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1 Executive Summary

This project has contributed to the promotion of issues in the monitoring of emissions of pollutants to air, and to ensure compliance with EU directives and national legislation that is key to enforcing emission limits and thereby enabling their reduction and control and reduce air pollution in order to protect European citizens and the Environment. Industry needs to measure and report emissions for regulatory purposes, including assessing stack emissions against concentration limit values, reporting annual mass emissions, and determining emissions of greenhouse gases (GHGs) from area sources. GHGs are gases in the atmosphere that absorb and emit radiation within the thermal infrared range and a fundamental cause of the 'greenhouse effect'.

Introduction

The cost of air pollution from the 10,000 largest polluting facilities in Europe is around 150 € billion per year. The European Climate Change Programme is targeting an 80-95 % reduction in greenhouse gas emissions by 2050 compared with 1990 levels, but currently Europe is not on track to meet this target. This means that more stringent industrial emission limits are needed, along with new measurements to enable the required increased monitoring and enforcement.

This project developed measurement and monitoring technologies for industrial emissions, methods and guidance to support industry, regulators and standardisation committees. Issues such as traceable stack emission measurements and the challenges of lower emission limit values were addressed. The results have helped to removed many of the current obstacles in the way of emissions reporting and to control emissions within the framework of tighter regulation.

The Problem

The emission of pollutants from industrial sources has a direct impact on air quality. As stated by the European Environment Agency (EEA), the EU's long-term objective is to achieve levels of air quality that do not result in unacceptable impacts on, and risks to, human health and the environment. These emissions also have an economic impact, the EEA state on their website that the cost of air pollution from the 10,000 largest polluting facilities in Europe was €102 to €169 billion in 2009. This project addresses the metrology needs in stack emissions monitoring, annual mass emission reporting and area source emission quantification.

The Solution

The project set out to investigate the monitoring of emissions of pollutants to air to ensure compliance with EU directives and national legislation is the key to enforcing emission limits and thereby enabling their reduction and control. Industry needs to measure and report emissions for regulatory purposes including assessing stack emissions against concentration limit values, reporting annual mass emissions, and determining emissions of GHGs from area sources. This need was met by; developing facilities and capabilities in within the European metrology community, such as a controlled release facility, an optical camera test facility and two stack simulators the development of protocol documents promulgated at the European Committee for Standardization to provide new methods for monitoring of stack and area source emissions, including a protocol for monitoring stack emissions by portable Fourier transform infrared spectroscopy (FTIR) - a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. A protocol was also developed for specifically monitoring SO₂ emission by optical techniques. And through research activities producing improved understanding of critical issues, such as the uncertainty in mass emission reporting and flow measurement in stacks and the performance and uncertainties in open-path optical measurement instruments.

Impact

Impact was achieved through a number of activities, for example;

NPL derived a protocol that was provided to CEN for potential incorporation into a full EN standard for monitoring of area sources by remote sensing techniques. This also fed into an invited presentation given by NPL at the annual plenary of CEN/TC 264 'Air Quality' covering a range of work carried out including; analysis of real-world emissions data to determine 'true' measurement capability for enforcing legislation, developing new measurement methods, providing new national facilities, and leading the authorship of a range of documentary standards.

The design and operation of a new Controlled Release Facility (CRF) that is able to recreate both the distribution and rate of emissions seen in actual industrial applications, and gives the results of a series of field validation experiments involving this facility and an infrared differential absorption lidar (DIAL) facility. The CRF is a transportable flow control system purposefully designed and configured for the creation of 'real-world' gaseous emissions scenarios. The system enables the operator to replicate a variety of gaseous emission fluxes at comparable scales to those found in industrial and agricultural scenarios, and thereby validate emissions monitoring methodologies at the levels and under the conditions they would be used in the field.

2 Project context, rationale and objectives

2.1 Context

Monitoring of emissions of pollutants to air to ensure compliance with EU directives and national legislation is the key to enforcing emission limits and thereby enabling their reduction and control. Industry needs to measure and report emissions for regulatory purposes including assessing stack emissions against concentration limit values, reporting annual mass emissions, and determining emissions of GHGs from area sources. The EU's Industrial Emissions Directive (IED) and Best Available Technique Reference (BREF) Documents are introducing lower emission limit values, in some cases requiring measurements not achievable by current standard methods, and novel reporting requirements – for example annual mass emission values for emissions trading and the quantification of emissions from area sources (e.g. fugitive leaks of Volatile Organic Compounds (VOCs) from industrial plant and GHGs from landfills).

Improved technologies, methods and protocols are required by industry (e.g. operators in the manufacturing, waste sectors), regulatory authorities, equipment suppliers and stack monitoring providers to enable these lower limits and novel emissions sources to be controlled.

Industry and regulators require a robust metrology infrastructure to underpin the monitoring and reporting framework. This work will remove many of the current technological obstacles to allow the reporting and therefore the control of industrial emissions within the framework of increasingly lower limit values.

2.2 Objectives

The project "Metrology to underpin future regulation of industrial emissions" aimed to provide validated reference measurement methods with ensured traceability of the metrology needs in stack emissions monitoring, annual mass emission reporting and area source emission quantification. This is of prime importance to consolidate the Industry and regulators requirements for a robust metrology infrastructure to underpin the monitoring and reporting framework.

One of the main challenges of the project was therefore to set-up a metrology infrastructure able to cover the wide range of parameters that needed to be addressed due to their lack of reliability. The outcomes of the project will benefit to field measurement laboratories for which reliable reference values will be provided, either through proficiency testing schemes or use of (certified) reference materials allowing the dissemination of the metrological traceability.

The project focused on five main objectives:

- Development of alternative methods / techniques to traceably calibrate (in-situ) on-line stack monitoring instrumentation
- Development of characterisation of uncertainties associated with combining infrequent, independent flow measurements with continuous concentration data
- To validate facilities able to test sampling proficiency
- Development of improved and robust remote sensing techniques for fugitive emissions
- Development of a suite of metrologically robust protocols / standards covering the use of open path techniques

Objective 1: "...development of alternative methods / techniques to traceably calibrate (in-situ) on-line stack monitoring instrumentation..." shall be met by carrying out development of techniques that have the future potential to be applied to stack monitoring (e.g. TDLAS - Tuneable diode laser absorption spectroscopy) and authorship of protocols to standardise the use of techniques already demonstrated as being in principle capable of meeting stack monitoring requirements. The protocols will be submitted to CEN for acceptance as Technical Specification documents to formerly allow the pan-European use of such techniques (e.g. FTIR - Fourier transform infrared spectroscopy) for regulatory purposes.

Objective 2: "...characterisation of uncertainties associated with combining infrequent, independent flow measurements with continuous concentration data" shall be met through developing a stack flow model using OpenFoam software which will be validated using real stack data. Using the model, sensitivities, for example spatial dependence, will be probed in order to identify key error sources. In addition, a key output will be a guidance document providing procedure for the estimation of flow uncertainties and subsequent propagation upon combination with continuous concentration data in order to provide robust estimates of uncertainties associated with annualised mass emissions.

Object 3: "...validate facilities able to test sampling proficiency..." shall be met through validation of new particulate capability augmented onto the existing NPL Stack Simulator facility and validation of a new stack simulator facility at VSL for gaseous sampling. Significant further value will be added in terms of analyses of historical proficiency testing data in order to determine the extent to which the EU's stack monitoring industry has kept pace with increasingly stringent regulation and how it will cope with further near future reductions in emission limits.

Objective 4: "...improved and robust remote sensing techniques.....for fugitive emissions..." shall be met by developing DIAL (Differential Absorption Lidar), TDLAS and IR (infrared) camera for application to open path measurements of area emitting sources. In addition, the NPL Area Source simulator will provide a key facility to determine the performance characteristics of such open path techniques.

Objective 5: "...suite of metrologically robust protocols / standards covering the use of open path techniques..." shall be met through drafting of protocols to provide methods for the application of DIAL, TDLAS and IR camera to monitoring emissions from area emitters. Furthermore, the developed techniques and protocols shall be tested in a field trial at an applicable industrial site (e.g. landfill) as part of determining the overall performance characteristics / uncertainty budgets.

3 Research results

3.1 Development of alternative methods / techniques to traceably calibrate (in-situ) on-line stack monitoring instrumentation

The aim of this objective was to investigate and develop alternative methods to traceably calibrate continuous emission monitoring systems (CEMS). These systems operate to provide gas measurements (concentration and flow) to be reported under the Industrial Emissions Directive (IED). The systems operate according to EN 14181:2014 (Stationary source emissions – Quality assurance of automated measuring systems), requiring regular calibrations to ensure the system meets the uncertainty requirements in the legislation. Current Standard Reference Methods (SRM) are unable to accurately measure to the levels

required by some new and upcoming legislation. Alternative methods for calibration like NDIR (nondispersive infrared spectroscopy), FTIR (Fourier-transform infrared spectroscopy) and TDLAS (tunable diode laser absorption spectroscopy) could achieve improved results for concentration measurements, required to meet tightening future uncertainty requirements, but need to demonstrate their equivalence to the existing methods. Flow tracer techniques were assessed as a potential alternative for flow measurement CEMS.

To achieve this objective protocol documents were developed for FTIR, optical techniques and equivalency testing of alternative methods. Additionally the project contributed to the development of a new version of EN14181, the calibration standard for CEMS. A trade journal article was produced by VSL to communicate the ability of tracer techniques for flow measurement.

Research undertaken

3.1.1 Protocols

In order to meet the uncertainty criteria in European legislation, measurements have to be carried out in a consistent and well-documented manner. Protocol documents set out the methodology for monitoring using a particular technique, ensuring that the requirements of relevant standards will be met. At the start of the project there were instruments that had been type approved under EN 15267-3 (Air quality – Certification of automated measuring systems – Part 3: Performance criteria and test procedures for automated measuring systems for monitoring emissions from stationary sources), but as there were no CEN standards covering their use for periodic monitoring they could not be adopted across Europe. NPL led efforts to develop protocols for:

- Periodic monitoring of stack and flues by FTIR spectroscopy
- Periodic monitoring of stack and flues for SO₂ by optical techniques
- Describing the statistics to determine if an alternative method can be considered as equivalent to SRMs

These protocol documents are submitted to CEN for acceptance as Technical Specification (TS), or where applicable, full EN standards, formalising the use of these techniques across Europe. Additionally NPL played a lead role in the CEN mandated re-drafting of EN 14181, the standard concerned with calibration of CEM using periodic monitoring techniques, which is the basis for the other protocols.

Local competent authorities in many jurisdictions in Europe (e.g. Environment Agency in England) have allowed the use of FTIR spectroscopy for periodic monitoring of stacks and flues since instruments have met the type approval requirements in EN 15267-3. However each competent authority had to make their decision based on a local methodology, so in order to standardise the technique across Europe as an official alternative method (AM) it was necessary to develop a widely accepted protocol for adoption by CEN. NPL, in collaboration with European partners and industrial stakeholders, investigated and field tested different methodologies to develop the best possible protocol for completing measurements using FTIR spectroscopy in order to satisfy regulatory requirements with respect to industrial plant compliance monitoring and in-situ calibration of CEM systems.

The SRM for SO₂ monitoring is a wet chemistry technique, which in some jurisdictions (e.g. Germany) is the only allowed option. As with FTIR some local competent authorities have accepted the use of instrumental techniques (e.g. NDIR) for monitoring SO₂ emissions, but again this requires the use of a local methodology approved by the competent authority. NPL produced a dataset of parallel measurements with an FTIR and the SRM for SO₂, which were analysed to demonstrate the equivalence of the technique. NPL led efforts to produce a protocol for instrumental methods of measuring SO₂ emissions from stacks and a working document has been created for CEN/TC 264 to form a draft TS for the monitoring technique.

In order to qualify as an AM the technique is required to demonstrate equivalence to the current SRM according to the requirements in CEN/TS 14793:2005 (Stationary source emission – Intralaboratory validation procedure for an alternative method compared to a reference method). This involves carrying out parallel measurements with both techniques simultaneously on a test bench and/or at a real industrial site. NPL independently validated all the calculations set out in this existing TS, demonstrating that the method was technically correct. During the course of the IMPRESS project, the CEN working group responsible for the existing TS decided it should be elevated to an EN document, which was released as EN 14793:2017 Stationary source emissions – Demonstration of equivalence of an alternative method with a reference method.

In order to produce protocols that will be adopted across Europe as CEN/TS or EN documents there has to be international collaboration to ensure that the best possible solution can be found. Consulting with not only NMI partners, but also with industry stakeholders allowed the most efficient development to occur, which would not have been possible outside the collaboration within this EMRP project.

3.1.2 Flow tracer technique

Reporting for the IED requires data to be in the form of mass emissions, requiring flow rate measurements alongside the concentration measurements discussed above. Flow measurements can be made directly or indirectly. The inhomogeneity and dirty nature of the gas substrate in stacks and flues makes it difficult to directly measure the flow, with fouling and particulate build up on in-stack instruments. As emission limit values allowed in new legislation are reduced it tightens the measurement uncertainty requirements. Flow measurement also contributes to emission quantification error, so the aim of this work was to produce a new flow measurement solution with uncertainty $\leq 1\%$.

