Guide on static dilution method 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 (SO2) 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 (NOx), 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 (NO2) and VOCs, typically emitted from road vehicles, lead to the formation of ozone (O3) 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 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 method that is applied in this document is the static dilution method.

The document gives guidance on how to generate SO_2, NO 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 [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)*

This guide is originally based on the international standard ISO 6144 [4] 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 STATIC DILUTION METHOD

Standard gas mixtures are prepared by adding parent gases (pure gases of known composition) quantitatively from supply cylinders to the reference cell of known volume in which the standard gas mixture will be contained. The amount of gaseous component added is calculated by using the known volume of a gastight syringe (volumetric injection), applying corrections due to the ambient pressure and temperature, determined with accurate pressure and temperature sensors. The final desired concentration is achieved by successive dilution steps, using accurate pressure and temperature recordings. A single step preparation method can only be applied for high concentrations because the suitable syringe volume in combination with the reference cell volume limits the achievable dilution ratios.

With the exception of nitrogen oxide, synthetic air or purified air is used in general as dilution matrix.

Due to the reaction of NO with oxygen at NO high concentrations, pure nitrogen gas (5.0) is used as a matrix material to prepare the standard gas mixtures of this compound.

3.1. PURITY ANALYSIS OF PARENT GASES

The purity of parent gases is of similar importance for uncertainty components of the standard gas mixture prepared, than the thermodynamic properties given by pressure, temperature, non ideal behaviour and mixing chamber volume. The accuracy of mixture composition is influenced by the amount of impurities and furthermore by the uncertainty of their measurement. Only metrological certified pure gases are used for the preparation of the standard mixtures. Special attention has to be paid on the composition of the dilution matrix with respect to the pure gas under investigation. As a general requisite, the dilution matrix should not contain detectable amounts of pure parent gas. The detection limit of the used analytical method, applied to measure the matrix composition, is used for the calculation of the uncertainty contribution of the dilution matrix on the total uncertainty of the prepared mixtures. A rectangular distribution of measurement results between zero and the detection limit value is assumed, whereby the mole fraction is set equal to half of the value of the detection limit. For the calculation of the standard uncertainty this value is divided by the factor of $\sqrt{3}$.

3.2. PREPARATION OF THE GAS MIXTURE

The composition of the final gas mixture is defined by the substance fraction. Gas compositions are preferentially expressed as an amount of substance fraction (mol/mol), because this quantity is invariant to pressure and temperature changes. If other quantities of composition are required (e.g. mass concentration) then the applicable conditions (pressure, temperature) shall be given in addition. No further uncertainty contributions need to be considered since the transformation is of numerical precision with fixed conversion factors for a given pressure and temperature condition.

It has to be assured that the dilution matrix is free of any reactive species which may influence the composition of the gas mixture. The preparation of NO standard gas mixtures requires oxygen free buffer gas, water vapour should not be present in concentrations higher than

150 μmol/mol and the absence of other, with the applied measurement technique interfering gases, even at trace level concentrations, should be guaranteed.

The uncertainty budget for standard gases prepared with concentration levels near the certification range of the individual monitors used for compliance checking under 2008/50/EC do not require the consideration of the additional uncertainty contribution due to the parent gas impurities in the dilution matrix, because its relative contribution stays, if the mole fraction is below the detection limit, well below 1%, and is therefore in further calculations neglected. If standard gas mixtures are prepared at concentration ranges at the limit values or even below, this uncertainty has to be added to the total uncertainty budget.

