Guide on dynamic dilution methods for NO, NO$_2$ and SO$_2$ 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 for the generation of SO_2, NO and NO_2 standard gas mixtures at concentration levels corresponding to the limit values given in the European Directive ut s hơt go gro gtj irkgtk golu   u k .8 5 5 l / lu nk s kg ks kt 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 that are applied in this document are the dynamic dilution method and the gas phase titration (GPT) method. The latter method is based on the chemical reaction of NO and O_3 forming NO_2. The method is applicable for calibration purposes of NO_2 and O_3 analyzers and also to determine the NO_2 converter efficiency in the chemiluminescence analyzers.

The document gives guidance on how to generate SO_2, NO and NO_2 standard gas mixtures applied with different flow measurement methods and sources of gas standards in concentration ranges and with associated uncertainties in accordance with the specifications given in the European Directive 2008/50/EC and relevant EN standards [2][3] (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	-	20 to 100	3
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, NO 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)_

3. DYNAMIC DILUTION METHOD

This guide is originally based on the international standard ISO 6145 (parts 1, 6 and 7) [4][5][6] and is completed with newer sources, the knowledge and the experience of the participating laboratories in the framework of the MACPoll project.

3.1. PRINCIPLE

Dynamic dilution methods are widely used to dilute gases from sources with higher concentration to lower concentration ranges for various applications in air quality measurements. They can be applied for the preparation of standard gas mixtures for calibrating and testing of analyzers for air quality measurements and for inter-laboratory comparisons.

The gas sources used for dynamic dilution methods are gravimetrically prepared gas standards (certified reference materials, CRM) and high purity gases. For controlling and measuring the calibration gas or reference gas mixture and the dilution gas flows, various types of flow elements are used: laminar flow elements, thermal mass flow controllers or meters and critical nozzles or combinations of these. The dilution methods are also regulated in standards made by e.g. the International Standardization Organization (ISO). In this guide the focus of the application is for ambient air quality measurements but the methods are also applicable to calibrate analyzers for emission measurements for example.

Since for all three types of flow elements the calibrated flow values are usually given as (standard volume) / (time unit) e.g. mL/min (usually at 0 °C and 1013.25 hPa), the complete mixing formula is established with the concentrations C_B of the Analyte B first. Corresponding abbreviations are introduced afterwards.

The complete mixing formula for dilution i can be expressed as follows:

$$C_{Bi} = \frac{C_{B1} \cdot q_{span} + C_{B2} \cdot q_{dil}}{q_{span} + q_{dil}}$$

(1)

With C_{Bi} the concentration of analyte B in dilution i

          C_{B1} the concentration of analyte B in gas 1 (span gas, standard ST, CRM)

          q_{span} the volume flow of span gas

          C_{B2} the concentration of analyte B in gas 2 (dilution gas)

          q_{dil} the volume flow of dilution gas

With the equation of the ideal gas the relation between the concentration C_B and the amount of substance fraction x_B of a substance B is:

$$C_{Bi} = \frac{n_{Bi}}{V} = \frac{x_{Bi} \cdot p}{R \cdot T}$$

(2)

With C_{Bi} the concentration of analyte B in dilution i
          n_{Bi} the amount of substance B in dilution I
          V the volume
          x_{Bi} the amount of substance fraction B in dilution i
          p the total pressure
          R *the* gas constant of ideal gas
          T the absolute temperature

With equal values for p and T for the reference and dilution gas, respectively, eq. 1 becomes

$$\frac{x_{Bi} \cdot p}{R \cdot T} = \frac{p}{R \cdot T} \cdot \frac{x_{B1} \cdot q_{span} + x_{B2} \cdot q_{dil}}{q_{span} + q_{dil}}$$

(3)

With x_{B1} the amount of substance fraction of analyte B in the span gas
              x_{B2} the amount of substance fraction of analyte B in the dilution gas

Under the above conditions the complete mixing formula with amount fractions can be written:

$$x_{Bi} = \frac{x_{B1} \cdot q_{span} + x_{B2} \cdot q_{dil}}{q_{span} + q_{dil}}$$

(4)

If x_{B2} is (or were zero), the dilution factor f_d can be introduced:

$$f_d = \frac{q_{span}}{q_{span} + q_{dil}}$$

(5)

eq. 4 can then be written as:

$$x_{Bi} = f_d \cdot x_{B1}$$

(6)

The span and dilution flows q are either expressed as a volume flows (q_V) or a mass flows (q_m) depending on the applied calibration method.

Various realisations of dynamic dilution devices using the different flow control and measurement methods exist. Commercials dilution devices integrate all components into one unit, as shown in Figure 1.

Figure 1:

3.2. FLOW MEASUREMENT INSTRUMENTS

3.2.1 Mass flow controllers and meters

Thermal mass flow controllers (MFC) or meters (MFM) are widely used for the controlling and measuring of gas flow rates. The flow ranges are within approximately 5 ml/min up to 500 l/min. Both thermal mass flow controllers and meters are designed in such a way that the flow is divided into two laminar flows: a sensor flow and a bypass flow. The sensor tube contains two thermal sensors, the first one (upstream) is heated and the second one measures the gas temperature. The gas flow passing the first, heated element causes a heat loss thus leading to a temperature difference between the two sensors. This temperature difference is proportional to the mass flow and the thermal properties of the gas. Therefore the indicated mass flow is dependent on the thermal properties of the measured gas. Only the sensor flow goes through the thermal sensors up to 5 ml/min of the full scale of the flow in order to have correct operation of the temperature sensors. Since the ratio of the sensor to the bypass flow is constant it allows the correct calculation of the total flow.

Mass flow controllers are designed to keep the flow rate constant at a pre-set value with the help of the pressure difference between the input and output flow, while the mass flow meter measures the flow in the prevailing conditions.

The performance characteristics of mass flow controllers and meters have been studied by a number of research groups [7][8] in which the uncertainty of the devices has also been evaluated [9][10]. In addition, the ISO 6145/7 standard for the use of mass flow controllers for calibration purposes is available [6].

3.2.2 Critical nozzles

An other method for obtaining standard gas mixtures by the dynamic dilution method is the use of critical orifices. The operation of the orifices is based on the characteristics of gas flow through an orifice (nozzle) at the velocity of sound. An ISO standard is available for the set up of critical orifices [5]. The performance characteristics of critical orifices have not been evaluated as widely in the literature as MFCs.

