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1 Overview

European Directives came into force setting increasingly stringent Emission Limit Values (ELVs) for key air pollutants to mitigate ~400 000 premature deaths and €330-€949 billion p.a. of costs attributable to air pollution. However, the emission monitoring industry faced an issue, as a metrologically robust framework of standardised measurement methods to enforce these directives was not fully in place. This project addressed this measurement gap by innovating measurement methods for new measurands (NH_3, formaldehyde, HF, PM, SVOC, OGC, PAH), addressed a lack of uncertainty characterisation in flow measurements and developed next generation techniques for increasingly stringent future legislation. These improvements and innovations in measurement and uncertainty assessment provide the capability to enforce further tightening of ELVs in future.

2 Need

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

3 Objectives

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

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

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

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

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

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

5. To provide input to the development and/or revision of standards related to the emissions of semi-volatile organic compounds (SVOCs), particulate matter (PM), polyaromatic hydrocarbons (PAHs) and

organic gaseous carbon (OGC). In addition, to facilitate the take up of the technology and measurement infrastructure developed in the project by standards developing organisations (such as CEN TC 264 and ISO TC 146 and those linked to the EU Eco-design Directive 2009/125/EC, MCP Directive 2015/2193 and IED 2010/75/EU) and end users (e.g. environmental monitoring and regulation bodies, the power generation sector, combustion equipment manufacturers).

4   Results

4.1   *Objective 1: Reference methods for HF, NH₃, formaldehyde, HCl and dust*

NPL and INERIS wrote a report summarising the available manual and certified automated systems for measuring formaldehyde, NH_3 and HF, assessing their relative strengths and weaknesses. The IMBiH guestworker at NPL (RMG1) carried out an assessment of current best available techniques – associated emission levels (BAT-AELs) which informed the evaluation in the report. This concludes that as ELVs are set at lower levels it presents a problem for current metrologically robust emission measurement techniques.

INERIS carried out a field based inter-comparison of manual and automatic methods to measure NH_3 concentrations. INERIS had two pairs of two manual sampling devices and the same number of FTIR instruments over three days. Measured emission matrices were varied daily to represent boiler flue emissions from natural gas, fuel oil and biomass fuels. The results showed the equivalence of the reference method and the Gasmet DX 4000 FTIR, however the slope of the regression line varied depending on the matrix of combustion gases. In particular, for biomass the measurement results were more variable.

DTU carried out laboratory and field testing of a prototype optical instrument for measuring formaldehyde and NH_3. This included testing at the INERIS test bench which demonstrated high sensitivity for NH_3/H_2CO and agreement with INERIS data.

NPL have produced procedures for in-field wet calibration method for HCl and NH_3. Along with this they have documented an uncertainty budget. This highlights that HCl remaining in sampling equipment can lead to increases in overall measurement uncertainty of up to 5 %, so it is important to properly purge equipment and allow sufficient time for the analysers to stabilise after concentration changes during the calibration process.

NPL have developed a facility to simulate a typical duct that would be sampled for dust measurements (Figure 1). The amount of dust in the duct can be precisely controlled and traceably quantified, making it an ideal test bench for testing the limits of current measurement techniques at low concentrations. Emission limits are continually being reduced to improve air quality, so emissions are also falling to meet the revised limits. Current measurement techniques have to be able to keep up with falling limit values, particularly with regards to the method uncertainty. This is specified in the industrial emissions directive (IED) to be a percentage of the limit value, so as limit values fall so must the measurement uncertainty. The limit of detection for current methods is still capable of detecting dust at the required levels, but measurement uncertainty is being challenged by the lower emission limit values.
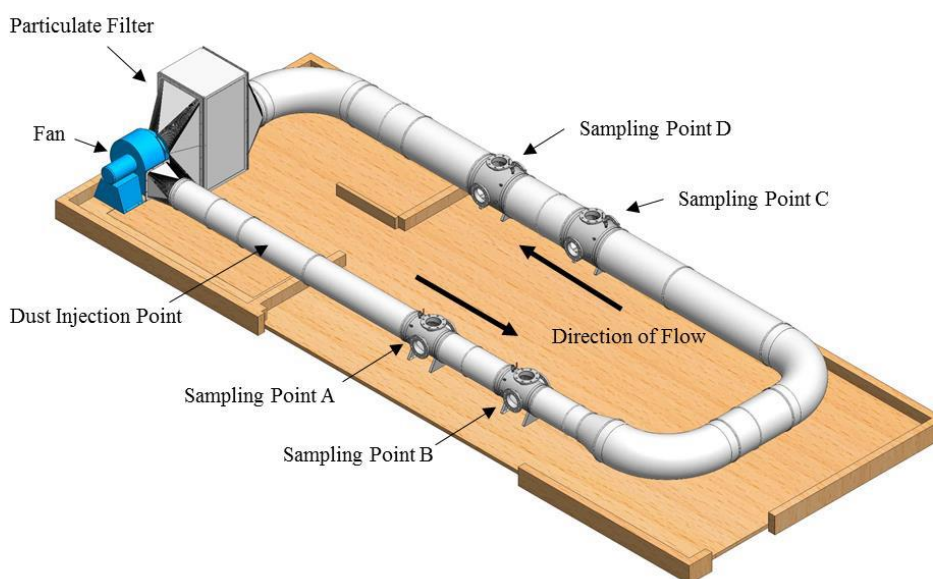
Figure 1: 3D engineering drawing of the constructed NPL facility indicating the positions of the four sampling points, each of which has three ports to allow sampling from above and both sides of the duct

Similar to dust, falling emission limits makes it difficult for the HCl reference method to meet the required uncertainties. The HCl reference method involves flowing the sample gas through impingers where the chloride is captured by a reaction. Laboratory analysis can then derive the concentration of chlorides in the stack. This laboratory analysis is a significant proportion of the overall uncertainty so it is important that accredited laboratories are meeting the uncertainty limits and where possible surpassing them to demonstrate that the uncertainty limits could be reduced in future. To test this NPL carried out a blind proficiency test, sending out a number of traceably prepared samples, labelled like standard stack samples, along with samples taken from the NPL stack simulator facility, to three accredited laboratories for analysis. The samples were the equivalent of 0-60 mg/m^3 concentration range. Once all the participants had returned results and their measurement uncertainties an analysis was carried out according to EN-5725, to identify any outliers and investigate the performance across the range of accredited laboratories.

