Instituto Português da Qualidade

Laboratório Central de Metrologia

UNCERTAINTY CALCULATION IN DYNAMIC GENERATION OF PRIMARY GAS MIXTURES

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ABSTRACT

The production of reference gas mixtures of environmental pollutants is an area that has been widely developed in recent years at the Instituto Português da Qualidade (IPQ) to ensure traceability at national level of the amount of pollutants present in the air. Dynamic Generation processes follow the international standard ISO 6145 [1] and include techniques to produce toxic gases in air at concentrations equivalent to those found currently in ambient air and workplace environments. Preparation of gas mixtures at the low-molar fraction (ppb (10^{-9} mol/mol)) can be achieved through the application of permeation techniques (ISO 6145-10) [2]. This technique is used for reactive unstable mixtures in low concentrations. In this work, emphasis is given to the technique of dynamic generation of gas mixtures of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2), in air. These gases are indicators of air quality and are found in atmosphere in molar fraction close to nmol/mol order of magnitude.

This communication describes the uncertainty calculation in dynamic generation process. The uncertainties have been calculated in accordance with GUM - Guide to the expression of uncertainty in measurement [3]. The uncertainty sources have been estimated and the combined uncertainty of the measurements was calculated. The expanded uncertainty is expressed by the combined uncertainty of measuring multiplied by the coverage factor (*k*) in order to correspond to a confidence interval of approximately 95 %.

INTRODUCTION

The work developed in the scope of the dynamic generation method was the production of reference gas mixtures of nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) in air, according to ISO 6145:10 [2]. Different mixtures were generated in the molar fraction range (40 – 200) $\times 10^{-9}$ mol/mol.

The analytical method defined for sulfur dioxide determination is molecular fluorescence and for nitrogen dioxide is chemiluminescence.

The molar fraction of each mixture is obtained by the equation:

$$x_A = \frac{q_m \times M_{total}}{q_{v,total} \times \rho_{total} \times M}$$

Where q_m is the permeation rate, $q_{v,total}$ is the total flow of the carrier gas and the diluting gas, ρ_{total} and M_{total} are the total density and total molar mass of the carrier gas and the diluter gas.

The permeation rate was determined from the slope of linear relationship between the mass losses of permeation tube and elapsed time.

Cooled nitrogen was used as carrier gas and the diluter gas was purified air.

All equipments and instruments used were calibrated by competent entities in order to ensure the traceability of the results.

Measurement uncertainty of the results obtained by dynamic generation was calculated according to GUM [3] and the main contributions were analysed.

UNCERTAINTY CALCULATION

The uncertainties of the dynamically generated mixtures were calculated according to standard 6145:10 [2] and the Guide to the Expression of Uncertainty in Measurement - GUM [3]. The measurement uncertainty associated with the input quantities are classified by how they are estimated as follows: "Type A" or "Type B". The sources of uncertainty with the greatest impact are the uncertainty in determining the permeation rate, the flow of carrier gas and diluter gas, the weight, the measurement of pressure, temperature and humidity. The uncertainty due to possible leaks and the presence of impurities and time measurement uncertainties are smaller contribution to the final uncertainty.

Uncertainty of permeation rate

The permeation rate is a type A uncertainty, determined by calculating the slope between the mass of the permeation tube, in grams, and time elapsed and is given by the equation:

$$u_{RP} = \frac{\sqrt{\frac{1}{(n-2)} \times \left[\sum (y-\bar{y})^2 - \frac{\left[\sum (x-\bar{x})(y-\bar{y})\right]^2}{\sum (x-\bar{x})^2} \right]}}{\sum (x-\bar{x})^2}$$

Where x is the time and y is the mass of the permeation tube, and $\bar{y}$, $\bar{x}$ their averages, respectively. *RP* is the permeation rate given in grams per liter.

Uncertainty of carrier and diluting gas flows

The uncertainty associated with the flow of carrier and diluting gas is calculated by the combined uncertainty due to momentary fluctuations in the flow meter and the calibration. The thermal flow controllers are strongly temperature dependent, so fluctuations in temperature originate fluctuations in the flow. The uncertainty caused by fluctuations is about 10 % of the variation of room temperature. It is an uncertainty of type B and follows a rectangular distribution.

$$u_{flut} = \frac{0{,}1 \times \Delta T}{\sqrt{3}}$$

ΔT is the temperature variation.

