Publishable Summary for 16ENV05 MetNO2
Metrology for Nitrogen Dioxide

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.

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.

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.

Progress beyond the state of the art

Measurement accuracy is strongly linked to the analytical methodology and the quality of the reference gas standards used for instrument calibration. NO_2 amount fractions in the atmosphere span several orders of magnitude and reference standards that encompass this range are necessary to minimise calibration uncertainties. However, NO_2 is very reactive, which limits the stability of static standards at low amount fractions in high-pressure cylinders making their dissemination highly challenging. The production of accurate standards at low amount fractions typical of the ambient atmosphere requires either the dilution of a stable higher concentration gas standards or direct production by a dynamic technique, such as one based on permeation tubes. This project progressed beyond the state of the art by improving the understanding of the kinetics of the reaction between NO_2 and H_2O, the major reaction leading to loss of NO_2 and formation of the undesired impurity, HNO_3. This project has substantially lowered the uncertainties and increased the stability of NO_2 reference standards. To achieve this required the full characterisation and minimisation of critical and significant NO_y impurities, most importantly nitric acid (HNO_3), which required the development of appropriate measurement methods for detection and quantification. Clearly, it is much better and more accurate to use techniques that specifically measure NO_2 as opposed to conversion and detection in another form and also to directly calibrate with NO_2 reference standards as opposed to indirectly through for example the gas phase titration of NO standards with ozone. Due to recent advances in selective NO_2 measurement techniques, direct NO_2 measurements were feasible, and there was an urgent requirement to critically evaluate the applicability of these methodologies for long-term ambient measurements and to compare them against the standard chemiluminescence method (EN 14211:2012). This was done in a side-by-side experiment where instruments could be compared using both controlled synthetic test atmospheres and ambient air. This project demonstrated the improved accuracy of the direct measurement and direct calibration of atmospheric NO_2 utilising static and dynamic reference standards supporting the direct NO_2 market. These standards ensured that atmospheric monitoring stations are able to comply with the requirements of the WMO-GAW programme supporting national, regional and global long-term NO_2 monitoring.

Results

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.*

The focus of this objective was on the production of new, accurate (≤ 0.5 %)) and stable (≥ 2 years) static reference standards of NO_2 in the low µmol/mol (1 – 10) range. These were needed to facilitate the atmospheric measurements of NO_2 that are used to meet the DQOs (≤ 5 %) established by the WMO-GAW programme. A best practice guide for the preparation of static primary reference standards of NO_2 has been produced to share the findings with the broader NMI community and the speciality gas industry.

Technical protocols were prepared for the accurate preparation and validation of the NO_2 gas standards and for the stability testing based on best available knowledge. A selection was made from various available suitable cylinder treatments (7 in total) for the preparation of the NO_2 standards and all 33 NO_2 gas standards were prepared by the partners (at amount fractions of 1 µmol/mol and 10 µmol/mol) in synthetic air and nitrogen matrices and these 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 the cylinder passivation chemistry used, which indicated 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.

NPL, LNE, VSL and TUBITAK sent NO_2 reference standards, which were developed in the project, to the BIPM as part of key comparison CCQM-K74.2018 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's results showed a bias of 0.5 % relative to NPL, LNE and VSL. The discrepancy for TUBITAK was likely because they used chemiluminescence to measure NO_2. As both NO_2 and its main impurity HNO_3 were measured together by the CLD method this analytical technique was unable to distinguish between these two compounds. This resulted 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.

Nitric acid (HNO_3) has been identified via a literature review as the sole NO_y impurity in low µmol/mol NO_2 gas standards and spectroscopic methods (cavity ring down spectroscopy and fourier transform infrared spectroscopy) to quantify this have been developed. This has been confirmed by results obtained by NPL and VSL. NPL developed an FTIR method to measure the temporal evolution of HNO_3 and nitrous acid (HONO) in seven NO_2 reference standards that have been deliberately spiked with known amounts of water vapour (0.3 µmol/mol – 20 µmol/mol). The time resolved behaviour of the loss and subsequent formation of HNO_3 within the cylinder has been 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. 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 partitioning of HNO_3 to the internal surface of the gas cylinder. 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. NPL have noted that there appears to a limited amount of HNO_3 formation that is not related to the availability of either NO_2 or water, which has implications for the production of HNO_3 standards from in-cylinder chemistry.