Laboratory measurements were generally better with the laboratory prepared samples that are normally used during proficiency testing. This could indicate that testing teams may have overly optimistic consideration of their uncertainties when making real world measurements. Additionally, when looking at results for emission limits for existing IED limits (10 mg/m^3; 0-15 mg/m^3 range) and future BAT Conclusion limits (3 mg/m^3; 0 - 4.5 mg/m^3 range), a significant proportion of samples (21.6 % and 54.9 % respectively) would not meet the overall uncertainty required. The next revision of EN 1911 should include more attention on the analytical uncertainty, including adding an overall uncertainty requirement for the laboratory analysis.

NPL and INERIS both have stack simulator facilities, but there are some differences between them. The NPL simulator is a recirculating system in a 1.5-metre-wide section of vertical duct with four sample ports, two on each side. The NPL system generates the gas stream from gas cylinders along with nitrogen and synthetic air generators. The INERIS facility is a horizontal duct with gas generated by three boilers firing on oil, natural gas and biomass, with the ability to spike the flow with additional analytes and twelve sampling points.

Each of these facilities are used for proficiency testing (PT) schemes to test the ability of participating stack testing organisations. This testing demonstrates competence and is used as evidence for maintaining accreditation granted by national accreditation bodies. The NPL scheme accesses participants against a reference instrument from which assigned values are taken using parallel measurements with the participants. For the INERIS scheme the assigned value comes from consensus values derived statistically from all participants, requiring at least ten participants measuring in parallel.

As part of the IMPRESS 2 project the stack testing teams for both INERIS and NPL took part in both schemes. The results demonstrated that both stack teams performed better in their home PT schemes, indicating that participants are likely to do better when they are more familiar with a scheme.

NPL created a computer model of an automated measuring system (AMS) operating on a stack according to the EN 14181 quality assurance regime. As part of the IMPRESS 2 project the model was expanded to include reference methods for HCl and dust measurements. The model uses Monte-Carlo simulation techniques to assess the effect of individual uncertainties on reported annual mass emissions.

The model was used to carry out sensitivity testing for the dust reference method. Evaporation losses have the most impact in terms of errors on annual mass emissions. Leak rate and the sampling nozzle angle to the flow in the duct also caused significant errors.

From the proficiency testing on HCl laboratory performance carried out by NPL, low, high and average lab analytical uncertainty values were derived. The model was used to look at the effect of using these uncertainties on the annual mass emission values. Average error is small, but the range is significant so attention should be paid to the contribution of lab analytical uncertainty when considering if the overall uncertainty requirement is being met. This supports the findings of the NPL laboratory inter-comparison work.

INERIS discussed the existing established and ad-hoc methods for the determination of NH_3, formaldehyde and HF and have highlighted some of the challenges associated with their measurement in industrial stacks. INERIS also assessed the benefits of using the available manual measurement methods and techniques.

Ammonia (NH_3), hydrofluoric acid (HF), and formaldehyde (CHOH) are subject to regulatory limit values, but for which no standardised reference method (SRM) is defined. These elements will enable the development of standards describing measurement methods.

It is essential to know the performance characteristics of measurement methods in terms of limit of quantification and measurement uncertainty to assess their suitability for emission sources monitoring, in relation with current emission limit values and in the perspective of a further lowering of these emission limit values in the future due to new directive requirements.

The document therefore provides information to assess the suitability of each measurement method for the monitoring of the 3 compounds mentioned above as well as for dust and HCl. For these last two compounds, the implementation of already existing standardised reference methods and the organisation of interlaboratory comparisons provide feedback to assess the limit of the reference methods.

Protocols capable of achieving measurement uncertainties of ≤30 % for HCl and dust, and ≤20 % for H-CHO, NH_3 and HF of the applicable ELVs need to be developed. Looking further ahead, in addition to establishing the state of the art for these measurands this project has also taken a further step forward in terms of developing next generation techniques and supporting spectroscopy. Laser-based techniques have the potential to achieve increased sensitivities more in line with the perspective of a further lowering of emission limit values in the future due to new directive requirements.

INERIS carried out an inter-laboratory comparison to assess the measurement performance of participants for CO, NO_x, TOC, dust, SO_2, HCl and HF. Using data from nine rounds of the ILC and some additional data produced for the project using the SRMs, INERIS and NPL have produced a paper to look at how the measurement uncertainty compares to requirements in current and future legislation. The AMS methods met the IED guidelines, but, focussing on the SRM measurements, the results demonstrated that the reference methods for CO, TOC and dust were already falling short of the IED requirements. For HCl (reaction with ammonia) and HF (too few results available) the results were inconclusive about the uncertainty requirement. Lower ELVs that have already been proposed in existing BAT conclusions will expand this issue, so new measurement methods, particularly new SRMs, are required to meet the upcoming measurement challenge.

The reference method for measuring HCl in stack gas is unable to measure at the lowest concentrations currently and likely to be required in future legislation. To address this need PTB, along with CNR, reviewed the potential of tunable diode laser (TDL) based cross-stack analysers to fill this gap. PTB went on to develop a direct tunable diode laser absorption spectroscopy (dTDLAS) for making HCl measurements using an inter-band cascade laser. Combining the instrument with a simulation model to account for other gases, in this case CO_2, it demonstrated results that meet the requirements of European legislation for HCl monitoring from combustion emissions. Further development of the simulation in future will allow the method to work in more complex gas matrices that will be more representative of real stack conditions.

CNR focused on measurement of NH_3 using direct absorption (DA) and wavelength modulation spectroscopy (WMS). Commercial analysers have been certified for this use, but research was required to understand the effects of experimental conditions on their calibration. CNR carried out experiments at the INERIS stack simulator facility at Verneuil-en-Halatte, measuring concentrations of NH_3 from 1-51 µmol/mol, with different background conditions (fuel type, moisture content, etc.). Most combustion plants have relatively stable

conditions, but for biomass burners carbon and moisture content can vary both over time and instantaneously, leading to the instrument operating well beyond the range provided by the calibration.

The CNR work shows that, among optical techniques, those which are not affected by the shape of the absorption profile should be preferred for this kind of measurement. They are DA, Cavity Ring Down (CRD) and Fourier Transform InfraRed spectroscopy (FTIR), which adopts an infrared lamp as its source and can be considered a DA over a large wavelength range simultaneously. CRD is the most effective technique but requires very clean samples (usually above 99.99 %), as the mirrors must maintain their reflectivity, however the tests showed fouling of the mirrors due to soot from fuel combustion.