By injecting a known quantity of a tracer gas into the flow upstream of the measurement location, it is possible to calculate the flow rate either from the delay before detection or the detected concentration. If the flow is faster the tracer gas will be diluted in a larger volume of gas so the detected concentration will be lower. VSL used this principle to develop and characterise a new technique using methane as the tracer for laboratory scale applications. Since the detector is measuring the concentration of the methane, dependant on the type of detector, it might be able to measure flow and concentration simultaneously, reducing the in-situ measurement requirements.

3.1.3 Equivalence investigations

NPL with the local competent authority, the Environment Agency, tested portable FTIR using the protocols developed in this project, to demonstrate equivalence as an alternative method for SO₂ and HCl calibrations according to the requirements of CEN/TS 14793. The validation exercise also included CO, NO_x and H₂O, allowing a single FTIR instrument to be used to carry out the annual validation or calibration on CEMS for all the key gaseous emission species regulated under the IED. The FTIR also provides real time data so problems with the CEMS can be quickly identified, improving the quality of the reported emission data.

Measurements were made on the NPL Stack Simulator facility, a recirculating stack with ports to accommodate multiple sets of gas sampling apparatus. The flow was run with a gas velocity of 12 m s⁻¹ and at a temperature of 180°C, representative of conditions within a real stack. Water was vaporised into the gas phase using an incumbent liquid injection system. Previous peer-reviewed publications have outlined testing and data to demonstrate homogeneous mixing within the simulator.

A series of fifty-four different test matrices were generated, covering the full concentration ranges for the measurands of interest: CO 0–100 mg m⁻³; NO 0–300 mg m⁻³; SO₂ 0–200 mg m⁻³; HCl 0–60 mg m⁻³; H₂O 0–14 vol%. Concentrations were varied uncorrelated across these ranges for the 54 tests; also, additional compounds were included in some of the test mixtures as potential interferences, specifically, 15 mg m⁻³ NH₃; 30 mg m⁻³ NO₂; volatile organic compounds (VOC) mixture (9 mg m⁻³ CH₄/8 mg m⁻³ C₂H₆/8.5 mg m⁻³ C₃H₈); 10 vol% CO₂. The interferents were selected based on compounds typically emitted from many process types and also on the operating principle of the FTIR; for example, NH₃ absorbs radiation in a region of the mid-infrared spectrum similar to that of SO₂. The diluent gas within the simulator was dry 10 vol% O₂/N₂, created by blending the gas flow from the facility's dry air and dry nitrogen generators in approximately equal ratio, and with the exception of water vapour all other gases were acquired from BOC Specialist Gases, UK. In accordance with the requirements of CEN/TS 14793, two SRMs were run for each measurand and were compared against two ProtIR 204m portable FTIR systems. Each sample run of the Stack Simulator was defined as averaging for 30 minutes.

NPL produced a peer-reviewed paper outlining the technique, results and analysis. The paper concluded that FTIR meets the equivalence requirements for SO₂ when compared with EN 14791 (Stationary source emissions – Determination of mass concentration of sulphur oxides – Standard reference method) (i.e. impinger train and ion chromatography), NO when compared to EN 14792 (Stationary source emissions – Determination of mass concentration of nitrogen oxides (NO_x) – Reference method: Chemiluminescence) (i.e. chemiluminescence), CO when compared to EN 15058 (Stationary source emissions – Determination of the mass concentration of carbon monoxide (CO) – Reference method: Non-dispersive infrared spectrometry) (i.e. NDIR) and HCl when compared to EN 1911 (Stationary source emissions – Determination

of mass concentration of gaseous chlorides expressed as HCl – Standard reference method) (i.e. impinger train and ion chromatography). It met the requirements over all required ranges under IED for waste incineration processes, and all but NO met the requirements for supplementary ranges required for some large combustion plants. As a result the FTIR has been accepted as an alternative method for the stated measurands in England and some other jurisdictions. The evidence has also been submitted to CEN for adoption as a formally recognised alternative method across the EU.

3.1.4 TDLAS monitoring on Stacks

PTB investigated the techniques of TDLAS and NDIR for their capabilities and limitations in stack emission monitoring applications.

Depending on the substances combusted, bypass ratio, the speed and dynamical properties of combustion and the geometrical properties of the combustion chamber the exhaust gas components and their concentrations vary. Typical main components are N_2 , CO_2 , CO , NO_x , SO_2 , H_2O and O_2 . Whilst the average stack pressure is typically roughly within ± 10 mbar at ambient pressure, the stack temperatures strongly vary depending on the technical flow and the combustion process. For example typical stack temperatures, thus differ between $160^\circ C$ and $260^\circ C$. The VDI3951 (Overview on relevant regulations on the performance of emission measurements) states regulations for the conduction of emission measurements.

Due to its cost-effectiveness and its long history NDIR is one of the methods mostly used for stack gas measurements and provides the technical basis for several standard reference methods for many analytes. In contrast, TDLAS is a comparatively new measurement technique, developed for gas concentration determination and which is still developing for common industrial monitoring, with potential to improve monitoring uncertainty.

NDIR is one of the most used methods for stack gas measurement. Manufacturers of NDIR analysers for stack gas analysis include ABB, HORIBA, Siemens, and Yokogawa. More than 10,000 NDIR analysers for stack gas analysis are installed world-wide from Horiba alone. In addition some details on the calibration mixtures for stack gas monitoring will be provided as, in particular for NDIR, there are well-established interference effects between different compounds.

A spectrally broadband infrared beam is directed via bandpass filters through a gas cell containing the infrared absorbing species. In a typical set-up for stack gas measurements NDIR is used to measure these CO , NO_x , SO_2 and H_2O , with an additional electrochemical or paramagnetic sensor for oxygen measurement.

TDLAS is a technique that is typically used to perform concentration fraction measurements, and sometimes temperature and pressure measurements as well. The TILSAM (Traceable IR laser-spectrometric amount fraction measurements) method describes how to achieve traceability in TDLAS amount fraction measurements. The components of a TDLAS setup are the laser with laser driver and function generator, detector with amplifier and data acquisition system and detectors to determine the temperature and pressure in the probe volume (Figure 1).

Depending on whether the probe is sampled into a spectrometer's gas cell where the absorption is measured, or whether the light travels through the free space between laser source and detector, TDLAS is separated into extractive methods and open path versions.

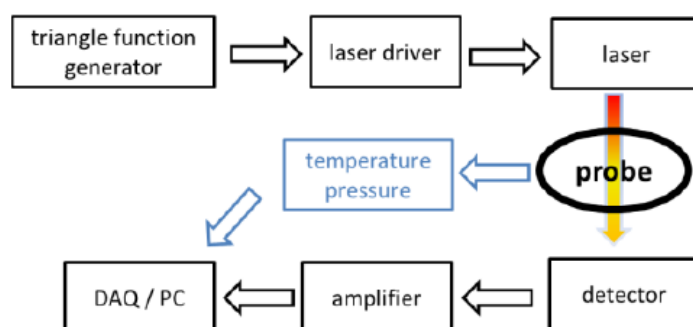


Figure 1: Principle of a TDLAS setup

A fundamental standardization for gas analysers is given in IEC61207-1 (Expression of performance of gas analysers – Part 1: General). Especially relevant for TDLAS is DIN IEC 61207-7 (Expression of performance of gas analysers – Part 7: Tuneable semiconductor laser gas analysers), which concerns the expression of performance of tuneable semiconductor laser gas analysers. In addition DIN 51866-1 (Temperature measurement – Part 1: Survey of laser spectroscopic methods) has to be taken in account, which concerns temperature measurements with laser spectroscopic methods. However it's worthwhile to note, these methods are others than TDLAS although TDLAS itself would be capable to be used for temperature measurements. TDLAS could act as standard reference method due to its high selectivity and, based on an appropriate spectral line selection, its ability to become less affected by interferences.

TDLAS is applicable for long range fence line detections as well as for in situ measurements. It is based on the absorption of light transmitted through the investigated gas. The laser wavelength is scanned over an absorption line of the gas, which was selected for the specific application. For the application in a stack it is important to correct for any changes in the effective transmission of the complete light path between laser and detector. For reliable concentration measurements it might be necessary to measure the temperature in the investigated stack volume simultaneously or rely on spectral lines with minimal possible temperature dependence in combination with an enlarged measurement uncertainty.

Another issue is possible cross interference from other spectral lines originating from gas components different than the targeted analyte. Also water is an interfering analyte in many cases. Especially when large area sources are investigated or the dispersion of the stack emission is high, for example because of high wind speed and turbulences, the determination of emitted volume rates is difficult.

Key research outputs and conclusions

NPL investigated the performance of the current SRM techniques in relation to the current and potential future reduction in emission limit values (ELV). The report indicates that better SRM techniques will need to be developed in order to meet the uncertainty requirements for monitoring with lower ELV. This evidence demonstrates the need for this project.

PTB, with assistance from VSL, produced a report outlining the capabilities of spectrometric techniques for stack measurement. PTB developed a state of the art new laboratory facility to test TDLAS based measurement techniques, using it to develop and test improved technologies that could result in lower monitoring uncertainties in future.

NPL, with assistance from VSL, then produced protocols for monitoring stacks using optical techniques and FTIR spectroscopy. NPL published a peer reviewed publication demonstrating the ability of portable FTIR to meet the requirements of an SRM for calibration of CO, NO_x, SO₂, HCl and H₂O, based on the protocols developed with VSL. This has allowed local competent authorities to accept FTIR as a suitable alternative method, meeting the objective.

3.2 Characterisation of uncertainties associated with combining infrequent, independent flow measurements with continuous concentration data

The aim of this objective was to investigate uncertainty in reported mass emissions. Under the IED polluters must submit a quantified mass emission value from their plant. In general they are required to use continuous emission monitoring systems (CEMS) to quantify the emitted concentrations, while the requirements are less stringent on the flow measurements to complete the mass emission calculation. EN 16911:2013 (Stationary source emissions – Manual and automatic determination of velocity and volume flow rate in ducts) sets the requirements for flow measurement, differing in a number of areas from EN 14181:2014 which sets the quality control methodology for concentration measurement. The validation studies for EN 16911 demonstrated that flow conditions (e.g. stability, inhomogeneity and flow profile) could have significant impacts on the flow measurements so further research is required to characterise these conditions.

Many CEMS are not fitted with flow monitors, and there are relatively few continuous flow monitors. Whilst combining a “snap-shot” flow measurement with continuous concentration data is permitted, there is insufficient guidance to plant operators on how to achieve this. Hence, propagation of error sources to derive uncertainties associated with annualised mass emissions is often incorrectly carried out, further

compromising the accuracy of national emission inventories. Furthermore, even when continuous flow measurement is carried out, with annual calibration of the flow CEMS, the uncertainty in the annual mass emission is not well understood.

Understanding how different sources of uncertainty contribute to the overall reported mass emissions is a complex and challenging task that this objective is to investigate. Reported emissions are a single value with no associated uncertainty, so the overall uncertainty is not well understood by operators who just assume that by following EN 14181 and EN 16911 they will achieve reliable results.

Research undertaken

Assessing flow uncertainty from direct measurements is a very challenging field. In general it is less challenging, but still difficult, to produce computer models of flow to investigate measurement uncertainty. CMI modelled flow in ducts to investigate flow uncertainty from swirl, where turbulence caused by obstructions or changes of direction in the duct causes non-laminar flow at the monitoring point. The scenarios investigated were based on stakeholder feedback on current flow measurement methods. NPL took a different modelling approach, focussing on the uncertainty of a gas analyser operating under EN 14181, using Monte Carlo Simulation to understand concentration uncertainty. The model uses a simplified flow uncertainty to demonstrate the propagation of uncertainty into the annualised mass emissions. JV used the uncertainties from both modelling processes to look at the effects of errors in combining data from flow and concentration measurement sources, producing a guidance document for users to help determine uncertainty sources.

3.2.1 Flow uncertainty: CMI CFD experiments

Measurement of smooth flow in a wide straight duct is relatively straight forward and the associated uncertainties are well understood. However these conditions are not often present at industrial plants. Ducts are narrow, particularly at medium combustion plants, creating difficulties with quantification of wall effects. Sampling ports for measuring flow cannot always be located on long straight sections of pipe where there will be no sources of uneven flow and swirl. To investigate the effect of this CMI used computational fluid dynamics (CFD), which is included in ISO 16911-2 (Stationary source emissions – Manual and automatic determination of velocity and volume flow rate in ducts – Part 2: Automated measuring systems) as a simulation tool to pre-investigate how variation in plant operating conditions can influence the stability of the flow profile, to model flows in a narrow duct downstream from obstructions including bends and t-pieces where flows merge. NPL supported these modelling efforts by providing realistic information on dimensions for ducting in large and medium combustion plants and typical flow rates.

This simulation work, performed by Czech Metrology Institute (CMI), clearly shows that the position and orientation of the measurement ports for Pitot tube can significantly affect the accuracy of the annual mass emission measurement since the relative error in flow rate contributes by the same amount to the relative error of mass emissions. The CFD can be useful to estimate the optimal installation of the flow measurement instrument. It is also possible to implement this method to estimate the related sources of measurement uncertainty for the installed pitot tubes.

The calculations have been applied to different shapes of supplying pipes generating different swirl pattern; 1- straight pipe 2- pipe with a single 90° elbow 3- a pipe with double 90° out of plain elbow. These supplying pipes are presented in figure 2.

