Publishable Summary for 16ENV08 IMPRESS 2
Metrology for air pollutant emissions

Overview

European Directives are coming into force setting increasingly stringent Emission Limit Values (ELVs) for key air pollutants to mitigate ~400 000 premature deaths and €330-€949 billion p.a. of costs attributable to air pollution. However, the emissions industry faces an issue as a metrologically robust framework of standardised measurement methods to enforce these directives is not fully in place. This project addresses this measurement gap by innovating measurement methods for new measurands (NH_3, formaldehyde, HF, PM, SVOC, OGC, PAH), addresses a lack of uncertainty characterisation in flow measurements and develops next generation techniques for increasingly stringent future legislation.

Need

Emission limits are enforced by measurements using techniques (instruments) operated in accordance with documentary standards published by CEN, these conventionally being referred to as Standard Reference Methods (SRMs) and either being passed into, or referred to, in member state legislation. There are now European directives regulating emissions from large scale processes, such as power stations, all the way down to domestic boilers burning fuels such as wood pellet. New directive requirements have a two-fold impact in that they are bringing in ELVs for previously unregulated emissions species and also increasingly stringent ELVs for species currently regulated. This is beginning to expose gaps in the capabilities of techniques and SRMs, potentially undermining the ability of national regulators for fulfil their legal responsibilities to enforce such limits. On the large scale there are no SRMs for HF, NH_3 and formaldehyde, and there are questions over whether the existing SRMs for HCl and dust will be able to enforce increasingly stringent ELVs. With respect to small-scale biomass, there are no SRMs for semi-volatile organic compounds (SVOCs), organic gaseous carbon (OGC), polyaromatic hydrocarbons (PAHs) or particulate matter (PM). There is no on-line measurement technique to apportion CO_2 emissions as renewable or fossil fuel derived. Also, cutting across all industrial processes there are some significant issues with flow uncertainty, as with small ducts there is a lack of any work identifying and quantifying sources (needed for dust measurements) and with large processes work is needed to validate existing uncertainty knowledge and develop novel lower uncertainty techniques. Lastly, as acknowledged by the EC, the current legislation will not meet WHO air quality guidelines, and so work is needed now on the next generation of techniques to enforce ELVs in future legislation.

Objectives

The overall aim of this project is to provide metrology to enable the enforcement of the Industrial Emissions, Medium Combustion Plant and Eco-design Directives, and the EU's Emissions Trading Scheme.

The scientific and technical objectives of the project are as follows:

1. To develop validated reference measurement methods where currently none exist for HF, NH_3, formaldehyde and to test the limitations of the existing HCl SRM (EN 1911) and dust SRM (EN 13284-1) for enforcing increasingly stringent ELVs**.** To develop next generation optical techniques laying the platform to enforce ELVs in future legislation.
2. To develop validated reference measurement methods for SVOCs, OGC, PAHs (including benzo[a]pyrene) and PM from small scale combustion sources meeting Eco-design directive uncertainty requirements.
3. To develop hyperspectral multispecies methods for the determination of emissions from biomass combustion including non-wood fuelled. To develop an on-line, real-time technique to apportion CO_2 emissions between renewable and fossil fuel in co-firing biomass plants.

4. To determine the uncertainty and traceability of mass emission measurement with respect to flow calibrations under field conditions. To establish the impacts of wall effects and sensor obstruction, particularly in small ducts. To investigate the use of multiple sensors in stacks and the potential to decrease flow uncertainties.
5. To provide input to the development and/or revision of standards related to the emissions of semi-volatile organic compounds (SVOCs), particulate matter (PM), polyaromatic hydrocarbons (PAHs) and organic gaseous carbon (OGC). In addition, to facilitate the take up of the technology and measurement infrastructure developed in the project by standards developing organisations (such as CEN TC 264 and ISO TC 146 and those linked to the EU Eco-design Directive 2009/125/EC, MCP Directive 2015/2193 and IED 2010/75/EU) and end users (e.g. environmental monitoring and regulation bodies, the power generation sector, combustion equipment manufacturers).