Provided that the critical conditions across the orifice are fulfilled, i.e., the ratio of upstream pressure to downstream pressure exceeds the value of 2 and the ratio of the diameter of the orifice to the diameter of the upstream tube remains below 0.2, the mass flow (q_m) passing isotropically through the sonic orifice can be expressed in the form [11]:

$$q_m = A_c C_d \cdot \frac{p_1}{\sqrt{T_1}} \cdot \sqrt{\frac{M}{R} \cdot \gamma \cdot \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \tag{7}$$

With
    q_m mass flow
    A_c the cross-section area of the sonic nozzle
    C_d the concentration coefficient of the gas jet (discharge coefficient)
    p_1 upstream pressure, absolute (hPa)
    T_1 upstream temperature (°K)
    M molar mass of the gas
    R gas constant of an ideal gas
    γ ratio of the mass thermal capacities c_p/c_v

Equation (7) can be expressed in the form:

$$q_m = \frac{A_c \cdot C_d \cdot C^* \cdot p_1}{\sqrt{T_1}}$$

(8)

Where in equation (8) the coefficient C^* is:

$$C^* = \sqrt{\frac{M}{R} \cdot \gamma \cdot \left(\frac{2}{\gamma + 1}\right)^{\frac{\gamma+1}{\gamma-1}}}$$

(9)

From equation (8) one can see that the mass flow through the sonic nozzle depends on the upstream temperature and pressure, and on the coefficients A_c, C_d and C^*, which depend on the geometry of the nozzle, characteristics of the flow dynamics (Reynolds number), on the thermal properties of the gas (the ratio of c_p/c_v) and on its molar mass, respectively. The discharge parameter is a smooth function on Reynolds number and depends on the geometric factors of the orifice. On commercial gas dilutors the manufacturer has defined the geometric factor, the conditions for the discharge coefficient and the gas properties. The pressure and temperature conditions should be controlled by the user.

3.2.3   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.

Following the Hagen-Poiseuille's law [11], the mass flow of a compressible medium through an annular pathway in the laminar regime can be expressed as:

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

(10)

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

3.2.4   Comparison of the flow measurement methods

The high accuracy of flow measurement is mostly due to the high performance of the flow control and measurement systems used for the dynamic dilution method. In the present case the best performance for gas flow measurements is achieved with the laminar flow elements with a standard uncertainty of 0.2 % and up to 1.0 % for mass flow controllers. The rather new solution of

mass flow controllers by CMOS technique improves the standard uncertainty down to 0.4 %. The standard uncertainty of the critical nozzles lies somewhere between the uncertainty ranges above. Technical solution of critical orifices can vary from sophisticated commercial solutions by accurate pressure control to a simple flow port made by drilling or by hammer the metal tube.

The cost of the flow measurement system applying the dynamic method can also vary orders of magnitude and mostly is connected with the performance characteristics of the flow measuring device, controlling unit and data acquisition system. In this respect laminar flow element system is most expensive. Depending on the technical requirements cheaper solutions are available by mass flow controllers or single critical nozzles.

3.3. IMPLEMENTATION OF DYNAMIC METHOD

The implementation of the dynamic method to generate low concentrations of NO, NO_2 (below 100 nmol/mol) and SO_2 (below 150 nmol/mol) requires some precautions to achieve the target uncertainty of 3%. The instructions are addressed both for the laboratory as well as for the transfer system applying the dynamic dilution method.

The various criteria to consider are listed below:

- Dilution system
    - Nature of the materials in contact with the different gases used to avoid reactions between materials and the different gases
    - Purging and conditioning procedure
    - Leak detection
- High concentration gas mixture
    - The concentration range to be used and the associated uncertainty
    - The pressure regulator (material, flushing and evacuation possibility)
- Quality (purity) of the dilution gas
- Regulation and measurement of the gas flows (span and dilution flow rates)
    - Calibration of gas flow meter
- Homogeneity of the generated standard gas mixture
- Stabilization time to obtain a reference gas mixture with a stable concentration

Note : Some guidances are given in the encyclopedia from Air Liquide [12] and on the website of Spectragases [13].

3.3.1 Dilution system

3.3.1.1   Nature of the materials

Before generating a standard gas mixture by dynamic dilution, it is advised to further check the suitability of the laboratory 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 the valve seats and seals. Such reactions should 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 and gas supplier handbooks.

Information on the most commonly used gases 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	S	S	S[a]	S[a]	S[a]	S
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.

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

It is recommended to use all metal sealed connections.

3.3.1.2   Purging and conditioning procedure

The transfer line integrity, including the leak tightness and cleanliness of all the components (pressure regulator, valves, transfer line, connections, etc.) shall be guaranteed to avoid contamination of the system and of the gas cylinder. In order to guarantee this, appropriate equipment, materials choice and purging procedure shall be used. For reactive gases it is advised to purge the transfer line with a flow higher than the flow used after to generate the reference gas mixture. For adsorbing molecules like NO_2 and SO_2 conditioning the entire gas system with the gas mixture for appropriate time (maximum two hours) saturates the adsorbing sites of the walls, resulting in more stable compositions.

It is recommended to sequentially pressurise, vent and evacuate all components of the transfer ks on nk mg s o k uhk kjh g sksh gtk s .ǫkgm u 7 s hg /. This method requires typically three cycles. In case evacuation is not possible, five to eight pressurising cycles are recommended. The insertion of a stop valve after the pressure regulator is recommended for safety reasons. An additional conditioning period of typically one to two hours followed by a last pressurising/venting cycle (not evacuation) further ensures the stability of the gas composition.

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[1] http://www.swagelok.com/downloads/webcatalogs/de/MS-06-64.pdf   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-Nom o ks øut j i u Sgt lgi ɗm rŏg ɑt

[2] For coating manufacturers see e.g. www.restek.com or www.SilcoTek.com

The choice of a low-volume pressure regulator for the high concentration mixtures is recommended. Reactive gases such as SO_2 and NO_2 k ok k kt ok mdm ul nk k kj areas of the transfer line and, in particular, the low-volume pressure regulator. The use of special regulators for ultraclean gases with separate pressure, vent and evacuation ports on the high pressure side are recommended.

In the laboratory the dynamic dilution system is complete and ready to use. It is recommended to leave the system pressurized in order to avoid the difficulties which may happen in transfer systems. However, when changing the Primary Reference gas Mixture (PRM), during the maintenance of the system or any time when the system has been in contact with the laboratory air the instructions given above are followed.

3.3.2 High concentration gas mixtures

3.3.2.1 Type of gas mixtures

It is recommended to use a Primary Reference gas Mixture (PRM) prepared by a National Metrological Institute (NMI) and/or by a accredited laboratories according to the standard ISO 17025 [14] and to the ISO Guide 34 [15]. This allows the use of gravimetric gas mixtures as described in the standard ISO 6142 [16] assuring traceability to the International System (SI) with adequate uncertainties even at low concentrations. Moreover in the certificate an expiry date is given according to the ISO Guide 34 specifying the stability time of the concentration of the gas mixture.

3.3.2.2 Concentration range and uncertainties

To generate gas mixtures with amount fractions below 100 nmol/mol for NO, NO_2 and below 150 nmol/mol for SO_2 it is recommended to use gravimetric gas mixtures in cylinders with concentrations and expanded uncertainties given in Table 3.