FTIR has, with respect to DA, the advantage of measuring several molecules simultaneously in the middle infrared, where absorptions are more intense than in the near infrared by almost two orders of magnitude. Yet, the frequency resolution of FTIR devices is generally lower than laser-based instruments. Therefore, changing the absorption frequency width could result in an interference among different molecular species, and smart software is required to separate the absorption of the different molecules.

DA is the least sensitive optical technique. Yet some important improvements with respect to the apparatus can easily be attained. The artificial stack available at INERIS has a diameter of 15 cm, but typical diameters of chimneys are at least 50 cm. So, even when maintaining the number of passes in the cell, longer pathlengths can easily be achieved. CNR selected a target wavelength in the near infrared, allowing the use of optical fibres. By proper technical design, it is possible to reach much stronger absorptions using a mid-infrared, free propagation laser. Finally, optical fibres operating in the mid infrared region are entering the market. In the future, the same optical arrangement used for the present measurements could be used for the middle infrared, allowing to position the laser in a safe place. All this means that the need for more sensitive techniques could be less and less important, and DA could be used without renouncing to sensitivity.

A multipass cell was inserted for the first time inside a stack, to verify the effects of exhaust composition on the readings of the two most widespread commercial detection techniques, "direct absorption" and "second derivative". An experimental apparatus was developed, suitable for both kinds of techniques. During a test of the artificial stack at INERIS, ammonia was measured, at concentrations in the range 3-60 ppm, at the temperature of 140 °C. This temperature was obtained either by using electrical resistors, or by burning methane. In the latter case, the exhaust mixture contained a significant amount of both carbon dioxide and water. The difference in the behaviours of direct absorption and second derivative is summarised in Figure 2. With increasing ammonia concentrations, the readings of direct absorption are linear, with respect to the reference analyser, and the points with methane burning are indistinguishable from those with electrical heating. On the contrary, with second derivative there is a well visible difference. The two sets of measurements are linear with respect to reference, but with different coefficients. Second derivative is a powerful detection technique, which anyway should be handled with care. Several calibration issues are always taken into account in practical devices, mainly electronics. But the mixture composition should be considered as well, especially in applications in which the content of water and/or carbon dioxide can vary appreciably.
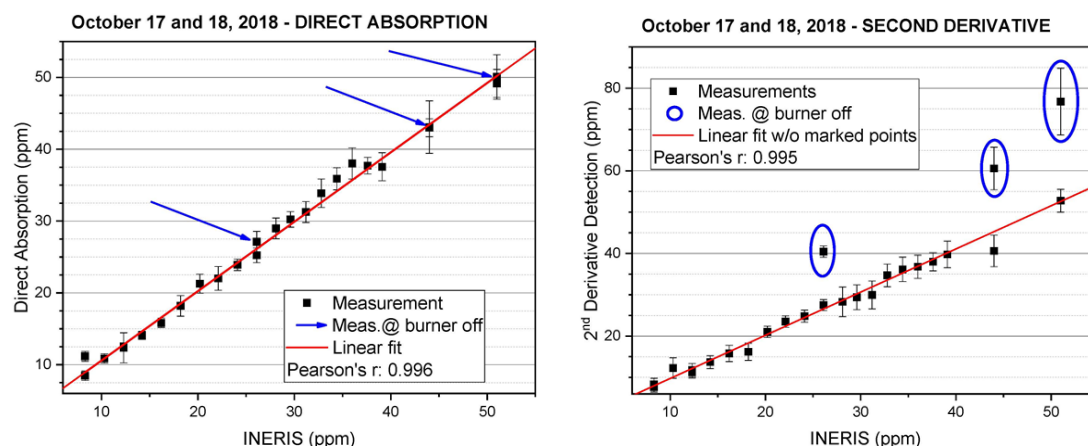

Figure 2: Results for direct absorption (left) and the second derivative (right). Direct absorption does not detect measurements made with the burner off, but these are clear when looking at the second derivative.

The key outputs of Objective 1 are:
- Results will support standardisation of HF, NH3 and formaldehyde
- Demonstrated the need for improvement of the current HCl and dust SRMs
- Development and demonstration of new optical measurement techniques
- 8 peer-reviewed publications

This objective was successfully achieved.

4.2 Objective 2: Reference methods for small scale combustion sources meeting the Eco-design directive uncertainty requirements

RISE looked at the use of biomass burners for domestic heating, which are covered under the Eco-design directive. Residential combustion of wood biomass is characterised by incomplete processes leading to high concentrations of gases and particles containing both organic and inorganic substances. There are many different standard methods for the measurement of combustion generated particle emission, some differ between different combustion sources. Most standards focus on the most straight forward measurement methods, collecting particles directly from the hot fumes, while in other standards the particulate collection is after a dilution of the exhaust gases, taking into account the condensation of organic gases. In particular for residential biomass heating appliances there is no European harmonised standard for measuring solid and condensed particles. Two methods are currently in use, one adapted from the standard used to measure particles produced by large combustion plants (just collecting solid particles at high temperatures), while the other method is based on the dilution of sampled gases to collect solid and condensed particles.

From reviewing the available literature RISE put forward a number of suggestions for PM and SVOC standardisation requirements.

- Including emission data on phenol, naphthalene and benzene would improve the estimates of formation of particle mass in biomass effluents (ambient particulates).

- It would be preferable to measure inorganic and organic particles differently, as the inorganics are mainly related to the fuel, while organics more to the combustion facility, thus abatement strategies for the different parameters will vary.

- Formation of secondary organic particles takes place both in the gas phase and the aqueous phase and the resulting compounds differ. In the aqueous phase the reactions are included in dark chemistry and other compounds are more important than in OH-driven chemistry. This might imply benefits of measuring other species than phenol, naphthalene and benzene in some areas.

- The partitioning between the gas and the particle phase can be calculated assuming instantaneous thermodynamic equilibrium at sufficiently good results.

- Particle number is important for cloud formation processes, but this data is highly related to dilution processes, requiring more research to be usable as a measurement standard at this level.

- If different standard methods on measuring particle emissions from biomass combustion are used, the reported emission data need to include information on what type of emission factor applies.

- Including organic analysis in the standard would allow it to include the particles that are condensed close to the source which can be missed by current procedures.

There are no standard reference methods for measuring SVOC, PAHs or condensable PM generated from small scale biomass like residential wood combustion. INERIS, RISE, ENEA, ISSI and DTI worked together to develop and validate three protocols/methods to characterise these sorts of emissions.

