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1 Overview

More accurate measurements of nitrogen dioxide (NO_2) were needed in order to understand population level exposure, to improve air quality models and emission inventories, to better discern long-term trends in NO_2 concentrations and to enforce air quality and vehicle emission legislation. This was essential for the timely evaluation of air pollution mitigation policies, and to improve our understanding of the influence of anthropogenic emissions on the climate system. This project achieved the necessary accuracy by developing and validating capabilities for the direct measurement of NO_2 using newly available selective NO_2 techniques, characterising the critical impurities (nitric acid and water vapour) and applying direct calibration with more accurate and stable primary reference standards of NO_2.

2 Need

Nitrogen dioxide (NO_2) is the air pollutant considered to have one of the greatest impacts on human health. A major source of NO_2 in cities is from fossil fuel combustion in motor vehicles. Diesel powered vehicles emit twenty times more NO_2 compared to their petrol-powered equivalent. In Europe, NO_2 in the air we breathe is becoming a massive issue due to large increases in diesel vehicle ownership, resulting from government driven tax incentives, in conjunction with emission standards not delivering the expected reductions under real world driving conditions. This was highlighted by the Volkswagen emissions scandal, recent health reports linking NO_2 exposure with adverse health outcomes and the continuing breach of annual mean and hourly limit values (NO_2 amount fraction maxima) set by European Union (EU) legislation (2008/50/EC), in the majority of EU member states. NO_2 emissions in Europe are not decreasing fast enough and lower NO_2 concentrations are needed in the future to improve the quality of life for European citizens and to reduce the economic burden of detrimental health outcomes resulting from exposure to NO_2. To enable this required greater confidence in measured trends in emissions and ambient air leading to better evidence-based policy and more effective mitigation policies, which are strongly dependent on measurement accuracy. At the outset of the project, to achieve the necessary improvements in measurement accuracy required the:

- Direct measurement of NO_2, because previous methodologies to measure it indirectly as the difference between NO and total NO_x were no longer fit for purpose because of their high uncertainties, e.g., > 10 %.
- Calibration of instruments with high accuracy NO_2 calibration gases at atmospherically relevant amount fractions, e.g., 10 nmol/mol – 500 nmol/mol. Current NO_2 reference standards were not sufficiently accurate or stable enough to fulfil the requirements of the monitoring community.
- Full characterisation and minimisation of impurities, such as water vapour and reactive nitrogen compounds (e.g., nitric acid), in reference materials, which increased uncertainty and decreased long-term stability.

3 Objectives

The overall objective of this project was to deliver a high accuracy SI traceable measurement infrastructure to underpin direct measurements of NO_2 amount fractions in the atmosphere to meet the Data Quality Objectives (DQOs) established by the World Meteorological Organisation Global Atmospheric Watch (WMO-GAW) programme. The project increased the accuracy and stability of NO_2 reference standards, which was challenging due to the highly reactive nature of NO_2. This required a more comprehensive characterisation of the impurities formed unintentionally during the preparation of reference standards, most importantly nitric acid (HNO_3) and the development of new methods designed to suppress the formation of critical and significant impurities. New and existing selective spectroscopic NO_2 measurement techniques were developed, characterised and validated with reference to the standard chemiluminescence method (EN 14211:2012).

The project was structured into the following objectives:

1. To develop high concentration traceable static reference standards for NO_2 (1 µmol/mol - 10 µmol/mol) with a target uncertainty of ≤ 0.5 % and stability of ≥ 2 years. To achieve these challengingly low uncertainties required the full characterisation of critical impurities and the development of new methods to minimise their formation during static standard preparation.
2. To develop high accuracy traceable dynamic reference standards for low amount fractions of NO_2 (10 nmol/mol – 500 nmol/mol) with a target uncertainty of ≤ 1 %. To achieve these challengingly low uncertainties required the full characterisation of critical impurities and the development of new methods to minimise their formation during dynamic standard preparation.

3. To develop analytical methods to quantify the main impurities formed unintentionally during the preparation of static and dynamic NO_2 reference standards. To validate selective spectroscopic methods for directly measuring NO_2 and compare them with the standard reference method as described in EN 14211:2012, using field trials at an atmospheric simulation chamber.
4. To engage with stakeholders to ensure the uptake of the reference standards, calibration methods and devices developed in this project by standards development organisations, atmospheric monitoring networks, speciality gas companies, instrument manufacturers and other measurement infrastructures.

4 Results

4.1 To develop high concentration traceable static reference standards for NO_2 (1 µmol/mol – 10 µmol/mol) with a target uncertainty of ≤ 0.5 % and stability of ≥ 2 years. To achieve these challengingly low uncertainties will require the full characterisation of critical impurities and the development of new methods to minimise their formation during static standard preparation.

Measurement accuracy is strongly dependent on the analytical methods employed and on the quality of the calibration gases used. Recent advances in selective NO_2 measurement techniques mean there is an urgent requirement to characterise and evaluate the applicability of these methodologies for long-term measurements and for the provision of appropriate reference standards of NO_2. High accuracy static reference gas standards in high pressure cylinders are needed for the direct calibration of instruments and also to provide independent validation of dynamic generation methods. The development of new primary standards of NO_2 will support the long-term global monitoring of atmospheric NO_2 for air quality and climate applications by ensuring stable, comparable and coherent datasets from national, regional and global monitoring stations and other mobile measurement platforms. Producing accurate and stable NO_2 reference standards is challenging because NO_2 is very reactive and can convert into other reactive nitrogen (NO_y) compounds, which reduces stability and increases uncertainty. There are two ways of preparing NO_2 standards. This can be from a dilution of a higher amount fraction NO_2 standard or from a pure nitrogen monoxide (NO) source. NO reacts spontaneously with oxygen (O_2) to form NO_2. One of the largest sources of problems in the preparation of static standards is the presence of water (H_2O) which reacts with NO_2 creating nitric acid (HNO_3). The reaction mechanism shown below for the hydrolysis of NO_2 under atmospheric conditions is well described in the literature to yield equimolar amounts of nitric acid (HNO_3) and nitrous acid (HNO_2):

$$2\ NO_2 + H_2O + \text{surface} \rightarrow HNO_3 + HNO_2$$

This reaction is thermodynamically favourable and is expected to proceed until one of the reactants is consumed. Due to the ubiquity of water (H_2O) and its affinity for surfaces, NO_2 hydrolysis within high pressure cylinders is expected to be a serious problem. The state of the art prior to this project for static primary reference standards of NO_2 was demonstrated by a key comparison CCQM-K74 that showed comparability broadly within 3 % for 10 µmol/mol NO_2 in nitrogen standards. This comparison assessed the NMIs abilities to value assign a traveling standard. In CCQM-K74, highly variable but non-negligible amounts of nitric acid (HNO_3; 1 % – 4 %) were observed in 10 µmol/mol static reference standards of NO_2. Similar levels of HNO_3 impurities in 1 µmol/mol NO_2 standards would represent a significant fraction (10 % – 40 %) and would be unacceptable. In order to improve the accuracy and stability of NO_2 reference standards it is important to understand the formation and evolution of major impurities and to develop methods or approaches that minimise their formation during the preparation of static NO_2 reference materials.

NPL, VSL, LNE and TUBITAK undertook a literature review in order to develop a protocol for the preparation and analytical certification of the NO_2 reference materials developed in this project based on the available information for the production of NO_2 reference materials. In total, these 4 partners produced 40 NO_2 reference materials between them in 7 different cylinder types with two different matrices (air and nitrogen) with NO_2 amount fractions of 1 (14 reference materials) or 10 (26 reference materials) µmol/mol. Only NPL and VSL produced reference materials at both amount fractions. Note that the nitrogen matrix also contained an excess of at least 1000 µmol/mol oxygen, which is recommended to force the equilibrium ensuring full conversion to NO_2. Working together these 4 partners were able to test a broader range of cylinder passivation’s and matrix gases than would have been possible if they were operating completely independently.

These NO_2 reference materials were compared against one another in the context of key comparison CCQM-K74.2018, coordinated by the BIPM, a repeat of the earlier CCQM-K74 comparison on NO_2. In contrast to the original comparison, where NMIs value assigned a travelling standard, participants sent their prepared mixtures to the BIPM who conducted the analytical comparison. NPL, LNE, VSL and TUBITAK sent NO_2 reference standards developed in the project to the BIPM and submitted uncertainties that were 0.4 %, 0.6 %, 0.6 % and 0.5 %, which were respectively consistent with the project's aim of 0.5 %. There was good agreement, within the uncertainties, between NPL, VSL and LNE from this comparison. TUBITAK results showed a bias of 0.5 % relative to NPL, LNE and VSL. The discrepancy for TUBITAK is likely because they used the chemiluminescence to measure NO_2. As both NO_2 and its main impurity HNO_3 are measured together by the CLD method this analytical technique is unable to distinguish between these two compounds. This results in an overestimation in the amount fraction of NO_2, as well as concealing any decay of NO_2 to HNO_3. NPL, VSL and LNE all used NO_2 specific analytical techniques that distinguished NO_2 and HNO_3. It is important to note that chemiluminescence should not be used to certify reference standards of NO_2 for these reasons, and a direct technique, e.g. non-dispersive ultraviolet (NDUV), should be used instead.