Progress beyond the state of the art

Cutting across the emissions species mentioned above and with regard to measurement methods the current state of the art is that member states have adopted differing approaches and overall the validation is incomplete. The exception is for HCl and dust where SRMs exist as described in EN 1911 and EN 13284-1, however, the validation – having been carried out some time ago - does not fully extend down to concentration levels consistent with the increasingly stringent ELVs that have / will come into force. Instrumentation (techniques) associated with such methods typically poses ppm level sensitivities, which are rapidly becoming insufficient. Hyperspectral monitoring of biomass emissions is not fully developed as a technique and with regard to apportioning CO_2 emissions from co-firing power stations the current measurement is based on an off-line technique. The SRM described in EN 16911-1 gives the state of the art for flow measurement, but this was not validated on a stack that had cyclonic flow, and uncertainty sources in narrow ducts have not been fully characterised as previously there was no requirement for such measurements.

The following new measurement knowledge and capabilities will be delivered under each objective:

1. New measurement methods for HF, NH_3 and formaldehyde and associated validation datasets acquired from measurements carried out on Stack Simulator facilities. New knowledge of limitation of HCl and dust SRMs for legislative enforcement. Next generation capability developed for tuneable diode laser (TDL) systems for future reductions in ELVs.
2. New measurement methods for SVOCs, OGC, PAHs (including benzo[a]pyrene) and PM, and associated validation datasets. Development of a new dilutor sampling approach to improve sampling capability for these difficult to sample measurands. An intercomparison of analytical chemistry laboratories proficiency for analysing collected samples of PAH.
3. Novel hyperspectral, multispecies capability to monitor emissions from both biomass and other combustion sources. Characterisation data and associated peer review publications. A new real-time, on-line instrumental technique based on optical isotope ratio spectrometry (OIRS) to apportion CO_2 emissions from co-firing power stations between renewable and fossil fuel types.
4. Some of the first flow studies in support of the MCP directive in terms of determination of flow uncertainty sources in narrow ducts. An intercomparison of flow test laboratories on a Flow Stack Simulator facility. Uncertainty budgets for flow measurements on full size and narrow ducts. An evaluation of a multiple sensor, in-stack approach to reducing flow uncertainties.
5. Promulgate above reference methods and dissemination of results on limitation of existing SRMs, and flow uncertainties directly to CEN/ISO Working Groups.

Building on previous EMRP/EMPIR projects

This project follows on in part from the preceding EMRP project ENV60: IMPRESS in terms of the work on emissions from industrial stacks. IMPRESS has provided new capabilities: Dust Stack Simulator; Flow Stack Simulator; model for calculating annualised mass emissions uncertainties; CFD model of stack flow. The work in this project, including testing limitations of the dust SRM and modelling flow uncertainties in narrow ducts, will exploit these capabilities and develop new knowledge. In addition, this project will provide complimentary work to EMPIR project 15NRM01 Sulf-Norm, which is addressing the chemistry of SO_2 sampling from stacks.

Results

Objective 1: *To develop validated reference measurement methods where currently none exist for HF, NH_3, formaldehyde and to test the limitations of the existing HCl SRM (EN 1911) and dust SRM (EN 13284-1) for enforcing increasingly stringent ELVs. To develop next generation optical techniques laying the platform to enforce ELVs in future legislation.*

Significant progress has been made on protocols describing measurement methods for HF, NH_3 and formaldehyde. Final technical outputs under this objective will include new measurement methods written into protocol documents passed to applicable standardisation working groups for promulgation as listed below under 'Impact'. A report on the review of ad-hoc measurement methods has been completed and initial activities related to the testing of the methods are underway. Data sets associated with the development and validation of the NH_3 and formaldehyde methods based on stack simulator facilities will be generated as well as test data sets on the limitations of both the dust SRM (EN 13284-1) on a unique dust simulator facility (developed under ENV60 IMPRESS), and the HCl SRM (EN 1911) from a blind inter-laboratory comparison. High impact publications will discuss the myriad of emissions regulations (highlighting gaps / ambiguities / conflicts), and the feasibility of further lowering emission limits values using current measurement capability. A report containing laboratory and field testing data discussing the capability of laser based systems for enforcing future legislation will be prepared.