- Method using a dilution chamber to simply characterise solid and condensable fraction of particulate matter

- Simplified method of characterisation for PAH emissions including BaP, a regulated compound in ambient air which is mainly generated by residential combustion

- Method for characterisation of SVOC emissions according to volatility characterisation

Using these methods would improve emission inventories and close the gap between observed and modelled PM in ambient air. Existing standards are not sufficient to characterise these, so the developed protocols are being put forward for adoption as new standards under CEN TC295.

Polycyclic aromatic hydrocarbons (PAH) are monitored according to ISO 11338:2003. The samples are extracted from the sampling apparatus using an organic solvent (e.g. hexane), then the solution is analysed by GC-MS or HPLC. NPL produced standard solutions of PAH in hexane which they sent to four European analytical laboratories, isolating the analysis stage of the process. The spread of results from the different labs calls into question the uncertainty currently stated for the method. On top of the analytical uncertainty, the sampling uncertainty and representativeness of sampling also need to be considered. There is currently no proficiency testing for this method and, given relatively few laboratories are accredited for PAH measurements, it is unlikely that one could be organised.

The key outputs of Objective 2 are:
- Clarified requirements for standardisation in the area
- Developed protocols/methods for characterising these emissions
- Identified a potential issue with the stated analytical uncertainty for PAH monitoring

This objective was successfully achieved.

4.3   *Objective 3: Biomass emission measurement and source apportionment*

Biomass combustion is viewed as carbon neutral since the carbon in biomass generally has been removed from the air as the plants grew over relatively short timescales. However, when biomass is co-combusted along with fossil fuels there is a need to account for the source apportionment of the emissions. The carbon isotope ratios are measurably different between biomass and fossil fuels, so looking at the ratios of isotopic CO_2 emitted by co-combustion is seen as a method for source apportionment.

VTT with help from NPL produced a report on expected isotopic ratio ranges from different biofuels. Several previous studies have characterised ratios from different sources, indicating both species and regionally specific varieties (e.g. Figure 3). Beyond this the report considers the instrument requirements to actively measure these levels of isotopic variation within emissions. A dilution system would be needed to keep the concentration of CO_2 in the instrument below 10 % as a higher range would reduce the sensitivity. The optical wavelength used by the spectrometer would have to avoid potential interferents H_2O, CO, SO_x, NO_x, VOCs and hydrocarbons. The combustion gas would also require filtration to avoid particulate matter entering the instrument.
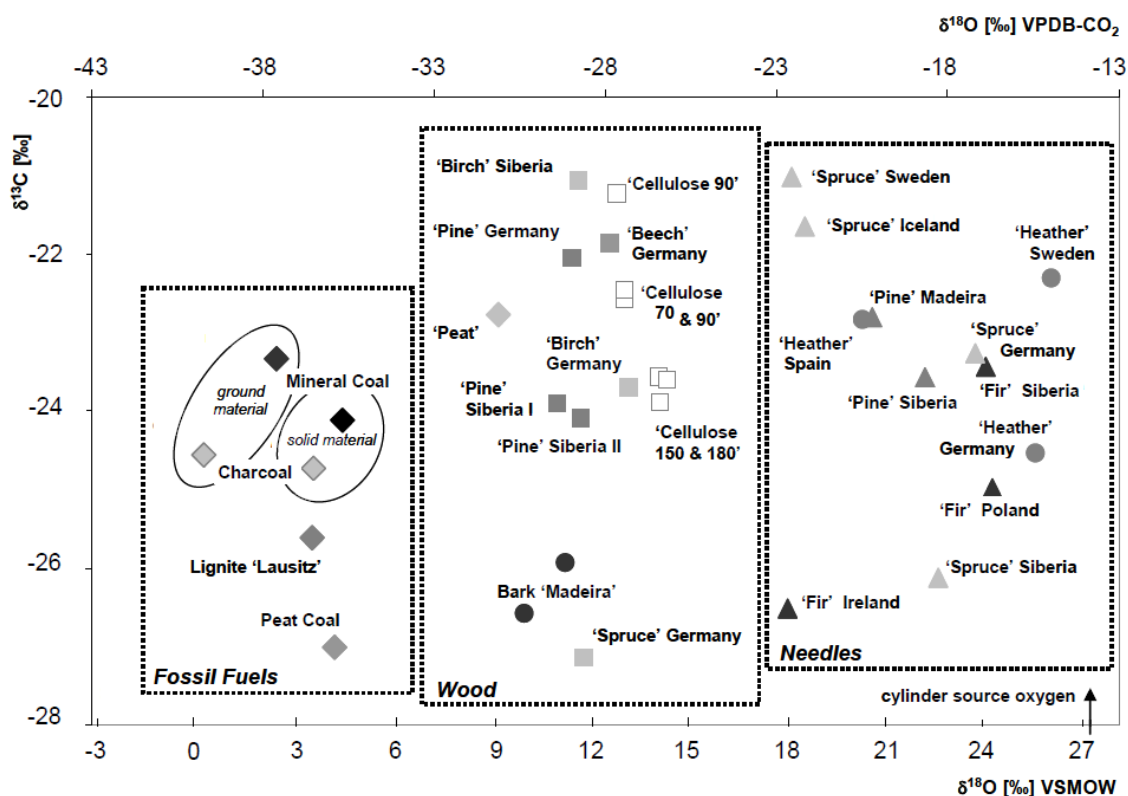
Figure 3: Isotopic signature of combustion-derived CO_2 from various kinds of fuels of different spatial origin. Triangles indicate needle material, squares wood material, diamonds fossil fuels, the varied species are additionally marked by different hues. Reproduced from Schumacher et. al.

VTT developed an isotope analyser which utilises CO_2 absorption lines around 2310 cm^{-1}. This region is free of interference of other absorbing species expected in the atmosphere, whilst providing sufficient absorption for the three main stable isotopologues. Precision below 0.5 ‰ would be necessary for sufficient distinction of the source materials, which is achievable with the VTT instrument. In a recent study where the biogenic content of mixed fossil-bio methane samples was determined, 0.5 ‰ was sufficient to determine the biofraction to within 1.5 %. Measurement times should be sufficiently fast so as to allow one measurement every minute.

The isotopic fingerprint of CO_2 emitted from a power station can be used to determine if the power station is using renewable or fossil fuel. Previously there was no online measurement technique to monitor isotopic composition of CO_2 ($^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios). VTT, with the help of NPL, developed and validated an online optical spectroscopic technique to measure the stable isotopologues of combustion-originated CO_2. The developed instrument was first tested with collected bag samples of stack emissions from different power stations using renewable, fossil or mixed fuel. These tests successfully demonstrated that the technique worked. During the final phase of the project, the instrument was tested in industrial conditions. VTT successfully monitored $^{13}C/^{12}C$ and $^{18}O/^{16}O$ ratios of CO_2 from stack emissions at a >500 MW power station. These results increase the potential to use online spectroscopic methods for apportion of CO_2 emissions between renewable and fossil fuels.

