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Traceable Dynamic Generation of Reactive Air Pollutants at Limit Values

Standard gas mixtures of reactive pollutants, such as nitrogen oxides and ammonia in nitrogen, are not stable at limit ambient levels in pressurized cylinders due to absorption, residual impurities and surface catalysed reactions. METAS has built up a traceable mobile permeation generator (TMPG) and a new two-step gas dilution system that allow generating dynamically and in-situ SI-traceable binary gas mixtures at ambient fractions. The TMPG was validated as travelling standard for producing NO_2 gas mixtures and used for the MACPoll measurement comparison. The long term stability of the generated NO_2 amount fractions is shown. For generating NO standard gas mixtures at ambient levels the two-step diluter based on the most recent digital CMOSens mass flow controllers from Sensirion was realized. For both methods all input quantities are metrologically traceable to National Standards. They are used to calibrate the chemiluminescence comparator (CLD) for NO_2 and NO and to transfer METAS reference values.

Introduction

In the framework of the MACPoll project METAS has realized and characterized: (1) a permeation generator (TMPG) with state of the art control of temperature, pressure and flow and (2) a new two-step dynamic dilution method. The aim of the project was to reach 3% uncertainty at limit values of the EU air quality directive for NO_2 NO and SO_2 [1]. The state of art for the realisation of the standards at limit values and their analysis were demonstrated in a multilateral comparison among the MACPoll partners using the TMPG as travelling standard for NO_2 and the dilution system to calibrate the NO CLD-analyser of the METAS laboratory.

Traceable mobile permeation generator (TMPG)

The TMPG is a calibrator for the production of reference gas mixtures with the permeation method, e.g. of NO_2, with all input quantities being traceable to national standards. State of the art components are used and the best possible concerning stability and representativeness. The set-up is designed to isolate the gas mixture generation process completely from ambient conditions.

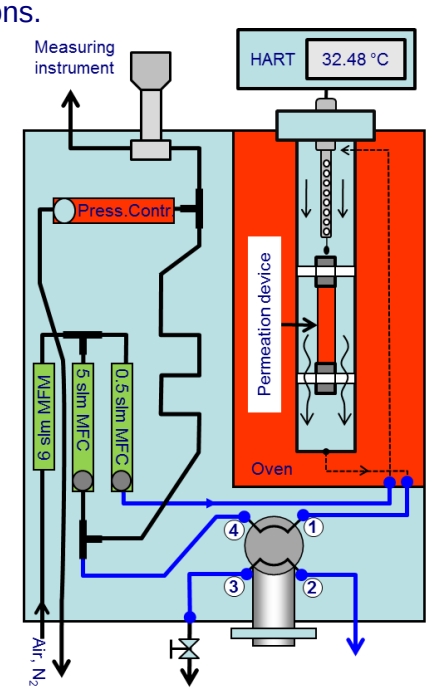

Fig.1: Flow schematics of 'Traceable mobile permeation generator' (TMPG)

The TMPG was used for the EMRP project MACPoll, work package 1 (WP1) comparison as travelling standard [2]. Two reference gas mixtures for NO_2 at 20 and 76 nmol/mol in synthetic air were produced at the four participating metrology institutes. The set values for the permeation temperature, the total carrier- and dilution gas flow and pressure were identical. From their actual values and the permeation rate closest to the dates of measurement the generated fractions were calculated for each laboratory.

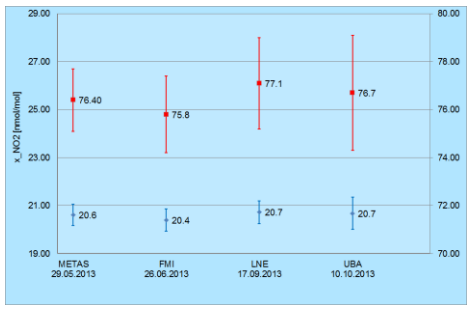

Fig.2: Reproducibility of the two generated x_{NO2} at the four labs during the MACPoll comparison over a time period of 4.5 months

The mean and the experimental standard deviation of the generated x_{NO2} values, expressed as relative reproducibility, were:

x_{NO2}	s_{rel}
(nmol/mol)	(%)
20.61	0.11
76.50	0.47

Table 1: Mean and standard deviation of the generated x_{NO2} values at the participating laboratories during the five months time period

With stated relative uncertainties realised by METAS of **2.2 %** and **1.7 %** for the two amount fractions the results mean a very good reproducibility of the generator in view of the different operators, locations and zero air used and the time period of 5 months. The permeation rates of the permeator were determined three times during the comparison and were within the stated uncertainties [3].