Protocols describing measurement method for HF, NH_3 and formaldehyde have all been completed and are now being promulgated under the applicable standardisation working groups (see list under Impact below). At the same time work validating a Stack Simulator for the production of formaldehyde emissions down to 0.2 $mg.m^{-3}$ has been completed allowing an intercomparison to be carried out involving both formaldehyde and NH_3. Various proposed measurement methods and techniques have been intercompared over a 1 week trial whilst generating realistic stack emissions including these two species. The methods / techniques compared were based on wet chemistry, Fourier transform infrared spectroscopy, ultra-violet absorption and tuneable diode laser absorption spectroscopy. This significant data set is currently being analysed and is expected to further support the standardisation process mentioned above.

Work analysing data from an HCl intercomparison to determine the capability of chemistry laboratories for chloride measurement to support increasingly stringent emission limits has been completed. An associated manuscript has been submitted for peer review publication. Also, the gaps, ambiguities and conflicts in the current regulatory framework have been researched and a peer review manuscript prepared.

With respect to work on next generation optical techniques two TDLAS systems have been built. One of these was included in the Stack Simulator intercomparison work described above, the results of which are currently being analysed.

A dataset of repeatability has been taken using a HovaCAL® (Hot-Vapor-Calibration) generator and a portable FTIR (Fourier-transform infrared spectroscopy). Work has also been completed in terms of estimating bias uncertainty terms associated with wet gas generation. Additional work under this objective has been the set-up of a 'mystery customer' test of ISO/IEC 17025 in accredited laboratories in the UK offering formaldehyde quantification by NPL. The results of this research are expected to be published in 2020.

Objective 2: *To develop validated reference measurements methods for SVOCs, OGC, PAHs (including benzo[a]pyrene) and PM from small scale combustion sources meeting Eco-design directive uncertainty requirements.*

The INERIS stack simulator facility equipped with 12 sampling ports has been validated and the experimental plan has been completed. An intercomparison exercise has been completed involving the proposed EN_PME_TEST method and a UV system for PM and OGC measurement. It is expected once analysis is complete that this intercomparison will be peer review published.

In addition, a report has been completed critiquing various ad-hoc measurement methods proposed for the characterisation of PM (solid and condensable) and SVOC emissions.

A dilution chamber method has been compared to a dilution tunnel and heated filter plus impinger method. Online and offline SVOCs determination methods have been applied to a wood log stove and a pellet stove each on a sampling platform. Four measurements campaigns have been performed on wood and pellet stove simulator facilities and two large data sets are being prepared, the first comparing a dilution chamber built under the project to heated filter and dilution tunnel methods for measuring condensable and solid PM, the second comparing the same dilution tunnel to alternative proposed methods for SVOC measurement. Measurement methods developed from knowledge from these data sets will be written into protocol documents for SVOCs, OGC, PAHs and PM, which will be passed to applicable working groups for promulgation as listed below under 'Impact'. The results of the comparison will be presented in a peer reviewed paper.

A paper from a blind inter-laboratory comparison of PAH analysis capability will be produced.

Objective 3: *To develop hyperspectral multispecies methods for the determination of emissions from biomass combustion including non-wood fuelled. To develop an on-line, real-time technique to apportion CO_2 emissions between renewable and fossil fuel in co-firing biomass plants.*

A survey of current hyperspectral techniques has been completed and an associated report written. Based on this acquired knowledge the optical isotope ratio (OIRS) instrument and optical parametric oscillator (OPO) source have both been designed. The build of the OIRS instrument, laboratory validation testing, as well as the OPO source have been completed. The latter one is now being tested at low power thresholds.

