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Long term stability of dynamic reference systems for NO_2 atmospheric monitoring

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The long-term monitoring of reactive gases, such as NO_2, provides significant challenges for the development of gas standards that can demonstrate fit-for-purpose stability and accuracy. Over the last fifteen years the BIPM's primary gas facility for the dynamic production of mixtures of nitrogen dioxide in nitrogen, operating over the range (1 µmol/mol to 15 µmol/mol) has been shown to operate with a relative standards uncertainty of 0.4%. The system is based on continuous weighing of a permeation tube and on the accurate impurity quantification and correction of the gas mixtures using FT-IR.

The operation of the system has been demonstrated in two international comparisons organized by the CCQM Working Group on Gas Analysis (CCQM-GAWG), in 2009 and 2018, with the former demonstrating the requirement to correct for HNO_3 impurities in gas standards produced in cylinders, and the more recent, the potential for non-linear decay in NO_2 concentration in gas cylinder standards in the first 100 to 150 days following their production.

The CCQM-K74 (2009/2010) was organized, with all cylinders prepared by the one NMI (VSL) with the same surface treatment and characterized for stability and with reference values provided by the BIPM dynamic reference facility. The initial comparison identified small decay rates in the circulated standards, accounted for by the addition of an uncertainty to the reference value, and calculated to have been no more than 0.1 nmol/mol per day loss of NO_2. However, the 2009 comparison did not examine standards maintained by individual participating institutes directly. The protocol of the CCQM-K74.2018 comparison, was modified so that the standards prepared by participating institutes (two per participant), were all directly measured at the BIPM against its dynamic reference facility. The modified protocol, although technically more challenging, has allowed the different decay rates in different cylinder preparations from different institutes to be identified, as well as the time dependence of these days rates.

The work has highlighted the challenges in NO_2 standard development, and that fit-for-purpose standards can be obtained following appropriate protocols. Further development of these protocols is the focus of a number of research programmes, for example METNO2 and MetroPEMS projects within the EMPIR programmes. Further activities at the BIPM facility are focused on validating the performance of NO_2 dynamic reference systems below 1 µmol/mol and into the nmol/mol range, with the comparison of different dynamic reference systems, in support of future international comparisons and knowledge transfer activities.