The standard gas mixtures are prepared in an inert vessel with known volume. This volume was determined by filling the cell with water at 20°C using certified volumetric flask. A total volume of 14.7356 L with a standard uncertainty of 0.0010 L was calculated using 5 independent measurements. Its contribution is considered in the total uncertainty budget. A photograph of the mixing vessel with pressure and temperature measurement instruments is shown in Figure 1.
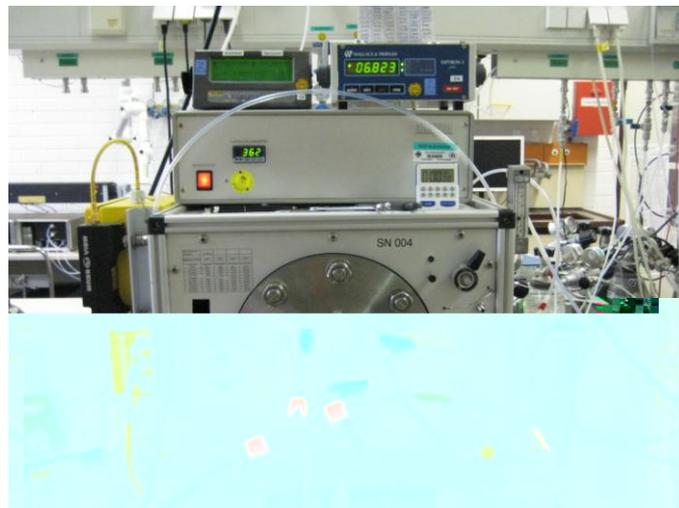

Figure 1: Mixing chamber used to prepare standard gas mixtures

The prepared mixtures are used directly after their stabilization period, which is currently based on the observation of the pressure and temperature values.

Needle valves in combination with Teflon lines and glass tubes are used to transfer the mixture to the monitors.

3.3. CALCULATION OF THE MIXTURE COMPOSITION

The amount of substance fractions of the component in the final mixture is calculated according to relation (1), as an example for the preparation of NO standard gas mixtures with one dilution step according to ISO 6144:

$$C = \frac{C_p \times V_s}{V_d} \times \frac{p_1}{p_2} \times \frac{p_3}{p_4}$$

(1)

List of Quantities:

Quantity	Unit	Definition
C	-	Volume fraction in the resulting gas mixture of NO
C_p	-	Volume fraction of the NO pure gas
V_s	l	Injected volume by syringe
V_d	l	Volume of the vessel (complementary gas)
p_1	kPa	Pressure in the syringe
p_2	kPa	Final pressure in the vessel (1st addition dilution matrix gas N_2)
p_3	kPa	Pressure static dilution (expansion step)
p_4	kPa	Final pressure static dilution (2nd addition dilution matrix gas N_2)

where temperature changes are assumed to be negligible.

4. IMPROVED METHOD FOR THE IMPLEMENTATION OF A STATIC DILUTION PROCESS TO ACHIEVE UNCERTAINTIES BELOW 3%

The implementation of the static dilution method to generate low concentrations of NO (below 100 nmol/mol) and SO_2 (below 150 nmol/mol) requires to consider additional effects which are currently assumed to be negligible in the application of ISO 6144 in order to achieve the low uncertainty of 3%.

The major additional points to take into account are listed below:

- Continuous records of pressure and temperature values, both from the measurement cell and the ambient conditions with high accuracy have to be provided.

- Pressure stabilized monitors to achieve concentration measurements which are invariant against changes to ambient conditions are necessary, which improve zero gas and span point measurements during long term observations.

- To prepare lower mixing ratios, multiple dilution steps are required. To achieve these mixing ratios in a single or maximum two step dilution process, a second high accurate pressure measurement sensor is needed to minimize the relative uncertainty contribution of this low pressure measurement reading on the total uncertainty budget. As an alternative a single pressure measurement device can be used with an accuracy of less than 0.01% of full scale (10 bar), commonly used at static dilution chambers, to maintain the uncertainty contribution to the total uncertainty of the pressure measurements nearly negligible compared to the major sources (see example uncertainty budget, paragraph 4.2.6).

- The detection limit of the parent gas in the dilution gas mixture will be one of the major parts of the total uncertainty budget. Therefore analytical equipment with enhanced performance with respect to the stability of zero gas measurements are required to minimize this effect. The use of instrumentation in a well controlled environment with respect to both, temperature and pressure variations, is a step in this direction. This is in line with attempts to get better specifications for dilution matrix gases used to prepare those standard gas mixtures.