VSL have developed and utilised a new cavity ring down spectrometer (CRDS) to measure HNO_3 and HNO_2 in NO_2 reference standards and have shown that the amount fraction of HNO_3 increases with the age of the reference standard indicating that HNO_3 formation continues over time following production and thus it substantially contributes to long-term instability. Interestingly, NPL and VSL both report that no HNO_2 was detectable (< 1 nmol/mol) suggesting it was a short lived intermediate assuming that the known atmospheric mechanism for the $NO_2 + H_2O$ is appropriate for high pressure cylinders. While it was possible to produce NO_2 reference materials with an accuracy of 0.5 %, a stability of 2 years was not possible at this uncertainty level. However, scientific knowledge has been advanced by the project in this area. 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. New procedures have been developed and implemented to minimise the presence of water vapour in the cylinders' valves, filling lines and matrix gases, which is critical to minimise HNO_3 formation in the cylinder. It is important to note that chemiluminescence should not be used to certify reference standards of NO_2 due to the interference of HNO_3, and if possible, a direct technique should be used.

It is notable that the loss of NO_2 (drift rate) changes as a function of time following preparation and appears to follow a power law dependence regardless of water vapour amount fraction. The results from this project show that after 150 days (5 months) the drift rates have substantially declined and this means that the best way to currently achieve longer stability periods maybe 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 correspondingly longer stability periods than would be possible from the gravimetry alone.

Overall, this objective was partially achieved in that NO_2 reference materials could be prepared with uncertainties ≤ 0.5 %, but at this uncertainty the stability periods were much shorter that the required 2 years. A greater understanding of the chemistry of nitric acid formation within high pressure gas cylinders demonstrates that as the kinetics follow a power law dependence it would be possible to provide certified reference materials (analytical assigned values) with longer stability periods and low uncertainties 150 days after 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.*

The focus of this objective was on the development of dynamic generation devices capable of producing accurate (≤ 1 %), low amount fraction (10 nmol/mol – 500 nmol/mol) reference standards of NO_2 for the calibration of instrumentation at air quality monitoring stations. The major impurities (e.g., HNO_3 and N_2O_4) have been fully characterised and methods have been developed to minimise impurity formation during standard generation. A best practice guide for the use of static and dynamic gas standards at monitoring stations has been produced in order to share the findings with the air quality monitoring community.

A critical requirement to meet the low uncertainties at the lowest amount fractions is the removal and characterisation of NO_y from the diluent gas. To address this, different purifiers (Hydrosorb, Microtorr, Monotorr, Sofnofil followed by activated charcoal) have been tested to remove NO_y from air and nitrogen matrices. Microtorr and monotorr cartridges appear to effectively remove NO_x to < 50 pmol/mol. The sofnafil and charcoal traps can also be effective depending on the age of the purifier material and on the leak tightness of the filter housing. Several different dynamic generation systems based on permeation (METAS, LNE) and dynamic dilution of higher amount fraction reference standards (UoY, NPL, IL, CMI) have been developed, and with the exception of CMI, were assessed and compared through a round robin comparison using a certified travelling standard. 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 all partners other than NPL. NPL reported an amount fraction of NO_2 lower than the reference value. The positive bias for most results suggested that either NPL's reference value was low, or the partners' dynamic systems generated lower amount fractions of the target gas than expected. There were several challenges to the 'round robin' approach for this intercomparison and in hindsight it would have 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.

METAS and LNE have tested the influence of temperature and pressure on the permeation rate. METAS have tested the influence of both variables on a unit with a thin permeation membrane and these results were compared against a unit with a thicker permeation membrane. These results 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, while also demonstrating the benefit of pre-conditioning the permeation tubes before use. METAS has determined the mass loss rates of NO_2 and HNO_3 using new permeation units, which have accurately quantified the water amount fraction from HNO_3 permeation units, using a calibrated cavity ring down spectrometer. LNE has developed analytical methods to measure NO_2 and the major impurities in dynamic systems (HNO_3 and N_2O_4) based on FTIR spectroscopy. These methods have been used to characterise the portable dynamic generator from METAS. The output of the UoY permeation device has been measured gravimetrically and by FTIR spectroscopy to equate mass loss with output component amount fractions. The FTIR measurements showed that water vapour was the dominant impurity emitted alongside HNO_3 but accurately measuring the amount of water vapour emitted depended on the ingress of ambient water vapour into the permeation system. The original housing providing by UoY suffered from significant ingress of ambient moisture. NPL designed a new and improved heated housing for the UoY permeation tube and demonstrated that it substantially minimised moisture ingress. 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.