Component	Concentration (µmol/mol)	Expanded uncertainty (%)
NO	5 to 10	≤1.0
NO_2	5 to 10	≤1.0
SO_2	5 to 10	≤1.0

Table 3: Concentration ranges and expanded uncertainties of gas mixtures in cylinders with high amount fractions

3.3.2.3 Precautions with the gas cylinders

The implementation of the high concentration gas mixture requires some precautions. Concerning the choice of the pressure regulator care shall be taken with respect to material compatibility. Moreover reactive gases such as SO_2 and NO_2 k ok nk k ul ru - ur s k km rg u nɸn reduces the wetted surface area and hence reduces the level of purging required. Re-connecting cylinders always has the danger of creating a leaking connection which shall be avoided for several reasons. In an optimum set-up, the pressure regulator should remain on the cylinder and the cylinder must be left with a minimum pressure inside. These measures will help to reduce the number of purge cycles for the pressure regulator prior to analysis. Environmental air diffuses back into the pressure regulator over time, even with this optimum set-up and if it is pressurized.

A minimum operating pressure specified by the CRM producer indicates, if applicable, the pressure value below which the gas should not be used. It has been reported that below a certain pressure,

gas molecules that were attached to the cylinder wall come off when the pressure drops in some cases, resulting in higher mole fraction. The precaution actions that the operators should take care of are presented in Table 4.

Component	Pressure regulator	Minimum operating pressure (bar)	Storage temperature (°C)
NO	Stainless steel Low dead volumes Seals compatible with NO	10 or higher (according to specification of manufacturer)	according to specification of manufacturer
NO_2	Stainless steel Low dead volumes Seals compatible with NO_2	10 or higher (according to specification of manufacturer)	according to specification of manufacturer
SO_2	Stainless steel Low dead volumes Seals compatible with SO_2	10 or higher (according to specification of manufacturer)	according to specification of manufacturer

Table 4: Implementation of the high concentration gas mixture

3.3.2.4   Storage

The storage and operation of gas mixtures in cylinders are often limited by the manufacturer to certain temperature ranges. If the cylinder is stored at or exposed to temperatures below the stated range given by the manufacturer, some components may condense and thus leading to a possible change in the composition of the mixture and voiding the values given in the certificate by the manufacturer. If this happen a more detailed guide is provided in 5.2.5.

It is recommended to avoid high temperatures (heating) close to the cylinder, e.g. from ovens or other intensive heat sources. High temperatures will result in higher pressures leading to potentially hazardous situations. In addition, elevated temperatures may result in decomposition of thermally unstable species.

3.3.2.5   Conditioning of gas cylinders

Mixtures may require to be homogenized again if stored for longer periods of time and if exposure to temperatures below the condensation point of one or more substances cannot be excluded. This may be done by bringing the cylinders up to ambient temperature and rotating them horizontally for an appropriate period of time, which may depend on the matrix gas and the components.

It is further advised to store the cylinders for minimum 24 h at laboratory temperature prior to their use.

3.3.3 Purity of the dilution gas

	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 and 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 5: 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.

3.3.4   Regulating and measuring the gas flows (span 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.

3.3.4.1   Common criteria for all flow elements

The method for controlling the flow depends on the specific properties of the gas (e.g. thermal capacity, viscosity). Therefore the flow elements need to be calibrated for the same specific gas as it is used. In order to be able to guarantee the stability and the composition of the flow some additional actions need to be taken care of. The dead volumes of the flow regulator elements (MFCs, sonic nozzle, valves) 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 electro polished 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 evacuatable 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 calibrating the flow elements in its operating mounting and configuration without e.g. 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.

Calibration of the flow elements should be conducted at least once a year by an accredited laboratory in the operating 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. To be sure that there is no matrix effect during calibration of the flow elements, calibration of the flow elements should be made by the same gas matrix as for generating the dynamic standard gas mixtures. The flow element for high concentration gas mixture should be calibrated by the parent gas of the cylinder (nitrogen) and the flow element for

dilution should be calibrated by dilution gas (synthetic air). In some of the flow elements the operator can change the setting for the gas in use even when calibrated with different gas. The operator needs to be careful when using these options in case of confusions. It is also recommended to compare the whole dynamic dilution system against the other method between the flow calibrations in order to avoid drift of the flow elements. Not only the correct calibration gas but also the calibration conditions should be the same as operation conditions, see below.

In case if a laminar flow element is used as flow meter it should be calibrated with the same gas composition as for generation of the dynamic standard gas mixture.

3.3.4.2   S l

It is recommended to use the flow meters not below 10 % of their maximum flow and to keep the minimum flow of the high concentration gas mixture above 15 ml/min to limit retention in the transfer system and to allow proper purging of the transfer lines. The foreline pressure set by the reducing valve is generally sufficiently stable but should be as specified during the calibration and lu nk k4 k u nk s in lg k k ut k os k ul S l   on 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 hk kk t nk s g k og r ul nk S l gt j nk mg g dm n u mm nk S l 4

3.3.4.3   Laminar flow elements

nk tkk j u hk u k g kj on i ut umk j   kgs k k gt j on gj joo t gr S l lu k dm 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 h dm nk g k l ti ot hklu k kgi n s kg   element according to the manufacturer procedure. If necessary the pressure sensors of the elements can be calibrated and adjusted.

3.3.4.4   Critical nozzles

The stability of the flow depends on the up- gt j ju t kgs k k km rg ot 4l ut k kt r o important to take care of the choice of robust pressure regulation elements (mechanical or electronic). Moreover due to the gas expansion the nozzle housings and tubings should be temperature stabilized to allow reasonable stabilisation times.

In commercial devices many nozzles are combined in various ways with the flow of the gas standard and the dilution gas, respectively, in order to obtain a great number of evenly distributed dilution ratios. It is worth to mention that the total flow for the different dilution ratios remains constant and that the operation of the nozzles is mechanical (no electronic signal is needed) and that the flow follows the physical theory. The calibration should be made at all discrete dilution ratios to avoid the need for interpolating values.

3.3.5 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 so k4Nus umk tko o jkl dkj ol O = : 8 7 a7=cg nk g k ul g mg so k nk kko d g rrul o ius utk t g k jo dk j t ou s r n u mmu nk ur s k uii dkjh nk mg so k4 Inhomogeneous mixtures manifest by long and unstable readings of the measurement instrument without obvious drifts.

Some precautions should be taken to ensure the homogeneity of the dynamic standard gas mixtures. It is recommended to use:
- Turbulent flow elements after the mixing point, like a meandering tube.
- A mixing chamber (material: glass, stainless steel) or commercial mixing nozzles.

The principle is injecting the (low) flow of a high concentration gas mixture perpendicular into the laminar to turbulent main flow of the dilution gas through fine nozzles into a mixing chamber (length l_R) with a sufficiently large diameter d_R. The necessary dimensions of the recipient (e.g. a tubing with a larger diameter than the inlet and outlet) for various flows can be calculated from the diffusion time of the analyte gas B in the dilution gas A in each element with the finite element method.