- The nature of the materials in contact with the prepared standard gas mixtures should not influence the composition. Trends in the concentrations observed should be analysed thoroughly. This implies an improved QA/QC procedure with continuous records of all relevant parameters used in the evaluation process with sufficient high time resolution.

- Purging of the mixing chamber requires more attention, if low concentrated standard gas mixtures are prepared.

An improved model equation which incorporates the temperature measurements from the mixing cell as well as from the laboratory, is given in equation (2):

$$C = \frac{C_p \times V_s}{V_d} \times \frac{p_1}{p_2} \times \frac{T_2}{T_1} \times \frac{p_3}{p_4} \times \frac{T_4}{T_3}$$

(2)

List of Quantities:

Quantity	Unit	Definition
C	-	Volume fraction in the resulting mixture of NO
C_p	-	Volume fraction of the NO pure gas
V_s	l	Injected volume by syringe
V_d	l	Volume of the vessel (complementary gas)
p_1	kPa	Pressure in the syringe (ambient pressure)
p_2	kPa	Pressure in the vessel (after 1st addition dilution matrix gas N_2)
p_3	kPa	Pressure static dilution (1st expansion step)
p_4	kPa	Final pressure static dilution (after 2nd addition dilution matrix gas N_2)
T_1	K	Temperature of the syringe (ambient)
T_2	K	Temperature of the mixing cell (after 1st addition dilution matrix gas N_2)
T_3	K	Temperature of the mixing cell (1st expansion step)
T_4	K	Final temperature of the mixing cell (after 2nd addition dilution matrix gas N_2)

4.1 PURITY ANAYSIS

The accuracy achievable by this method depends significantly on the purity of parent gases and balance (dilution matrix) gas used for the preparation of the standard gas mixtures. Furthermore it is important to evaluate critical impurities that may react with relevant components (see paragraph 3.2).

When an impurity, likely to be present in parent gas or dilution gas, is not detectable by the applied analytical method, the mole fraction of the expected impurity shall be set equal to half of the value of the detection limit of used analytical method. The assumption, that there is an equal likelihood for all concentration levels up to its detection limit, is taken. Hence, the content of undetected impurity forms a rectangular distribution from which its standard uncertainty is defined as half of the value of detection limit divided by √3.

4.2 Transfer system

4.2.1 Nature of the materials

Before generating a standard gas mixture via static dilution method, it is advised to further check the suitability of all components of the transfer system. Special consideration shall be given for corrosive gases such as SO_2 and the interaction with metals and possible reactions with elastomers and greases used, for example, in the valve seat and seals. In order to minimize any effect a stainless steel (SS) needle valve is used to adjust the flow rate of the prepared mixtures to the analysers.
Transfer lines made from stainless steel (SS) or glass are suitable for all parent gases considered here.
In any case, it is advised to use short transfer lines to minimize memory effects.

4.2.2 Purging procedure

The mixing cell and the transfer-line integrity, including the leak tightness and cleanliness of all the components should be tested on a regularly basis. Therefore the system shall be purged with dilution matrix gas to guarantee contamination free operation of the preparation system. It is recommended to sequentially pressurize and vent the mixing cell, whereby the transfer system should be flushed continuously with the dilution gas to be used. A shut off valve (SS) is placed in front of the needle valve in order to reduce the risk to damage the needle if used as closing valve. Leak tightness of the transfer system is checked on a continuous basis by recording the humidity of the gas reaching the analysers. Even small leaks can be detected in that way.
The collector unit of the pure gas cylinders and the syringes in use are generally flushed several times with the parent gas (3-8 times, depending on nature of gas) before the syringes are finally filled with slight over pressure to their nominal volume. The syringe is directly, after expansion to ambient pressure, injected "pressure less" into the mixing cell, which is filled with the dilution gas (synthetic air, purified air, or nitrogen 5.0) to nearly ambient pressure, whereby a 2-3 mbar overpressure is applied.

4.2.3 Concentration range and uncertainties

For the preparation of low concentrated gas mixtures of NO below 100 nmol/mol and SO_2 below 150 nmol/mol, it is required to optimize the procedure as given in ISO 6144.