The uncertainty from the calibration is of type B and follows a normal type probability distribution.

$$u_{cal} = \frac{U_{cc}}{k}$$

Where *k* is the coverage factor and U_{cc} the expanded uncertainty presented in the calibration certificate.

The combination of these two uncertainties leads to uncertainty associated with each flow controller:

$$u_{flow} = \sqrt{u_{flut}^2 + u_{cal}^2}$$

which will later be converted to relative uncertainty by dividing by the minimum flow rate of each gas used in their analysis.

Uncertainty from the pressure reading, temperature and humidity

The uncertainty from the measurement of temperature, pressure and humidity are also recorded. These uncertainties are Type B, with a normal type probability distribution (are from the calibration certificate for each equipment) and are calculated according to:

$$u_{cond} = \frac{U_{cc}}{k}$$

Where *k* is the coverage factor and U_{cc} is the expanded uncertainty presented in the calibration certificate.

Uncertainty in the weighing tube

The uncertainty due to periodic weighing of the permeation tube counts with the uncertainty from the maximum error in the balance, the air impulsion and equipment calibration. All uncertainties are Type B, the first two follow a rectangular distribution and the latter follows a normal distribution. The contribution from the balance error and of air impulsion is calculated according to the equation:

$$u = \frac{y}{\sqrt{3}}$$

In the uncertainty from the error of scale "*y*" takes the value of "0,1 mg", which is the maximum error of the scale. In the uncertainty of air impulsion from "*y*" is calculated according to the expression (ρ_{max}-ρ_{min}) × V_{tube}.

The relative contribution to the calibration of the balance is calculated by the uncertainty expressed in the calibration certificate, divided by the coverage factor, since it follows a normal distribution.

The uncertainty in weighing is given by:

$$u_{weighing} = \sqrt{u_{erro}^2 + u_{imp}^2 + u_{cal}^2}$$

Uncertainty of time and leakage

The uncertainty arising from leaks at the one associated with the measurement of time are both type B and follow a rectangular distribution. They are calculated according to the expression

$$u_{leak/time} = \frac{y}{\sqrt{3}}$$

Since the value of *y* is the maximum error and is 0,1 nmol/mol in the first case and 5 min in the second.

The relative uncertainty due to leakage is the uncertainty divided by the minimum concentration measured by the analyzer. The relative uncertainty in the measurement of time is given by the uncertainty associated with the measurement of time divided by the average time between weighings.

Uncertainty arising from the presence of impurities

The main sources of impurities in this work are the permeation tube, the carrier gas and diluter gas. These uncertainties are Type B, following a rectangular distribution and can be calculated according to the equation:

$$u_{imp} = \frac{V_{imp}}{\sqrt{3}}$$

The volumes of impurities in the air, in the nitrogen and in the permeation tube considered were 0,5 ml; 0,2ml and 0,02 ml, respectively. Since the first results from a study carried out by the Netherlands National Metrology Laboratory (VSL) and other are from technical specifications of the manufacturer.

All uncertainties are converted in relative uncertainties.

The relative combined uncertainty of the method is calculated according to the equation :

$$u_{r,comb} = \sqrt{u_{r,flow}^2 + u_{r,RP}^2 + u_{r,leak}^2 + u_{r,time}^2 + u_{r,imp}^2 + u_{r,cond}^2 + u_{r,weighing}^2}$$

The relative expanded uncertainty was calculated by multiplying the combined uncertainty on the coverage factor *k*.