A strong collaboration between three partners involved in the objective, UC3M, VSL & CEM, was necessary to produce an extensive and rigorous literature survey entitled "Current technologies for hyperspectral detection of pollutant emissions". This covered books, review articles, peer-reviewed papers and other literature sources, along with highlighting the main research groups in the field and current commercial systems.

VSL developed an instrument with an infrared source based on a narrow line width continuous wave optical parametric oscillator (OPO). Testing demonstrated that this could be used to detect HCl by focussing on the absorbance line centred at 2963.29 cm^{-1}. The current OPO has limited continuous scanning range but this can be extended in several ways, with the most promising being using a pump laser rather than a continuous one

and/or making use of electro-optic spectral tuning to improve output. This work demonstrates the potential of OPO for emission measurement, but still requires further development.

Taking into account the air pollutants availability for preparation and certification by CEM as well as the capabilities of the hyperspectral techniques on the other partners' facilities (UC3M & VSL) a group of gas mixtures at agreed concentrations was defined (and subsequently prepared by CEM) for the validation measurements.

Excellent results in quantification of air pollutants have been achieved by UC3M with an improved stand-off hyperspectral imaging method. Figure 4 demonstrates what can be achieved with the method. Two aspects of this method should be highlighted:

- Mid-Infrared spectral noise and quantification lack-of-accuracy problems could be significantly reduced by using post-processing techniques like the well-known statistical method called Principal Component Analysis (PCA). PCA is applied to noisy experimental transmittance spectra in order to retrieve cleaner spectra without degrading neither its infrared signature, the key element in the further pollutant quantification, nor the spatial resolution.

- The application of an air pollutant-customised Nelder–Mead minimisation algorithm to retrieve column density values with low error was very important to finally retrieve a concentration accurately related to the nominal value of the gas mixture preparation (maximum error ~9 %, typical error ~4 %). These results were obtained in the form of a column density (ppm·m) map, in which spatial resolution provides an important added value.
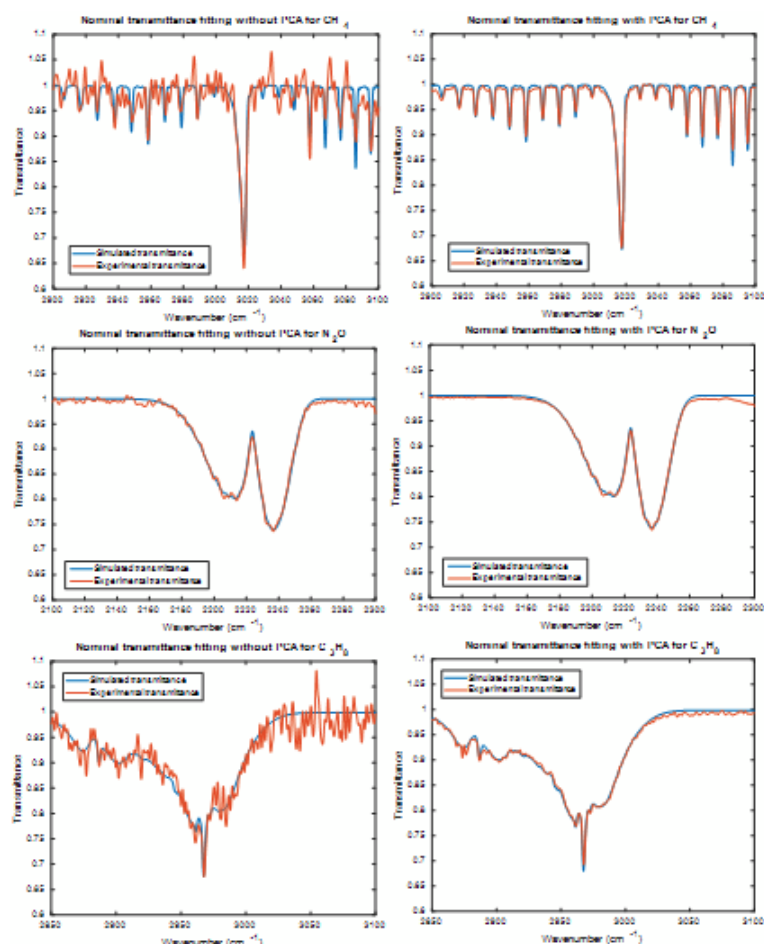

Figure 4: Transmittance spectra before (left) and after (right) applying the method. Original noisy transmittance spectra for one pixel of each air pollutant under measurement and their fitting by theoretical spectra are on the left, while the PCA-processed spectra on the right show a notable improvement in signal to noise ratio without losing its infrared signature, making possible a better fitting.

The key outputs of Objective 3 are:
- Demonstrated instrument to attribute biomass proportion in fuel from measuring emissions
- Comparison of hyperspectral techniques for monitoring air pollutants
- 1 peer-reviewed publication

This objective was successfully achieved.

4.4   Objective 4: Contribution of flow uncertainty to reported mass emissions

While the IED sets out concentration limits, emissions are generally reported as annualised mass emissions. Mass emissions are calculated by combining concentration and flow measurements of stack emissions. Like concentration measurements, flow measurements must be made following the relevant standard, EN 16911:2013. EN 16911-1 sets out the manual reference methods that can be used to calibrate continuous flow monitoring instruments. Unlike most concentration standards that include one or two reference methods, EN16911-1 covers many methods spanning differential pressure techniques (L-, S- and 3D-Pitot tubes), vane anemometers, tracer gas dilution, tracer transit time and calculation from energy consumption. Validation studies were carried out as part of the standardisation approach, however characterising the uncertainties of many different methods was challenging and required further investigation.

A review of the uncertainties relating to each of the methods was carried out. This highlighted current understanding of the issues and benefits of each of the available reference measurement solutions. A Monte-Carlo simulation model was created to investigate the propagation of uncertainty due to different flow calibration reference method choice. This model was extended from a model created in the previous (IMPRESS) project just covering the concentration measurement uncertainty. The model covers a flow AMS and a concentration AMS operating in a stack, covering all measurements and calibration for both under EN-14181 and EN-16911. In the model individual uncertainty characteristics can be modified to investigate the effects and by setting all uncertainty characteristics to zero it is possible to isolate the effect of a single uncertainty source. Vane anemometer, L-type Pitot, S-type Pitot and hot-wire anemometer are implemented in the model as reference methods for flow calibration, based on the accepted uncertainties highlighted in the review. These were tested to see their effect on annual mass emission uncertainties under different flow and reference method uncertainty regimes. The uncertainties tested were partly based on results fed back from the experimental testing on the impact of swirl and wall effects carried out within this project.