The following improvements have been adopted to achieve acceptable uncertainties, i.e. below 3% :
- Pressure and temperature recording with high accuracy to evaluate equilibrium state of the prepared mixtures,
- Improved detection limits due to enhanced analyser performance by pressure compensated operation,
- Reduced number of dilution steps in using a second, high accurate pressure sensor for the low pressure measurements, or a single instrument with relative uncertainties of less than 0.01% full scale,
- Improved procedure to evaluate the leak rate of mixing chamber,
- Non ideal behaviour of the primary gases should be included by calculating the compressibility factor, which is significant for SO_2 at ambient pressure. This is basically a constant factor with negligible contribution to the uncertainty and therefore not included in the uncertainty calculation, but has a significant effect on the calculated mixing ratio. Depending on the highest pressure used for the dilution matrix, the

compressibility of air or nitrogen should also be considered. This may account for about 0,3% at 10 bar total pressure for air matrix gas for a single step dilution process. For multiple step dilutions with 1/10 (bar/bar) ratios the compressibility factors should be used to calculate the concentration of the final gas mixture. As for the primary gas, the contribution of the uncertainty on the compressibility factor to the total uncertainty is negligible.

The relative contribution of individual parameters influencing the total uncertainty budget could improve slightly the total uncertainty budget, whereby relative contributions could be reduced to nearly insignificant values.

Improvement	Target concentration NO (nmol/mol)	Parameter	Uncertainty contribution (mol/mol)	Relative improvement
Pressure sensor Mensor 2500	20	Low pressure value in dilution step	0.72×10^{-12}	Factor 10
Equilibrium state	20	Temperature record in each dilution step	10.0×10^{-12}	Factor 2

Table 2: Major improvements and relative improvement compared to the process described in ISO 6144

A slight improvement could be achieved for the total uncertainty budget for the dilution process only, even for low concentration mixtures in the range of 20 nmol/mol by using the improved process. An expanded uncertainty of 1.2% could be calculated with 10% improvement.

This value currently does not include the uncertainty contribution due to the dilution matrix purity with respect to the parent gas, calculated by the detection limit of the applied analytical technique. This part is negligible for high concentration standard gas mixtures prepared at 70% of the certification range. For low concentration mixtures this part becomes more and more important and reaches, with a detection limit of 0.47 nmol/mol for test gas concentrations of nitrogen oxide at 20 nmol/mol values (EN 14211) which exceeds the required specifications. Therefore it is not possible to achieve with the current method, standard gas mixtures at concentrations below 40 nmol/mol with an expanded uncertainty below or equal to 3%.

It should be noted that this limitation is not due to the static dilution process itself. It is a more general problem which can only be improved by using analytical instrumentation with higher sensitivity and stable zero readings. The operation of the equipment in a stable temperature and pressure regime helps to improve the detection limit. Currently technical measures are taken to install the analytical instrumentation for the measurement of standard gas mixtures in a climate rack system with low specifications on the allowed temperature variation.

4.2.4 Purging procedure

During the preliminary tests to evaluate the pressure temperature equilibrium state in one of the mixing cells in use it was detected that the operation of the mixing fan has a small influence on the calculated equilibrium.
This behaviour is shown in Figure 2. If the mixing fan located inside the mixing cell is switched on, the pressure and temperature sensors detect a quick change in the measured values with a slight different equilibrium state.
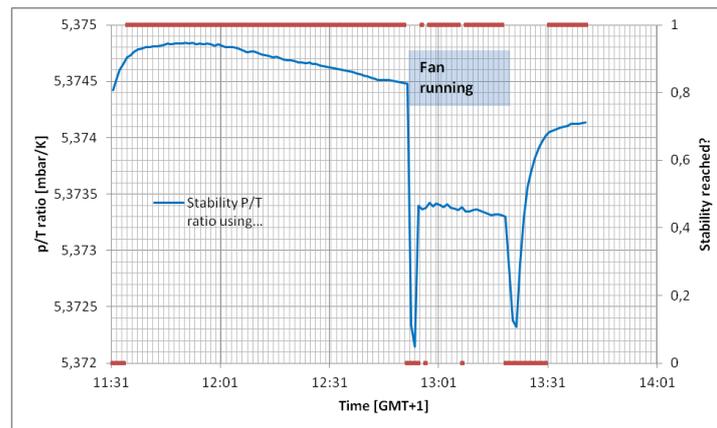
Figure 2: Change in equilibrium state with and without mixing fans