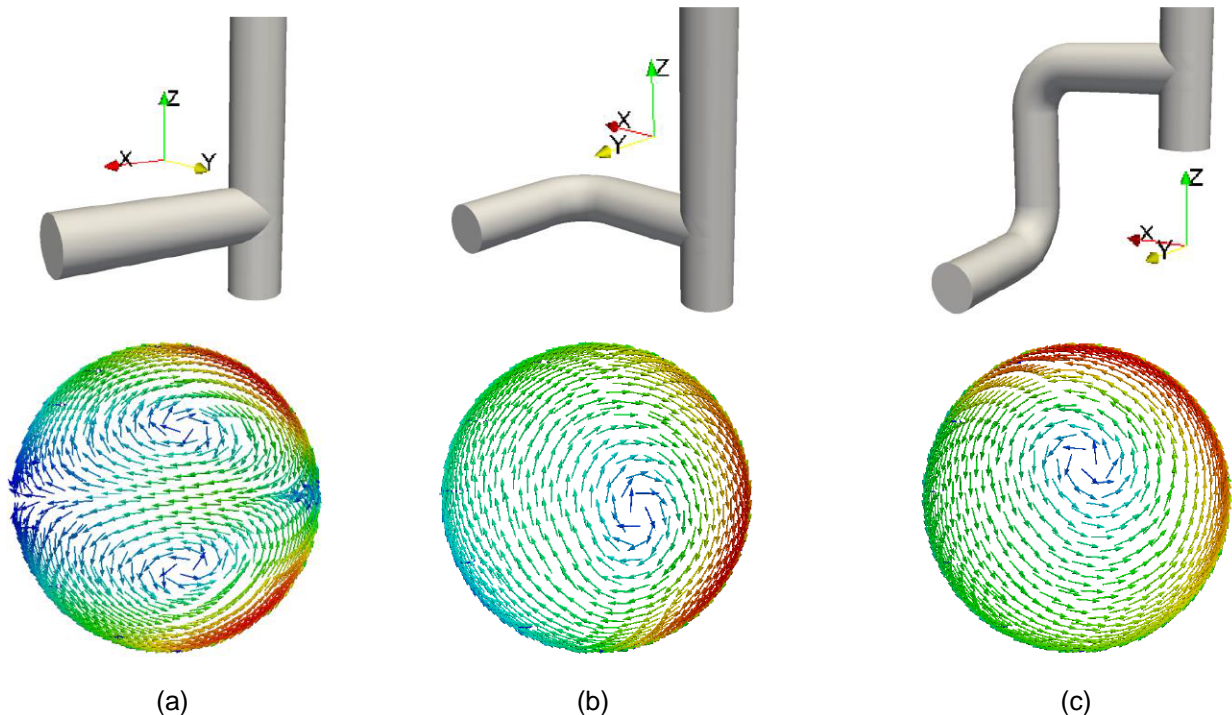


Figure 2: (a) The straight supplying pipe. Length of the pipe is 5m from the inlet to the stack wall. The pipe generates two counter rotating swirls in the stack. (b) Supplying pipe with a single 90° elbow. Radius of the elbow is 1.5m. Length of the straight parts upstream and downstream of the elbow is 3m. Pipe generates a single clockwise (view from the stack outlet) swirl in the stack. (c) Supplying pipe with double 90° out of plain elbow. Radius of both elbows is 1.5m. Length of straight parts upstream, downstream and between the elbows is 3m. Pipe generates single counter clockwise (view from stack outlet) swirl in the stack.

Information on these scenarios will enable pitot tubes to be deployed where they will generate representative flow velocity measurements.

3.2.2 Concentration Uncertainty: NPL Monte-Carlo Model

The Industrial Emissions Directive (IED) sets out the required frequency of emissions monitoring, with some species only requiring periodic measurement while many require constant monitoring with automated measurement systems (AMS). Each species will have one or more international standards outlining procedures for obtaining suitable measurements.

The standard will outline a standard reference method (SRM). Demonstrating equivalency of an alternative method (AM) requires comparison with the SRM according to the procedure set out in EN 14793:2005, *Stationary source emission - Intralaboratory validation procedure for an alternative method compared to a reference method*.

The AMS must be operated according to a procedure to ensure measurements are consistent and meet uncertainty requirements. Quality assurance procedures for AMS on stationary sources are set out in EN 14181:2014. This consists of four levels of validation testing, quality assurance level 1 (QAL1), QAL2, QAL3 and annual surveillance testing (AST). QAL1 ensures the instrument is suitable for the application and is installed correctly. These international standards are enforced by local competent authorities, e.g. Environment Agency (EA) in England. Such bodies often produce guidance documents to help operators interpret the standards.

Quantifying the uncertainty of these processes is important since the measurements are used to enforce the legislation. However very little attention is paid to the overall uncertainty of the annualised emission totals, with uncertainty assessments tending to focus on one part of the process. These assessments help build confidence in the ability of EN 14181 and the other standards to meet the uncertainty requirements of the legislation. However the use of such piecemeal studies could lead to many systematic sources of uncertainty being missed, potentially resulting in underestimation of actual overall uncertainty.

In order to address this issue NPL have developed a Monte-Carlo model of an instrument operating under the procedures in EN 14181 over a period of years, representing a full 5-year cycle allowed for AMS at large combustion plants (LCP) under the IED between QAL2 calibrations (Figure 3).

MCS (Monte-Carlo Simulation) involves mathematically modelling a process, then running the model many times with input conditions that are sampled from Probably Density Function (PDF). The PDF for each input parameter is defined according to the individual uncertainties of each input parameter within the model. If there are sufficient repeats within the model run then the spread of the output will represent the range of potential results that can be achieved with those input parameters and their associated uncertainties. The standard deviation of the results of a model run is therefore an indication of the overall uncertainty of the whole process.

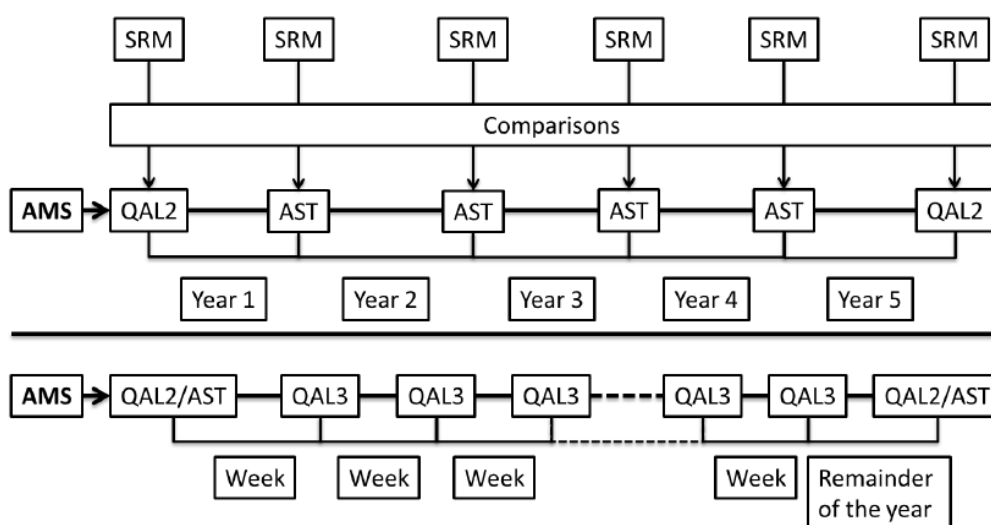


Figure 3: Frequency of quality assurance testing. Top section shows the required frequency of tests involving intercomparison with an SRM. Lower section indicates an example of QAL3 frequency, but the timing is based on the product conformity certification so the week shown here is just an illustrative example

Random sources of uncertainty will change with every repeat of the measurement, but if the measurement was repeated enough times the resulting error would average out. In contrast systematic sources of uncertainty will affect measurements in the same way over time, an offset from the measurand that will not average out over multiple measurements of the same thing.

The sources of uncertainty within the process are encapsulated within the model, so for each repeat in the MCS the measurement input parameters are adjusted by a random error, the magnitude of which is controlled by the uncertainty of the operation. The model is based on the real use of a gas analyser instrument under EN 14181 like any model, it has to include some assumptions in order to function.

The model takes 30 minute average measurements, assuming that there is no downtime, including timeless quality assurance testing, so every measurement is made regardless of procedural requirements. Errors for each interference source are calculated separately and added together to form the total cross interference error on an individual measurement.

The model has been designed in order to allow the modification of many of the variables and influence factors, so there are plenty of opportunities to investigate the effects of alternative changes on overall uncertainty of emissions monitoring. NPL plans to look into possibilities for altering testing frequency and what effect that would have on meeting the uncertainty limits, this is currently being addressed in EMPIR project 15NRM01 Sulf-Norm.

When SRM uncertainty moves above 15% there is a marked increase in AST failures due to the poor quality SRM. The sensitivity testing showed that the growth in overall uncertainty stayed linear even when SRM uncertainty moved above 20%, demonstrating that having a limit at that point makes very little difference. Lowering the limit on SRM uncertainty to $\pm 15\%$ would reduce potential difficulties with good quality CEMs failing due to poor SRM performance.

Improvements to overall uncertainty would be minor, but the real benefit would be fewer failed ASTs and the subsequent additional QAL2s, something that will be welcomed by operators. The AMS repeatability demonstrated a reduction over time in the overall uncertainty. The maximum uncertainty of any measurement continues to increase as the AMS repeatability uncertainty rises, but over time a mix of QAL3 and AST failures leads to recalibrations that improve the overall performance in subsequent years.

The AMS linearity uncertainty leads to cumulatively larger overall uncertainty, with relatively high numbers of QAL3 failures between ASTs causing discontinuities in the concentration measurement uncertainty. Interestingly while the resets due to failing QAL3 tests tend to make overall uncertainty worse, resets performed due to failed ASTs appear to reduce the overall uncertainty. For cross interfering species, where the magnitude of the related errors is affected by the effectiveness and concentration of one or more conflicting species, the effects on overall uncertainty varied according to the number of species and their influence on the measured value.

Extra interfering species increased the overall uncertainty, although the direction of the influence had little impact on the magnitude of this effect, as the tests with three species partly cancelling each other out caused similar overall uncertainty to runs where all three species generated complimentary errors, with both achieving a mass emission uncertainty ~3.5% when set to 10% characteristic uncertainty. Higher detection limits lead to higher overall uncertainty, although the sensitivity of this attribute is lower than many others.

With a mass emission uncertainty of 3.1%, only SRM uncertainty and cross interference with a single species had less impact on overall uncertainty at 10% intensity than AMS detection limits. The use of quarterly QAL3 testing caused the model to encounter step changes in temperature between tests, resulting in failures even at low temperature offset uncertainties.

The more frequent recalibrations will have affected the modelled overall uncertainty for temperature effects so the overall uncertainty of 42% for zero and 71% for span might not be directly comparable with other factors. The high sensitivity of the overall uncertainty to the ambient temperature demonstrates the need to calibrate instruments at representative conditions to keep offsets low. At low drift rates the QAL3 adjustments are successful in restricting measurement uncertainty.

In later years of a run the model indicates a potential for some failed ASTs, but this ensures the AMS operates within the required uncertainty limits. Failures maintain uncertainty levels, but more frequent QAL3 testing would likely prevent this from becoming an issue until much higher drift rates.

3.2.3 Synchronization error: JV

For their simulation, JV used the NPL Monte Carlo simulation tool to combine PDFs for flow- and concentration measurements to obtain a PDF for mass emission. In this simulation, the real data of flow and concentration measurements of a stack emission were sampled and combined to obtain PDFs that shows the dispersion for the mass emissions. The investigations by JV have been limited to a time shift of ± 15 minutes between flow and concentration measurements. The mentioned time is a maximum realistic value for the lag when an AMS based measurement system is used. On the other hand, this can be also realistic when manual based methods are used.

The effect of lag between flow and concentration measurements are reported as relative change in the 95 % confidence level for the PDF obtained for different lags. This analysis shows that the lack of synchronization for the used dataset has symmetrical effect for positive and negative shifts. The most significant effect on the relative uncertainty in mass emission can be seen in SO₂ data.

It is clear from this evaluation that the estimated measurement uncertainty can be significantly influenced if flow and concentration measurements are not correctly synchronized according to the actual measurement time. Minute resolution is used in our observed real emission data from industry. These results indicate that calculations of the mass emission should be implemented for this time increment (1 minute) to avoid large calculation errors for the estimated mass emissions. As periodic averaged concentration calculations will also be a weighted mean, synchronization of the data will be required for these calculations.

The evaluations performed on a situation where the emissions are monitored by AMS (for both concentration measurements (AMSC) and flow measurements (AMSQ) are also relevant for manual based methods. Manual based methods can an option for monitoring when the risk level is small or if the design gives physical obstacles that makes it practically impossible to install a proper AMS. For such situations, representativeness shall be regarded carefully. The measurement plane should be defined and proper

measurement methods considered. It is clear that the measurement of flow and concentration in a measurement plane defined for some duct or ventilation hatch will increase the measurement uncertainty. Nevertheless, it is also clear that the lack of representativeness in time should be considered. A worst case scenario would be that flow and concentration measurements are not planned and executed as one measurement process.

