# Title: Metrology for Nitrogen Dioxide

## Abstract

Nitrogen dioxide ($NO_2$) is a toxic gas with direct implications for public health, it also has implications on the environment as it influences the oxidative capacity of the atmosphere. It plays a critical role in air quality and as such is regulated through the Air Quality Directive 2008/50/EC and National Emission Ceilings (NEC) Directive 2001/81/EC. The World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) programme is committed to maintaining a long term global measurement programme for $NO_2$, in order to improve the accuracy of air pollutant models and emissions data; and ensure legislative compliance. However, in order to support the WMO-GAW programme and EU regulation the metrology for $NO_2$ needs to be urgently improved and developed. In particular, the direct measurement of atmospheric $NO_2$ needs to be advanced with the development of new, high accuracy reference standards and methods, as well as a comparison with existing indirect $NO_2$ measurement methods.

## Keywords

Nitrogen dioxide, dynamic methods, nitrogen oxides, monitoring networks, air quality, atmospheric composition.

## Background to the Metrological Challenges

In Europe, air pollution is responsible for more than half a million premature deaths per year and has an associated economic costs that equates to 5 - 10 % of European GDP. $NO_2$ is a key air pollutant that directly affects human health, and is also a key precursor in the formation of two other key air pollutants ozone and fine particulate matter. $NO_2$ also has serious environmental impact as it has greatly affects the oxidative capacity of the atmosphere which in turn affects the way in which the atmosphere deals with other pollutants and ozone depletion. The EU sets legal limits for $NO_2$ concentrations as part of the Air Quality Directive 2008/50/EC and upper limits for annual $NO_x$ emissions as part of the NEC Directive 2001/81/EC and the United Nations Economic Commission for Europe (UNECE) Gothenburg Protocol. Compliance with such legislation is assessed through a combination of data from monitoring networks and the results of air pollutant modelling. However, these air pollutant models depend upon measurement data, and so the accuracy of the measurement data is critical for minimising uncertainty and maximising confidence in the outputs of the air pollutant models. More accurate measurements of $NO_2$ are needed to understand population level exposure and improve air pollutant models.

The most common method for measuring $NO_2$ is by chemiluminescence detection, as described in EN 14211:2012. However, this method is an indirect measurement technique making $NO_2$ the only regulated air pollutant that is not directly measured. Direct measurements of $NO_2$ are now possible as a result of recent advances in more selective $NO_2$ measurement techniques, e.g. quantum cascade laser absorption spectrometry (QCLAS), cavity ring-down spectrometry (CRDS), cavity attenuated phase shift spectroscopy (CAPS), cavity-enhanced absorption spectroscopy (CEAS), and these direct measurements should be a far more accurate and reliable method of measuring $NO_2$. There is an urgent need for reference standards and an improved SI traceable infrastructure for $NO_2$ based on such direct measurements.

Concentrations of $NO_2$ in the atmosphere vary from pmol/mol to high nmol/mol and standards that encompass this range are necessary to minimise calibration uncertainties. However, $NO_2$ is a challenging molecule due to its reactive nature, which can result in the instability of calibration mixtures. Dynamic reference standards for $NO_2$ are currently based on the dilution of stable high concentration static $NO_2$ standards, however permeation and diffusion tubes and gas phase titration of NO with ozone are alternative methods of generating low amount fraction calibration gas mixtures of $NO_2$. In fact, the EMRP ENV01 MACPoll project has already demonstrated that dynamic methods, based on permeation and diffusion tubes, can generate amount fractions at the EU regulated limit values for $NO_2$ with uncertainties typically around 3 %.

Recent results from a BIPM key comparison (CCQM-K74) have shown comparability within 3 % of the reference value for a static standard of 10 µmol/mol $NO_2$ in nitrogen. But, in order to provide the most reliable data for air pollutant models and to meet the data quality objectives defined by the WMO-GAW of ≤ 5 % for ambient $NO_2$ concentrations (pmol/mol to nmol/mol), reference standards for $NO_2$ with significantly lower uncertainties of ≤ 1 % are required.

## Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on the traceable measurement and characterisation of $NO_2$ in the atmosphere.

The specific objectives are

1. To develop highly accurate, traceable dynamic reference standards for trace amount fractions of $NO_2$ (10 – 500 nmol/mol) with a target uncertainty of 1 %.
2. To develop high concentration static reference standards for $NO_2$ (1 – 10 µmol/mol) with a target uncertainty of 0.5 % and stability of > 2 years.
3. To develop methods and reference standards to quantify the main components of $NO_y$, (other than $NO_2$) that are formed as impurities during the preparation of $NO_2$ reference standards. The effect of $NO_y$ on the uncertainty of the $NO_2$ amount fraction in the reference standard will be minimised and within the requirements set out by the Air Quality Directive 2008/50/EC.
4. To validate selective methods for directly measuring $NO_2$ (such as QCLAS, CRDS, CAPS, CEAS). This will include the characterisation of the analyser zeros and interferences as well as the demonstration of the equivalence of the methods to EN 14211:2012, using field trials at monitoring sites.
5. To collaborate with stakeholders e.g. instrument manufacturers and speciality gas industry to ensure the uptake of the reference standards, methods and devices developed in this project by standards development organisations (such as those linked to the Air Quality Directive 2008/50/EC and NEC Directive 2001/81/EC), end-users, atmospheric monitoring networks, programmes and other measurement infrastructures (e.g., WMO GAW, the European Monitoring and Evaluation Programme (EMEP), In-service Aircraft for Global Observing System (IAGOS), Aerosols, Clouds, and Trace gases Research Infrastructure 2 (ACTRIS II), the London Air Quality Network (LAQN) and Network of Air Quality Reference Laboratories (AQUILA)).

These objectives will require large-scale approaches that are beyond the capabilities of single National Metrology Institutes and Designated Institutes. To enhance the impact of the research, the involvement of the appropriate user community such as industry, standardisation and regulatory bodies is strongly recommended, both prior to and during methodology development.

Proposers should establish the current state of the art, and explain how their proposed research goes beyond this. In particular, proposers should outline the achievements of the EMRP JRP ENV01: MACPoll and how their proposal will build on those.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 2.0 M€, and has defined an upper limit of 2.3 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 35 % of the total EU Contribution to the project.

Any industrial partners that will receive significant benefit from the results of the proposed project are expected to be unfunded partners.

## Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the “end user” community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the "end user" community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,
- Feed into the development of urgent documentary standards through appropriate standards bodies,
- Transfer knowledge to the atmospheric and environmental monitoring sectors.

You should detail other impacts of your proposed JRP as specified in the document "Guide 4: Writing Joint Research Projects (JRPs)"

You should also detail how your approach to realising the objectives will further the aim of EMPIR to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work

## Time-scale

The project should be of up to 3 years duration.