Title: Metrology for chemical pollutants in air

Abstract

The European Union's Directive 2008/50/EC on 'ambient air quality and cleaner air for Europe' forms a strong impetus for further development of the metrological infrastructure for measurement of chemical pollutants in air. Joint Research Projects (JRPs) submitted for this topic should improve the metrological infrastructure for (1) the preparation methods of air pollutants gas mixtures for calibration purposes, (2) validation of measurement methods for challenging gaseous pollutants, and (3) validation of micro- and compact optical sensors for air quality measurements.

Conformity with the Work Programme

This Call for JRPs conforms to the EMRP 2008, section on "*Grand Challenges"* related to *Environment* on pages 8, 24 and 25.

Keywords

Dilution methods, gaseous pollutants, zero gas, micro- and optical sensors

Background to the Metrological Challenges

Air quality measurements are required for the implementation and further development of the EU Air Quality policies (e.g., Directive 2008/50/EC and 2004/107/EC), and metrological aspects such as method development/validation, uncertainty and traceability constitute key elements for these policies. Additionally in the light of emerging challenges, there is a need for underpinning research and new measurement methodologies. Among these, the following themes need to be addressed:

- Development of preparation methods of air pollutants gas mixtures for calibration purposes

- Validation measurement methods for challenging gaseous pollutants

- Validation of micro- and compact optical sensors for Air Quality measurements

Development of preparation methods of air pollutants gas mixtures for calibration purposes

Directive 50/2008/EC states that National Reference Laboratories (NRLs) are responsible for providing traceable calibration standards to the air quality networks for each of the regulated pollutants. The lowest level of concentration that NMIs can provide is restricted by the "How Far The Light Shines" statements of each of the key comparisons. At present, the lowest level starts with ozone from zero, whilst for NO and SO_2 the lowest level is 100 nmol/mol, and for CO the lowest level is 1 µmol/mol.

The use of dilution methods can provide a way to reach lower calibration concentration ranges. Dilution methods applied for the preparation of calibration gas mixtures are based on the dynamic dilution and the static volumetric dilution method. The dynamic dilution method applies to a wide variety of gas compounds e.g. inorganic gases (CO, NO, SO_2, H_2S) and VOCs. Gas sources can be gravimetrically prepared gas standards, or based on permeation or diffusion sources.

Comparisons of gas mixtures preparation with the same method as well as with an independent method (cross studies) is essential to avoid drift of the calibration level, to test the comparability between different calibration methods as well as to validate the methods. Recent CCQM key-comparisons (CCQM-K26b, CCQM-K46) have shown significant differences in results between gravimetric and dynamic methods and the reason why is not yet well understood. NRLs, Air Quality

Networks (AQN) and research groups will all benefit from a better understanding of the use of dilution methods for the preparation of gas mixtures, for a large range of gas compounds and concentration levels, with traceability to SI units and with known uncertainty.

Extending the lower limit of calibration ranges using the dilution approach is limited by the quality of the zero gas used for dilution. At present no zero-gas standards (nitrogen and air gas containing traceable and accurately measured trace level of impurities) are available and therefore accuracy of gas mixture preparation and ultimately the measurement results is negatively affected.

Directive 50/2008/EC (Annex 1 paragraph C) specifies that all measurements undertaken in relation to the assessment of ambient air quality pursuant to Article 6 and 9 shall be traceable and in accordance with the requirements of ISO/IEC 17025:2005. Calibration of emission analysers normally requires a so-called span gas (90 % of measurement range) and a zero gas. The limits for air pollutants subject to regulation are reducing further and the limit of detection of current analysing equipment is only just acceptable. Current EN standards for reference methods of air pollutants include specifications around or below 1 nmol/mol (parts-per-billion).

For both zeroing of the measuring instrument and dilution it is very important to accurately and traceably quantify the presence of any of these pollutants or compounds that may provide analytical interference. The challenge in producing zero-gas standards is to find extremely sensitive and accurate analysers that have preferably a potentially primary method of operation.

Validation methods for challenging gaseous pollutants

Several relevant air pollutants are difficult to quantify due to their chemical properties (reactivity, adsorption), including PAHs, (V,S) VOCs, formaldehyde, and ammonia.

For PAHs, the current CEN reference methodology, based on the determination of particulate PAHs in the PM10 fraction, is known to suffer from important limitations due to the reactivity of ozone and nitrogen dioxide with PAHs during sampling. The measurement uncertainty of the reference method amounts to 50 %, rendering the assessment of compliance with the target value inefficient or unclear. A better methodology that would include the full range of PAHs, including gaseous and particulate, nitro- and oxy-PAHs is therefore needed.

International standards (ISO 16000-3, ISO 16000-6, ISO 16000-9) are available for the determination of VOC emissions, but there is a lack of methods for the measurement of VVOCs and SVOCs in air. With regard to standards (“Blue Angel” environmental label) and legislation (European building product directive), current inter-laboratory comparisons for test chamber measurements of building products reveal a large unsatisfying variation (more than one magnitude) of results. For the health related evaluation of VOC emissions the AgBB-Scheme is used in Germany[i], but the detection of some important compounds which are currently not included in routine analysis for this scheme must be added in the near future. This enlargement of the test procedure is important and must be developed and checked by inter-laboratory comparison tests.

