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Concepts and challenges in the dynamic generation of SI-traceable nitrogen dioxide reference gas mixtures at ambient air amount fractions

Daiana Leuenberger, Myriam Guillevic, Céline Pascale, Guillaume Baur, Andreas Ackermann, and Bernhard Niederhauser

Federal Institute of Metrology METAS, Laboratory Gas Analysis, Bern, Switzerland (daiana.leuenberger@metas.ch)

Nitrogen dioxide (NO_2) is an important trace gas in the atmosphere playing a key role in ozone and secondary particle formation, acidification and eutrophication. Furthermore, it changes the oxidative capacity of the atmosphere and is thus negatively affecting air quality and climate. Atmospheric concentrations are strongly affected by exhaust gas emissions from fossil fuel combustion in motor vehicles, airplanes, firings and power stations. Upper emission limits for annual nitrogen oxides (NO_x, the sum of NO_2 and nitrous oxide (NO)) emissions in the European Union are regulated in the National Emission Ceilings (NEC) Directive 2016/2884/EU. In addition to environmental impacts, NO_2 can affect the human respiratory system at long-term exposure to NO_2 concentrations above the legal annual immission limits ($NO_2 \leq 40\ \mu g \cdot m^{-3}$ ($NO_2 \leq 21.28\ nmol \cdot mol^{-1}$)) according to Air Quality Directive 2008/50/EC). 98 % of measurement stations with values above the annual limit values were urban (or suburban). Therefore, reductions in NO_2 concentrations need to be focused on traffic (particularly on diesel powered motor vehicles) and urban locations for the annual limit value to be met.

To control the effectiveness of emission reduction measures and mitigation policies the data obtained by air quality networks have to be sufficiently accurate to capture small trends with lowest possible uncertainty and the comparability of the data needs to be improved. Currently applied measurement techniques measure NO_2 indirectly as the difference between NO and total NO_x which leads to uncertainties $\geq 10\%$.

In the framework of the European Metrology Programme for Innovation and Research (EMPIR) project on the topic "Metrology for Nitrogen Dioxide" ($MetNO_2$), European national metrology institutes have joined to deliver a highly accurate measurement infrastructure, traceable to the international system of units (SI), to underpin direct measurements of atmospheric NO_2.

To achieve comparability in the NO_2 data obtained at different monitoring stations, all measurements have to be made traceable to the SI by calibrating measurement instruments with SI-traceable reference material, i.e. NO_2 gas mixtures at the relevant amount of substance fractions (10 – 500 nmol mol^{-1}) with a relative expanded uncertainty $U_{NO2} \leq 1\%$ ($k = 2$ or 95 % confidence interval).

Here, we present the primary method as well as a field deployable transfer method developed to dynamically generate NO_2 reference gas mixtures for the calibration of analysers. The methods are making use of the temperature and pressure dependent permeation of the pure substance liquefied in a tube (here NO_2) through a selective polymer membrane into a constant flow of carrier gas. Subsequently, this mixture is diluted with a system of thermal mass flow controllers in one or two consecutive steps to desired ambient air amount fractions of the order nmol mol^{-1} (ppb). All components are fully traceable to SI standards. The challenge lies in the characterisation and reduction of the major uncertainty contributions. These are the purities of the matrix gas and of NO_2 in the permeation tube and the quantification of associated impurities, e.g. nitric acid (HNO_3) and dinitrogen tetroxide (N_2O_4).