There was a tendency for the modelled techniques to calibrate in a small negative bias for the flow measurements, something that would result in systematic under reporting of emissions. When the uncertainties are kept low the two Pitot tube types provided the best reference methods for calibrating with. Based on the current best available characterisations, all flow calibration techniques have their limitations and further development is required to improve the metrology sufficiently to close the gap and produce methods which can consistently and reliably provide accurate calibrations free from bias, as is assumed in the measurement standards for emission concentration and flow measurements.

VSL designed and performed experiments to investigate wall effects and sensor obstruction in Pitot tube measurements. Results indicate that sensor obstruction represents a relatively small uncertainty source for these types of measurements, while wall effects seem to affect S-type Pitot tubes, but only when measuring very close to the wall (closer than allowed according to the standardised methods). These findings were complimented by simulations of TU Delft, which produced similar conclusions. Part of the work was performed by a MSc-thesis student who was jointly supervised by VSL and TU Delft.

VSL designed a stack simulator (Figure 5) which was used to investigate the effects of flow disturbances (including swirl) on emission flow measurements. As the relevant standard had not been validated using stacks that included swirl, the experiments were an important test of the suitability of the relevant standard and its associated uncertainty. Project partner CMI performed computer modelling simulations on these geometries and carried out experiments to determine the angle dependency of the used Pitot tube. The results were combined in a joint paper by VSL and CMI indicating that the current standardised methods can result in very significant errors in emission flow rate measurement, particularly due to the low number of sampling points required (one for narrow ducts).
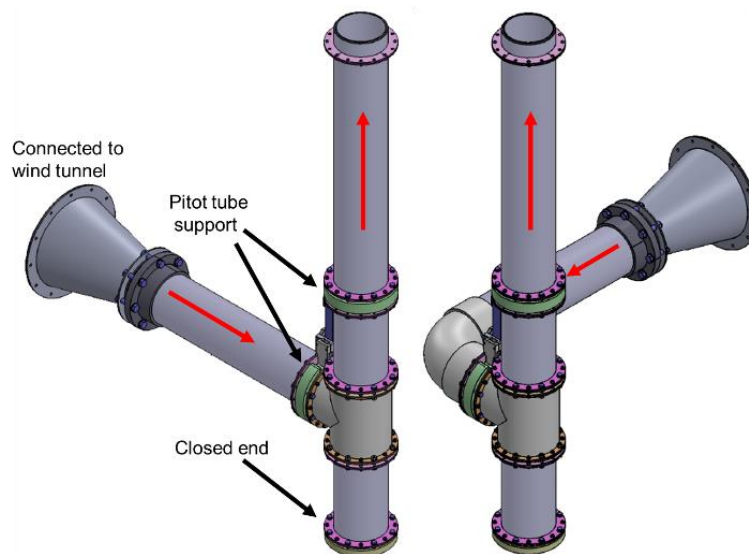
Figure 5: New VSL stack simulator facility, developed as part of the project to test the effects of flow disturbances such as swirl caused by varying duct geometries.

Two different sources of error of flow rate measurement in stacks have been investigated assuming the flow rate is measured according to the Standard Reference Method (EN ISO 16911-1) using Pitot tubes in a grid of points. The error due to a Pitot tube sensitivity to inclined flow direction and the error due to number and position of the sampling points have been discussed using the measured data and data from numerical simulations.

The first type of error which relates to the flow inclination with respect to a Pitot tube, e.g. due to swirl, was discussed for both L-type and S-type Pitot tubes with different angular dependencies. It was found both types of Pitot tube have comparable sensitivity to the flow angle. The errors are less than 2 % for distance from T-junction larger than 3D.

The second type of error related to the number and position of sampling points used for the flow rate measurement is significantly larger than the error due to flow angle. The error can reach 20 % using one sampling point located in the centre of the measuring cross-section of the stack and about 10 % using 16 sampling points according to the tangential method for grid sampling (according to EN 15259). The minimal requirements of the SRM of having one sampling point for narrow ducts and five or more hydraulic diameters straight duct upstream from the sampling plane, do not exclude potential errors around 10 % and 15 % for straight and elbowed supply pipe, respectively.

Based on the results (Figure 6), it can be concluded that both the number and location of sampling points need an appropriate assessment, also considering the shape of supply pipe.
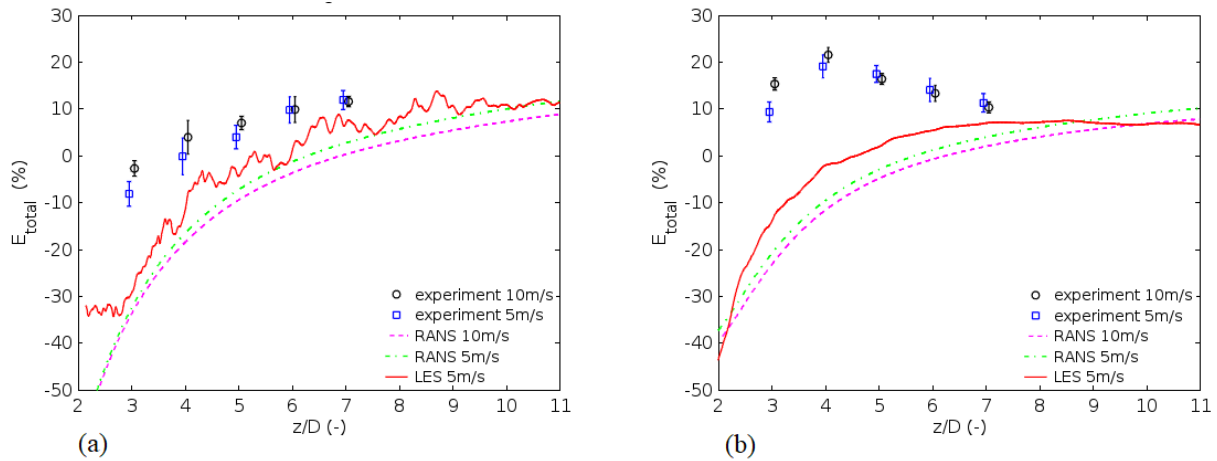
Figure 6: Relative error of flow rate determined from one sampling point in the centre ($U_r \equiv U_{center}$) of stack cross-section in a stack with straight supply pipe (a) and with the elbowed supply pipe (b). Uncertainty bars represent the (total) flow measurement uncertainty (k = 2) of the experiment.