An estimation for the necessary tube diameter d_R i gt hk mokt h g r dm d kd jd out equation (eq. 11). The diffusion time t_D of the analyte molecule B for the smallest dimension d_R of the chamber (perpendicular to the main flow direction) and the residence time t_R of the dilution gas in the chamber (eq. 12) are calculated. This estimation is for the worst case not considering turbulence and convection.

$$t_D = \frac{d_R{}^2}{2 \cdot D_{B,A}} \tag{11}$$

with $D_{B,A}$ the diffusion coefficient of substance B in substance A

$$t_R = \frac{V_R}{q_V} = \frac{d_R{}^2 \cdot \pi \cdot l_R}{4 \cdot q_V} \tag{12}$$

with V_R, the volume of the mixing recipient and l_R its length

The necessary criterion for homogeneous mixing by diffusion only is that t_D t_R

As an example: for O_2 diffusing in N_2 at 20 °C and 200 kPa for a distance d_R of 0.4 cm a t_D of 0.7 s results. For a mixing chamber volume of 22 mL and a volume flow of 400 mL/min, t_R is 3.3 s, thus the criterion is well fulfilled. For further details and references see the publication by Haerri [18].

3.3.6 Stabilization time

O œ u gt u k dynamically diluted 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 stabilization times for obtaining standard gas mixtures with a stable concentrations are linked to:
- The pretreatment of the cylinders, the nature and the implementation of gases
- The transfer system (design, dimension, flows)
- The mixing system and the components used (materials, volumes)

Orders of magnitude for stabilization times are given in Table 6.

Component	Concentration range (nmol/mol)	Dilution ratios	Stabilization time (min)
NO	20 to 100	1/2000 to 1/100	up to 15
NO$_2$	20 to 100	1/2000 to 1/100	up to 120
SO$_2$	40 to 150	1/2000 to 1/100	up to 120

Table 6: Orders of magnitude for stabilization times (dilution ratios are given for a CRM with 5-10 µmol/mol)

3.4. UNCERTAINTY OF DYNAMIC DILUTION METHOD

3.4.1 Calculation of the expanded uncertainty

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

$$u_c^2(y) = \sum_i \left(\frac{\partial f(x_i)}{\partial x_i} \right)^2 u(x_i)^2$$
(13)

where y is the estimate of the measurand ($Y = f(x_1, x_2, \ldots, x_n)$) 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 $f(x_1, x_2, \ldots, x_n)$.

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

$$U = k \cdot u_c(y)$$
(14)

where $u_c(y)$ is the combined standard uncertainty of the measurand (Y) and k is a 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 the dynamic dilution method can be expressed applying the equation (13) to the equation (1). The detail of the calculation is given in Annex 1.

$$u_c^2(C_{Bi}) = \left(\frac{q_{span}}{q_{span} + q_{dil}} \right)^2 \cdot u^2(C_{B1}) + \left(\frac{q_{dil}}{q_{span} + q_{dil}} \right)^2 \cdot u^2(C_{B2})$$

$$+ \left(\frac{q_{dil} \cdot (C_{B1} - C_{B2})}{(q_{span} + q_{dil})^2} \right)^2 \cdot u^2(q_{span}) + \left(\frac{q_{span} \cdot (C_{B2} - C_{B1})}{(q_{span} + q_{dil})^2} \right)^2 \cdot u^2(q_{dil})$$
(15)

If C_{B2} is equal to zero, the equation (15) becomes :

$$u_c^2(C_{Bi}) = \left(\frac{q_{span}}{q_{span} + q_{dil}} \right)^2 \cdot u^2(C_{B1}) + \left(\frac{q_{dil} \cdot C_{B1}}{(q_{span} + q_{dil})^2} \right)^2 \cdot u^2(q_{span}) + \left(\frac{q_{span} \cdot C_{B1}}{(q_{span} + q_{dil})^2} \right)^2 \cdot u^2(q_{dil})$$
(16)

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

$$U = 2 \cdot u_c^2(C_{Bi})$$

Equation (16) is slightly complicated when several flow measurement devices are connected at the same time for preparation of the gas mixture for calibration purpose and when impurity of the dilution gas and/or in the gas standard are taken into account.

The concentration C_{Bi} and the associated expanded uncertainty are given in the calibration certificate of the high concentration gas mixture. The standard uncertainty on C_{Bi} is calculated as following:

$$u(C_{Bi}) = \frac{U(C_{Bi})}{2}$$

(17)

3.4.2 Standard uncertainty on q

3.4.2.1 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 laboratu ᴋ u TSO gtj u nk u ik ul tik gᴅ .ᴅlr ktik ul ks k g k2j ᴆ /4 nk tik gᴅ igt hk k k kj g g kᴍg ok gr k 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.

3.4.2.2 Critical nozzle

- **Calibration by an accredited laboratory**

In the case the critical nozzles are applied with dynamic dilution method to regulate span and dilution flows, the standard uncertainties of each critical nozzle can be obtained from the calibration certificate issued by an accredited calibration laboratory. It can be expressed as a relative value of the full scale which is a

Since the analytical evaluation is cumbersome and not all quantities are measurable, e.g. A_c and C_d, the uncertainty analysis with the flows from the certificate with a gas flow standard is practical and widely applied.

3.4.2.3   Laminar flow element

- **Calibration by an accredited laboratory**

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

- **Calibration with theoretical function**

The flow of a medium through a laminar flow element is analytically described by the laws of flow dynamics, see eq. 10. In comparison with the flow through a critical nozzle more parameters characteristic of the gas are associated and more physical quantities both upstream and downstream of the flow element need to be known. The variance of the combined standard uncertainty for a single laminar flow element can be expressed in the following form, for details see Annex 3.

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

$$+ \left(\frac{q_m}{T_N}\right)^2 \cdot u(T_N)^2 + \left(\frac{q_m}{Z_N}\right)^2 \cdot u(Z_N)^2 + \left(\frac{q_m}{C_g}\right)^2 \cdot u(C_g)^2 + \left(-\frac{q_m}{T}\right)^2 \cdot u(T)^2 \qquad (20)$$

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

4.   GAS PHASE TITRATION (GPT) METHOD

The gas phase titration method is based on the international standard ISO 15337 [20] and this guide is completed with the latest knowledge and the experience of the participating laboratories in the framework of the MACPoll project.

4.1. PRINCIPLE

The gas phase titration of nitrogen monoxide by ozone is a simple gas phase bimolecular reaction between NO_2 and oxygen (O_2). The titration can be presented as:

$NO + O_3 \rightarrow NO_2^* + O_2$, (R1)

$\quad\quad\quad\quad\hookrightarrow NO_2$ λ: 600 nm   2400 nm
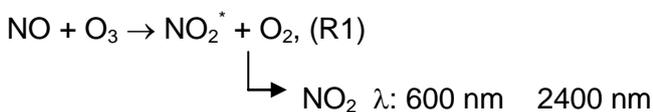
The nitrogen dioxide formed in reaction (R1) can be in the excited state, NO_2^*, which decays to the ground state. The wavelength, , of the transition energy occurs between 600 nm and 2400 nm, with an intensity peak at 1200 nm. The rate constant, k_{R1}, of the reaction (R1) has been studied quite intensively over a wide temperature range by a number of research groups. The reaction rate constant of $k_{R1} = (1.8 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 298 K [20] is used. The reaction (R1) is also an important reaction in the atmosphere. Once NO_2 is formed through the reaction (R1), nitrogen dioxide dissociates into nitrogen monoxide and oxygen in the presence of sunlight; this is the most important photochemical reaction occurring in the atmosphere.