The change in the p/T ratio (blue line) corresponds either to a pressure change of 0.35 mbar (equal to 0.02 %) or a temperature change of less than 0.1 K. The observed decrease of the equilibrium is mainly due to the leak rate of the mixing cell which is small but noticeable. For the preparation and use time of the mixture of about 3h, a maximum loss of substance of about 0.2 mbar is calculated. The relative contribution to the uncertainty is less than 0.1% and currently not considered. However, QA/QC procedures require to test on a regularly basis the loss rate to ensure a gas tight operation with negligible effect on the uncertainty.

For the stability criterion a step function with two values (0 = unstable; 1 = stable) is used and indicated on the graph (Figure 3, red line). The calculation is based on the pressure and temperature values recorded during the dilution process. Therefore a software tool takes the individual data point from the database, calculates the p/T ratio [mbar/K] and compares two individual consecutive data points with the standard deviation of unperturbed measurements in equilibrium. For high pressures above 200 mbar a standard deviation of $7.4 \cdot 10^{-6}$ mbar/K could be obtained and for pressures below 200 mbar the standard deviation is equal to $5,0 \cdot 10^{-7}$ mbar/K. Stability is reached when the absolute difference between two consecutive measurement points is less than 3 times the standard deviation as given above.
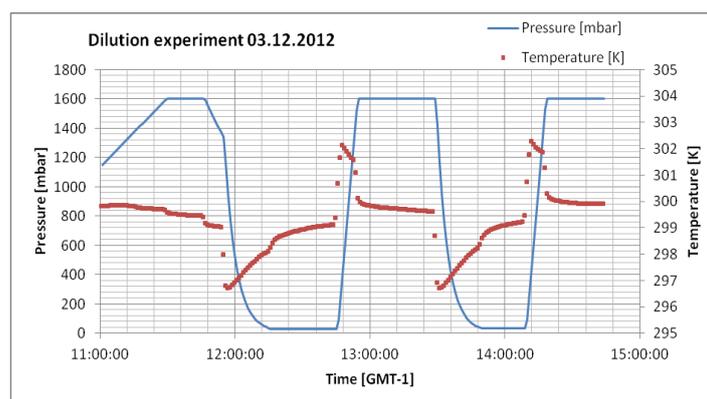
Figure 3: Pressure and temperature changes recorded during flushing of the mixing cell with dilution matrix gas

ISO 6144 requires that temperature changes during the dilution should be smaller than 0.2 K. In practise this is difficult to achieve, as it can be seen on Figure 3. In this diagram the temperature and the corresponding pressure profiles for typical flushing under normal laboratory conditions are given. The evacuation of the reference cell is partly an adiabatic expansion of the gas mixtures and therefore reduces the measured temperature. The minimum

temperature is reached in about 4 minutes with an overall depletion of 3 K. After the minimum is reached, the temperature of the residual gas increases with a much longer time scale and has even after 30 minutes not reached the starting temperature. With start filling the cell with the dilution matrix gas the temperature rises sharply until a maximum value is reached, which is 4 K higher than the value before the buffer gas addition. The buffer gas is added during 10 minutes and the mixture reaches the equilibrium state for P/T ratio within the next 5 minutes after finalizing the buffer gas injection. This equilibrium state is reached much earlier than the temperature and pressure sensors show stable signals. The currently used standard operating procedures (SOPs) based on ISO 6144 requires to wait for the next dilution step sufficient time until the reading of the temperature sensor is stable and does not deviate more than 0.2 K from the starting value. In practise this requirement is difficult to achieve since careful analysis of the temperature data records shows that under normal operating conditions, the difference in temperature is significant higher, partly due to the fact that the buffer gas is adiabatic compressed. The heat transfer to the chamber walls is slow, even with the mixing fan running and the additional heat has increased the cell temperature. In addition, the laboratory temperature generally tends to increase during the dilution process which adds an additional error contribution to the total uncertainty budget. High precision temperature sensors should be used to minimize the contribution of the individual temperature readings to the total uncertainty budget.