Representativeness according to process variations should be also carefully taken into account, when planning the measurement schedule. The study of real emission data both by the use of a Monte Carlo simulation tool developed by NPL and calculation done by JV shows that the lack of synchronization of flow and concentration can significantly increase the measurement uncertainty, and alter the emission calculation results.

Despite substantial standardization for monitoring industrial emissions with AMS or by other means, it seems that the need for securing estimated emissions is not completely supported by proper guidance documents. These results indicate that it is important to assure the quality in respect to timing from the measurement of flow rate and concentration sampling and analysis through signal processing and the final mass flow calculations with respect to the timing. Even if the measurement task is to establish time averaged values for concentration for a given period, it is necessary to give a weighting factor to the different concentration measurements based on the flow rate.

Key research outputs and conclusions

CMI with assistance from NPL and JV got feedback on the scenarios that needed investigation regarding flow measurement in stacks. This was used to guide their CFD modelling work to answer the topics raised, which will help reduce uncertainty in stack flow measurement from swirl effects. Initial results of the flow modelling work were presented at the FLOMEKO 2016 conference and a full peer-review paper has been submitted in order to communicate the findings.

Monte-Carlo modelling has been used before to investigate process uncertainty, but the scale and complexity incorporated in the NPL model is a step beyond anything described in peer-reviewed publications. The model has provided a test bench to investigate the effects of changing uncertainty on single input parameters and how that impacts overall uncertainty in annual mass emissions. The NPL report provides a sensitivity analysis for key uncertainties when determining the annualised mass emissions.

JV used the uncertainty information provided by the NPL Monte-Carlo model to look at the level of error that can occur if the concentration and flow data are not correctly synchronized when they are combined. JV also considered the feasibility of using surrogate parameters for flow monitoring, but found it was not something that could be realistically achieved using the methods they investigated while meeting the uncertainty requirements. The guidance document produced by JV, with input from CMI and NPL, provided users with an understanding of the uncertainty sources and the propagation of this into the annualised mass emissions. Expertise from different partners helped to provide a broad range of guidance that would not have been achievable by any one organisation.

3.3 To validate facilities able to test sampling proficiency

The aim of this objective was to develop and validate new facilities capable of testing sampling proficiency of stack testing companies. In order to get a true indication of the sampling ability of a test team it is necessary to know the concentration and flow rates that are present in the duct. This is not possible in an industrial setting (otherwise there would be no need for measurement), so stack simulation facilities are required for proficiency testing.

Stack simulation facilities play an important role in supporting our understanding of the correct measurement of emissions in industrial stacks. Currently some stack simulation facilities are in use at NMI's or research institutes. Two noteworthy examples include:

A. Stack simulator of NPL (focused on gas emission)

"The stack simulator has an across-stack path length of 1.5 m. It has two 5-inch ports at one end of the path-length and two ports at the other end, which are positioned similarly to allow two cross-stack instruments to

be attached. The simulator allows flows of air, nitrogen and a selection of 'pollutant' gases into the 'stack' at controlled rates to create predictable mixture concentrations. It also incorporates a water injector to provide a controlled water vapour concentration." <http://www.npl.co.uk/measurement-services/environmental-monitoring/stack-simulator>

B. Smoke Stack Simulator of NIST (focused on flow)

"Set-up built to critically test conventional and alternative ways of measuring the flow of stack gases. The inlet cone and reference section of the simulator draw in ambient air and generate a swirl-free, fully-developed turbulent flow. The reference section features an ultrasonic flow meter calibrated with an uncertainty of 0.5%." <https://www.nist.gov/programs-projects/smoke-stack-simulator>

For the future underpinning of technique development and testing monitoring industry proficiency, new stack facilities are required which mimic industrial stacks as closely as possible. VSL is working towards realizing a simulator focused on gas emissions, while NPL have developed a particulate stack simulator to complement their existing gaseous stack simulator.

Research undertaken

3.3.1 Proficiency Testing Database

Proficiency testing (PT) schemes are used to demonstrate the ability of stack testing organisations to make the required measurements. Where available these use stack simulator facilities (i.e. NPL facility mentioned above) to test the full sampling and analysis ability. Where facilities are not available PT schemes will consist of blind measurements of gas cylinders, testing only the calibration and analysis without sampling systems. NPL (simulator & cylinder), PTB/HLUG (simulator) and VSL (cylinder) provided historical PT scheme performance data to investigate historical performance of the industry across Europe. NPL led efforts to combine the datasets so they could be analysed for trends.

Participant results in PT schemes are based on their performance compared to the reference values for the gas matrices being measured. The z-score, as defined in ISO 13528:2015 (Statistical methods for use in proficiency testing by interlaboratory comparison), is a performance score derived by dividing the deviation from the assigned value by an allowable deviation (Equation 1):

$$z = \frac{x - AV}{\sigma} \quad \text{Equation 1}$$

where:

z	z score
x	value obtained by participant
AV	assigned value for test sample
σ	assigned value for standard deviation

Z-scores are used as the acceptability criteria, with $|z| > 3$ graded unsatisfactory, while $2 < |z| < 3$ is questionable and $z \leq \pm 2$ is satisfactory. Assuming the allowable deviation is consistent the z-score can be used to compare any measurements. To assess performance over time NPL recalculated z-scores for SO₂, NO, CO and VOC using the strictest allowable deviation values for each species. In most cases the allowable deviations will have got smaller over time to reflect the tightening of regulations, so by framing the z-scores in this way the results indicate relative performance of stack testing organizations over time.

The results show some improvement over time, but indicate that further tightening of ELVs and associated uncertainty requirements may push beyond the current industry wide measurement capability limits. Comparisons were also made between simulator and cylinder schemes, demonstrating the expectation that performances are better for cylinders as there is no error from sampling and conditioning equipment. In order to get a true representation of an organization's testing ability conditions have to be close to those in a real stack, demonstrating the need for the development of additional stack simulator facilities.

3.3.2 VSL Gas Stack Simulator

VSL developed, built and validated a gas emissions simulator within the IMPRESS project. The validation experiments were carried out using methane and nitrous oxide. These results provide an indication of the maximum allowable uncertainties of the facility in order to be useful for testing and validation experiments. An open-source computational fluid dynamics software called OpenFoam was used to simulate the correct dimensions of the stack for the target flow rates in the simulator.

The facility was designed as an add-on to the existing flow meter calibration facility at VSL. This facility can generate a wide range of flows with a very low uncertainty. The stack flow simulator design is depicted in Figure 4 together with the dimensions. (diameter 31.5 cm and a total length slightly over 2 meter). The simulator material is aluminium.

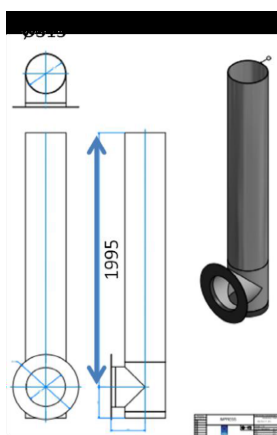


Figure 4: Stack flow simulator (Design)

In some of the experiments an additional mixer was installed in the tube before the stack simulator. The gas can be sampled from the stack on 3 different heights via small ports which can be opened to insert the measurement port.

For the injection of pollutant gas, mixtures in cylinders are used in combination with mass flow controllers. For the measurement of the injected pollutants in the stack, a transportable Fourier Transform InfraRed spectrometer, model 301-x from Interspectrum OU was used in combination with a multi-pass absorption cell which provides absorption path lengths up to 8 meters.

Some preliminary tests were performed on flow. The wind tunnel is capable of producing uniform flow speeds from less than 1 m/s to more than 5 m/s at its exit.

The fog generator for flow visualization was used to check the performance of flow straightness in the upstream diffusers. The seeding of the flow with the fog is shown in Figure 5.

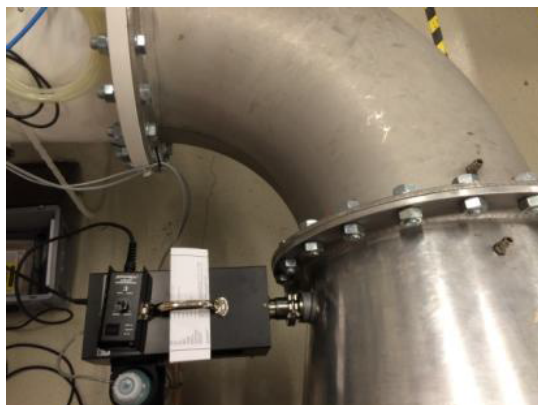


Figure 5: Seeding of the flow using Safex Fog-Generator F2010.

The seeding was used to investigate the flow profile coming out of the wind tunnel. However the flow visualization of the seeding using fog-generator Fog Switch revealed non uniformities at flow speeds ranging from 0.5 to 5 m/s. With the stack installed the flow at the exit appeared much more uniform then at the exit of the wind tunnel. This suggests that when pollutants are added to the flow the distribution of the pollutant in the flow will be uniform at least at the stack exit.

For the experiments the flow facility generated a range of different flows. Different amounts of a pollutant were added to the flow before the stack. For some of the experiments, an additional mixer was added to the flow tube before the stack. This was to investigate if the flow was already fully developed in the stack or not.

In all experiments the flow was set and kept constant for a number of experiments in which for example pollutant injection rates or probe depths were varied. When the flow was changed new experiments were only started after a pause of at least a 1 minute in order to have a stable flow during the experiments. The standard deviation of the flow data is typically 0.1%.

Figure 6 shows an example of the derived absorption signals for a range of different flow, seeding and probe insertion conditions.

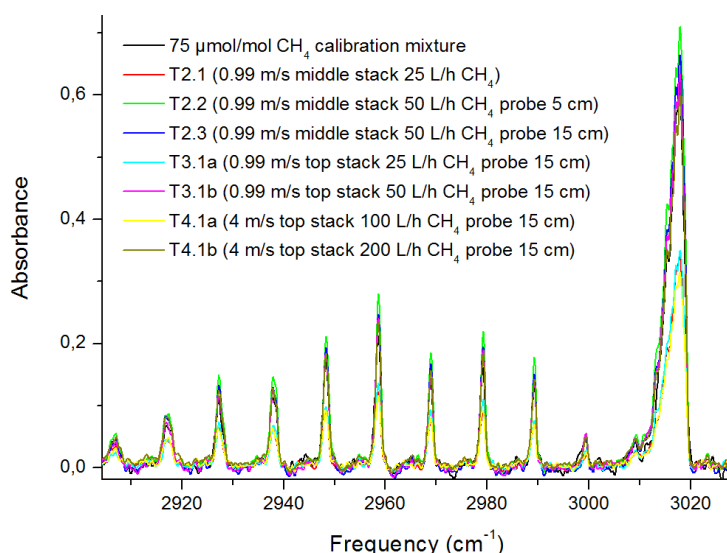


Figure 6: Results of one of the measurements series. FTIR spectra are shown for 2 different winds speeds (1 and 4 m/s at the exit of the wind tunnel) and different injection rates of CH_4 (25-200 L/h) and probe insertion depths.

During the experiments it became clear that an important limiting factor of the current set-up lies in the repeatability of the FTIR. This affects both the background signal and the signal with the pollutant added. For the N_2O measurements the standard deviation of the background signal is about 0.8%. For the N_2O signal itself, the relative error in the measurements depends on the selected absorption lines.

Limitations which are due to restrictions in the current laboratory include: The temperature of the gas and stack is fixed. Higher temperatures are not allowed in the laboratory as they may impact the daily work of flow meter calibrations. Humidity level is currently fixed. In order to get a more realistic gas emissions simulator it is necessary to build up the facility in a dedicated lab which facilitates use of high temperatures and higher levels of pollutants.

3.3.3 NPL Dust Stack Simulator

NPL currently runs a PT scheme for dust using foil shims and sodium chloride solutions to stand in as filters and washings for analysis. This is similar to the cylinder schemes for gas measurement in that it does not test the sampling, only the laboratory analysis. Modifying the existing NPL facility to allow dust was not possible due to the current design, so a completely new facility has been developed to allow full dust PT measurements to be made. The facility will be used for the controlled testing of methods and instrumentation

involved in the sampling of particulate from stack atmospheres, in the concentration range between 1 - 40 mg/m³ in the size range 1 - 10 µm.

The facility is of a looped duct design such as the air matrix, and any entrained particulate, is contained (Figure 7). Velocity within the loop is produced by the operation of a variable speed centrifugal fan (Stockbridge Airco, 350 CBL T2) providing a maximum design output of 1.65 m³/s at 9 mbar of static pressure. Immediately downstream of the fan the duct is 0.35 m diameter with a circular cross section, and has a linear run of 6.5 m. The duct diameter then increases to 0.5 m and then contains two 90° bends with a curvature radius of 1.5 x duct diameter. A second linear run of 6.5 m followed by a third 90° bend then connects to a filter housing, containing an EN779:2012 (Particulate air filters for general ventilation – Determination of the filtration performance) F9 class filter, completing the loop. Particulate matter is injected downstream of the fan using a solid aerosol generator (Topas SAG 410/L) with aerosol generated in a nominally dry air matrix with low particulate levels, provided by a compressor, and water, oil and particulate scrubber system (Compair L07RS-FS compressor, A9 XSDS Dewpoint Dependent Desiccant Dryer). The aerosol generator sits atop a Sartorius Cubis analytical balance, aerosol mass injection rate is determined by measuring the mass loss from the aerosol generator.