Formaldehyde is considered to have carcinogenic/mutagenic properties and proper chemical analysis of its concentration in air is required. Legislation may require measurement of occupational exposure, emission from wood products like particle board and emissions from gas or oil powered turbines, however, accurate and traceable calibration standards for formaldehyde are currently lacking.

Accurate measurement of trace levels of ammonia is particularly problematic due to its strong adsorption onto surfaces. This is exemplified by the results of the recently held key comparison CCQM-K46 of 30 μmol/mol ammonia in nitrogen which showed dispersion in the results as large as –6 % to +1.5 % relative.

Validation of micro- and compact optical sensors for Air Quality measurements

The EU Air Quality legislation contains a number of provisions concerning the Data Quality Objectives (DQO) that need to be respected for the assessment of the air quality levels. The DQO are expressed in terms of maximum measurement uncertainty, minimum data capture and coverage. The current performances of micro-sensors and compact optical sensors make both methods eligible as indicative measurement method under EU Air Quality legislation, and in certain cases as equivalent methods to the reference methods proposed by the Air Quality legislation. Verification of the possible agreement of the current performances of both type of sensors with the DQO of the EU Air Quality legislation and assessment of their applicability in air quality research activities is needed.

Micro-sensors are very small sensors with physical dimensions of a few millimetres or less that can be used to monitor the concentration levels of air pollutants in ambient air. They are based on either the variation of the resistance of a semi-conductor or consist of miniaturized electrochemical cells. Micro-sensors have been tested at the concentration levels found in ambient air since the end of the 1980s, however, there is a hesitancy to use these sensors to monitor air pollution in ambient air because of their lack of accuracy, sensitivity and reliability. In the last years, technological progress has led to improvements in the manufacturing of micro-sensors that resulted in reliable sensors having the correct sensitivity for ambient air monitoring. The use of more theoretical models to describe the phenomena involved in the detection process need to be studied in order to improve the applicability of micro-sensors to a wide range of field conditions.

The recent emergence of compact solid-state sources in the most important spectral regions (UV and infrared) for gas analysis has boosted the development of optical gas sensors. Optical sensors have a high potential to be made compact and integrated into sensor networks and coupled monitoring and modelling systems. However, essential knowledge about the sensitivity to cross-interferences, long-term stability or the impact of operating conditions on these systems is still.

In order to fill the gap between the potential applications of both types of sensors and their lack of implementation, it is proposed to validate both methods and their suitability in the light of the new EU Air Quality Directive's requirements.

Scientific and Technological 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 JRP protocol.

The core objective is to provide validated and reliable measurements/methods with traceability wherever it is practicable to do so for chemical pollutants in ambient air (not particles/aerosols).

The specific objectives are to:

1. Develop dilution methods for preparation of gas mixtures for calibration purposes.
2. Develop traceable methods for validation of zero gas standards (nitrogen and air).
3. Achieve significantly lower uncertainties in the measurement of chemical pollutants in air
4. Develop traceable measurement of 'challenging' chemical pollutants (e.g. trace pollutants like (V,S)VOCs and PAHs, reactive pollutants such as formaldehyde, ammonia, hydrogen sulphide)
5. Develop compact optical sensors and micro-sensors for monitoring ambient air pollutants.

The proposers need to carefully prioritize methods and species to be addressed, given the lifetimes and budgets of a typical joint research. The proposers shall describe which stakeholder input their prioritisation is based on. Proposers shall give priority to work that meets documented stakeholder needs and may include measures to facilitate the development of European standards and Directives.

Proposers should establish the current state of the art, and explain how their proposed project goes beyond this.

Potential Impact

Proposals must demonstrate adequate and appropriate participation/links with the "end user" community. This may be through the inclusion of unfunded JRP partners or collaborators, or by including links to industrial/policy advisory committees, standards committees or other bodies. Evidence of support from the "end user" community (eg letters of support) is encouraged.

Where a European Directive is referenced in the proposal, the relevant paragraphs of the Directive identifying the need for the project should be quoted and referenced. It is not sufficient to quote the entire Directive per se as the rationale for the metrology need. Proposals must also clearly link the identified need in the Directive with the expected outputs from the project.

In your JRP submission please detail the impact that your proposed JRP will have on existing Air Quality Directives of the European Commission and in particular on “Ambient air quality and cleaner air for Europe” (2008/50/EC).

You should also detail other impact of your proposed JRP as detailed in the document “Guidance for writing a JRP”

In response to the need for standardised measurement techniques you should detail how your JRP results are going to:

- feed into the development of documentary standards and guidelines through CEN, other standards developing bodies or other appropriate bodies
- transfer knowledge to the industry, regulators and policy makers.

You should also detail how your approach to realising the objectives will further the aim of the EMRP to develop a coherent approach at the European level in the field of metrology. 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 Member States and countries associated with the Seventh Framework Programme whose metrology programmes are at an early stage of development to be increased
- outside researchers & research organisations other than NMIs and DIs to be involved in the work

Time-scale

The project should be of 3 years duration.

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[i] Umweltbundesamt, 2008 http://www.umweltbundesamt.de/building-products/archive/AgBB-Evaluation-Scheme2008.pdf