During the GPT, number of reactions with nitrogen dioxide and ozone may take place with the wall material of the reaction chamber. These reactions have been studied in the literature [21]. In order to avoid the other reactions than (R1) the reaction chamber and the tube materials in the measurement system need to be made of inert material to avoid detectable loss of reactants.

The reaction (R1) is allowed to proceed in an excess concentration of nitrogen monoxide compared to the concentration of ozone, in order to consume the ozone completely in the reaction. The reverse situation, ozone in excess of nitrogen monoxide, would leave ozone in the system. As a reactive molecule it would react again with the nitrogen monoxide after the NO_2 NO conversion causing nonlinear behaviour of the results.

From the conservation of nitrogen in the reaction (R1), the sum of nitrogen monoxide and nitrogen dioxide is a conservative quantity, i.e.,

$$[NO] + [NO_2] = [NO]_o + [NO_2]_o = [NO]_o \tag{21}$$

On the right-hand side of the equation, an initial situation $[NO_2]_o = 0$ has been used. The reaction (R1) takes place in a stochiometric condition, i.e., the changes in the ozone concentration equals to the changes in the nitrogen monoxide concentration:

$$a_{3}] = [O_3]_o \quad [O_3] = [NO]_o \quad \text{aT} \quad cC \quad \text{aT} \quad c \tag{22}$$

The titration takes place normally in a reaction chamber where the reaction time must be long enough to allow the titration reaction to go to completion. The rate constant of reaction (R1) is well-documented in the literature over a wide temperature range [21]. The rate of change of nitrogen monoxide in reaction (R1) using the condition of Equation (22) can be calculated according to:

$$-\frac{d[NO]}{dt} = k[NO][O_3] = k[NO]\left([O_3]_0 - ([NO]_0 - [NO])\right) \tag{23}$$

Integration of Equation (23) with the initial condition of Equation (21) gives the reaction time:

$$t = \frac{1}{k \cdot ([O_3]_0 - [NO]_0)} \ln\left(\frac{[NO]_0([O_3]_0 - [NO]_0 + [NO])}{[NO][O_3]_0}\right) \tag{24}$$

where
t   the time of reaction (min)
k   the rate constant (nmol/mol^{-1} min^{-1})
$[O_3]_o$ the initial O_3 concentration (in nmol/mol)
$[NO]_o$ the initial NO concentration (in nmol/mol)
$[NO]$ the final NO concentration (in nmol/mol)

An important aspect of the GPT method with nitrogen monoxide is that the amount of ozone introduced into the system can be calculated from the change of nitrogen monoxide. This gives the possibility of tracing the ozone concentration to a reference standard of nitrogen monoxide made by a gravimetric method. However, there are some problems along the way. First, the reaction (R1) has to go to completion with respect to ozone. The materials of the GPT system have to be inert to ozone as well as to nitrogen compounds, in order to prevent the loss of reactants with the wall and tube materials. The best way is to build a very compact system of inert material and use high concentrations of both gas components to minimize the required delay time according to Equation (24) for the complete reaction (R1).

Laboratory studies have been performed to demonstrate GPT as a method to trace the ozone reference standard to a gravimetrically-prepared nitrogen monoxide standard. In order to reach a complete reaction (R1), an empirical parameter, the so-called dynamic parameter [22] is used. This parameter, P_R, is a product of the concentration of nitrogen monoxide and the residence time, t_R, of the reactants in the reaction chamber. It should fulfil the criteria:

$$P_P = [NO]_{RC} \cdot t_R = [NO]_{RC} \cdot \frac{V_{RC}}{f_{ozone} + f_{NO}} > 2.75 \mu mol / mol \cdot \min$$

(25)

where V_{RC} is the volume of the vessel (reaction chamber), and f_{ozone} and f_{NO} are the flows of the ozone and the nitrogen monoxide, respectively.

The volume of the reaction chamber shall designed in such a way that $t_R > t$, where the reaction time, t, is calculated from Equation (24). The commercial dilutors which are equipped with the options for performing the GPT, can be designed in such a way that the concentration of nitrogen monoxide in the reaction vessel, $[NO]_{RC} = [NO]_{STD}$, i.e., no dilution with zero air takes place before the reaction with ozone. When the concentration of NO is high, the reaction time is short enough to make the reaction (R1) complete with ozone. Dilution of the reactants should take place after the reactions in the dilution chamber. As an example of the commercial gas dilutors equipped with facilities for conducting the GPT, the flow rate of ozone can be f_{ozone} = 50 to 200 ml/min and f_{NO} varies depending on the dilution rate, being from 3 to 200 ml/min. The size of the reaction chamber can vary from 10 cm^3 up to couple of hundreds of cm^3 and the concentration of the gas standard of nitrogen monoxide can be 50 μmol/mol or higher. The dynamic parameter, P_R is thus 10 a s ur5s ur s dc gqdm nk ru k   gr k ul kgi n g ghrk l rdm nk i ck out ul   g ut .8 /4O can also be lower than the criterion of Equation (25) depending on the combination of the values for each of the variables.

Dilution of the nitrogen dioxide produced by the reaction (R1), need to be made rapidly after the completed reaction. The concentration of the nitrogen dioxide produced can be calculated with the help of Equations (21) and (22):

$$[NO_2]_{prod} = [NO]_o - [NO] = [O_3]_o - [O_3] = \frac{[NO]_{STD} \cdot f_{NO}}{f_{NO} + f_{dil}} - [NO]_{actual} = \frac{[O_3]_{STD} \cdot f_{ozone}}{f_{ozone} + f_{dil}}$$

(26)

The two similarities on the right-hand side of Equation (26) describes the production of $[NO]_o$ and $[O_3]_o$ for reaction of NO + O$_3$ in the GPT system. The $[NO]_{STD}$ and $[O_3]_{STD}$ are the sources for preparation of the initial concentrations of $[NO]_o$ and $[O_3]_o$ by dilution method from gravimetric standard of NO and from the ozone source (e.g. by Standard Reference Photometer or by other UV-lamp). The flow rates f_{NO}. f_{ozone} and f_{dil} are the flow rates used for preparation of the gas concentrations. Dilution flow needs to be large enough to have excess of flow at least of 10 % of the total flow of the GPT system including the sample flow of the analyzer(s). In the GPT system the ozone is consumed completely and therefore $[O_3]$ = 0 in Equation (26). However, *[NO]=[NO]$_{actual}$,* is not zero and is the actual concentration which is not reacted with the ozone i.e. is not titrated.