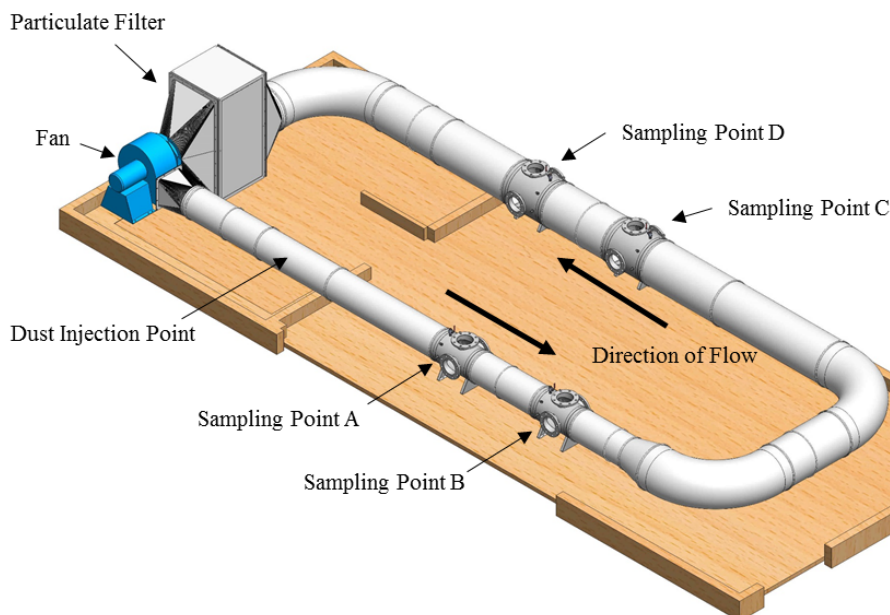


Figure 7: 3D engineering drawing of the NPL dust stack simulator facility show positioning of sampling points

Four sampling points are included within the loop, two within the 0.35 m diameter section and two within the 0.5 m diameter section. Each sampling point has three ports (BS10 Table E 6" flange) at -90°, 0 and +90° to the vertical plane, and all are perpendicular to the sampling plane. In addition to the main sampling ports, six ¾" BSP ports are situated on the upstream edge of each sampling section at -90°, -45°, 0°, +45°, +90° to the vertical plane. An example sampling point layout is shown in Figure 8. All sampling points are positioned at least 5 hydraulic diameters downstream and at least two hydraulic diameters upstream of any changes in duct size or direction recommended by EN13284-1:2002 (Stationary source emissions – Determination of low mass concentration of dust – Part 1: Manual gravimetric method).

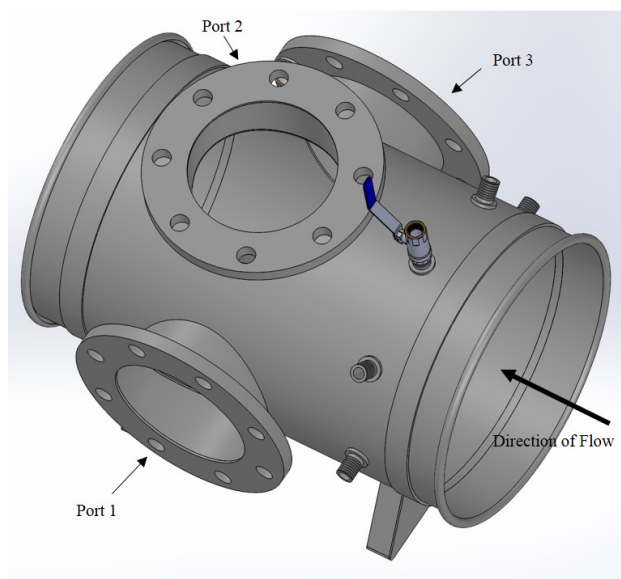


Figure 8: 3D engineering drawing of sampling point

As part of the validation process a preliminary flow survey was carried out in order to establish any mass flow variation from port to port and across the sample plane. A number of fan speed settings were used to establish characteristics over various flow rates in the ducting. Flow, swirl and temperature measurements were taken according to EN 16911-1. A total of 10 points per sampling plane were measured as per EN 13284-1:2002 using the general method for circular ducts. Once the flow conditions had been validated dust was introduced, with measurements made from multiple ports simultaneously to indicate any potential variation (Figure 9).



Figure 9: Comparison of measured concentration against reference concentration for two measurement ports

Key research outputs and conclusions

The new facilities at VSL and NPL were validated and a report describing the validation was prepared. These new facilities will enable proficiency testing (PT) schemes to take place that can include participant's sampling uncertainty. This will help improve stack monitoring performance across Europe and further afield (the NPL gaseous stack simulator PT scheme is open to test teams from any country). Collaboration between participants helped ensure that the new facilities were suitable for the intended requirements, sharing expertise to avoid bad decisions during the development and ensure that validation experiments ran smoothly.

The historic PT results provided an indication of relative performance of the wider stack testing industry compared to the increasingly stringent monitoring requirements. A single scheme's results would not have provided a representative indication of performance across Europe so collaboration with international partners was essential to the successful completion of this aim that has been achieved by this project.

3.4 Development of improved and robust remote sensing techniques for fugitive emissions

The aim of this objective was to produce new techniques for identifying and quantifying fugitive emissions, since this is an area that is known to be under developed. There are limited approaches used for area source emissions and uncertainties on measurements were typically high.

Existing monitoring approaches of acquiring point measurements and scaling up to represent an area have been shown to be unreliable as with many sources there are high spatial and temporal variances in emission, i.e. the measured quantity is heterogeneous in nature. An important part of area emissions is leaks, which given that these by definition are unexpected often escape measurement and hence are generally absent from reports. In Houston, USA it has been reported that local air pollution is far higher than can be accounted for from emissions from known sources alone, which has led to proposals that the shortfall is due to leaks. It has been proposed that this same rationale explains why DIAL emission measurements from an oil refinery storage facility near Rotterdam were 3-fold higher than values determined by calculation via emission factors from the Dutch Emission Registration System.

Such observations have led many to question if the status-quo is adequate for demonstrating compliance with emission limits. In addition to the environmental impact, there are also potential political and financial benefits for capability to measure an area capturing all emissions. Whilst remote sensing offers a potentially very powerful method of monitoring area emissions, work is first needed to address some technological issues and equally importantly to develop protocols for standardization in application.

In order to develop improved and robust remote sensing techniques NPL carried out research into improving the DIAL measurement technique by investigating improved analysis approaches to estimate the background concentrations of the target pollutants. Test data sets were compiled for emissions plumes measured by DIAL which were then assessed using different approaches for background removal. A paper describing this was published. This work is described in Section 3.4.1. In order to develop an improved approach for open path-integral optical techniques PTB investigated TDLAS open path techniques. Specifically they identified from a concept review that temperature and pressure variation along the measurement path have not been routinely addressed as an uncertainty source. They carried out laboratory and field research and developed an improved uncertainty approach based on this work which is described in Section 3.4.2. Infrared cameras with suitable wavelength filters are able to visualize fugitive hydrocarbon emissions and they are increasingly being used in a regulatory context. VSL and the internal REG (DCMR) undertook a review on the use of IR cameras and carried out research activities to improve the understanding of this technique. Specifically they developed a model of the performance of the camera and developed a test facility to enable the cameras to be assessed. This work is described in Section 3.4.3. In order to assess and validate the performance of techniques used to measure fugitive and diffuse emissions NPL developed a controlled release facility, able to generate known and traceable emission rates with characteristics which replicate real word emission sources. This is described in Section 3.4.4.

Research undertaken

3.4.1 Estimation of background gas concentration from differential absorption lidar measurements

Differential absorption lidar, which is based on the optical analogue of radar, provides the capability to measure remotely the concentration and spatial distribution of compounds in the atmosphere. The ability to scan the optical measurement beam through the atmosphere enables pollutant concentrations to be mapped and emission fluxes to be determined. The infrared measurements at wavelengths of around 3 μm target a range of hydrocarbon gases, including methane that has a significant background concentration level.

A critical part of the analysis of the measured data provided by the DIAL system is to estimate, and subsequently correct for, the background concentration level of the target species along the optical measurement path. This section is concerned with approaches to analysing the measured data provided by the DIAL system to estimate the background concentration level of the target species.

This section has been concerned with approaches to analyse the recorded measured data obtained using NPL's DIAL system to estimate the background concentration level of a target species in the atmosphere. The estimation of the background concentration level is necessary for an accurate quantification of the concentration level of the target species within a plume, which is the quantity of interest.

The section has focussed on methodologies for estimating the background concentration level and, in particular, contrasting the assumptions about the functional and statistical models that are part of those methodologies. An approach to estimating the background concentration level has been described.

It uses a functional model for the path-integrated concentration level that allows for the presence of a plume. The functional and statistical models are then used to formulate a generalised least squares problem whose solution provides estimates of the background concentration level and other model parameters, including the path-integrated concentration level of the target species in the plume.

From an analysis of the measured data recorded beyond the plume the results show reasonable consistency between the statistical models for the noise and between the estimates of the background concentration level corresponding to the different elevation angles. The estimates of the background concentration level are influenced by the inclusion of measured data before the plume.

There is benefit in trying to refine and improve that knowledge to obtain a short window containing the plume and to increase the amount of data available to estimate the background concentration level. The presented results have not included an assessment of the quality of the estimate of the background concentration level in the form of a statement of uncertainty, which is a necessary part of the quantification of the background concentration level.

A complete description of the noise is necessary if the part of the signals before the plume are to be used to obtain a reliable estimate of the background concentration level supported by an associated uncertainty. Making an assumption about the dependence of the background concentration level - for example, that it is a constant or slowly varying function - would allow the measured data for the different elevation angles to be aggregated and analysed together. Additional experimental data - for example, direct measurement of the background concentration level undertaken independently, such as in situations where a plume is known not to exist - would assist in the validation of the results of the analysis.

The data are part of a field measurement undertaken using NPL's DIAL system to quantify the concentration level of methane in a plume produced by a methane source, and as such they are commercially sensitive. The data are used here to demonstrate and compare the described methods for the estimation of the background concentration level of methane in the proximity of the source.

3.4.2 Concept and Functionality for Area Source Emissions Monitoring Using TDLAS

The principle setup of a Tunable Diode Laser Absorption Spectroscopy system is described in Section 3.1. TDLAS is a technique that is typically used to perform amount of substance fraction measurements, and sometimes temperature and pressure measurements. The TILSAM method, which was developed in the EUROMET 934 project describes how to achieve traceability in TDLAS amount fraction measurements.

TDLAS technique directly measures sample gas absorption by tuning the laser over an absorption line of a molecule. A multi-pass absorption cell can be used as well as open path measurement. High temporal resolution allows the TDLAS to be used for investigation of fast changing systems. The following influence quantities are required for converting a line spectrum from a spectrometer raw data to an amount fraction.

There are several possibilities to realize an open path TDLAS system. Within the IMPRESS project a monostatic configuration was set up by PTB. This principle is visualized in Figure 10:

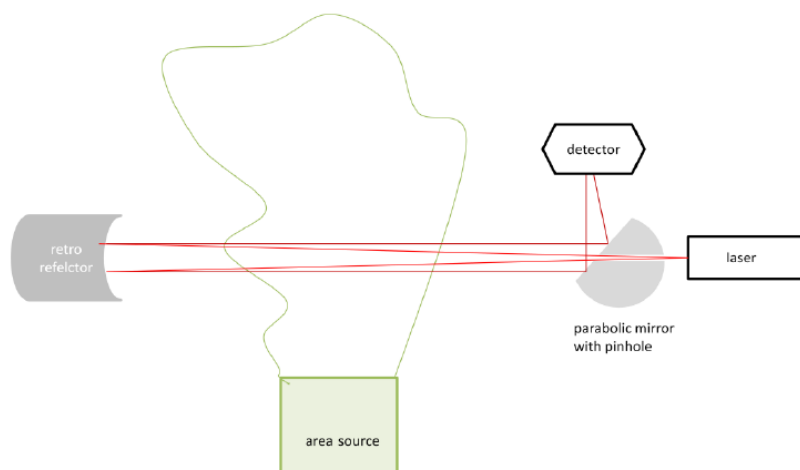


Figure 10: schematic of the TDLAS setup

The gas temperature is measured independently with a sensor for which measurement values are traceable to the SI. Typically, the gas temperature is measured with a temperature sensor placed in the measurement volume. The gas pressure is also measured independently using a pressure sensor which measures pressure values traceably to the SI. Capacitance diaphragm gauges are typically used for gas pressure measurements.

The optical path length is determined by an independent measurement to achieve traceability of the measured length to the SI. Optical path lengths can be determined using e.g. mechanical measurements or interferometry.

Line parameters such as the line strength of a probed species absorption line are measured in separate experiments in order to achieve traceability of the measured line parameters to the SI. The line strength of the probed transition is seen as the most important influence parameter based on previous metrology studies. The line strength links the measured interaction of photons to the molecule.