The developed NO_2 reference materials were assessed for stability over the course of 1 – 2 years by NPL, LNE, VSL and TUBITAK. For the 10 µmol/mol a decrease in NO_2 amount fraction was observed for all mixtures after 15 months – 26 months (1 % – 4 %) but this varied depending on cylinder passivation chemistry, indicating the critical importance of selecting the correct passivated gas cylinder for NO_2 reference materials. The NO_2 loss was greater (approximately a factor of two) in an air matrix than in a nitrogen matrix, which could be related to the larger presence of H_2O impurities in oxygen compared to nitrogen.

The work carried out on reference standards of 1 µmol/mol NO_2 reference materials was very challenging. For the NPL produced mixtures, losses of NO_2 in the order of 10 % – 15 % were observed in the first month. For measurements carried out by NPL and VSL, the reference point standards were often low, producing results that were higher than the gravimetry. VSL demonstrated good evidence for stability over two years within 3 % for 1 µmol/mol NO_2 standards. For all cylinder types the results obtained, by comparing reference standards against a set of in-house standards, tended to give more variable results, with results sometimes above the gravimetric amount fraction for the standard under test. Results against in-house standards also appeared to be more stable over time, however as the reference points used were low amount fraction NO_2 standards (1 µmol/mol – 4 µmol/mol) it is possible that any changes in the reference points would hide any changes in the standards under test. In comparison, the results obtained by comparing reference standards to a dynamic dilution seemed to give much more consistent results, showing a decrease in NO_2 amount fraction over time. As a higher amount fraction NO_2 standard is used as a parent for the dynamic dilution it is likely to be more stable over time, so the reference point is less likely to change making this a much more robust comparison technique. NPL also faced additional measurement challenges with stabilisation times preventing measurements from being taken. This work has highlighted the importance of having a stable reference point for doing stability measurements, as a reference point that changes over time can conceal changes in the standards being tested. This is especially important for low amount fraction NO_2 standards, where having a reliable and robust dynamic standard system is essential. The use of molblocs/molbox laminar flow elements to generate NO_2 reference standards proved problematic due to extremely long stabilisation times and losses due to significant surface areas, such that these approaches are not recommended. It is suggested that low surface area systems, e.g., sonic nozzles, are developed and used for this purpose in the future or permeation based systems.

NPL and VSL undertook a literature review to ascertain what the major reactive nitrogen (NO_y) impurities were likely to be and also to determine the feasibility of developing reference materials to improve their quantification. Normally for gas standards, prepared following ISO 6142, the molar fraction of impurities in the prepared mixture can be derived from the purity analysis of the pure gases used for the preparation. However, for NO_2 mixtures this is not possible using the current preparation methods as typically many more NO_y components are present in the prepared mixture than can be expected based on the purity of the pure gases (i.e. the NO_y components are created during the preparation process). As a result, it was important to quantify the major identified impurities directly in the prepared NO_2 reference materials. NPL, Empa, PTB, VSL and DWD quantified the major impurities (HNO_3, NO, HNO_2, other NO_y) in the NO_2 reference standards. Working together these 5 partners were able to bring their specific instrumental approaches and analytical methods together to facilitate a complete analysis of all possible impurities. NPL also produced HNO_3 reference materials in high pressure gas cylinders for the first time. Unfortunately it was not possible to produce HNO_3 standards through the use of UoY's HNO_3 permeation device because the permeation rates were too low, however they were produced by the deliberate reaction of 10 µmol/mol NO_2 with varying amounts of added H_2O (0.5 µmol/mol and 2 µmol/mol). The observed evolution of the gas phase HNO_3, NO_2 and H_2O relative to the gravimetric preparation data was determined using FTIR spectroscopy over 1 year. The observed gas phase HNO_3 amount fractions increase rapidly for approximately 150 days. The increases in HNO_3 amount fraction coincide with similar behaviours in the decrease of both NO_2 and H_2O amount fractions. After 150 days the rate of increase becomes much slower and the HNO_3 amount fraction begins to stabilise even though there is still plenty of NO_2 and H_2O available to react. This clearly demonstrates that there is a limit to the amount of HNO_3 that can be formed through in cylinder chemistry. This has implications for the development of HNO_3 reference materials implying that these could not be produced without also containing substantial amounts of NO_2 and H_2O that were present as impurities, which has implications for long-term stability. The limit in HNO_3 formation does not appear to be related to the availability of either of the reactants and it was not possible to force the reaction to completion by heating and rolling of the cylinder. The amount of HNO_3 formed appeared to be limited to 10 % – 15 % of the NO_2 amount fraction irrespective of the availability of H_2O, whether this was at 33:1, 20:1, 10:1, 5:1, 1:1 and 1:2 (NO_2:H_2O). As the reaction is catalysed by a surface, the availability of surface sites may be the limiting factor affecting the conversion, but further work is needed to confirm this. As a result, the preparation of stable reference materials of HNO_3 appears to be limited.

The presence of small and variable amounts of HNO_3 in the NO_2 reference materials was confirmed by VSL, NPL, LNE and DWD and was observed to be correlated to the decrease of observed NO_2 amount fractions. VSL observed HNO_3 in NO_2 mixtures with all tested cylinder treatments and NO_2 amount fractions. The observed HNO_3 amount fraction was observed to increase with the NO_2 amount fraction. Also, the HNO_3 amount fraction seemed to increase with time (the oldest mixtures were four years old and these had very high HNO_3 amount fractions). The literature review did not find evidence of the presence of HNO_2 in NO_2 standards. Analyses performed by NPL and VSL confirmed that HNO_2 is not present at appreciable amount fractions in NO_2 gas mixtures contrary to that expected from the known chemical mechanism of NO_2 hydrolysis, which requires further investigation beyond the scope of this project. NPL modelled the expected N_2O_4 (NO_2 dimer) amount fraction based on the known rate constants that control the equilibrium ($2\ NO_2 <=> N_2O_4$). The NPL model shows that for NO_2 amount fractions < 100 µmol/mol that N_2O_4 is a negligible impurity (< 0.1 %) even at lower temperatures (10 °C) and this showed good agreement with analytical data reported by the BIPM in CCQM-K74. N_2O_4 only becomes a significant impurity at amount fractions > 100 µmol/mol, e.g., at 1000 µmol/mol it is ~1 %, which was confirmed by the FTIR measurements made by PTB. DWD reported that other major NO_y components, alkyl nitrates and peroxy acetyl nitrates were not detectable at any significant levels in static NO_2 reference standards.

The following contributions are important when estimating the uncertainty associated with reference standards of NO_2:

- Purity analysis of pure NO and matrix gases
- Gravimetric preparation (weighing and atomic weight uncertainties)
- Analysis of additional impurities formed *in situ*
- Repeatability of measurements
- Analytical uncertainty in assigning a value

Certification of the HNO_3 amount fraction contributes the most to the uncertainty due in part to a lack of reference standards and thus reliance of HITRAN line data that results in uncertainties of > 10 %. The future development of a more accurate method for the characterisation of HNO_3 in NO_2 standards would be greatly beneficial.

As a result of the importance of the role of the reaction of NO_2 with H_2O for the accuracy and stability of NO_2 reference materials, NPL and VSL focussed on evaluating the effect of water vapour on the conversion of NO_2 to HNO_3 in the cylinder. NPL developed a series of 10 µmol/mol NO_2 reference materials that contained different known amounts of added water in the range of 0.3 µmol/mol to 20 µmol/mol and studied the evolution of NO_2 and several key impurities (HNO_3, HNO_2, NO and H_2O) in these reference materials over a year. HNO_3 was the only major observed impurity present in the NO_2 reference standards, which was consistent with previous work. The time resolved behaviour of the loss and subsequent formation of HNO_3 within the cylinder was characterised for the first time and provides important insights into the impacts of water vapour on the stability and accuracy of NO_2 reference standards. In all of the mixtures, the HNO_3 amount fractions increased exponentially following preparation for approximately 150 days. After this initial period the increase became much slower and increased linearly over time. These increases in HNO_3 amount fraction coincided with similar behaviours in the decrease of both NO_2 and H_2O amount fractions. The reaction was observed to slow over time and followed an apparent power law dependence over the first 5 months. A mass balance approach between the loss of NO_2 and the presence of gas phase HNO_3 did not match with the expectations from the known reaction mechanism, indicating that this analysis was complicated by the partitioning of HNO_3 to the internal surface of the gas cylinder. No HNO_2 was observed above the detection limit (< 100 nmol/mol) and based on the known mechanism for the $NO_2 + H_2O$ reaction, this suggests it was a short lived intermediate.