In Figure 2 a typical set up for performing the GPT to calibrate ozone analyzer or to determine the NO$_2$ converter efficiency of the chemiluminescence NO-NO$_x$ analyzer is presented.
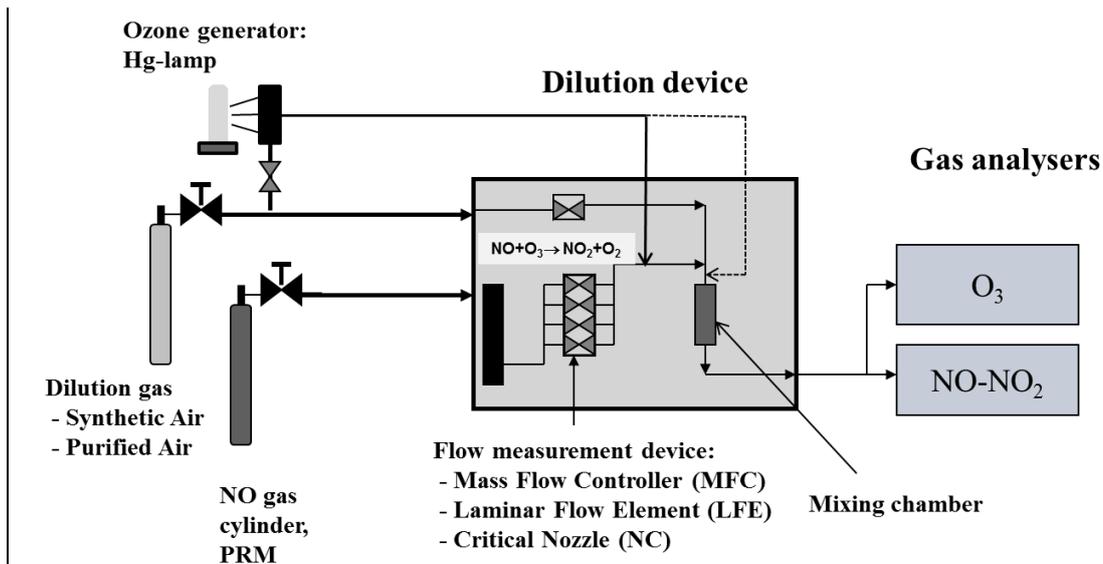
Figure 2: Typical set up for the GPT system. The ozone generator can be an external or integrated part of the dilution device. The ozone concentration can be injected directly into the mixture of high NO concentration line (solid line) or into the mixture of low (diluted) NO concentration line (dashed line).

O cs u gt u tuk ng nk u utk iutikt g ut igt hk dpki kj konk on nk nom NO concentration or with the diluted concentration line. The advantage of the former way is that the reaction time is very short in order of seconds or less while in latter case the reaction time is order of tens of seconds. In latter case the mixing (reaction chamber) chamber needs to be large enough in order to have the reaction (R1) in completion.

There is also clear evidence (Viallon et al. 2006 [23], Tanimoto et al. 2006 [24]) that the agreement between the performance of the primary ozone photometer i.e. Standard Reference Photometer (SRP by NIST) and the GPT are not consistent but rather has a bias of 2 to 3 %. The committee "ACSO" ("Absorption Cross Sections of Ozone") established in spring 2009 is a joint ad hoc commission of the Scientific Advisory Group (SAG) of the Global Atmosphere Watch (GAW) of the World Meteorological Organization (WMO) and the International Ozone Commission (IO_3C) of the International Association of Meteorology and Atmospheric Sciences (IAMAS).
The mandate of ACSO includes:
- Review of the presently available ozone absorption cross sections with a priority on Huggins band.
- Determination of the impact of modifying the reference ozone absorption cross sections for all of the commonly used (both ground-based and satellite) atmospheric ozone monitoring instruments.
- Recommendations whether a change needs to be made to the presently used WMO/IO_3C standard ozone absorption cross section data (by Bass and Paur, 1985).

The recommendations are to be discussed between the community of the involved experts. Until now the final decision of the change of the cross section which will change the concentration level obtained from the SRP has not been made by The International Bureau of Weights and Measures (BIPM).

4.2. IMPLEMENTATION OF GPT METHODS

The implementation of the GPT method to generate low concentrations of NO_2 (between 20 to 100 nmol/mol) requires some precautions to achieve the target uncertainty of 3%.

The instructions which are addressed both for the laboratory as well as for the transfer system applying the GPT method are listed below:

- GPT system
  - Nature of the materials in contact with the ozone, nitrogen monoxide and nitrogen dioxide
  - Purging and conditioning procedure
  - Leak detection

- High concentration gas mixture: NO
  - The concentration range to be used and the associated uncertainty
  - The pressure regulator (material, flushing and evacuation possibility)

- Stability of the ozone source

- Quality (purity) of the dilution gas

- Regulation and measurement of the gas flows (O_3 flow, NO flow and dilution flow)
  - Calibration of gas flow meter

- Homogeneity of the generated standard gas mixture of NO

- Reaction time for the completion of the reaction (R1) in the GPT system to obtain a stable concentration of NO_2

4.2.1 GPT system

4.2.1.1   Nature of the materials

Before applying the GPT system, it is advised to further check the suitability of the laboratory and the transfer system against the possible chemical reactions of mixture components. Special consideration shall be given to avoid the attack by corrosive gases such as NO_2 on metals and possible reactions with elastomers and greases used, for example, in the valve seats and seals. Such reactions should 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 and gas supplier handbooks.

Information on the most commonly used gases and their level of compatibility with a range of materials is outlined in Table 7. 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	Silica-lined stainless steel	Polytetra-fluoroethylene (PTFE)	Perfluoroalkoxy copolymer resin (PFA)	Fluorinated-ethene-propene (FEP)	
NO	S	S	S[a]	S[a]	S[a]	S
NO$_2$	Possible[c]	S	S[a] Possible[c]	S[a]	N[b]	S
O$_3$	N	S	S[a]	S[a]	N	S

Table 7: 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.

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

It is recommended to use all metal sealed connections.

4.2.1.2   Purging and conditioning procedure

The transfer line integrity, including the leak tightness and cleanliness of all the components (pressure regulator, valves, transfer line, connections, etc.) shall be guaranteed to avoid contamination of the system and of the gas cylinder. In order to guarantee this, appropriate equipment, materials choice and purging procedure shall be used. For reactive gases it is advised to purge the transfer line with a flow higher than the flow used after to generate the reference gas mixture. For adsorbing molecules like NO$_2$ conditioning the entire gas system with the gas mixture for appropriate time (maximum two hours) saturates the adsorbing sites of the walls, resulting in more stable compositions.

It is recommended to sequentially pressurise, vent and evacuate all components of the transfer ks on nk mg so k uhk kj h g sks h gtk s .ǿkgm 7 s hg /4 no s k nuj requires typically three cycles. In case evacuation is not possible, five to eight pressurising cycles are recommended. The insertion of a stop valve after the pressure regulator is recommended for safety reasons. An additional conditioning period of typically one to two hours followed by a last pressurising/venting cycle (not evacuation) further ensures the stability of the gas composition.

In the laboratory the GPT system is complete and ready to use. It is recommended to leave the system pressurized in order to avoid the difficulties which may happen in transfer systems. However, when changing the Primary Reference gas Mixture (NO standard), during the maintenance of the system or any time when the system has been in contact with the laboratory air the instructions given above are followed.