Temperature dependence, expressed by means of an exponent j , is important for any application outside the laboratory and at gas temperatures different from 296 K. Typically in laser-spectrometric - the amount fraction measurements, a single absorption line from an isotopologue is probed but the amount fraction is reported for the sum of all isotopologues of this gas species.

Line strength values for isotopologue absorption lines in literature, e.g. those of HITRAN (high-resolution transmission molecular absorption database), are typically not reported for the pure isotopologue, but for a certain "Natural" conventional abundance value e.g. that given by HITRAN. For a gas sample, the abundance of the probed isotopologue could differ from this conventional value at which the line strength value was reported.

Uncertainty sources which can be caused by an area source are:

- 1) Limited capture efficiency due to changing wind direction and speed
- 2) Inhomogeneous distribution of the analyte and integration in the line of sight
- 3) Not exactly known measurement distance
- 4) Unknown temperature distribution

- 5) Parasitic analytes
- 6) Vibrations of the setup or parts of the setup
- 7) Dazzling of the detector due to changing sun light

To address points 1 and 2, one has to distinguish between small, bounded area sources and large area sources, such as landfills, where the emission zone can exceed the size of optical configuration leading to difficulties in relating measured fluxes to emissions per unit area.

In 2006, the U.S. Environmental Protection Agency posted a test method on its website called OTM 10 which describes direct measurement of pollutant mass emission flux from area sources using ground-based optical remote sensing.

To avoid the influence of temperature special care has to be taken to choose a spectral line which shows minimum temperature dependence. The distance of laser and detector can be measured with optical distance meters aligned parallel to the laser beam used for TDLAS measurements or for example by using a chopped laser beam. These special conditions have to be addressed depending on the measurement environment and the uncertainty one needs to reach.

3.4.3 Survey on thermal imaging cameras for optical gas imaging (OGI)

Infrared imaging techniques are currently considered as one of the state-of-the art gas detection methods. IR-gas finding cameras, a relative new IR-technique, became popular in the oil and gas industry because it is more effective than the widely used 'sniffing' techniques, such as method 21 (Method 21 – Determination of Volatile Organic Compound Leaks).

The IR-camera visualize gas leaks and it enables scanning of large areas. One of the major disadvantages of the IR-camera is that it can only demonstrates the presence of a gas. It does not provide quantification information of the gas concentration or emission rates. Several studies have identified the sensitivity of IR-cameras to detect gas, i.e. the minimum detectable concentration under different laboratory conditions.

The minimum detectable concentration under different laboratory conditions has not been extended to estimate the gas emissions rates. The monitoring team found 72 leaks and 40 of these leaks were bagged for identifying the mass emission rate. The test did not determine a definitive reason why the instrument missed some leaks at rates that it might be expected to detect, because lower leak rates were detected. The detection sensitivity of the instrument depends strongly on the match between the laser wavelength and the wavelength of strongest absorption by the gas of interest.

Bagging analysis shows that the SNL camera was able to detect gas leaks as low as approximately 2 g/hr. The visibility of the gas leaks decreased with increasing stand-off distance. The detection limit of 100% natural gas, propane, n-pentane and benzene was lower than 0.22, 0.6, 1.96 and 2.75 g/h, respectively. Experiments with the Flir GF-320 IR-camera where the flow of 100% natural gas, n-pentane, propane and benzene were diluted with by 25%, 50% and 75% air revealed that the visibility of the emissions decreased with increasing dilution. Natural gas was emitted at two flows of 300ml/min and 2000ml/min from a leak with a diameter of 4mm and 55mm. All flows were clearly visible with the IR-camera and the different flows were easy distinguished with the camera.

Experiments with temperature difference ΔT of 0, 5, and 15 °C between 100% natural gas and ambient air showed that the visibility increased with increasing ΔT . In a laboratory with a standoff distance of 2 meters, an ambient temperature of 26 to 29 °C and a relative humidity 29 to 25%.

Benayahu et al showed with the Opgal EYE-C-GAS gas find camera that a temperature difference of 3 °C between the gas and the background was enough to visualize a methane mass flow of 0.76 g/h in normal mode. In the enhanced mode, a temperature difference of 2 °C between the gas and the background was enough to visualize a methane mass flow of 0.35 g/hr. Similar tests with butane, showed that the temperature difference of 3 °C between the gas and the background was enough to visualize a Butane mass flow of 1.84 g/h in NOR mode. In ENH mode a temperature difference of 1 °C between the gas and the background was enough to visualize a butane mass flow of 0.86 g/h.

Natural gas was released with 2m³/h at a distance of 5, 10 and 30 meters from the IR-camera. Natural gas

was still detected at a distance of 30 meters. Tests in a fume hood with a background made of paper, wood and plastic revealed that the gas plumes were less visible by the camera. A flexible gas tube with an inner size dimension of 6mm was attached in front of the blackbody; the gas flow through the tube was controlled via a flow controller verified and measured with a flow meter, the ambient temperature and humidity were measured at all times with an electronic thermometer. The gas was supplied from an equipped cart with methane cylinder with gas at 99.995% purity and a butane cylinder with gas at 99.995% purity. The tests were performed by placing two cameras side by side as a matter of redundancy to get results from similar cameras and proof of minimum leak rate detection.

Lev-On et al. 2007 describes the development of new "Leak/no-leak" emission factors that are suitable for estimating facilities' fugitive emissions when using an alternative work practice that is based on optical gas imaging technology for detecting leaking piping system components.

3.4.4 New Facility to Simulate Area Sources

The Controlled Release Facility (CRF) is a transportable flow control system purposefully designed and configured for the creation of replicate gaseous emissions sources. The system enables the operator to replicate a variety of gaseous emission fluxes at comparable scales to those found in industrial and agricultural scenarios, and thereby validate emissions monitoring methodologies.

Four separately controlled emission sources can be created, each fed by the output of a thermal mass flow controller (MFC) (Brooks Instruments SLA5853S) allowing a full scale output of 35 kg/h of methane or 50 kg/h of propane. Two secondary MFCs allow for the introduction of purge or tracer gases into the primary flow channels. All MFCs can be isolated from pressure and flow streams directed via a system of solenoid valves. All MFCs and valves are controlled via a computer running Brooks SMART Interface software, which also records each instrument status approximately every 4 seconds. The flow control system for the CRF is shown in Figure 11.

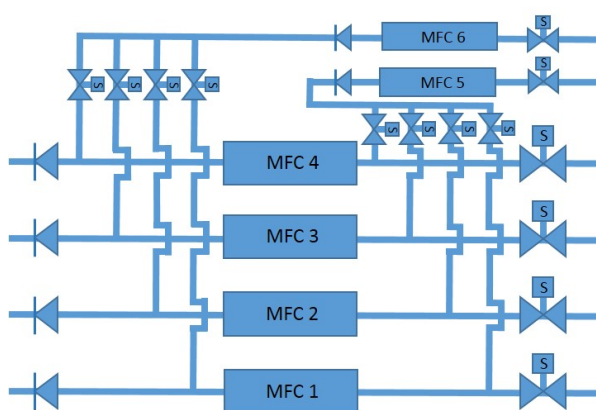


Figure 11: Photograph (left) and schematic (right) of the CRF flow control system

Calibration of the CRF is achieved through flow measurement using a primary piston flow meter (Mesa Labs ML-1020), full scale 500 litres per minute. The output of each MFC is connected in turn, while the gas of interest is flowed at a MFC set points reflecting the intended operational range. This calibration routine is usually conducted before and after tests to identify any instrument drift.

The facility is computer controlled and monitored, allowing for the execution of pre-written operational programs and analysis of flow data post-test. Communication to the instrument is made via a low voltage umbilical cable allowing the operator to control the system from a distance of up to 50m from the gas blending equipment. Figure 12 shows the typical configuration for a field validation experiment using the CRF.

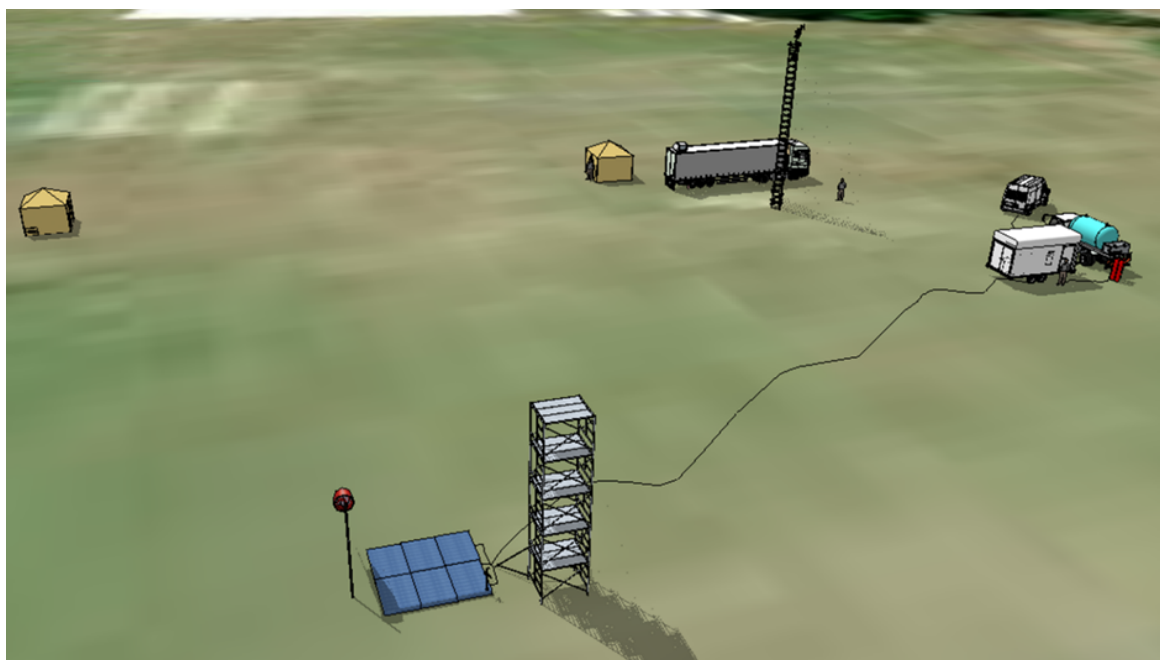


Figure 12. Typical operational layout for CRF with wind coming from the bottom of the figure creating a measurable plume where open-path FTIR and DIAL measurements are taking place

3.4.5 Key research outputs and conclusions

NPL developed the CRF to allow controlled testing of different methods for fugitive emission identification and quantification. This provides a unique capability to produce a realistic and configurable area source with metrologically traceable emission rates. Without this facility quantifying the abilities of the alternative measurement techniques would have been very difficult.

NPL improved the background detection rates for DIAL, publishing a paper about the methodology in the peer-review journal *Atmospheric Measurement Techniques*. VSL, working with DCMR, produced a facility for characterisation and calibration of IR VOC camera systems. VSL and DCMR developed a camera response model which enables camera performance to be characterised. PTB developed the concept of using TDLAS for fence line monitoring. Each developed uncertainty budgets for area source monitoring with their respective techniques, which were incorporated into a protocol for VOC monitoring, including the results of field testing the techniques using the CRF. The collaborative nature of the programme allowed a direct comparison of the different methods in a metrologically traceable way, giving a data based indication of the strengths and weaknesses of all techniques.

3.5 Development of a suite of metrologically robust protocols / standards covering the use of open path techniques

The aim of the objective was to standardise the use of different open path techniques to ensure that measurements would be traceable and comparable. International standardisation of measurement techniques provides confidence in results and sets out ways to control uncertainty in a consistent manner.

In order to ensure the uptake and use of the state of the art techniques for measurement of fugitive and diffuse emissions NPL, PTB and VSL developed protocols for the use of DIAL, TDLAS and OGI cameras respectively. These protocols have fed into standardisation where appropriate, in particular into CEN TC 264 WG38 which is chaired by NPL and which is developing a standard for the measurement of fugitive VOC emissions. Section 3.5.1 describes the DIAL protocol in more depth. Section 3.5.2 covers TDLAS and 3.5.3 describes the OGI techniques. In order to validate these protocols field validation studies were undertaken. Section 3.5.4 describes the use of the CRF developed by NPL to validate the protocols.

With the DIAL technique new methods for, and uncertainties associated with, spatial extrapolations are required. Generally, DIAL is operated by taking a series of scans either in the vertical or horizontal plane, hence concentration is known along lines of sight each at an increasing angle from the first. DIAL can scan over distances of up to ~1 km, hence even with relatively small angular steps there are large distances between the lines of sight at this range. Work is needed to evaluate different methods of extrapolation between these lines of sight, in order to optimise performance and fully characterise uncertainties. Combining DIAL concentration measurements with wind direction and velocity data to quantitate in terms of flux is relatively well established.