4.2.5 Storage

It is recommended to use the prepared standard gas mixtures directly after their preparation with the static dilution method.

4.2.6 Uncertainty budget example

The uncertainty budget for a sample gas mixture preparation at 40 nmol/mol of SO_2 is given as an example in this section.
The model equation used to calculate the expanded uncertainty for a three step dilution process includes the major parameters which have a significant influence on the uncertainty budget. These parameters are, in addition to the pressure and temperature measurements: the primary gas purity, the syringe volume and the mixing chamber volume as summarized in Table 3. The compressibility factors (constant at a given pressure and temperature) used to calculate the composition of the mixture contribute only minor to the total uncertainty and are therefore not included in the model equation. The GUM workbench 2.4 (www.metrodata.de) was used to calculate the uncertainties.

Model Equation:

$C = C_p * V_s / V_d * p_1 / p_2 / T_1 * T_2 * p_3 / p_4 * T_4 / T_3 * p_5 / p_6 * T_6 / T_5$

List of Quantities:

Quantity	Unit	Definition	Contribution in GUM budget
C	mol/mol	SO_2-gas concentration (mixing ratio)	
C_p	mol/mol	Concentration of SO_2 pure gas	Type B rectangular distribution Value: 0.99979 mol/mol Half width of limits: 0.004 mol/mol
V_s	l	Volume of the syringe	Type B rectangular distribution Value: $50 \cdot 10^{-6}$ l Half width of limits: $5 \cdot 10^{-7}$ l
V_d	l	Volume of the vessel	Type A Method of observation: Direct Number of observation: 5 Observations: 14.736 l; 14.733 l; 14.738 l; 14.734 l; 14.737 l Arithmetic Mean: 14.735600 l Standard Deviation: $2.1 \cdot 10^{-3}$ l Standard Uncertainty: $927 \cdot 10^{-6}$ l Degrees of Freedom: 4
p_1	kPa	Ambient pressure	DPI 141 Type B rectangular distribution Value: 101.3 kPa Half width of Limits: 0.005 kPa
p_2	kPa	First dilution step	PACE 1002 Type B rectangular distribution Value: 911.7 kPa Half width of limits: 0.05 kPa
T_1	K	Temperature at the beginning	Type B rectangular distribution Value: 293 K Half width of limits: 0.25 K
T_2	K	Temperature at the 1. dilution step	Type B rectangular distribution Value: 293.6 K Half width of limits: 0.25 K
p_3	kPa	Pressure after blow off (expansion)	Type B rectangular distribution Value: 300 kPa Half width of limits: 0.02 kPa
p_4	kPa	Second dilution step	Type B rectangular distribution Value: 700 kPa Half width of limits: 0.04 kPa
T_4	K	Temperature after 2. dilution step	Type B rectangular distribution Value: 293.6 K Half width of limits: 0.25 K
T_3	K	Temperature before 2. dilution step	Type B rectangular distribution Value: 293 K Half width of limits:: 0.25 K
p_5	kPA	Pressure after blow off (expansion)	Type B rectangular distribution Value: 200 kPA Half width of limits: 0.02 kPA
p_6	kPa	Third dilution step	Type B rectangular distribution Value: 800 kPa Half width of limits: 0.04 kPa
T_6	K	Temperature after 3. dilution step	Type B rectangular distribution Value: 293 K Half width of limits: 0.25 K

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Quantity	Unit	Definition	Contribution in GUM budget
T_5	K	Temperature before 3. dilution step	Type B rectangular distribution Value: 293 K Half width of limits: 0.25 K