4.2.2 High concentration gas mixtures

4.2.2.1   Type of gas mixtures

It is recommended to use a Primary Reference gas Mixture (PRM) prepared by a National Metrological Institute (NMI) and/or by a accredited laboratories according to the standard ISO 17025 [14] and to the ISO Guide 34 [15]. This allows the use of gravimetric gas mixtures as described in the standard ISO 6142 [16] assuring traceability to the International System (SI) with adequate uncertainties even at low concentrations. Moreover in the certificate an expiry date is given according to the ISO Guide 34 specifying the stability time of the concentration of the gas mixture.

4.2.2.2   Concentration range and uncertainties

To generate gas mixtures with amount fractions below 100 nmol/mol for NO it is recommended to use gravimetric gas mixtures in cylinders with concentrations and expanded uncertainties given in Table 8.

Component	Concentration (µmol/mol)	Expanded uncertainty (%)
NO	5 to 10	≤1.0

Table 8: Concentration ranges and expanded uncertainties of gas mixtures in cylinders with high amount fractions

4.2.2.3   Precautions with the gas cylinders

The implementation of the high concentration gas mixture requires some precautions. Concerning the choice of the pressure regulator care shall be taken with respect to material compatibility. Re-connecting cylinders always has the danger of creating a leaking connection which shall be avoided for several reasons. In an optimum set-up, the pressure regulator should remain on the cylinder and the cylinder must be left with a minimum pressure inside. These measures will help to reduce the number of purge cycles for the pressure regulator prior to analysis. Environmental air diffuses back into the pressure regulator over time, even with this optimum set-up and if it is pressurized.

A minimum operating pressure specified by the CRM producer indicates, if applicable, the pressure value below which the gas should not be used. It has been reported that below a certain pressure, gas molecules that were attached to the cylinder wall come off when the pressure drops in some cases, resulting in higher mole fraction. The precaution actions that the operators should take care of are presented in Table 9.

Component	Pressure regulator	Minimum operating pressure (bar)	Storage temperature (°C)
NO	Stainless steel Low dead volumes Seals compatible with NO	10 or higher (according to specification of manufacturer)	according to specification of manufacturer

Table 9: Implementation of the high concentration gas mixture

4.2.2.4   Storage

where $u_c([NO;O_3])_{max}$ is the larger of the two uncertainties that should select as for the uncertainty of the GPT method. In case where all the measurements are based on the measurements of both of the gas compounds the uncertainty of the analyzer, including the uncertainty of the calibration need to be included into the uncertainty budget i.e. into the standard uncertainties of $u([NO]_{STD})$, $u([NO])_{actual}$ and $u([O_3]_{STD})$.

The flow measurement system that can be used for preparation of the gas concentration can be based on mass flow controllers, critical orifices and laminar flow elements or combination of these. The performance characteristics and uncertainty sources that give the major contributions to the expanded uncertainty can be find in paragraph 3.4.2.

5.   CONCLUSION

Dynamic dilution is an accurate and commonly used method for preparing standard gas mixtures at amount of substance fractions starting from the nmol/mol range. Commonly used compounds for dynamic dilution cover stable and only moderately reactive inorganic gas mixtures like CO, NO, SO_2 and H_2S in N_2, as well as a wide list of volatile organic compounds (VOCs).
In the case of NO, NO_2 and SO_2 it is recommended to use high concentration gas mixtures (CRM) with amount of substance fraction between 5 to 10 µmol/mol with a relative expanded uncertainty lower than 1 %. By using dilution ratios from 1/2000 to 1/100, this means that the amount fraction of the dynamic gas mixture covers the range from 2.5 nmol/mol to 100 nmol/mol. Concerning the flow rates, care shall be taken of the performance of the flow control and measurement systems used for the dynamic dilution method.
The uncertainty for dynamic dilution methods depends on the uncertainty of the CRM concentration, on the analyte concentration and impurities in the dilution gas and on the uncertainty of the flow rates. The relative expanded uncertainties U_{rel} (k=2) for the dynamic dilution methods operated at the various laboratories (FMI, LNE, METAS) within the MACPoll project are lower than 3 % in the range 150 nmol/mol down to 20 nmol/mol.
The amount of substance fraction range and the associated uncertainties fulfil the requirements of the   u kgt oki ok ut   s hȼt go   gro gt j iɪkgt k go lu   u k .8   5 5 l / lu nk   s kg   ks kt ul gs hȼt go uɯ gt   and the relevant EN standards (EN 14211 and EN 14212) for calibrating gas analyzers.

The Gas Phase Titration (GPT) method is a method that can be used for calibration purpose of ozone analyzer, determining the conversion efficiency of the NO_2 converter in NO-NO_x analyzers by chemiluminescence method. In addition the method is applicable to check the consistency of the concentration of NO gas mixtures prepared by dynamic dilution method and the ozone concentration prepared by Standard Reference Photometer.

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ANNEX 1: CALCULATION OF THE COMBINED STANDARD UNCERTAINTY FOR THE DYNAMIC DILUTION METHOD

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

$$\frac{\partial C_{Bi}}{\partial q_{span}} = \frac{(q_{span} + q_{dil}) \cdot C_{B1} - 1 \cdot (C_{B1} \cdot q_{span} + C_{B2} \cdot q_{dil})}{(q_{span} + q_{dil})^2} = \frac{q_{dil} \cdot (C_{B1} - C_{B2})}{(q_{span} + q_{dil})^2} \tag{A1}$$

$$\frac{\partial C_{Bi}}{\partial q_{dil}} = \frac{(q_{span} + q_{dil}) \cdot C_{B2} - 1 \cdot (C_{B1} \cdot q_{span} + C_{B2} \cdot q_{dil})}{(q_{span} + q_{dil})^2} = \frac{q_{span} \cdot (C_{B2} - C_{B1})}{(q_{span} + q_{dil})^2} \tag{A2}$$

$$\frac{\partial C_{Bi}}{\partial C_{B1}} = \frac{q_{span}}{q_{span} + q_{dil}} \tag{A3}$$

$$\frac{\partial C_{Bi}}{\partial C_{B2}} = \frac{q_{dil}}{q_{span} + q_{dil}} \tag{A4}$$

The variance of the combined standard uncertainty according to equation (6) can now be expressed in the form:

$$
\begin{aligned}
u_c^2(C_{Bi}) = & \left(\frac{q_{span}}{q_{span} + q_{dil}}\right)^2 \cdot u^2(C_{B1}) + \left(\frac{q_{dil}}{q_{span} + q_{dil}}\right)^2 \cdot u^2(C_{B2}) \\
& + \left(\frac{q_{dil} \cdot (C_{B1} - C_{B2})}{(q_{span} + q_{dil})^2}\right)^2 \cdot u^2(q_{span}) + \left(\frac{q_{span} \cdot (C_{B2} - C_{B1})}{(q_{span} + q_{dil})^2}\right)^2 \cdot u^2(q_{dil})
\end{aligned} \tag{A5}
$$