Research undertaken

3.5.1 Protocol for the application of Differential Absorption Lidar (DIAL) to remote sensing of area source emissions

For practical applications in order to be able to monitor hydrocarbons, specifically VOC, the DIAL shall be able to operate in the 3 μm region. To specific monitor aromatic compound like benzene and toluene, the measurements shall be made in the UV region. In order to characterise emissions from an industrial scale site, the DIAL system shall be:

- Mobile
- Transmitted beam should be eye safe, according to IEC 60825-1 ed3.0 (Safety of laser products – Part 1: Equipment classification and requirements).
- Able to scan in the vertical and horizontal plane with an absolute pointing accuracy better than one degree. The relative movement precision in a vertical and horizontal scan shall be better than 0.1° .
- Able to record all the relevant information needed for the data analysis and quality controls.
- Able to perform the required calibrations and quality checks.
- Able to produce a narrow optical bandwidth in order to maximise sensitivity and reduce cross interference. The optical bandwidth should be equal or less than the gas absorption line. In the near infrared this is approximately 0.1 cm^{-1} .
- Able to ensure pulsed laser wavelength stability to avoid the selected differential absorption to drift. This can be achieved with stability better than the laser optical bandwidth that in the near infrared is approximately 0.1 cm^{-1} .
- Able to tune and control the on and off wavelengths.
- Able to ensure fast switching ($>10\text{ Hz}$) between on and off wavelengths to avoid atmospheric backscatter variation between the on and off return signals.
- Able to achieve a spatial resolution of 10-30 meters. This place requirement on the laser pulse length ($< 10\text{ ns}$) and detector bandwidth ($>2\text{ MHz}$).
- The transmitted beam energy shall be such that the system is able to record a vertical scan in 10 min - 20 min with an acceptable signal to noise ratio close to the detection limit reported in B.3.1.
- Able to deploy several wind sensors at different elevations.

As an example, these requirements would be met by a DIAL system with the following characteristics:

- Transient digitizer with a 10 MHz – 20 MHz bandwidth.
- Infrared detector with 2 MHz – 10 MHz bandwidth.
- 0.5 m collection system.
- Laser power output greater than 1 mJ.

3.5.1.1 Application of the Method: Measurements Planning

A plan is required to clearly define the measurements to carry out. This includes the species to be measured, experimental arrangements (field setup) and likely interfering species.

- Selection of measuring locations: identification of suitable measurement locations from a technical viewpoint and also from a site logistics (parking and potential obstructions etc.).
- Identification of likely emission sources: this requires information from the site, usually including site plans and existing emissions information. Potential sources off-site should also be considered.
- Identification of potential interfering species: for complex sites this may require process information or preliminary air-sample analysis taken as part of the pre-site visit in order to identify species with potentially interfering absorption features. With this information it is also possible to advise the site if ethane measurements are necessary in order to improve VOC measurements accuracy.

- Assessment of wind field: pre site planning includes an assessment of the likely wind conditions, and what existing meteorological data are available.

3.5.1.2 Application of the Method: Selection of wavelengths

For each species to be measured, the on and off DIAL wavelengths shall be selected such that:

- The differential absorption between the wavelengths is of an appropriate level to achieve the required sensitivity. This requires pre assessment of the likely emission rate and the system performance.
- There are no absorption features from interference species, this requires knowledge of likely emission sources. As minimal the wavelengths shall be checked for common atmospheric species interference. This can be achieved with an appropriate spectral database such as HITRAN.
- The on and off wavelengths should be as close as possible to minimize possible interferences.

3.5.1.3 Application of the Method: Measurement strategy

Identification of the meteorological mast location in a clear area. If site topography is complex, evaluate the possibility to deploy a second meteorological station. Identification of ideal wind conditions, DIAL locations and line-of-sights to measure each different site areas. This and the weather forecast during the measurements period would help to plan when to measure a specific site area and from which location. When measuring at close distance from the emission source, i.e. close to buildings, a portable wind sensor should be deployed along the DIAL measuring line-of-sight.

Selection of the DIAL scan speed such as it is as fast as possible within the limit imposed by the detection limit (signal to noise) at the range where a plume from the area under investigation is expected.

3.5.1.4 Application of the Method: Measurement procedure

If the detector bandwidth can be varied, select the most appropriate value. Higher the bandwidth (i.e. higher spatial resolution) greater is the noise. Higher spatial resolution can therefore be selected in favourable atmospheric conditions. In unfavourable conditions when the DIAL signal to noise ratio is low, smaller bandwidth should be selected.

- Carry out a set of three or four DIAL scans for each line-of-sight in order to minimise the uncertainty.
- To decrease the uncertainty associated with a set of measurements repeat one or two extra sets of measurements of the same area along different scan lines or from different locations or on a different day.
- Measure upwind sources if present.

While measuring record the following information:

- Measurement locations, met location and lines-of-sight on site map.
- File name, time, scanner azimuth and elevation, other specific information of the scan.
- Site information
- Time when periodic measurements to check detection and acquisition system response are made.

3.5.1.5 Quality Control

Quality assurance of the emission measurements is necessary. These procedures require detailed project planning and progress monitoring with project subject to regular internal reviews and quality audits at measurement institutions. A crucial requirement for high quality DIAL measurements is accurate knowledge of the actual differential absorption coefficients that are appropriate for a particular measurement. The following calibration procedures should be employed to ensure the spectroscopic quality, and therefore the accuracy of the differential absorption measurement. The three key elements that need to be verified through these checks are that:

- A suitable calibration reference cell prepared with a known (concentration*pathlength) parameter.
- The laser source is operating with a suitably narrow linewidth to properly resolve the spectral feature of interest.
- The wavelength of the laser source is fixed and stable on the appropriate on and off resonant wavelengths.

A standard gas mixture of the target gas should be used to provide the reference for the spectroscopic measurements. Having established that a suitable reference cell is available and the laser source linewidth is correct, the on- and off-resonant wavelengths are set to their chosen values for the DIAL measurements. The calibration certificates may provide a calibration factor for the wind speed and wind direction readings. If data loggers are used to store the meteorological data, then analogue sensors, cabling and data loggers should be checked annually using a reference voltage generator. When known voltages are applied directly to the output terminal of the sensors and voltage readings are taken at the data loggers, a calibration factor is then obtained.

3.5.1.6 Data Analysis

The data acquired has to be analysed to give the range-resolved concentration along each line-of-sight. The integrated concentration profiles are piecewise differentiated with a selectable range resolution, to give the range-resolved concentration along the line-of-sight. Range-resolved concentration measurements along different lines-of-sight are combined to generate a concentration profile.

- The product is formed of the gas concentration measured with the DIAL technique at a given point in space and the component of the wind velocity perpendicular to the DIAL measurement plane at the same location, taking into account the wind speed profile as a function of elevation.
- This product is computed at all points within the measured concentration profile, to form a two-dimensional array of data.
- This array of flux results is then integrated over the complete concentration profile to produce a value for the total emitted flux.

A logarithmic wind profile can be used to describe the vertical distribution of the wind by using at least two wind speed sensors at different heights. It is advisable to use more wind speed sensors at different heights in order to calculate the variation of wind speed with height, as a function of various parameters. The ground elevation where the wind measurement system is located needs to be checked to establish if it is similar to the ground level downwind of the source; if not, the ground elevation along the scan line where the plume is detected should be used as the reference point for establishing the wind profile.

3.5.2 Protocol for the application of Tuneable Diode Laser Absorption Spectroscopy (TDLAS) to remote sensing of area source emissions

In order to characterise emissions from an industrial scale site, the TDLAS system shall be:

- Portable
- Transmitted beam should be eye safe, according to IEC 60825-1 ed3.0.
- Multiple optical path capability.
- Able to record all the relevant information needed for the data analysis and quality controls.
- Able to perform the required calibrations and quality checks.
- Able to tune and control the laser wavelength.
- Able to avoid ambient light (e.g. sun light) effects.
- Able to deploy several wind, temperature and pressure sensors at different locations or elevations.
- The path-average amount fraction (ppm) or column density (ppm-m) is provided.

As an example, these requirements would be met by a TDLAS system with the following characteristics:

- Infrared detector with 1 MHz – 10 MHz bandwidth.
- 2 inch optical collection system.
- Laser beam divergence less than 1.5 milliradians full angle.
- An alignment scope

3.5.2.1 Application of the Method: Measurements Planning

It is necessary to clearly define the measurements to carry out. This includes the species to be measured, experimental arrangements (field setup) and likely interfering species.

- Campaign logistics: including pre-site visits (if required) and checklists for ensuring the site are aware of the logistics of a TDLAS measurement such as clear obstruction free optical path. A method statement covering the TDLAS may be provided if required.

- Health and safety: requirements for site specific health and safety, for example safety inductions or hot work permit systems. Also requires a risk assessment for site specific hazards, e.g. provision of suitable PPE. The TDLAS system should have a fire prevention system, which is maintained and tested (EN 54 (Fire detection and fire alarm systems)). All electrical equipment should be routinely tested accordingly to IEC 60364 (Low voltage electrical installations).
- Selection of measuring locations: identification of suitable measurement locations from a technical viewpoint and also from a site logistics (parking and potential obstructions etc.).
- Identification of likely emission sources: this requires information from the site, usually including site plans and existing emissions information. Potential sources off-site should also be considered.
- Identification of potential interfering species: for complex sites this may require process information or preliminary air-sample analysis taken as part of the pre-site visit in order to identify species with potentially interfering absorption features. With this information it is also possible to advise the site if other species measurements are necessary in order to improve the measurements accuracy.
- Assessment of wind field: pre site planning includes an assessment of the likely wind conditions, and what existing meteorological data are available.

3.5.2.2 Application of the Method: Selection of wavelengths

For each species to be measured, the TDLAS wavelengths shall be selected such that:

- The absorbance at the selected wavelength is of an appropriate level to achieve the required sensitivity. This requires pre assessment of the likely emission rate (amount fraction) and the system performance.
- There are no absorption features from interference species, this requires knowledge of likely emission sources. As minimal the wavelengths shall be checked for common atmospheric species interference. This can be achieved with an appropriate spectral database such as HITRAN.
- The wavelengths should be low temperature dependence to minimize possible interferences.

3.5.2.3 Application of the Method: Measurement strategy

Identification of the meteorological mast location in a clear area. If site topography is complex, evaluate the possibility to deploy a second meteorological station.

- Identification of ideal wind conditions, TDLAS locations and line-of-sights. This and the weather forecast during the measurements period would help to plan when to measure a specific site path and from which location.
- For a given wind direction the line-of-sight to measure should be chosen considering the range capability of the TDLAS system, clearness of the line of site and the assessment of any upwind sources
- When measuring at close distance from the emission source, i.e. close to buildings, a portable wind sensor should be deployed along the TDLAS measuring line-of-sight.
- Carry out all the necessary quality assurance measurements.

3.5.2.4 Application of the Method: Measurement procedure

If the detector bandwidth can be varied, in unfavourable conditions when the TDLAS signal to noise ratio is low, smaller bandwidth should be selected. The Lorentz width should be fixed when using Voigt fitting.

- Carry out a long period measurement for each line-of-sight in order to minimise the uncertainty.
- To decrease the uncertainty associated with a set of measurements repeat 1-2 extra measurement sets of the same area along different line-of-sight, from different locations or on different days.
- Measure upwind sources if present.

3.5.2.5 Quality Control

The equipment is calibrated annually or cal-checked as part of standard operating procedures. Certificates of calibration are kept on file. The following calibration procedures should be employed to ensure the spectroscopic quality:

- A suitable calibration reference cell prepared with a known (concentration*pathlength) parameter.
- The wavelength of the laser source is scanned and covers the transition line of interest.

- The laser tuning behaviour.

A standard gas mixture of the target gas should be used to provide the reference for the spectroscopic measurements. Direct measure of the transmission through a calibration cell filled to atmospheric pressure with the reference gas. This ensures that the pressure broadening, and therefore the linewidth, is the same for the calibration gas as in the ambient environment.

A spectral scan of the relevant absorption feature should be carried out on a daily basis. The measured absorption feature is fitted with a Voigt function. This provides confirmation that the cell has been filled correctly and that the laser tuning is correct. If the measured width of the absorption features differs significantly from the expected widths then this indicates an issue with the laser source or calibration cell and a number of checks should be carried out.

The checks can be accomplished using the absorption signal provided by the calibration gas cell added to the open path field absorption signal. The signal increases above the open path signal, proportionally to the gas concentration and path length of the gas cell. The instrument response is checked using the difference of the measurements with and without the gas cell.

Calibration certificates may provide a calibration factor for the wind speed and wind direction readings.

3.5.2.6 Data Analysis

The data acquired has to be analysed to give the concentration along each line-of-sight. The data analysis process consists of the following steps:

- Background subtraction
- Spectral Analysis
- Calculation of path-averaged concentration/column density. The absorption line intensity used in this calculation is derived from HITRAN or measured separately.

The emitted flux is calculated by integrating over the complete concentration profile

3.5.3 Protocol for the application of Optical Gas Imaging (OGI) cameras to remote sensing of area source emissions

IR camera that is used for OGI shall at least meet the following requirements:

- The presence of a specified filter which is suited for the hydrocarbons to be studied
- The IR camera shall be designed for detecting the gases of interest (filter!),
- The IR camera shall be designed to be used on industrial plants,
- A detector that has cooled down to the right operating temperature,
- It shall be possible to make gases visible in real time,
- 'Thermal sensitivity' equal or better than 25 mK,
- Detection limits for common gases like methane and propane shall have been studied and documented,
- The possibility to record IR videos,
- The possibility to record (or extract) images.