Table 3: List of quantities used to calculate the uncertainty of a standard gas mixture at a nominal concentration of about 40 nmol/mol

C: SO_2-gas mixing ratio

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
C_p	0.99979 mol/mol	$2.31 \cdot 10^{-3}$ mol/mol	rectangular	$41 \cdot 10^{-9}$	$94 \cdot 10^{-12}$ mol/mol	13.3 %
V_s	$50.000 \cdot 10^{-6}$ l	$289 \cdot 10^{-9}$ l	rectangular	$810 \cdot 10^{-6}$	$230 \cdot 10^{-12}$ mol/mol	83.1 %
V_d	14.735600 l	$927 \cdot 10^{-6}$ l	normal	$-2.8 \cdot 10^{-9}$	$-2.6 \cdot 10^{-12}$ mol/mol	0.0 %
p_1	101.30000 kPa	$2.89 \cdot 10^{-3}$ kPa	rectangular	$400 \cdot 10^{-12}$	$1.2 \cdot 10^{-12}$ mol/mol	0.0 %
p_2	911.7000 kPa	0.0289 kPa	rectangular	$-44 \cdot 10^{-12}$	$-1.3 \cdot 10^{-12}$ mol/mol	0.0 %
T_1	293.000 K	0.144 K	rectangular	$-140 \cdot 10^{-12}$	$-20 \cdot 10^{-12}$ mol/mol	0.6 %
T_2	293.600 K	0.144 K	rectangular	$140 \cdot 10^{-12}$	$20 \cdot 10^{-12}$ mol/mol	0.6 %
p_3	300.0000 kPa	0.0115 kPa	rectangular	$140 \cdot 10^{-12}$	$1.6 \cdot 10^{-12}$ mol/mol	0.0 %
p_4	700.0000 kPa	0.0231 kPa	rectangular	$-58 \cdot 10^{-12}$	$-1.3 \cdot 10^{-12}$ mol/mol	0.0 %
T_4	293.600 K	0.144 K	rectangular	$140 \cdot 10^{-12}$	$20 \cdot 10^{-12}$ mol/mol	0.6 %
T_3	293.000 K	0.144 K	rectangular	$-140 \cdot 10^{-12}$	$-20 \cdot 10^{-12}$ mol/mol	0.6 %
p_5	200.0000 kPA	0.0115 kPA	rectangular	$200 \cdot 10^{-12}$	$2.3 \cdot 10^{-12}$ mol/mol	0.0 %
p_6	800.0000 kPa	0.0231 kPa	rectangular	$-51 \cdot 10^{-12}$	$-1.2 \cdot 10^{-12}$ mol/mol	0.0 %
T_6	293.000 K	0.144 K	rectangular	$140 \cdot 10^{-12}$	$20 \cdot 10^{-12}$ mol/mol	0.6 %
T_5	293.000 K	0.144 K	rectangular	$-140 \cdot 10^{-12}$	$-20 \cdot 10^{-12}$ mol/mol	0.6 %
C	$40.552 \cdot 10^{-9}$ mol/mol	$257 \cdot 10^{-12}$ mol/mol				

Table 4: Individual contributions to the total uncertainty budget calculated by the GUM workbench

As it can be seen from the Index column for the improved method, only purity and the syringe volume have a significant influence on the uncertainty budget. Pressure and temperature readings, even for multiple dilution steps, are nearly negligible and therefore the preparation of low mixing ratios is not limited by the preparation methods. The required uncertainty of about 3% could be reached with this technique.

Results for the mixing ratio:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
C	~$40 \cdot 10^{-9}$ mol/mol	1.3 % (relative)	2.00	manual

The contribution which is due to the determination of the target gas concentration in the used matrix or zero gas is not considered in the uncertainty calculation.

The analytical equipment used has a detection limit of 0.36 nmol/mol (SO_2) and has for low mixing ratios a major influence on the total uncertainty budget, as outlined for NO in paragraph 4.2.3.