It is clear that the preparation of NO_2 reference materials differs from what is described in ISO 6142 and the formation of impurities, specifically HNO_3 from the hydrolysis of NO_2, is a tremendous challenge to their accuracy and stability. Due to the importance of impurities of water and their resultant effects on the accuracy and stability of NO_2 reference materials it is important to select pure gases with the lowest water content. For the N_2 this could be e.g. N_2 BIP-plus from Air Products. For the O_2, the water content of four major providers is nominally the same (< 0.5 µmol/mol). Additional analysis of O_2 using suitable instrumentation is recommended as are mitigation steps to reduce the water content as much as possible. It is suggested to apply (in the following order of relevance) the following methods to minimise the presence of water vapour during the preparation of NO_2 reference materials:

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NPL, VSL, TUBITAK and LNE produced 40 NO_2 reference materials and while it was possible to produce these with an accuracy of 0.5 %, a stability of 2 years was not possible at this uncertainty level due to losses of NO_2 within the cylinders of 1 % – 4 %. The major impurity was identified and confirmed to be HNO_3 formed from the hydrolysis reactions of NO_2. The consortium has progressed the knowledge in this area and now have a much better understanding of the kinetics of the reaction between NO_2 and H_2O. The presence of water as an impurity has a profound effect on the loss rate of NO_2 within the mixtures and so must be minimised as far as possible in order to achieve the lowest uncertainties. It is also notable that the loss of NO_2 (drift rate) changes as a function of time following preparation and it appears to follow a power law dependence, regardless of the water amount fraction. The results within this project show that after 150 days (5 months) the drift rates have substantially declined and this means that one approach to currently achieve longer stability periods would be to analytically certify the amount fraction of NO_2 after this time. These certified reference materials (CRMs) would then be able to be disseminated to end users with much lower uncertainties and corresponding longer stability periods than would be possible from the gravimetry alone.

4.2 To develop high accuracy traceable dynamic reference standards for low amount fractions of NO_2 (10 nmol/mol – 500 nmol/mol) with a target uncertainty of ≤ 1 %. To achieve these challengingly low uncertainties will require the full characterisation of critical impurities and the development of new methods to minimise their formation during dynamic standard preparation.

High accuracy dynamic generation standards are needed to generate atmospherically relevant NO_2 amount fractions. The current state of the art for producing accurate standards at low amount fractions typical of the ambient atmosphere requires either the dilution of a stable higher concentration gas standard or direct production by a dynamic technique, such as one based on permeation, or production by a dynamic technique, such as the gas phase titration of NO standards with ozone. The current state of the art for the uncertainty of dynamic NO_2 standards of 100 nmol/mol is 3 %. One limitation preventing lower uncertainties at lower amount fraction NO_2 is the presence of trace amounts (≤ 1 nmol/mol) of NO_2 which are present as an impurity in the diluent gas. Generating more accurate lower NO_2 amount fractions will require better removal, or quantification of very low levels of NO_2 impurities (< 50 pmol/mol), and in order to achieve lower uncertainties accurate quantification of impurities, such as water, HNO_3, NO_y and N_2O_4 in the dynamic reference standards, is required. When generating dynamic reference standards from higher amount fraction NO_2, impurities in the parent standard typically become negligible as a result of the large dilution ratios used to produce standards at ambient amount fractions. However, impurities can be produced through surface reactions in the gas streams (e.g. between NO_2 and H_2O that may be present on the surface of the tubing), although due to the dynamic nature of these standards these effects are short-lived and are minimised during the equilibration of the dynamic system. Regarding the permeation method, the major source of impurities is from the composition of the permeation tube and the diluent gas, with recent work by Flores *et al.*[1] showing that HNO_3 and N_2O_4 were the major impurities present in the dynamic standards that were produced from NO_2 permeation tubes.

METAS and NPL provided commercially available purifiers to Empa and UoY to test using their very sensitive CLD and QCLAS instruments. METAS provided Empa with three different purifiers: Hydrosorb® (Messer GmbH, Part No. 123326) for zero air and N_2, Microtorr ® (SAES Pure Gas model MC 400-203 V) for dry air and N_2, and Monotorr ® (SAES Pure Gas model PS3-MT3-N-2) for N_2. NPL provided UoY with a Microtorr ® (SAES Media 906) and UoY also tested several custom-made purifiers consisting of Sofnofil (Molecular Products; to oxidise NO to NO_2) followed by activated charcoal (to adsorb NO_2). Data from Empa showed that the combination of two or three purifiers efficiently reduced 10 nmol/mol – 100 nmol/mol of NO or NO_2 to below the detection limit of 60 pmol/mol. The SAES Media 203 microtorr purifier is the critical purifier for removing NO and NO_2 to trace levels. The Hydrosorb purifier used a Molsieve 5Å adsorbant to remove H_2O to < 20 nmol/mol. However, if the specification of the input gas is already set to match this purity level, for example with Air Products BIP+ N_2 that is specified to contain < 20 nmol/mol H_2O, then the use of this trap is unnecessary. The Monotorr purifier did not appear to improve NO_y removal, but this is not surprising as it is intended more for the removal of other compounds such as CO, CO_2, O_2 and CH_4. The NO_x levels in the custom-made traps tested by UoY were limited by the ability to seal the refillable traps and so it is possible that a commercially available trap with sealed fittings would be better. However, Sofnofil/charcoal works effectively as a trapping material, but it must be tested each time the material is replaced, as getting the trap to be leak tight appeared to be the limiting factor, rather than the actual materials. The commercially available SAES Media 906 Microtorr purifier proved to be excellent at removing NO_2, but not NO, which showed an approximate 2 % breakthrough relative to the input gas mixture.

LNE and METAS tested the effect of temperature and pressure variations on permeation rates from permeation tubes from KIN-TEK (LNE) and Fine Metrology (METAS). Data from both LNE and METAS showed that the permeation rate of the tubes tested increased with temperature, with data for the KIN-TEK permeation tubes showing a maximum change in permeation rate of ~166 % over the temperature range 21 °C – 34 °C for one permeation tube, and ~ 42 % for a second tube over the temperature range 30 °C – 34 °C. METAS tested three different permeation tubes from Fine Metrology and data showed a maximum increase in permeation rate of 32 % over the temperature range 35 °C – 40 °C for an uncoated and thin membrane permeation tube with a thin membrane (0.75 mm thickness), and 27 % for a SilcoNert 2000 coated permeation tube with a thick membrane (1.5 mm thickness) over the same temperature range. LNE tested the influence of pressure on the permeation rate over the pressure range of 1040 mbar – 1100 mbar. An initial test showed the permeation rate to increase with pressure, however on repeating the test the permeation rate was much lower for all pressures tested and then continued to decrease with an increase of pressure, by ~ 2 %. METAS tested the permeation rate over a larger pressure range of 1013 mbar – 2600 mbar and data also showed a decrease in the permeation rate with an increase of pressure, with the largest decrease in the permeation rate of 12 % for the SilcoNert 2000 coated tube (with a 1.5 mm thick membrane), and a decrease of 9 % for the uncoated tube (with a 0.75 mm thick membrane). METAS also tested the temporal stability and found that after 25 months – 30 months the permeation rate of the tube tested increased outside of the uncertainty range at both 35 °C and 40 °C, with the permeator being more stable over time at 35 °C.

Data from METAS highlighted the difference that pre-conditioning the permeation tubes made on the permeation rate. As a control, after storing the thin membrane (0.75 mm thickness) permeation tube at room temperature, the permeation rate stabilised after 3000 minutes. The permeation tube was then stored in the fridge for 6 hours; however the permeation rate fluctuated a lot and it did not seem to stabilise over the 8000 minutes tested. The thick membrane (1.5 mm thickness) permeation tube was tested after being stored at room temperature and the permeation rate was found to stabilise after 1200 minutes, however after conditioning the temperature and pressure, the permeation rate was found to stabilise after 710 minutes. These tests highlighted the importance of closely controlling the temperature and pressure of the permeation system when using these permeation tubes for the dynamic generation of NO_2, whilst also demonstrating the benefit of pre-conditioning the permeation tubes before use.

The dynamic dilution systems developed by NPL, LNE, IL, UoY and METAS were compared in a round robin intercomparison over a period of 16 months. CMI did not participate in this comparison because they did not have an instrument capable of measuring NO_2. It was intended that CMI would bring their dilution system to NPL to test however this was not possible due to travel restrictions and lab access issues resulting from

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[1] E. Flores, J. Viallon, P. Moussay, F. Idrees and R. I. Wielgosz, “Highly accurate nitrogen dioxide (NO_2) in nitrogen standards based on permeation”, Analytical Chemistry, vol. 84, no. 23, pp. 10283-10290, 2012.

COVID-19. A commercial 50 L cylinder, containing nominally 300 nmol/mol NO_2, was shipped between these 5 partners, with stability measurements being taken at the start and at the end of the round robin intercomparison. This allowed a reference value as a function of time to be determined, facilitating the comparison of the performance of the different dynamic dilution systems. Initially reference standards of NO_2 and NO were used by NPL for the stability measurements on the comparison cylinder, however, it was found that NO_2 was unsuitable for use with the Molbloc dilution facility. This was because the large internal surface area of the Molblocs and Molbox terminals led to stabilisation issues resulting in significant differences between repeated measurements of the comparison cylinder. For the stability measurements, at the end of the intercomparison NPL used gas phase titration to convert a stable amount fraction of NO to NO_2 by the addition of ozone.