Going forward, new retrieval algorithms for the interpretation of spectra recorded of a scene by hyperspectral imagers are being devised, along with a calibration method for hyperspectral images which will be published in a peer review journal. A dataset of an OIRS based instrument tested under real field conditions have been developed and an associated report written comparing the performance to the regulatory requirements under the EU's Emissions Trading Scheme.

An OIRS (Optical Isotope Ratio Spectrometry) instrument has also been developed and validated under the objective. Three emission samples have been collected from power plants and measured with the developed OIRS instrument, and the results have been reported. A new FTIR (Bruker Vertex 70v) has been installed and some modifications are now being made on the sampling handling system. After this, three gas mixtures (containing propane, N_2O and CH_4 in N_2) will be measured.

An OPO (optical parametric oscillator), based on an intracavity design in which the OPO is operating within the cavity of a Nd-YVO4 laser is working well with low pump power threshold of 1.5 W (while 30 W is available).

Objective 4: *To determine the uncertainty and traceability of mass emission measurement with respect to flow calibrations under field conditions. To establish the impacts of wall effects and sensor obstruction, particularly in small ducts. To investigate the use of multiple sensors in stacks and the potential to decrease flow uncertainties.*

A model and associated validation data set for probing uncertainties in flow measurement in small ducts due to flow sensor obscuration and wall deceleration are being developed, with test plans completed. The NPL Monte Carlo model of uncertainties has been extended to include multiple reference flow measurement techniques to determine the impact of the determined uncertainties on the accuracy of annualised mass emission reporting with conclusions published in a paper.

The project will develop an alternative approach for flow measurements in small ducts based on an optical tracer transit time methodology and comparison to the existing SRM (EN 16911-1) on a small duct stack simulator facility. An inter-comparison of stack testing organisations ISO/IEC 17025 accredited for carrying out the flow SRM (EN 16911-1) on a Field Test Stack Facility operated at low flow rates will be conducted. A model and associated validation dataset of a full scale stack will be produced to evaluate the performance of an in-stack embedded multi-sensor approach for measuring flow.

A report critiquing various portable stack flow monitoring devices has been completed. A Monte Carlo model for propagating uncertainties in concentration measurement of in-situ systems calibrated via comparison of portable systems has been successfully extended for the analogous flow scenario (i.e. in-situ flow monitors calibrated via comparison to portable flow monitoring devices). Thus far the model has been run for L- and S-type pitot tubes and vane anemometers, while 3D-pitot tubes and hot-wire anemometers have been added to the model for continuous testing.

Measurements and modelling the effect of wall deceleration on flow measurement in narrow ducts are well progressed and have already resulted in the successful completion of an MSc on this topic (http://empir.npl.co.uk/impress/wp-content/uploads/sites/29/2018/07/Thesis_Final_Alouette.pdf).

Measurements have been carried out determining the impact of swirl on stack flow measurement and it has been found that there is a dependency on distance from the entrance to the stack. A peer review paper (see list below) has been published on this topic.

The intercomparison of test laboratories using hot wire anemometers and vane anemometers at low flow rates in a Stack Simulator has been completed and is due to be reported soon. This data on low flow rate measurement uncertainties will feed into the Monte Carlo model to assess the impact of such measurements on the reported mass emissions.

Impact

The impact objective aims to use the project deliverables to realise improvements to the measurement infrastructure to facilitate the enforcement of European directives covering emissions from the large scale down to domestic combustion processes.

Partners have participated in 22 conferences where the project and its results were presented. Two peer-reviewed technical reports and a master thesis have been published, in order to disseminate the outputs of the project. A tutorial and a workshop have been held to provide training based on the outputs of the project.