Additional contributions considered to uncertainty budget:
1. Standard deviation at 159 nmol/mol: 0,36 nmol/mol
2. Standard deviation at 40 nmol/mol: 0,22 nmol/mol

4.3 HOMOGENEITY OF 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 7504:2001 [5] as the "state of a gas mixture wherein all of its components are distributed uniformly throughout the volume occupied by the gas mixture".
The non homogeneity of the gas mixtures can be detected by following the measured values during its use. The standard deviation of the values measured with the monitors to follow the trace gas concentrations should not differ from those obtained using pressurized cylinders and no trends should be found during the measurement. This should be checked on a regularly basis.

4.4 STABILIZATION TIME

The stabilization time depends on the used instrumentation. The values given from the manufactures or as given in the corresponding EN standards should be followed. Trend analysis, see paragraph 4.3, helps to detect problems arising from not equilibrated instrumentation. The enclosure in a temperature controlled housing and the operation of pressure stabilized instruments minimize times required to stabilize the measured signals and improve the long term stability of the measurements.

5. CONCLUSION

The static dilution method for the preparation of low mixing ratios is an accurate and especially valuable method achieving lowest mixing ratios, using multiple static dilution steps. Currently the preparation of those gas mixtures is not limited by the accurate pressure and temperature measurements preformed to calculate the correct mixing ratios. The used compounds cover only stable organic and inorganic gases which do not react on the surfaces of the mixing cell and the sample tubes. The applicability for a special gas can be checked easily by measurements over a longer time period which should not show any trend in the recorded data.

Nevertheless it is important to take several points into account during the preparation process.

- It is recommended to apply pressure and temperature measurement sensors with high long term stability and high accuracy to minimize the contribution of the individual readings to the uncertainty budget of the prepared mixing ratios.

- A continuous recording of pressure and temperature inside the cell as well as the ambient conditions for p and T with similar accuracy is necessary to observe and check the stability of the gas mixture.

- Special precautions should be taken to detect temperature gradients within the cell. This can be checked if a mixing fan is located inside the dilution chamber. The P/T ratio can be used as a criterion to follow the stability of the diluted gas mixture because it is proportional to the amount of gas enclosed inside the mixing chamber and should only change if either the system is not in equilibrium or the gas mixture is lost by leakage. If the mixing fan is switched on and off and the p/T ratio is stable, the system is in equilibrium and no temperature gradient exists. Nevertheless minor changes can always be found whereby the magnitude of the change in the P/T-value can be calculated as an additional contribution to the uncertainty either of the temperature or pressure readings. Homogeneous and stable environmental conditions, especially with respect to temperature, help to minimize those effects.

In addition to the preparation of standard gas mixtures from pure compounds, gases or liquids for hydrocarbons, the method can be applied to prepare low concentration mixtures using Certified Reference Materials (CRM) with relative uncertainties lower than 1%. The accuracy of the static dilution process in this case is high enough so that the dilution process itself does not contribute significantly to the uncertainty of the diluted mixture even if multiple dilution steps are involved. Under these circumstances the relative expanded uncertainty is dominated by the uncertainty of the CRM and the analyte concentration in the dilution gas which for low concentrations is limited by the detection limit of the applied measurement techniques.

The static dilution method covers in amount of substance fraction range and the associated uncertainties 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 and the relevant EN standards (EN 14211 and EN 14212) for preparing standard gas mixtures for the calibration of gas analyzers. Limitations arise by the uncertainty associated with the determination of detection limit of the target compound in the dilution matrix gas for low concentrated gas mixtures.

6. REFERENCES

[1] http://ec.europa.eu/environment/air/quality/legislation/existing_leg.htm

[2] EN 14211:2012. Ambient air quality - Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence

[3] EN 14212:2012. Ambient air quality - Standard method for the measurement of the concentration of sulphur dioxide by ultraviolet fluorescence

[4] ISO 6144:2006. Gas analysis – Preparation of calibration gas mixtures – Static volumetric method

[5] ISO 7504:2001. Gas analysis - Vocabulary