LNE, METAS and IL tested dynamic dilution systems using NO_2 permeation tubes and magnetic suspension balances, while UoY tested the gas phase titration of a NO reference standard with ozone, and NPL tested a sonic nozzle dilution system with a certified NO_2 reference standard. LNE, UoY, IL and NPL used direct analytical techniques (e.g. IBB-CEAS, CAPS and CRDS) to measure NO_2, whereas METAS used CLD. The reported uncertainties for the comparison were 0.9 %, 1.2 %, 3.7 %, 1.8 % and 17 % for LNE, METAS, UoY, IL and NPL, respectively. The repeatability of individual NPL measurements was affected by downstream pressure restrictions that affected flows through the sonic nozzles. This issue was not identified until after the measurements were complete and is responsible for the poor uncertainty achieved with this method. The results from the intercomparison highlighted a positive bias in the absolute difference between reported amount fractions of NO_2 and the reference value for METAS, UoY, LNE and IL reporting values that were 4.4 %, 9.5 %, 13.5 % and 20.8 % higher respectively. In contrast, NPL reported an amount fraction of NO_2 16.8 % lower than the reference value. The positive bias for most results suggested that either NPL's reference value was low, or METAS, UoY, LNE and IL's dynamic systems generated lower amount fractions of the target gas than expected. Possible sources of error which could lead to dynamic systems generating different amount fractions than expected include the following:

- Permeation tubes may contain impurities of water resulting in larger mass losses being measured
- If mass flow controllers have drifted significantly from their calibrated value, then the amount fraction of NO in the dynamic standard used in gas phase titration will be calculated incorrectly
- Restriction downstream could change the pressure difference across the sonic nozzle leading to a change in the flow
- Errors in purity analysis of any gases used could result in inaccuracies in the amount fractions calculated from the dynamic standards

There were several challenges to the 'round robin' approach for this intercomparison. Firstly, with the stability measurements, issues with NPLs ozone generator meant that stability data points using gas phase titration of molbloc/molbox diluted NO was not possible before the mixture was dispatched from NPL. Secondly, the cylinder was away from NPL for much longer than originally planned (1 year versus 6 months) which meant that the duration of the stability measurements was not really long enough to adequately characterise the drift. In hindsight it would have probably been better to have brought all the dynamic dilution systems together at a single institute to use the same comparator (NO_2 instrument) to compare them. This would have removed any differences from the use of different instrumentation and it would also have removed the need for a travelling standard, which due to stability drifts added considerable uncertainties to the comparison reference value.

While generating dynamic standards, impurities are often generated unintentionally during operation. These impurities can have an influence on the accuracy and the uncertainty of dynamic standards and so it is necessary to develop and validate analytical methods for quantifying these impurities. METAS, LNE, Empa, DWD and NPL aimed to quantify impurities such as the H_2O, HNO_3 and NO_y species present in NO_2 permeation tubes, and the H_2O and NO_y species present in HNO_3 permeation tubes.

Work was carried out by METAS and LNE to quantify the water vapour and HNO_3 permeation rates from NO_2 permeation tubes. METAS tested two wafer type NO_2 permeation units (99 % purity) from Fine Metrology and expected the main impurity to be HNO_3. Dynamic standards of NO_2 between 100 – 500 nmol/mol were generated and analysed using FTIR, however the amount fraction of HNO_3 was most likely too low to be detected, possibly due to the optical path length of the sample cell being too short. Results presented by Flores *et al.*[1] corresponded to the analysis of NO_2 reference standards between 5 – 15 µmol/mol, 1 – 2 orders of magnitude greater than those tested here, with an optical path length of the cell being 10 times longer than the gas cell used by METAS (48 ± 1.2 m). Better optimisation of the FTIR system and upgrading to a longer optical path gas cell might allow the identification and quantification of HNO_3 and other impurities in generated dynamic standards at low amount fractions (< 500 nmol/mol). LNE generated NO_2 amount fractions using the METAS permeation system ReGaS1 and a NO_2 permeation tube (Fine Metrology) calibrated with a magnetic suspension balance at METAS. Data using the ReGaS1 permeation system showed the formation of 2.5 nmol/mol HNO_3 in the presence of 150 µmol/mol water vapour for an amount fraction of NO_2 generated at 390 nmol/mol. For 210 nmol/mol NO_2 the amount fraction of HNO_3 was equal to 1.5 nmol/nmol. The formation of HNO_3 was insignificant (0.3 nmol/mol) when the amount fraction of water vapour was below 5 µmol/mol. The ReGaS1 permeation system was also tested by Empa to quantify the NO impurity, and it was determined to be 0.06 %. DWD also tested the ReGaS1 permeation system to characterise any potential impurities in the NO_2 dynamic reference standards, such as peroxy nitrates, alkyl nitrates and HNO_3 using thermodissociation. Data showed the NO impurity to be < 0.09 %, the HNO_3 impurity to be < 1.1 %, and peroxy nitrates were quantified to be 0 ± 0.6 %. Impurities of alkyl nitrates could not be quantified due to instrumental problems.

Work was carried out by METAS and DWD to quantify the impurities present in HNO_3 permeators. METAS tested two tube HNO_3 permeation units (68 % purity, azeotropic concentration) from Fine Metrology. Due to the azeotropic properties of the mixture of HNO_3/H_2O in the HNO_3 permeation tubes the major impurity expected was H_2O (22 % H_2O), however METAS found that the H_2O content of the HNO_3 permeators was much higher than expected (4 times higher than expected). DWD tested HNO_3 standards generated using the ReGaS1 permeation system and quantified the NO impurity to be < 0.9 %, the NO_2 impurity to be < 1.4 %, and the peroxy nitrates impurity to be < 0.9 %. Impurities of alkyl nitrates could not be quantified due to instrumental problems. NPL characterised the dynamic reference standards of HNO_3 generated from the UoY HNO_3 permeation device and found that comparing emission rates of permeation tubes using different permeation systems over time is very difficult (from gravimetric data assignment from KIN-TEK, UoY and NPL). Using the gravimetric emission rate as an estimation of the amount of HNO_3 generated in a dynamic mixture led to a significant overestimation to what was observed when assuming 100 % HNO_3 emission (by ~25 %), showing that there were significant impurities within the reference gas mixture. The FTIR measurements showed that water vapour was the dominant impurity emitted alongside HNO_3, but accurately measuring the amount of water vapour emitted was dependent on the ingress of ambient water vapour into the permeation system. Once ambient water vapour was effectively removed from the permeation system, the FTIR measurements showed that the proportion of HNO_3 and H_2O was similar to the proportion of HNO_3/H_2O within the permeation tube based on the HNO_3 purity. Clearly, the presence of water as an impurity needs to be considered by the user when using such devices.

Another key challenge is to improve the accuracy and comparability of the NO_2 measurements performed at monitoring stations. This was investigated by evaluating direct calibration with NO_2 reference standards with the conventional gas phase titration method at several different monitoring stations. Empa applied three calibration methods (dilution of a VSL prepared 1 µmol/mol NO_2 in N_2 standard, gas phase titration (GPT) of a 20 µmol/mol NO in N_2 standard and reference gas mixtures generated by permeation using a NO_2 permeation tube calibrated in a magnetic suspension balance) to four instruments: a molybdenum converter Chemiluminescence Detector (CLD), a Cavity Attenuated Phase Shift spectrometer (CAPS), a commercial Quantum Cascade Laser Absorption Spectrometer (MIRO) and a custom made one (MINAS) at the Dübendorf NABEL suburban station. The analysis of the calibration data showed that for a given method, the four instruments agreed within a range of 2 %. The ReGaS1 and cylinder calibration parameters differed significantly (up to 10 %) compared to the gas phase titration (GPT) calibration, which is the currently established reference method. The CAPS and the two QCLAS ambient NO_2 amount fraction datasets were in very good agreement, with slopes ranging from 0.994 to 1.002 using the factors from the direct calibration methods (cylinder and ReGaS1). The GPT calibration parameters yielded the least agreement between these three instruments. Regardless of the calibration method used, the CLD data showed the least agreement with the other three instruments with slopes around 1.06. Analysis of the uncertainty data showed that the lowest uncertainties were obtained with the cylinder and GPT calibrations and with the direct measurement instruments (CAPS, MIRO, MINAS). For the cylinder calibration method, the final ambient NO_2 amount fraction measurement uncertainties were mostly limited by the relatively high uncertainty on the NO_2 amount fraction in the gas cylinder. For the GPT method, the uncertainty was limited by the uncertainty on the NO measurements used to derive the span amount fraction. For the ReGaS method, the situation lay in between the two other methods: the ReGaS calibration work resulted in an instrument offset parameter fit with a high uncertainty causing the relatively big spread in the data.