METAS provided a portable generator (ReGas) to DWD together with a calibrated permeation unit, calibrated using their magnetic suspension balance and these were used to calibrate a Cavity Attenuated Phase Shift (CAPS) spectrometer for the direct measurement of NO_2. Empa purchased a ReGas portable generator from METAS, which was deployed successfully in the field at one of the NABEL monitoring stations in November 2019. This coincided with field calibrations using a new 1 µmol/mol NO_2 reference standard developed by VSL. UoY, KCL and IC have conducted side-by-side field trials of a direct NO_2 instrument (CAPS) against a reference instrument (CLD using heated molybdenum converter) at both an urban roadside site (Marylebone Road, London) during winter and an urban background site (Honor Oak Park, London) during summer to evaluate instrument biases of the current reference method. Interestingly, at the roadside site the slower response time of the CAPS instrument meant that some highly dynamic features (sharp spikes in amount fraction) were not fully captured when compare to the faster time response of the CLD instrument. NPL provided KCL and IC with five 1 µmol/mol NO_2 reference materials and five zero air cylinders which were deployed to 2 suburban and 3 urban London Air Quality Network (LAQN) monitoring stations, which use chemiluminescent methods. 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. Given what we now understand about the power law dependent decay, in the future it would be advisable to have at least 150 days between preparation and certification, which should provide more stable and accurate values for use at field stations.

Overall, this objectives was achieved but with uncertainties that were higher than the goal of 1 %. The best of these was for the METAS portable generator which was ≤ 3 %.

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.*

Spectroscopic methods for the measurement of major impurities such as NO, H_2O and HNO_3 in NO_2 reference gas standards have been developed and used to fully characterise impurities in the static and dynamic reference gas standards developed in this project. A literature review summarising commercially available selective NO_2 instruments has been completed and in addition to CAPS, IBB-CEAS, QCL, CRDS and CEAS 5 further instruments were identified; TDLAS, ICOS, OFCEAS, PAS and FTIR. The development of spectroscopic systems and methods was completed and a report was written. In summary, a novel dual wavelength QCLAS system for simultaneous direct NO and NO_2 measurements has been developed and the measurement requirements have been met. A QCLAS system has been adapted for the measurement of NO impurities in NO_2 reference standards. LNE developed an IBB-CEAS instrument and evaluated its linearity in the 20 nmol/mol – 500 nmol/mol range using their own permeation system. DFM developed a compact laser spectrometer for NO_2 detection and the long-term stability assessment of the instrument was not completed during the project due to a flood in DFMs laboratories in August 2020. PTB performed NO_2 line data measurements employing an 8m pass cell. UoY validated and optimised their CAPS instrument which has subsequently been deployed in two field experiments in London. Spectroscopic methods for impurity analysis in NO_2 reference standards have been developed and applied for impurity characterisation. These results have been written up into a report. In summary, PTB applied their FTIR method to characterise HNO_3, N_2O and CO_2 impurities in a 1000 µmol/mol NO_2 standard. DWD developed a four-channel thermal dissociation inlet combined with a CAPS instrument (TD-CAPS) to measure HNO_3, total alkyl nitrates and total peroxy nitrates. A CRDS system has been adapted for HNO_3 and HNO_2 detection, and the first measurements have been performed on NO_2 reference standards.

A protocol for the laboratory characterisation and evaluation of selective NO_2 instruments for direct NO_2 measurements was developed and agreed and a side-by-side comparison at the SAPHIR atmospheric simulation chamber at FZJ took place in October 2019. Fifteen instruments were evaluated, these comprised chemiluminescence detectors, cavity attenuated phase shift (CAPS) instruments, but also Iterative Cavity-enhanced DOAS (ICAD) systems and newly developed Quantum Cascade Laser Absorption Spectrometers (QCLAS). 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 everyday NO and NO_2 standard

gas was added into the sampling inlet 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 intercomparison showed that the measurements data agree, provided the instruments are well calibrated and characterised.

Overall, this objective was achieved in that nitric acid and water vapour have been identified as the major impurities in NO_2 reference standards and methods have been developed to quantify these impurities. A comprehensive comparison experiment demonstrated the measurement data from a range of direct NO_2 instruments agreed well (< 5 %) provided that these were well calibrated and characterised. This indicated the importance of calibration and quality assurance requirements to ensure measurement data is of the highest quality.

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.

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/

Project start date and duration:	June 1st 2017, 42 months	
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Internal Funded Partners: 1 NPL, UK 2 CMI, Czech Republic 3 DFM, Denmark 4 IL, Finland 5 LNE, France 6 NILU, Norway 7 TUBITAK, Turkey 8 VSL, Netherlands	External Funded Partners: 9 AU, Denmark 10 DWD, Germany 11 FZ-Juelich, Germany 12 KCL, UK (withdrawn from 30 June 2020) 13 UoY, UK 14 IC, UK (joined from 1 July 2020)	Unfunded Partners: 15 Empa, Switzerland 16 METAS, Switzerland 17 PTB, Germany
RMG: -		