_m}{\partial Z_{p,T}} = -\frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T}^2 \cdot \eta_{p,T} \cdot p_N} \cdot C_g = -\frac{q_m}{Z_{p,T}}$$

(A9)

$$\frac{\partial q_m}{\partial \eta_{p,T}} = -\frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T}^2 \cdot p_N} \cdot C_g = -\frac{q_m}{\eta_{p,T}}$$

(A10)

$$\frac{\partial q_m}{\partial p_N} = -\frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N^2} \cdot C_g = -\frac{q_m}{p_N}$$

(A11)

The variance of the combined standard uncertainty for the laminar flow element can now be expressed in the form:

$$u^2(q_m) = \left(\frac{q_m}{p}\right)^2 \cdot u(p)^2 + \left(\frac{q_m}{(p_1 - p_2)}\right)^2 \cdot u(p_1)^2 + \left(-\frac{q_m}{(p_1 - p_2)}\right)^2 \cdot u(p_2)^2 + \left(\frac{q_m}{\rho_N}\right)^2 \cdot u(\rho_N)^2$$

$$+ \left(\frac{q_m}{T_N}\right)^2 \cdot u(T_N)^2 + \left(\frac{q_m}{Z_N}\right)^2 \cdot u(Z_N)^2 + \left(\frac{q_m}{C_g}\right)^2 \cdot u(C_g)^2 + \left(-\frac{q_m}{T}\right)^2 \cdot u(T)^2 \qquad \text{(A12)}$$

$$+ \left(-\frac{q_m}{Z_{p,T}}\right)^2 \cdot u(Z_{p,T})^2 + \left(-\frac{q_m}{\eta_{p,T}}\right)^2 \cdot u(\eta_{p,T})^2 + \left(-\frac{q_m}{p_N}\right)^2 \cdot u(p_N)^2$$

Added references:

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e.g. SEMI F20-0305, „Specification for 316L Stainless Steel Bar,Forgings, Extruded Shapes, Plate, and Tubing for Components used in General Purpose, High Purity, and Ultra-High Purity Semiconductor Manufacturing Applications"

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