NPL provided a 1 µmol/mol NO_2 in N_2 standard to DWD to calibrate CLD and CAPS analysers at the Hohenpeissenberg monitoring station. The currently applied conventional calibration concept using GPT of NO and O_3 was compared to the NPL developed static reference standard for NO_2. Calibrations using the NPL

NO_2 cylinder were performed directly after the GPT calibrations. The uncertainty budget of the two different calibration methods was calculated by the uncertainty of the mass flow controllers (U (2σ) = 2.8 %), the uncertainty of the NO cylinder amount fraction (Air Liquide NO U (2σ) = 2 %), the reproducibility of the CLD NO_2 converter efficiency (1.52 %, determined from four consecutive calibrations) and the reproducibility of the CAPS sensitivity (1.2 %). These uncertainties propagated to an uncertainty of the measured NO_2 values of 3.8 % for the chemiluminescence detector and 4.5 % for the CAPS detector, when applying the GPT calibration method. For the NO_2 calibration using the new static reference standard generated by NPL (cylinder #S413 with a NO_2 amount fraction of 1.03 µmol/mol ± 0.05 µmol/mol). The estimation of the uncertainty for the NO_2 measurement with the CAPS instrument is analogous to the calibration operating gas phase titration with NO and O_3 using the same uncertainties for the dilution system ($U_{MFC´s}$(2σ)= 2.8 %) and the uncertainty of the cylinder concentration (NPL U_{NO2} (2σ) = 5 %). These uncertainties propagated to an uncertainty of the measured NO_2 values of 5.8 % for the CAPS analyser.

NPL provided KCL with five 1 µmol/mol NO_2 reference materials and five zero air cylinders that were deployed to five (2 suburban and 3 urban) London Air Quality Network (LAQN) monitoring stations, which use chemiluminescent methods, between 12th February 2020 and 10th September 2020. These NO_2 cylinders were used in conjunction with routine calibrations using NO in N_2 GPT and zero air scrubbers. It was observed that the NO_2 amount fractions measured by field instruments were considerably less than the certified amount fraction measured prior to the field test. This difference ranged between 17 % and 50 % of the certified amount fraction and is representative of the challenge of preparing 1 µmol/mol NO_2 reference materials. The field instruments took more than 12 minutes to stabilise when challenged with the NO_2 test gas and over the duration of the field deployment, two cylinders showed increases over time. Three cylinders showed relative stability. Rates of change were between +0.78 nmol/mol/day and -0.22 nmol/mol/day. Due to COVID restrictions, it was not possible to re-test the cylinder amount fraction in the laboratory at the end of the project. Results from this project suggest that calibration with the traceable and certified NO_2 cylinders would not be suitable for traceable calibrations of instrumentation in the field. The reasons for this are unclear. The cylinders may have experienced a one-off rapid change in the NO_2 amount fractions soon after certification or during field installation. It is also possible that NO_2 was lost in the site regulator and pipework, affecting the amount fraction delivered from the certified cylinder to the instrument. The increase in instrument response to NO_2 during each calibration and (at some locations) over the whole project may have been due to gradual conditioning of the regulator and pipework.

NPL, Empa, METAS and UoY demonstrated that with the correct choice of gas purifier NOx free (< 60 pmol/mo) diluent gas could be produce for dynamic generation systems. METAS and LNE optimised the permeation method for the dynamic preparation of NO_2 reference materials focusing on the temperature, pressure, preconditioning and membrane thickness. A round robin comparison of dynamic NO_2 reference standards demonstrated that the consortium had produced dynamic systems with uncertainties of 1 % - 4 % although there was a positive bias relative to the reference (gas phase titration of NO with ozone) that warrants further investigation and possible repetition with stringent QA/QC controls possibly as part of a Euramet comparison exercise. The deployment of these new NO_2 reference standards illustrated some challenges in their utilisation with respect to stabilisation and drift and that there are still improvements required before direct calibration can displace the indirect gas phase titration method.

4.3 To develop analytical methods to quantify the main impurities formed unintentionally during the preparation of static and dynamic NO_2 reference standards. To validate selective spectroscopic methods for directly measuring NO_2 and compare them with the standard reference method as described in EN 14211:2012, using field trials at an atmospheric simulation chamber.

Selective spectroscopic methods to directly measure NO_2 are necessary to decrease the uncertainty associated with ambient measurements in order to meet the data quality objective of ≤ 5 % stated by the WMO. Currently the standard technique for measuring NO_2, as described in EN 14211:2012, is chemiluminescence. This measurement technique works by converting NO_2 in the sample to NO for measurement, thus making NO_2 a regulated air pollutant that is indirectly measured. The major drawback with this technique is the bias that is introduced if other nitrogen oxides (e.g. HNO_3) are present as impurities. These impurities are also converted to NO in this technique and as a result the amount fraction of NO_2 can be overestimated by up to

50 %[2]. Recent improvements in spectroscopic methods have allowed direct measurements of NO_2 to become feasible with spectroscopic techniques such as QCLAS, CRDS, CAPS, CEAS, and FTIR being shown to be capable of performing accurate and reliable direct NO_2 measurements.

DFM, Empa, PTB, LNE and UoY undertook a literature review to summarise commercially available selective NO_2 instruments and identified the following instruments:

- Cavity attenuated phase shift spectrometer (CAPS)
- Incoherent broadband - cavity enhanced absorption spectrometer (IBB-CEAS)
- Quantum cascade laser absorption spectrometer (QCLAS)
- Cavity ring-down spectrometer (CRDS)
- Cavity enhanced absorption spectrometer (CEAS)
- Tuneable diode laser absorption spectrometer (TDLAS)
- Integrated cavity output spectrometer (ICOS)
- Optical feedback – cavity enhanced absorption spectrometer (OF-CEAS)
- Photoacoustic absorption spectrometer (PAS)
- Fourier transform infrared spectrometer (FTIR)

Empa developed a novel dual wavelength QCLAS system for the simultaneous direct measurement of NO and NO_2 and adapted the system to allow the measurement of NO impurities in NO_2 reference standards. The target precision of 0.03 nmol/mol and the target sensitivity of 0.1 nmol/mol was achieved. After averaging 200 s of data the Allan deviation was found to be 20 pmol/mol which corresponded to the best precision of the instrument. Averaging any further data did not increase the precision of the instrument due to drifts in the mixing ratio signal, this was thought to be partially caused by the thermal dilation/contraction of the optical elements. The QCLAS system was compared to a commercial CAPS instrument over a seven-month period and the overall agreement was very good, producing a slope of ~0.98. The difference between the data for the two analysers was likely due to a systematic error on the measurements by the QCLAS linked to errors in the absorption spectrum used (HITRAN). The biggest source of uncertainty in the measurement (~ 6 %) was due to the uncertainty on the NO_2 absorption spectrum which was estimated to be around 5 %.

A Fourier transform spectroscopy setup for NO_2 measurement was developed by PTB. The optimum spectral window was selected considering the amount fraction of NO_2 in available static primary reference standards and the optical path length of available optical gas cells and was selected to be the v_3-fundamental band absorbing in the range from 1540 cm^{-1} – 1670 cm^{-1}. An advantage to selecting this spectral window was that there was no significant interference with HNO_3 or NO, with only slight interference from water vapour. The optimal sample pressure was also determined to be about 1 mbar or lower in order to help resolve the complex rovibrational spectral structure of NO_2 with its high number of transitions. Due to the reactive nature and strong surface adsorption of NO_2, special optical components were installed inside PTB's FTIR, along with passivated gas lines and components. Corrosion-resistant materials were also necessary due to the tendency of NO_2 to produce highly corrosive HNO_3 through reaction with residual water vapour within the measurement volume. The developed method was tested through a set of measurements of a 979 µmol/mol commercial static gas standard with a spectral resolution of 0.002 cm^{-1} at 296.1 K and a pressure of 10 mbar. The resulting spectra showed the v_3-fundamental band of NO_2 with separated rovibrational transitions suitable for line-by-line modelling for spectral line data determination.

DFM developed a compact laser spectrometer for NO_2 detection with the aim to target a sensitivity of < 100 pmol/mol and an uncertainty of < 2 nmol/mol. Initial measurements performed using a 100 µmol/mol NO_2 reference standard at 10 mbar showed an acceptable background that could be subtracted. Deviations from the expected line shape were observed and attributed to strong water lines present in the wavelength range covered by the laser used. Even after continuous pumping for a week, strong water lines were still present in the spectrum, however as the feature was localised and small, no problems in relation to determining the amount of substance were anticipated. The presence of the lines could also serve as a frequency reference. The long-term stability assessment of the instrument was not completed during the project period due to a flood in DFMs laboratories in August 2020. The consequences of this flood was that repair had to be

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[2] M. Steinbacher, C. Zellweger, B. Schwarzenbach, S. Bugmann, B. Buchmann, C. Ordóñez, A. S. H. Prevot, C. Hueglin, "Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques", Journal of Geophysical Research, vol. 112, D11, 2007. DOI: doi:10.1029/2006JD007971

made to the building and to several instruments. New instruments had to be purchased as well. These actions were not completed in due time before the finishing date of the project.