Impact on industrial and other user communities

Large scale plant operators are legally required to demonstrate compliance with directive ELVs as are manufacturers of small scale boilers. To do this they need provision of measurement infrastructure to give confidence in the validity and comparability of the data that are reported. The accuracy of emission inventories, protection of the environment and improvement in the health of EU citizens is reliant on development of measurement capability able to successfully enforce increasingly stringent emission limits. For example, successful enforcement of the Industrial Emissions Directive is projected by the EC to reduce premature deaths/years of life lost by 13 000 and 125 000, respectively, and realise associated cost benefits of €7-€28 billion p.a. Work on the emissions species identified above is critical if such benefits are to be fully realised.

Impact on the metrology and scientific communities

One of the key impacts on the community will be to bring metrology to the field, directly to the point of use. Traditionally the metrology community has focussed considerable attention on producing artefacts (e.g. certified reference materials), but arguably has devoted insufficient time to directly developing metrology in the field. This project will develop metrology in terms of the underpinning measurement capability to link emissions back to artefacts and to the SI, with well characterised uncertainties. This capability will provide the scientific community (and most importantly policy makers) with emissions data enabling the progress of directives in reducing emissions to be robustly measured and tracked, and also capability and information specifying how much further it is possible to reduce emission limits in future legislation.

Impact on relevant standards

The impact on documentary standards will be significant with the project directly supporting the following working groups:

- CEN/TC 264/WG 3 HF and HCl; CEN/TC 264/WG 40 Formaldehyde; ISO/TC 146/SC 1/WG 33 Ammonia; ISO/TC 146/SC 1/WG 31 Individual VOC in waste gas; CEN/TC 295 WG5 Residential solid fuel burning appliances (SVOC, OGC, PAH, PM); CEN/TC 57 Central heating boilers (SVOC, OGC, PAH, PM); CEN/TC 264/WG 5 Dust; CEN/TC 264/WG 36 Measurement of stack gas emissions using FTIR instruments; CEN/TC 264/WG 9 Quality assurance of automated measuring systems; CEN/TC 264/WG 23 Flow; CEN/TC 264/WG 45 Proficiency testing involving semi-tech stack simulator facilities

The project partners have attended and provided input into the following: the CEN TC264 Working Groups, WG45, WG40, WG9 and Task Force Emissions and ISO TC146 SC1, WG 31, WG33 and the 2018 plenary meeting and the BIPM CCQM working groups on gas analysis and isotope ratios.

Longer-term economic, social and environmental impacts

This project is addressing key metrological issues across the IED, MCP, Eco-design and EU ETS Directives that represent significant barriers to successful implementation. This project will facilitate the realisation of a raft of societal, economic and environmental benefits, many of which are outlined above, and which relate to the Clean Air Policy Package for Europe. In addition to a reduction in premature deaths, better air quality for those with respiratory problems and the creation of jobs to facilitate implementation of the Directives; a cleaner European ecosystem is expected to lead to higher crop yields equivalent to €230 million worth of product.

Future use of the project outputs will include the publication of new documentary standards within CEN and ISO, which will be used to enable the monitoring and reporting of emissions in support of regulations. The development of new methods for monitoring wood burning stoves will support the implementation of the ECO Design directive.

List of publications

Qu, Zhechao ; Werhahn, Olav ; Ebert, Volker. Towards a TDLAS based optical gas standard for the absolute HCl measurements in flue gases from combustion process, 2019. Physikalisch-Technische Bundesanstalt (PTB). DOI: https://doi.org/10.7795/810.20191105

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van Hove, Alouette. Towards effective emission regulations: A numerical and experimental study on flow measurement uncertainty in stacks. Master thesis, 2018. Delft University of Technology (TU Delft). https://doi.org/10.4233/uuid:f56ff5c1-8a9c-4b5c-b404-ab421b7ede59

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RMG1: IMBiH, Bosnia and Herzegovina (Employing organisation); NPL, United Kingdom (Guestworking organisation)		