With the availability of reproducible, traceable and stable NO_2 reference mixtures at ambient ground levels NO_2 analysers can be directly calibrated and the observed discrepancies to NO gas phase titration be eliminated [4].

Besides the permeation rate the stability and reproducibility of the input quantities temperature, gas flow and pressure of the TMPG were extensively validated. The storage of the permeation device after weighing and the possible influence of its vertical orientation in the magnetic suspension balance versus horizontal in the TMPG were investigated.

Two-step dilution device

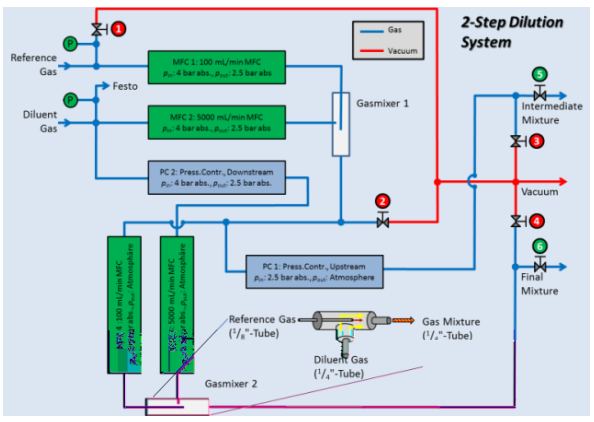

Fig.3: Flow schematics of two-step-dilutor, detail: gas mixing device ensuring homogeneous mixtures

Even in specially prepared gas cylinders, gravimetric gas mixtures of NO in the nmol/mol range showed unexpected reductions in concentration [5]. The most promising approach to reach low uncertainties is by diluting mixtures of higher concentrations. Starting from gravimetric mixtures around 50 µmol/mol two dilution steps are necessary to reach the lower amount fraction of 20 nmol/mol of the MACPoll comparison.

Repeatability and stability experiments by diluting a 150 µmol/mol gravimetric NO mixture show very quick response (< 1 minute), ultra stable and repeatable mixtures (< 0.1 %) and very low NO_2-formation even with air as diluent gas.

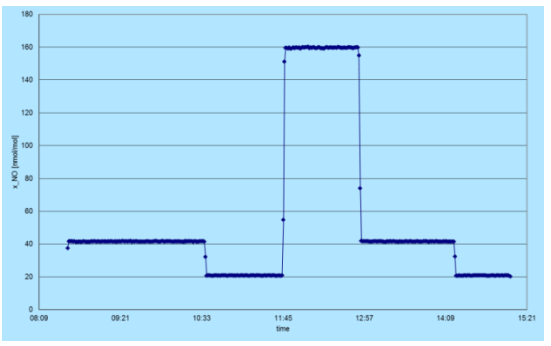

Fig.4: Indicated x_{NO} values of the repeatability and stability tests at 20, 40 and 160 nmol/mol in nitrogen

The validity of the dilution system has been demonstrated in the current comparison for NO at 20 and 100 nmol/mol. A gravimetric mixture with (20.305 ± 0.203 (k=2)) µmol/mol NO from the METAS set of national gas mixture standards was diluted to the two ambient levels. The degree of equivalence and the stated uncertainties were excellent [3].

Conclusions

Dynamic methods have the potential for primary generation of gas mixtures in the nmol/mol-range for reactive gas components. They can even be realized in form of mobile devices. Theoretical and experimental uncertainty evaluations show that 3 % relative expanded uncertainty can be achieved at limit values.

Acknowledgements

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References

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[2] www.macpoll.eu
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[5] International comparison CCQM-K26a: Nitrogen monoxide, 720 nmol/mol

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