LNE developed an IBB-CEAS instrument with a resolution of 0.1 nmol/mol and evaluated its linearity in the 20 nmol/mol – 500 nmol/mol range using their own permeation system. The calibration curve obtained over this range showed reasonable linearity with an R^2 value of 0.9996, however when fitted with a polynomial function (order 2) the agreement was much stronger, with an R^2 value of 0.999999.

UoY evaluated and validated the performance of their CAPS instrument by testing the instrument limit of detection, linearity, drift and response times. The limit of detection was calculated by multiplying the standard deviation of the NO_2 response during zero air sampling by three (3σ), and was found to be 61.6 pmol/mol. The linearity was tested over the range of 10 nmol/mol – 100 nmol/mol and the calibration curves obtained showed good linearity with strong positive correlation (R^2 values ranged from 0.9999 – 1). The drift in the instrument signal was monitored over a period of five days and the average drift was found to be 0.1 nmol/mol per day (the sample gas temperature varied from 43.5 °C – 43.9 °C). When the data was separated into three data collection periods with average gas temperatures of 43.9 °C, 43.7 °C and 43.5 °C, the respective average instrument drift was 0.05 nmol/mol, 0.10 nmol/mol and 0.15 nmol/mol per day. This suggested that the CAPS analyser experienced higher levels of drift at lower sample gas temperatures, however more evidence is needed to confirm this observation. Increased drift also correlated with the amount of time since starting the zero-air sampling, so it is important to assess any additional factors potentially affecting instrumental drift. Instrument response time tests were performed using 100 nmol/mol NO_2, and the average rise time, fall time and lag time were determined to be 18.7 s, 21.3 s and 2.3 s respectively.

Spectroscopic methods for the measurement of major impurities such as NO, H_2O and HNO_3 are required in order to fully characterise the impurities present in static and dynamic reference standards of NO_2. Due to rapid developments in infrared laser technology (in particular quantum cascade lasers) highly sensitive measurement for impurities, such as HNO_3 and HNO_2, have been developed based on mainly multi-pass absorption cells. An alternative for HNO_2 is to use UV absorption methods, however a drawback is the strong overlap with the NO_2 absorption band. Therefore, regular broad-band CEAS is probably less suitable and high-resolution measurements at low pressure are probably needed to overcome the NO_2 interference. Other possible useful spectroscopic methods include LIF.

Empa, PTB, VSL and DWD developed a range of spectroscopic methods for the analysis of impurities in NO_2 reference standards. Empa developed a NO_x device based on QCLAS to quantify NO and estimated the precision of the analyser from the Allan deviation to be 70 pmol/mol in 1 s, and 20 pmol/mol in 20 s (1σ). Their QCLAS was compared to a commercially available CLD over a period of 10 days at a Swiss Air Quality Monitoring Network (NABEL) station, and the correlation was fairly strong (R^2 value of 0.98578).

PTB applied their static FTIR method to characterise NO (using fundamental band at 1880 cm^{-1}), N_2O (using v_3 band at 2224 cm^{-1}), CO (using fundamental band at 2143 cm^{-1}), CO_2 (using v_3 band at 2349 cm^{-1}) and HNO_3 (using v_2 band at 1709.5 cm^{-1}) impurities in NO_2 reference standards. PTB found that the static method used, based on integrated intensities, had lower spectral noise, used less gas and had a more straightforward and faster integration process when compared to spectral simulation. Another advantage of the static method was that if there was sufficient data for reliable extrapolation, the concentration of a species can be determined even if it was initially too weak for an evaluation. However, if the amount of an impurity was small and decreased with time then the extrapolation method encountered complications and could only be used with caution. The integrals were also very sensitive to the baseline choice and it was not always easy to justify or draw unequivocal conclusions. Systematic error due to $t = 0$ being the time of filling the gas cell and not the beginning of the first measurement also leads to values being somewhat underestimated.

VSL developed a spectroscopic method to measure HNO_3 and HNO_2 using CRDS. The strongest fundamental absorption band of HNO_3 could not be accessed by the optically pumped oscillator so the OH stretch band at 3550 cm^{-1} was used (3580 cm^{-1} – 3520 cm^{-1}). This band was not listed in the HITRAN (high-resolution transmission molecular absorption) database so the PNNL (Pacific Northwest National Laboratory) database was used to obtain the absorption cross-sections of HNO_3, and as PNNL data is only valid for atmospheric pressures, measurements were performed at atmospheric pressure. Due to the strong absorption of water vapour in this region a large part of the absorption band could not be used, so the region around 3540 cm^{-1} was used. The detection limit for HNO_3 was found to be in the order of 2 nmol/mol and varied somewhat over time depending on mirror reflectivity, optically pumped oscillator stability and cell alignment. For measuring HNO_2, the OH stretch at 3590 cm^{-1} was selected (3650 cm^{-1} – 3550 cm^{-1}), however this band was approximately three times weaker than the HNO_3 stretch band, partly overlapped with HNO_3 and water vapour also strongly absorbed in this region. As such the region around 3574 cm^{-1} was measured, however no HNO_2 was detected in any of the samples run by VSL.

DWD developed a four-channel thermal dissociation inlet combined with a CAPS analyser (TD-CAPS) to measure HNO_3, total alkyl nitrates and total peroxy nitrates. The thermodissociation temperatures for peroxy nitrates, alkyl nitrates and HNO_3 were determined to be 150 °C, 350 °C and 550 °C respectively, and the conversion efficiencies were simulated to be 65 %, 80 % and 100 % respectively. The HNO_3 conversion efficiency was quantitatively determined to be 98 % (± 4 %) by applying a known amount of HNO_3 from a permeation device to the instrument.

A protocol for the laboratory-based characterisation and evaluation of selective NO_2 instruments was developed and a round robin comparison was carried out by LNE, DWD, DFM, METAS, Empa, IL, UoY, AU and NPL. The partners tested the following instruments:

- Custom-made IBB-CEAS analyser (LNE)
- CAPS NO_2 Monitor, Aerodyne Research Inc. (DWD)
- Custom-made QCLAS analyser (Empa)
- AS32M NO_2 CAPS analyser, Envea SA (IL)
- T500U CAPS NO_2 analyser, Teledyne API (UoY)
- M200E Chemiluminescence NO_x analyser, Teledyne API (AU)
- NO_2-*11r*-EP CRDS analyser, Los Gatos Research (NPL)
- CLD 780 TF chemiluminescence analyser, ECOPHYSICS AG (FZ-Juelich)

All instruments were tested following the protocol to test for response time, Allan deviation, long-term drift, linearity, inlet pressure effect and NO interferences. All instruments were found to show similar rise and fall response times at NO_2 amount fractions of 100 ± 10 nmol/mol, with values below 20 s (except for IBB-CEAS – LNE, < 45 s). The acceptance criterion (in laboratory conditions) for the response time from the EN14211 standard is ≈ 80 s with a difference between rise and fall time of 3 s. This criterion was fulfilled for all tested instruments.

For the Allan deviation, two different types of curves were observed. Four instruments (IBB-CEAS – LNE, CAPS – DWD, CRDS – NPL and QCLAS – Empa) showed an initial linear decrease of Allan deviation as a function of the integration time. This was expected and indicated a reduction of (white) signal noise by data averaging. This trend was followed by a progressive increase of the Allan deviation after reaching a local minimum. After this local minimum, data averaging caused an increase in the difference between the data subsets, which was caused by drifts in the zero signal of the instrument. The second type of curve (seen for CAPS – IL, CAPS – UoY, CLD – AU, CLD – FZ-Juelich) showed an initial increase. This was untypical and unexpected and was attributed to the presence of a high frequency filter in the DAQ process (low-pass filter) which was not documented and therefore could not be discussed any further. As such, the short-term noise (or precision) of these instruments should not be compared. However, after a local maximum was reached, the Allan deviation decreased again to reach a local minimum similar to the other instruments. All direct NO_2 detection instruments showed a minimum Allan deviation of < 12 pmol/mol and performed better than the CLD instruments.

The maximum long-term drifts (≈ - 1.5 nmol/mol NO_2) were observed for the IBB-CEAS and CRDS instruments. The best stability obtained without drift correction was observed for the CAPS and QCLAS instruments, which were comparable with the stability of the drift corrected CLD. The acceptance criterion (in laboratory conditions) for the maximum drift at zero NO_2 in 12 h given in the EN14211 standard is 1 nmol/mol. This was respected by nearly all instruments even with no internal zeroing, which is usually part of the normal operating conditions. Even the IBB-CEAS, which was drifting faster than the other instruments, would comply with the 1 nmol/mol criterion, except for one short period around 24 h, where the drift was just slightly above 1 nmol/mol. The acceptance criterion (in laboratory conditions) for the maximum drift at non-zero NO_2 in 12 h given by the EN14211 standard is 2.4 nmol/mol. This criterion was respected by all instruments (at their respective span concentration) except for the CAPS – DWD.