$$U_r = K \times u_{r,comb}$$

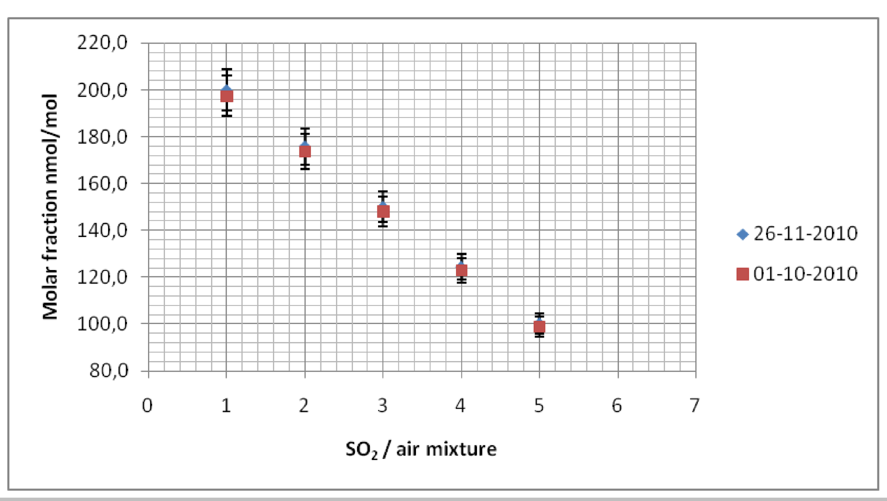
RESULTS

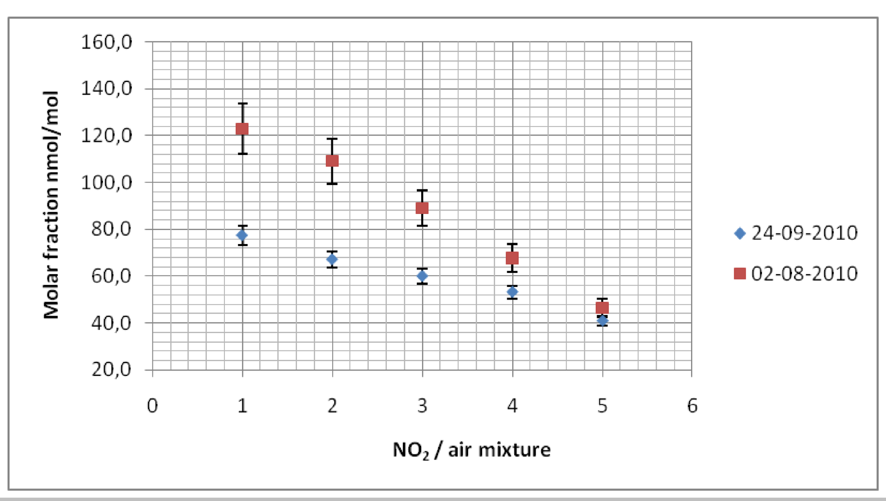
SO_2 mixtures

2010-11-26					
x nmol/mol	199,9	175,8	150,0	124,3	100,2
U nmol/mol	8,8	7,7	6,6	5,5	4,4
U_r %	4,4	4,4	4,4	4,4	4,4
2010-10-01					
x nmol/mol	197,3	173,6	148,1	122,8	98,9
U nmol/mol	8,6	7,5	6,4	5,3	4,3
U_r %	4,3	4,3	4,3	4,3	4,3

NO_2 mixtures

2010-09-24					
x nmol/mol	77,4	67,1	60,0	53,2	40,9
U nmol/mo	4,0	3,5	3,1	2,8	2,1
U_r %	5,2	5,2	5,2	5,2	5,2
2010-08-02					
x nmol/mol	123	109,1	89,0	67,8	46,4
U nmol/mo	11	9,5	7,8	5,9	4,0
U_r %	8,7	8,7	8,7	8,7	8,7





CONCLUSIONS

The choice of these systems presents an advantage comparing to the static system that is the possibility to modify the ratio of compound/carrier gas during the preparation process. The method is versatile and practical to produce reference gas mixtures, especially for reactive and unstable mixtures. It is however a method with relatively high uncertainty, it has many sources of uncertainty, over 4 % for SO_2 and more than 5% for NO_2, as this gas is highly unstable.

REFERENCES

[1] ISO 6145 – "Gas Analysis – Preparation of calibration gas mixtures – Dynamic volumetric methods", 1986.

[2] ISO 6145-10 – "Gas Analysis – Preparation of calibration gas mixtures using dynamic volumetric methods Part 10: Permeation method", 2002.

[3] Guide to the expression of uncertainty in measurement – GUM, BIPM et al., 1993.