The IR camera may additionally have a high sensitivity mode that enables smaller amounts of VOC to be made visible by manipulating images. Whether a high sensitivity mode is necessary will depend on the purpose for which the IR camera is used.

3.5.3.1 Factors affecting detectability

The following factors should be optimized in order to improve the OGI performance:

- Background properties (e.g. infra-red reflectivity and emissivity)
- Detection distance
- Detection angles (different backgrounds)
- Environmental: wind speed, temperature, water, steam, sun, stainless steel, density sources
- Methodology: number of sources per day, using high sensitivity mode or not, daily operation test, parameters to set up
- Camera (or filter) characteristics in relation to the VOC's to be studied.

3.5.3.2 Application of the method

Carrying out the test procedure for the use of the IR camera.

- The basic principle is that an IR recording will be made only if an emission is detected.
- Only make IR recordings of all emission sources if laid down specifically in the detection plan.
- Before accessing the detection zone, first do a quick safety scan from an ample distance for very large and potentially hazardous leaks. If there are no such leaks, continue with the following steps:
- Inspectors follow detection procedures in order to control some uncertainties
- Perform an accurate and systematic round of detection on the basis of the measuring plan, while preventing exposure to released VOC emissions as much as possible.
- Record a continuously emitting source for at least 20 s
- Record a fluctuating emission source for at least 20 s or for as much longer as is necessary to make its fluctuating character visible
- Make a visible picture (non-IR) of the emission source. The visual recording of the source shall also make the surroundings of the source visible, so that the reason for the leak becomes as clear as possible.

Base your choice of sensitivity settings for the IR camera on what is being detected and the detection strategy.

3.5.3.3 Quality control

No calibration (from provider) is required for OGI used in "gas detection". On the other hand, a functional test is required. This functional test consists of validating the ability of the IR Camera to detect a certain determined flow rate of a certain substance, from a certain distance, under certain weather conditions.

3.5.3.4 Data analysis

All gathered pieces of information on site are recorded in a database.

The direct mass flow quantification using OGI technology is not - yet - possible. In order to quantify leaks, several methods can be implemented:

- FID (Flame Ionisation Detector) measurement and quantification using specific correlations
- Bagging

3.5.4 Field validation campaign

A field validation campaign was carried out at an industrial site, embedding the NPL CRF in a decommissioned refinery unit (Figure 13). The CRF source nodes released propane gas while embedded within the structure of a cracking/reforming plant. The DIAL was used to measure the emissions following the protocol developed in this project, along with TDLAS and OGI techniques.



Figure 13 Decommissioned cracking/reforming plant where the CRF source nodes were deployed

Figure 14 shows the locations inside the selected decommissioned unit of the five controlled release nodes. The released gas was mainly propane (about 91%) with a small percentage of propene, i butane and n butane. The release rates were not known to measurement technique operators. The maximum achievable emission rate was about 30 kg/hr.

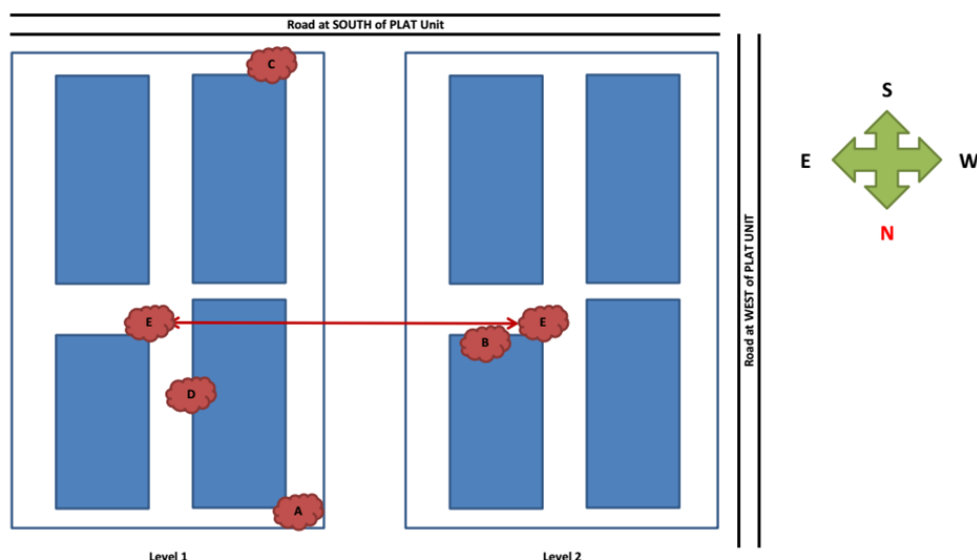


Figure 14 Locations of the five controlled release nodes

The DIAL measured background sources in most of the scans, but could generally isolate these plumes from the plume of the intended release. The DIAL was able to measure 18 of the 20 controlled releases as shown in Table 1. Tests 7 and 13 were not measured as the DIAL was parked in non-ideal locations as consequence of the low wind speed and variable wind direction.

The DIAL measured relatively high background sources in most of the scans, but it could generally isolate their plumes from the plume of the intended release. Nonetheless, background scans were carried before and after each test and analysed in the same region as the test scans showing some contribution from upwind sources. The values reported in Table 1 are after the subtraction of the background contribution from the test scans and the standard deviation is the sum in quadrature of the two sets of measurements. For this reason the reported standard deviations are relatively high, particularly when the test emission rates are low.

During Test 5 it was not possible to carry out background scans since the wind direction changed after the test release stopped, therefore Test 5 emission rate probably overestimate the actual controlled release rate and it should not be used.

3.5.4.1 Summary of the DIAL controlled release test results

Emission Area	Average Emission Rate	Standard Deviation
	kg/hr	kg/hr
Test 1	5.41	1.83
Test 2	16.06	1.95
Test 3	9.83	2.33
Test 4	8.36	2.61
Test 5 *	11.42	1.86
Test 6	9.18	1.43
Test 8	9.56	1.13
Test 9	13.27	4.37
Test 10	18.47	5.60
Test 11	10.23	4.46
Test 12	8.46	4.47
Test 14	14.96	3.66
Test 15	3.68	2.52
Test 16	1.22	3.05
Test 17	9.68	1.14
Test 18	17.09	5.46
Test 19	8.01	4.55
Test 20	10.89	5.13

Table 1 DIAL results and standard deviations.

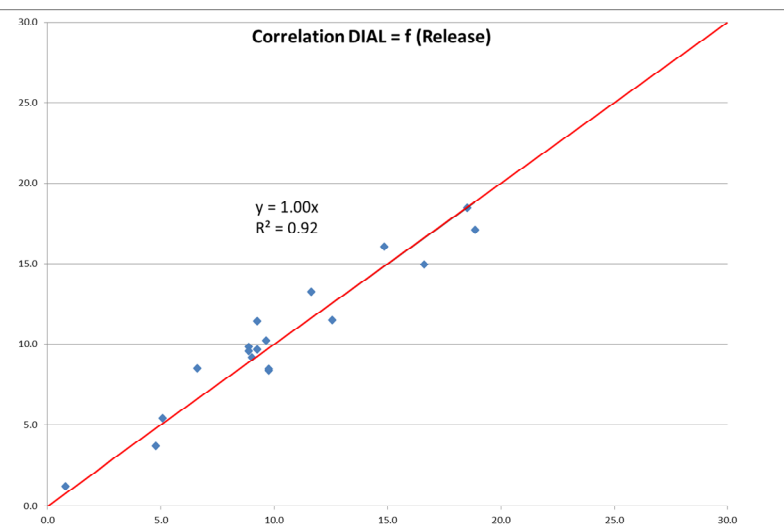


Figure 15 DIAL measured emission rates (kg/hr) against CRF emission rates (kg/hr)

A regression plot of the DIAL emission rates compared to the CRF emission rates shows excellent agreement, with a very linear response (Figure 15). The slope of the fit is 1, showing the DIAL has almost no systematic effects, and the scatter is very small.

Key research outputs and conclusions

Partners have taken widespread actions to develop and standardise methods, taking active roles in relevant CEN technical committees and working groups. Field work has been carried out to provide data for validation and demonstration of the new methods. Without the collaborations in this project such efforts to improve working practices would take longer to develop and be unsupported by validated measurements.

4 Actual and potential impact

The project developed a robust metrology infrastructure to underpin the monitoring needed for enforcement of point (stack) and area (e.g. fugitive) emissions regulation. As part of this the project developed protocols used as input by CEN/TC 264 in draft standards, stack simulator facilities, and the development of DIAL, TDLAS and IR camera monitoring techniques.

Dissemination of results

Articles were published in six journals including Remote Sensing of Environment, Atmospheric Measurement Techniques, and the Journal of Air and Waste Management Association.

Presentations on the project were also given at six conferences including the American Geophysical Union meeting and the Conference on Emission Measurement and Air Protection.

A workshop on the application of differential absorption lidar (DIAL) for pollution emissions monitoring was hosted by NPL and the Chinese NIM and attended by 50 stakeholders.

An e-learning course on emission monitoring measurement entitled 'Uncertainty calculation of flue gas velocity and volume flow rate under EN ISO 16911-1' is available on the project website.

Contribution to standards

The work of this project has provided input to the following working groups, for inclusion in draft documentary standards:

- CEN/TC 264/WG 36, 'Measurement of stack gas emissions using FTIR instruments'. Input from the project: Protocol for the measurement of stack emissions by FTIR (objective 1).

- CEN /TC 264/WG 16, 'Reference measurement methods for NO_x, SO₂, O₂, CO and water vapour emissions'. Input from the project: Protocol for the measurement of stack emissions of SO₂ using optical techniques including TDLAS (objective 1).
- CEN/TC 264/WG 38 Determination of fugitive VOC emissions. Input from the project: Protocols for DIAL, TDL and IR camera. The determination of fugitive VOC emissions working group are operating under an official EC mandate formally requesting that CEN produce this documentary standard for the enforcement of fugitive related legislation (objective 5).

In the future all measurements by FTIR and for SO₂ using optical techniques carried out across the EU for regulatory compliance purposes will have to follow the methods produced by CEN/TC 264/WG 36 and WG16, using input from the project's FTIR and SO₂ protocol documents.

The work on modelling flow uncertainties and concentration measurement uncertainties has fed into the production of an industry guidance document 'Framework for determining uncertainty sources and the propagation of uncertainty contributions in reported annualized mass emission', available via the project website (objective 2).

Early impact

- A gas stack simulator is now available at VSL (objective 3).
- A particulate simulator is now available at NPL, designed to deliver synthetic dust where particle size can be controlled, and giving a measure of sampling proficiency (objective 3).
- A tool that can model the effect of temperature and pressure on remote sensing techniques is freely available for download from <https://www.ptb.de/cms/en.html> (objective 1).
- The Controlled Release Facility (a transportable facility based at NPL) provides a unique tool that has already been used by manufacturers to properly validate fugitive emission measurement techniques under the conditions that are actually present in real measurement situations (objective 4).

Future potential impact

The results of this project have fed into CEN standards including EN14181. Wider beneficiaries of the work include manufacturers of high-technology products such as remote sensing devices, who will benefit from the project's new measurement methods, standards and validated protocols.

5 Website address and contact details

A public website has been open, where the main public deliverables have been made available for the end-users and keep them informed about project meetings and events: <http://projects.npl.co.uk/impress/>

The contact person for general questions about the project, management and coordination is Garry Hensey, NPL (garry.hensey@npl.co.uk)

The contact person for the development of work on stack emissions – performance of existing SRMs and development of next generation of protocols, techniques and facilities is Stefan Persijn, VSL (Spersijn@vsl.nl)

The contact person for the development of the work on the uncertainty of flow and annual emission determination is Jan Geršl, CMI (jgersl@cmi.cz)

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The contact person for the development of work in creating impact is Zhechao Qu, PTB (zhechao.qu@ptb.de)

6 List of publications

- [1]. Coleman, M.D., Render, S., Dimopoulos, C., Lilley, A., Robinson, R.A., Smith, T.O.M., Camm, R., Standring, R., Testing equivalency of an alternative method based on portable FTIR to the European Standard Reference Methods for monitoring emissions to air of CO, NO_x, SO₂, HCl, and H₂O. Journal of the Air & Waste Management Association, 65:8 (2015) 1011-1019.
- [2]. Zhechao Qu, Olav Werhahn, Volker Ebert, The thermal boundary layer effects on line-of-sight TDLAS gas concentration measurements. To be submitted.
- [3]. Coleman, M.D., et al., Combining UK and German Emissions Monitoring Proficiency Testing Data Based on Stack Simulator Facilities to determine if Increasingly Stringent EU Emission Limits are Enforceable, to be submitted to Accreditation and Quality Assurance.
- [4]. Harris, P., Smith, N., Livina, V., Gardiner, T., Robinson, R., and Innocenti, F., Estimation of background gas concentration from differential absorption lidar measurements, Atmospheric Measurement Techniques, 9 (2016) 4879–4890.
- [5]. Gardiner, T., et al., In-field validation of remote sensing emission measurements, to be submitted to Remote Sensing of Environment.
- [6]. John C. Korsmana,*, Stefan T. Persijnb, Edgar M. Vuelbanb, VOC measurements by passive IR cameras: Operational boundaries and model estimations, submitted to Journal of Loss Prevention in the Process Industries.