Linearity tests were carried out by spanning the instruments with NO_2 amount fractions ranging from 0 nmol/mol – 100 nmol/mol, and all instruments were found to perform well, with coefficient of determination values (R^2) ≥ 0.998. The best linearity coefficient was found for the CLD, CAPS and QCLAS instruments. The acceptance criterion (in laboratory conditions) for the maximum normalized residual from the EN14211 standard is 1.5 % of the measured value above zero. This criterion was not fulfilled by the IBB-CEAS – LNE, CRDS - NPL, CLD – FZ-Juelich, CAPS – IL and CAPS – DWD instruments.

The instruments were tested for a pressure inlet of 80 %, 100 % and 120 % of atmospheric ambient pressure (recommended values). The acceptance criterion (in laboratory conditions) for the pressure sensitivity given by the EN14211 standard is 0.01 nmol/mol/hPa. The CAPS and the CRDS instruments exceeded this limit. However, in order to get comparable results, all instruments were required to deactivate any pressure regulation mechanism, so it is very likely that the acceptance criterion would be fulfilled by using appropriate pressure regulation mechanisms.

Six of the seven instruments tested were based on direct NO_2 detection via direct light absorption, and as such, no interferences from NO were expected. In contrast, the CLD measurement technique is based on conversion of NO_2 to NO followed by detection of NO. It is therefore possible that co-sampling of NO could affect measurements of NO_2 in case of non-linearity in any step of the CLD measurement process. The test at 0 nmol/mol NO_2 was done to estimate the impurities of NO_2 in the NO source. The maximum significant deviation of $\Delta[NO_2]_{0,X}$ from 0 observed was 0.5 nmol/mol for the CAPS – UoY device. The same test done at 100 nmol/mol NO_2 revealed $\Delta[NO_2]$ values similar to the test at 0 nmol/mol NO_2 (within the 1σ measurement standard deviation) indicating no interferences from NO.

Alongside the laboratory evaluation of the NO_2 instruments, a side-by-side comparison at the SAPHIR atmospheric simulation chamber at FZ-Juelich took place in October 2019 with DWD, Empa, UoY, IL, AU, and FZ-Juelich. Fifteen instruments were evaluated, comprising CLD detectors, CAPS instruments, iterative cavity-enhanced DOAS (ICAD) systems and newly developed QCLAS instruments. The intercomparison was hosted by the World Calibration Center for Nitrogen Oxides (WCC-NOx) who provided the reference instrument. The setup at the atmospheric simulation chamber SAPHIR and the JULIAC tower allowed for ambient measurements as well as photochemical experiments. The participants calibrated their own instruments before the campaign, but NO and NO_2 standard gas was added into the sampling inlet daily which allowed for monitoring changes in sensitivity over time. NO_2 in gas cylinders is more prone to degradation than NO, therefore the oxidation of NO by gas phase titration with ozone has been the preferred method to produce NO_2 for calibration purposes. However, this method requires the simultaneous measurement of NO which cannot be done by e.g. CAPS instruments. Therefore, the production of stable NO_2 calibration mixes was one of the main foci of this project. The NO_2 gas cylinder from NPL prepared within the project was found to contain the expected mixing ratio within the stated uncertainty. Also, the recovery rate of the NO_2 from the permeation source was very good, as the sample had to be diluted to be measured by all the instruments. Likewise, the measurements of the NO_2 produced from gas phase titration were in accordance with the expected value. Two other NO_2 standards from cylinders on the other hand were found to contain only 80 % and 90 % of the stated concentration, respectively.

The sensitivity of the instruments was tested, and the data for four instruments (CLD – FZJ, ICAD – FZJ, CAPS – IL) agreed to better than 5 % with the expected value, however some test gas measurements differed by up to 30 %. The NO_2 data obtained with the rather recently developed QCLAS and ICAD instruments agreed quite well with the expected values. These instruments also showed little change in sensitivity over time, as did two out of the three CAPS systems (CAPS – IL, CAPS – DWD). In contrast, response factors of three CLDs (CLD – DWD, BLC – UoY, PLC (diode) – UoY) and one CAPS (CAPs – UoY) changed significantly over time.

The instruments were also tested for humidity and nitrate and nitrite interferences. The CLDs tested showed loss of sensitivity under humid conditions due to quenching, however this effect can be corrected for. CAPS measurements can also be biased from humidity. One QCLAS system and the ICAD analyser showed no effect from humidity. All CLDs were found to have interferences with isobutyl nitrite and therefore potentially with HNO_2, while molybdenum and one photolytic converter showed interferences with nitrates.

The consortium developed new methods to enable the accurate measurement of impurities, most critically HNO_3, and they reviewed, developed and validated direct NO_2 measurement methods and compared these under controlled synthetic and ambient conditions. The intercomparison showed that the measurement data agreed provided the instruments were well calibrated and characterised. It was also suggested that the accuracy of measurements could be greatly improved by improving the calibration procedure by calibrating with reference standards containing NO and CO_2 and tracking the dilution with precise CO_2 measurements.

5 Impact

(To promote the uptake of the new primary reference materials of nitrogen dioxide, and to share knowledge and insights into the production and application of these reference materials generated throughout the project, results were shared broadly with academic, scientific and industrial end users. The project website is hosted by NPL (http://empir.npl.co.uk/metno2/). The website has a dedicated news and events section. A successful first stakeholder workshop was hosted at CMI in Prague in February 2018. Ten stakeholders came from as far away as Japan, with representatives from ENVEA, TROPOS, WMO, FORCE, Picarro, FINE metrology and Takachiho in attendance. Following presentations on the MetNO2 project from the partners, Edgar Flores of BIPM gave a pre-recorded presentation discussing CCQM-K74.2018 10 umol/mol NO_2 in Nitrogen. Kjetil Torseth (NILU) then presented on WMO-GAW and EMEP perspectives on the $MetNO_2$ project and how to maximise impact. The final presentation was given by Thierry Tonnelier (ENVEA), describing their work with NO_2 as a European manufacturer of continuous environmental pollution analysis systems. The stakeholder committee had 14 members, not including partners, (EMEP, WMO GAW, Picarro, Ecoscientific, Takachiho, BOC, Air Monitors, Mirico, Environnement S.A., Fine Metrology, TROPOS, Force Technology, BIPM, Ricardo Energy and Environment) from 6 EU countries (UK, France, Denmark, Germany, Norway, Italy). A second stakeholder webinar workshop was held virtually in October 2020 with more than 70 attendees where an overview of the results was presented. Stakeholder MIRO Analytical Technologies gave an overview of the new multi-compound laser-based spectrometer instrument that can make simultaneous measurements of NO and NO_2 as well as a series of other air quality and climate related gases. Outputs from the project have been disseminated to the academic and atmospheric communities via a dedicated session at the EGU conference in Vienna, Austria and to industrial stakeholders at the Biennial Gas Analysis conference in The Hague, The Netherlands. NILU have also made numerous presentations to the EMEP steering body and the task group on measurements and modelling. NPL have presented updates on the project at the Euramet TCMC meeting and also a special workshop to celebrate the 25th anniversary of the CCQM.

METAS organised a 4 day workshop and training course for users of magnetic suspension balances applied to the generation of dynamic standards through the use of permeation devices. The event consisted of one day of training and discussion, led by METAS, in which expertise and experiences were shared between the participants in setting up MSB systems coupled to permeation devices. The training was followed by a two day workshop, again lead by METAS, in which key aspects were addressed concerning the generation of dynamic standards using MSB instruments. These topics included factors influencing: the mass measurement; validation; uncertainty budgets of the mass measurement; results from international comparisons; permeation devices; dynamic generation; and limits of the technology. Separate contributions made by participants from METAS, NPL, VSL, LNE, BIPM, TA Instruments (formerly Rubotherm) and Fine Metrology were made via presentations of their work. The outputs of this workshop include the formation of an unofficial working group of stakeholders using the MSB technique applied to dynamic standard generation. The aim of the group was to share experience/data using the MSB to help the members identify and trouble shoot difficulties associated with the technique and optimise their systems.