ANNEX 2: CALCULATION OF THE COMBINED STANDARD UNCERTAINTY FOR THE CRITICAL NOZZLE

First order derivate of equation (8) with respect of the variables can be expressed according to:

$$\frac{\partial q_m}{\partial A_c} = C_d \cdot C^* \cdot \frac{p_1}{\sqrt{T_1}} = \frac{q_m}{A_c} \tag{A6}$$

$$\frac{\partial q_m}{\partial C_d} = A_c \cdot C^* \cdot \frac{p_1}{\sqrt{T_1}} = \frac{q_m}{C_d} \tag{A7}$$

$$\frac{\partial q_m}{\partial C^*} = A_c \cdot C_d \cdot \frac{p_1}{\sqrt{T_1}} = \frac{q_m}{C^*} = 0 \tag{A8}$$

The right hand identity follows if C^* is constant.

$$\frac{\partial q_m}{\partial C_d} = A_c \cdot C^* \cdot \frac{p_1}{\sqrt{T_1}} = \frac{q_m}{C_d}$$

$$\frac{\partial q_m}{\partial p_1} = A_c \cdot C^* \cdot C_d \cdot \frac{1}{\sqrt{T_1}} = \frac{q_m}{p_1} \tag{A9}$$

$$\frac{q_m}{T_1} \quad A_c \quad C_d \quad C^* \quad (\;\frac{1}{2}\;) \frac{p_1}{\sqrt{T_1}} \quad \frac{1}{2} q_m \tag{A10}$$

The variance of the combined standard uncertainty for the critical nozzle can now be expressed in the form:

$$u^2(q_m) = \left(\frac{q_m}{A_c}\right)^2 \cdot u(A_c)^2 + \left(\frac{q_m}{C_d}\right)^2 \cdot u(C_d)^2 + \left(\frac{q_m}{C^*}\right)^2 \cdot u(C^*)^2 + \left(\frac{q_m}{p_1}\right)^2 \cdot u(p_1)^2 + \left(\frac{1}{2} q_m\right)^2 \cdot u(T_1)^2 \tag{A11}$$

ANNEX 3: CALCULATION OF THE COMBINED STANDARD UNCERTAINTY FOR THE LAMINAR FLOW ELEMENT

First order derivate of equation (10) with respect of the variables can be expressed according to:

$$\frac{\partial q_m}{\partial p} = \frac{(p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{p} \tag{A12}$$

$$\frac{\partial q_m}{\partial p_1} = \frac{p \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{(p_1 - p_2)} \tag{A13}$$

$$\frac{\partial q_m}{\partial p_2} = -\frac{p \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = -\frac{q_m}{(p_1 - p_2)} \tag{A14}$$

$$\frac{_m}{_N} \quad \frac{q \ (p \quad p \ ) \ T_N \ Z_N}{T \ Z_{p,T} \quad_{p,T} \ p_N} \ C_g \quad \frac{q_m}{_N} \tag{A15}$$

$$\frac{\partial q_m}{\partial T_N} = \frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{T_N} \tag{A16}$$

$$\frac{\partial q_m}{\partial Z_N} = \frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = \frac{q_m}{Z_N} \tag{A17}$$

$$\frac{\partial q_m}{\partial C_g} = \frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} = \frac{q_m}{C_g} \tag{A18}$$

$$\frac{\partial q_m}{\partial T} = -\frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T^2 \cdot Z_{p,T} \cdot \eta_{p,T} \cdot p_N} \cdot C_g = -\frac{q_m}{T} \tag{A19}$$

$$\frac{\partial q_m}{\partial Z_{p,T}} = -\frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T}^2 \cdot \eta_{p,T} \cdot p_N} \cdot C_g = -\frac{q_m}{Z_{p,T}} \tag{A20}$$

$$\frac{\partial q_m}{\partial \eta_{p,T}} = -\frac{p \cdot (p_1 - p_2) \cdot \rho_N \cdot T_N \cdot Z_N}{T \cdot Z_{p,T} \cdot \eta_{p,T}^2 \cdot p_N} \cdot C_g = -\frac{q_m}{\eta_{p,T}} \tag{A21}$$

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

<div align="right">(A22)</div>

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

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

$$+ \left(\frac{q_m}{T_N}\right)^2 \cdot u(T_N)^2 + \left(\frac{q_m}{Z_N}\right)^2 \cdot u(Z_N)^2 + \left(\frac{q_m}{C_g}\right)^2 \cdot u(C_g)^2 + \left(-\frac{q_m}{T}\right)^2 \cdot u(T)^2 \qquad \text{(A23)}$$

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

ANNEX 4: PARTIAL DERIVATIVES FOR THE UNCERTAINTY CALCULATIONS OF THE CONCENTRATIONS FOR THE GAS PHASE TITRATION METHOD (GPT)

$$[NO_2]_{prod} = \frac{[NO]_{STD} \cdot f_{NO}}{f_{NO} + f_{dil}} - [NO]_{actual} = \frac{[O_3]_{STD} \cdot f_{ozone}}{f_{ozone} + f_{dil}}$$

The standard uncertainty components of the gas phase titration method can be calculated as follows:

$$\frac{\partial C_i}{\partial f_i} = \frac{[C_i]_{STD} \cdot (f_i + f_{dil}) - [C_i]_{STD} f_i}{(f_i + f_{dil})^2} = \frac{[C_i]_{STD} f_{dil}}{(f_i + f_{dil})^2} \tag{A24}$$

$$\frac{\partial C_i}{\partial f_{dil}} = -\frac{[C_i]_{STD} \cdot f_i}{(f_i + f_{dil})^2} \tag{A25}$$

$$\frac{\partial C_i}{\partial [C_i]_{STD}} = \frac{f_i}{f_i + f_{dil}} \tag{A26}$$

$$\frac{\partial C_{NO}}{\partial [NO]_{actual}} = -1 \tag{A27}$$

where the index $i = NO, O_3$. The variance of the combined standard uncertainty of the concentration of the gas mixture prepared by the gas phase titration method can be calculated as follows

$$u_c^2([NO_2]) = \sum_{i=1}^{N} \left(\frac{\partial E}{\partial x_i}\right)^2 \cdot u^2(x_i)$$

$$= \left(\frac{[NO]_{STD} f_{dil}}{(f_{NO} + f_{dil})^2}\right)^2 \cdot u^2(f_{NO}) + \left(\frac{[O_3]_{STD} f_{NO}}{(f_{NO} + f_{dil})^2}\right)^2 \cdot u^2(f_{dil}) + \left(\frac{f_{NO}}{(f_{NO} + f_{dil})}\right)^2 \cdot u^2([NO]_{STD})^2 + u^2([NO]_{actual})$$

$$\tag{A28}$$

The similar uncertainty can be calculated for ozone:

$$u_c^2([O_3]) = \sum_{i=1}^{N} \left(\frac{\partial E}{\partial x_i}\right)^2 \cdot u^2(x_i)$$

$$\tag{A29}$$

$$= \left(\frac{[O_3]_{STD} f_{dil}}{(f_{ozone} + f_{dil})^2}\right)^2 \cdot u^2(f_{ozone}) + \left(\frac{[O_3]_{STD} f_{ozone}}{(f_{ozone} + f_{dil})^2}\right)^2 \cdot u^2(f_{dil}) + \left(\frac{f_{ozone}}{(f_{ozone} + f_{dil})}\right)^2 \cdot u^2([O_3]_{STD})^2$$