VSL successfully completed all activities relating to this objective, resulting in an extensive report, an MSc thesis and a peer reviewed paper. Much insight was gained into the uncertainty sources of emission flow measurements and the potential to decrease them using multiple sensors (or additional measurement points).

Modelling by TU Delft, supported by experiments carried out at the VSL facility investigated issues with blockage. The experiments suggest that the effects of blockage are relatively small (less than 2 %), especially when following the standard which stipulates no more than 5 % of the duct area can be blocked by the measurement device. However, it is relatively easy to correct for blockage by measuring or calculating the blockage area of the device. Hence, the uncertainty of mass emission measurement could be reduced if the correction is implemented. It would then be of importance to also clearly specify how the blockage area can be calculated for the different measurement methods described in the standard (e.g. different L- and S-Pitot tubes). Additional research may be necessary to validate such methods.

The experiments suggest that when the standard is followed (distance from the wall > 5 cm), results from S- and L-Pitot tubes align. This is not the case when approaching the wall, where S-Pitot measurements consistently report lower velocities, suggesting larger wall effects for these instruments, as L-Pitot measurements match the expected flow profile more closely. Differences were as large as 16 % for measurements at 1 cm from the wall.

Corrections available for L-Pitot tubes near the wall appear to be insignificant to the overall measurement uncertainty, especially when following the standard. Position corrections are less than a millimetre, while velocity corrections can be around 2 % for measurements closer to the wall than 2 Dp. Since most Pitot tubes have $Dp \lesssim 1$ cm, these corrections are not of importance for measurements done at 5 cm from the wall, as required by the SRM. Furthermore, the wall effect corrections are more difficult to implement than the correction for blockage, which is especially true for the position correction which requires knowledge of the flow field. Hence, implementing these corrections in the SRM does not seem sensible.

In agreement with the experimental results, the simulations of S-Pitot measurements support the claim that S-Pitot tubes near walls tend to under-report the velocity. Average velocities reported by the S-Pitot can be as much as 14 % lower compared to the reference, with this error increasing as the orifices get closer to the wall, similarly to what is observed experimentally.

Narrow stacks exhibit higher levels of flow disturbance. This was investigated experimentally on a stack simulator by VSL and through computational fluid dynamics (CFD) modelling by CMI. Similar duct/port characteristics were used in both sets of experiments so the results would be comparable allowing CMI to validate their model using the VSL experimental measurements. Cyclonic flow, created by changes in flow direction, is clear in the CFD modelling by CMI (Figure 7). This can have significant impact on flow uncertainty if an insufficient number of measuring points are used, e.g. a single central point in the narrowest stacks, as this is unlikely to capture the varying flow rates across the stack, even significant distances downstream of the source of the disturbance (Figure 8).
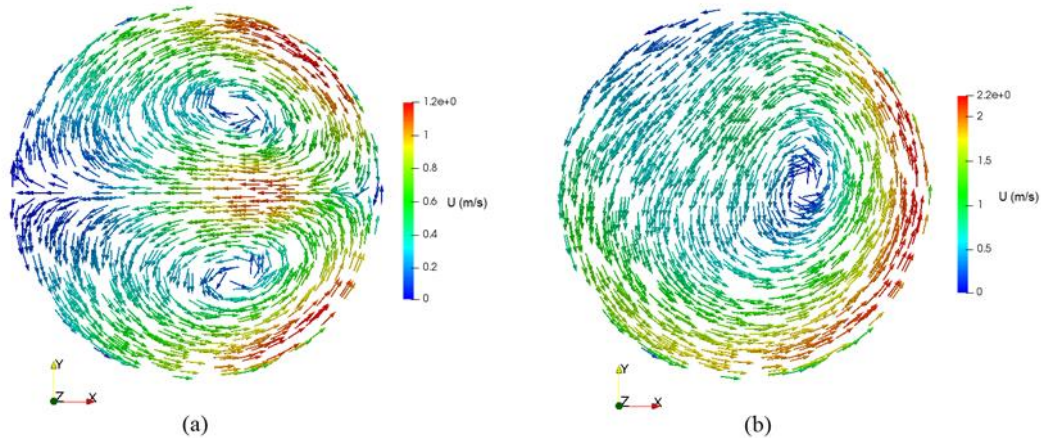
Figure 7: Resulting swirl structures appearing in the stack with the straight supply pipe (a) and elbowed supply pipe (b). Cuts are in distance of 3D from T-junction.
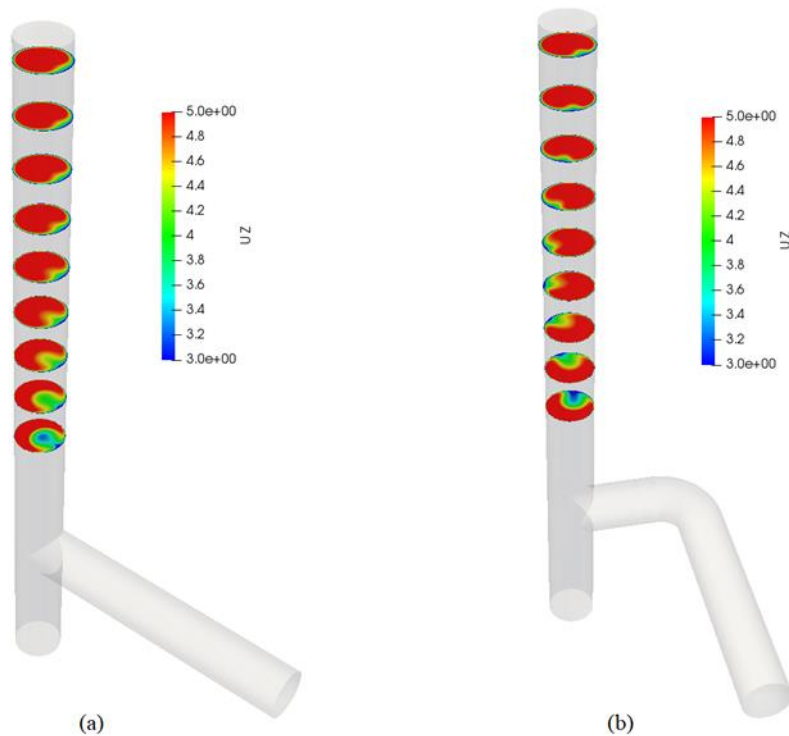

Figure 8: Distribution of the axial velocity component in cuts along the stack for the straight supply pipe (a) and the elbow supply pipe (b). The lowest cut is at height 3D, the highest at height 11D from T-junction.