Impact on industrial and other user communities

Eight one day knowledge exchanges have been held between NPL and major speciality gas companies (Air Liquide, Air Liquide UK, Air Products, BOC/Linde and Effectech) to discuss the project's efforts to improve NO_2 reference standard production and the advances in cylinder passivation that could help to achieve the project's goals. One trade journal article has been published in Gasworld magazine on the challenges around the preparation of NO_2 reference standards. A second article was published in the Viewpoint section of the prestigious Journal of Environmental Science and Technology (American Chemical Society) entitled “Future Adoption of Direct Measurement Techniques for Regulatory Measurements of Nitrogen Dioxide: Drivers and Challenges”. This article described the importance of atmospheric nitrogen dioxide (NO_2) and that as a result of the chemiluminescence (CLD) measurement technique typically used to demonstrate regulatory compliance it remains the only regulated air pollutant that is not directly measured or calibrated. With the CLD method the NO_2 amount fraction is estimated as the difference between two channels, one that measures NO only and the other that measures total nitrogen oxides ($NO_x = NO + NO_2$) after NO_2 is either catalytically or photolytically converted to NO prior to detection. Interferences in the NO_x channel from other reactive nitrogen compounds (NO_y) result in inaccuracies in the estimated NO_2 amount fractions, which limits the applicability of this data to improve atmospheric models and satellite retrievals. With recent advancements in adsorption spectroscopy commercial instruments capable of direct NO_2 measurements are now readily available and the challenges to widespread use of direct NO_2 instruments for regulatory compliance have been identified and discussed. The project developed an Intellectual property (IP) exploitation plan. Empa co-founded a spin off company, MIRO Analytical

Technologies, to exploit the IP, some of which was developed during the project, related to their mid-IR laser technology and they are already marketing a new compact laser spectrometer that directly measures up to 10 gases simultaneously including NO_2.

Impact on the metrology and scientific communities
NPL co-organised (in collaboration with project partner METAS and stakeholder BIPM) and chaired a special metrology focused session at the European Geosciences Conference in Vienna in April 2018, April 2019 and April 2020 (held virtually). There were 15 presentations in this metrology focused session in 2018 including one on this project, 24 presentations in 2019 including three from this project and 20 presentations in 2020 including 5 from this project. These sessions were entitled ‘Atmospheric gases and particles: metrology, quality control and measurement comparability’ and the session description was as follows: “*Measurements of gaseous compounds and particles in the atmosphere play a critical role in our understanding of air quality, human and ecosystem health and the mechanisms governing the Earth’s climate. Monitoring long term spatial and temporal changes in amount fractions of regulated air pollutants, greenhouse gases, precursors to secondary pollutants (e.g. ozone and particulate matter) and particle number and size distributions are essential to establish the scientific links and feedbacks between atmospheric composition, air quality and climate and to ensure legislative compliance. Ambient amount fractions and stable isotope ratios of many trace gases as well as particle number concentrations and size distributions are routinely observed within networks of monitoring sites and on mobile measurement platforms around the globe. Ensuring the quality and comparability of all these datasets is critical to improve reliability and reduce uncertainty in our understanding of the Earths system. This session invites contributions that seek to address the fundamental metrology needed to underpin long term ambient monitoring of trace gases and particles ensuring coherent and comparable measurements*.” This provided an excellent forum to disseminate project outputs to the atmospheric chemistry community and the academic community as it is one of the largest geoscience conferences in the world.

A peer reviewed paper has been published in the Journal of Spectroscopy on a new approach for purity analysis using a novel OPO-CRDS instrument. Another peer review paper has been published in Applied Sciences that describes advances in direct NO_2 measurements using laser spectroscopy. Six more peer reviewed publications are in preparation which are expected to be submitted for publication during 2021.

A partner was present at each of the following committee meetings: CEN TC264 WG12 where revisions to EN 14211 were discussed and a proposal was made to recommend to the European Commission to change the standard reference for NO_2 measurements from chemiluminescence to direct detection. A new work item was prepared and it was supported by the working group. The CCQM-K74.2018 10 µmol/mol NO_2 in N_2 comparison and the CCQM-P172 Spectroscopic methods for HNO_3 value assignment were discussed at the CCQM GAWG. Improvements in the development of NO_2 reference standards generated within the project have been exploited by several of the partners during the production of standards for the CCQM-K74.2018 international comparison on 10 µmol/mol NO_2 in N_2 that will result in new and/or improved calibration and measurement capability claims for NO_2. Scientists from NPL, LNE, PTB and METAS were seconded to BIPM for training in FTIR for between 1 and 12 weeks in Autumn 2017, Summer 2018 and Summer 2019 for knowledge exchange and training.

The direct involvement of representatives from the key atmospheric monitoring communities (WMO-GAW, EMEP, AQUILA, LAQN, NABEL) ensured the rapid dissemination of new reference materials, measurement guidelines and recommendations ensuring the early impact of the project’s outputs. NILU has made several presentations about the project and its aims to the EMEP steering body and to the WMO-GAW scientific advisory group on reactive gases. They have also played the leading role in the revision and development of the EMEP monitoring strategy for 2020-2029, that has been endorsed by the EMEP Steering Body, where they have tried to more clearly state the importance of metrology, which is now referenced within the document. Project outputs will also be used to provide updates to the EMEP ‘Manual for Chemical Analysis’, the WMO-GAW measurement guidelines for ‘Global long-term measurements of nitrogen oxides and recommendations for GAW nitrogen oxides network’ and the Global Atmospheric Watch Training and Education Centre (GAWTEC) which are used to train air quality monitoring station personnel in the standard operating procedures. DWD hosted GAWTEC 35 providing training on reactive gases, data assurance and quality control. Activities in this project are well coordinated with existing members of the Horizon 2020 funded Aerosol, Clouds and Trace Gases Infrastructure (ACTRIS) II and In-service Aircraft for a Global Observing System (IAGOS) research infrastructure projects ensuring that it will complement and contribute to efforts within these communities to improve reliability and traceability of NO_2 measurements. This project contributed positively to ongoing data harmonisation activities improving the comparability of future NO_2 measurements in Europe by strengthening and enhancing the impact of the European funded ACTRIS II and IAGOS projects.

NPL has become an associated partner of the ACTRIS-2 and EUROCHAMP-2020 measurement infrastructure projects, through which NPL can now attend meetings and influence these key stakeholder projects. The provision of new more accurate reference materials will support the very extensive network of NO_2 measurement sites within Europe allowing Europe to maintain its position at the forefront of NO_x measurement research. This project will also support the work of the World Calibration Centre (WCC) for NO_x of the WMO-GAW located at Research Center Jülich, Germany.

Impact on relevant standards

The developments and outputs from the project are being used to revise reference methods and documentary standards under ISO/TC158 (Gas Analysis) and CENTC/264 (Air Quality). New methods developed in this project for the preparation of reference materials will be proposed for inclusion in the next revisions of ISO 6142 and ISO 6145 (production and certification of reference materials) and ISO 19229 (purity analysis). A revision of EN 14211:2012 is currently being undertaken by CEN TC 264 WG12 and there has also been discussion on initiating a new work item, which has already been prepared, to develop a standard reference method for direct NO_2 measurements that has support from within the working group.

Longer-term economic, social and environmental impacts

Society needs better NO_2 measurements to understand the health impacts of NO_2 as well as its critical role in global atmospheric chemistry and climate. This project will have a direct impact on the quality of life of citizens as it will underpin the atmospheric monitoring of NO_2 supporting monitoring networks and the direct NO_2 market. More accurate and better harmonised data and greatly improved air quality models will result in cost effective mitigation strategies reducing the economic burden of air quality related disease and policy implementation costs and financial penalties from breaching EU legislation ultimately improving the quality of life for citizens. This project will develop clear tangible outputs (new static and dynamic reference materials, instrumentation, methods, best practice guides and recommendations) to address the requirement for the maintenance of short and long-term stable values of NO_2 at unprecedented levels of precision and accuracy to meet the DQOs established by the WMO-GAW programme. This project will:

- Improve the long-term atmospheric monitoring of NO_2 through the promotion of more accurate direct measurement techniques and direct calibration through the provision of accurate and stable NO_2 reference standards.
- Support data harmonisation across Europe by providing an accurate SI traceable infrastructure which is needed to ensure stable, comparable and coherent datasets.
- Improve evidence-based legislation for motor vehicles based on better trend and concentration analysis leading to more effective mitigation strategies.
- Ensure the most cost-effective compliance with EU legislation through lower uncertainty and more comparable measurements.
- Enable the enhanced competitiveness of European NMIs and companies based in Europe with institutes outside of Europe by considerably improving European capabilities and positioning Europe at the frontier of metrology.
- Improve quality of life for European citizens and reduce economic burden of health effects of NO_2 exposure through facilitating the rapid evaluation of the effectiveness of pollution abatement strategies.

6 List of publications

[1] S. Persijn (2018). Purity Analysis of Gases Used in the Preparation of Reference Gas Standards Using a Versatile OPO-Based CRDS Spectrometer. Journal of Spectroscopy, vol. 2018, Article ID 9845608. https://doi.org/10.1155/2018/9845608

[2] D. Worton (2020). Future Adoption of Direct Measurement Techniques for Regulatory Measurements of Nitrogen Dioxide: Drivers and Challenges. Environmental Science and Technology, 54, 23, 14785–14786 https;//doi/10.1021/acs.est.0c04709.

[3] N. Sobanski, B. Tuzson, P. Scheidegger, H. Looser, A. Kupferschmid, M. Iturrate, C. Pascale, C. Hüglin, L. Emmenegger (2021). "Advances in High-Precision NO_2 Measurement by Quantum Cascade Laser Absorption Spectroscopy." Applied Sciences 11(3): 1222. https://doi.org/10.3390/app11031222

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/