The results indicated that measurement errors due to misalignment of the flow with typical measuring probes (Pitot tubes) are small compared to errors resulting from the positioning of these probes in the measurement plane. Errors of up to 15 % are reported using the standardised methods, while the measurement error is both smaller and more predictable when using additional measurement points.

The data from this study can be used to inform revisions of these standards, in particular with respect to flow disturbances in narrow stacks, helping law- and policy-makers to obtain insight into the uncertainties of emission measurements in these specific situations.

A spectroscopic analyser was implemented and deployed by CNR onto the artificial stack facility at ISSI for the measurement of flow velocity with dilution and transit time methods (Figure 9). Acetylene was used as the tracer. For the tracer transit time method the passage of a concentration burst was monitored in "second derivative" detection mode at two cross-sections of the stack, 3.54 m apart (Figure 10).
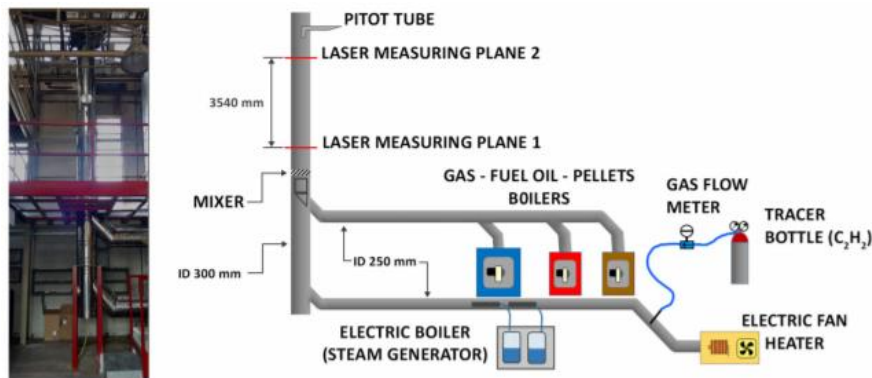
Figure 9: Layout of the ISSI stack simulator facility for the transit time and dilution tracer flow measurement testing, with results compared to an S-type Pitot tube beyond the second measuring plane.
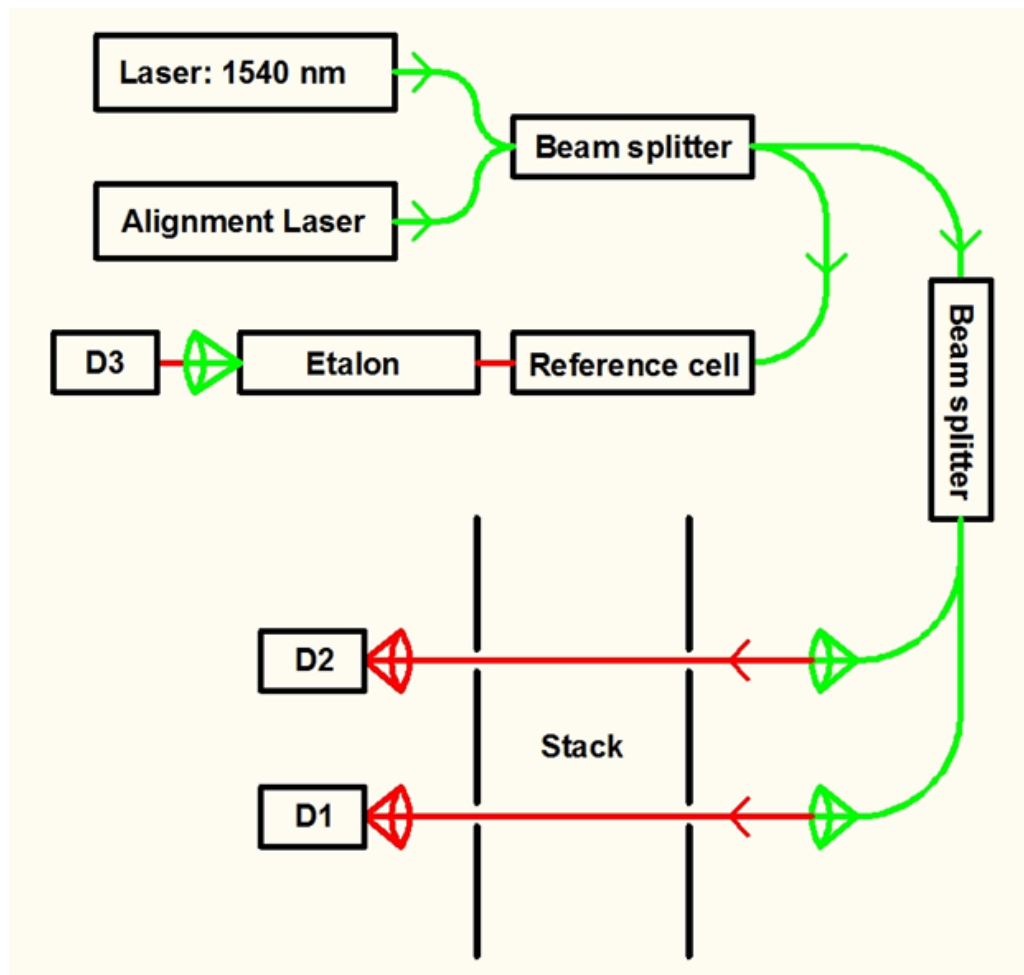

Figure 10: Schematic of the tracer transit method equipment.

The flow speed was obtained from the formula:

$$z = (T2-T2)/D$$

where T1 and T2 are the transit times at the two cross-sections, and D their distance apart. No difference was found among different methods to identify the peak transit time: peak of the concentration burst, it's median, or maximum slope of the peak rise.

With the dilution method the concentration of acetylene, constantly injected at the beginning of the stack at a known rate, was measured along a diameter, yielding the flow speed from the formula:

$$v = ST/C$$

where S is the duct section, T is the injection rate of the tracer, and C the measured concentration.

Optical methods were in perfect agreement between themselves. They also exhibited very good linearity when compared with a Pitot tube located downstream from the detection diameters at the duct centre, regardless of the environmental conditions such as gas temperature and water content (Figure 11). Nevertheless, the slope of this linear behaviour was not unity, because of the effects of turbulence on the Pitot probe.
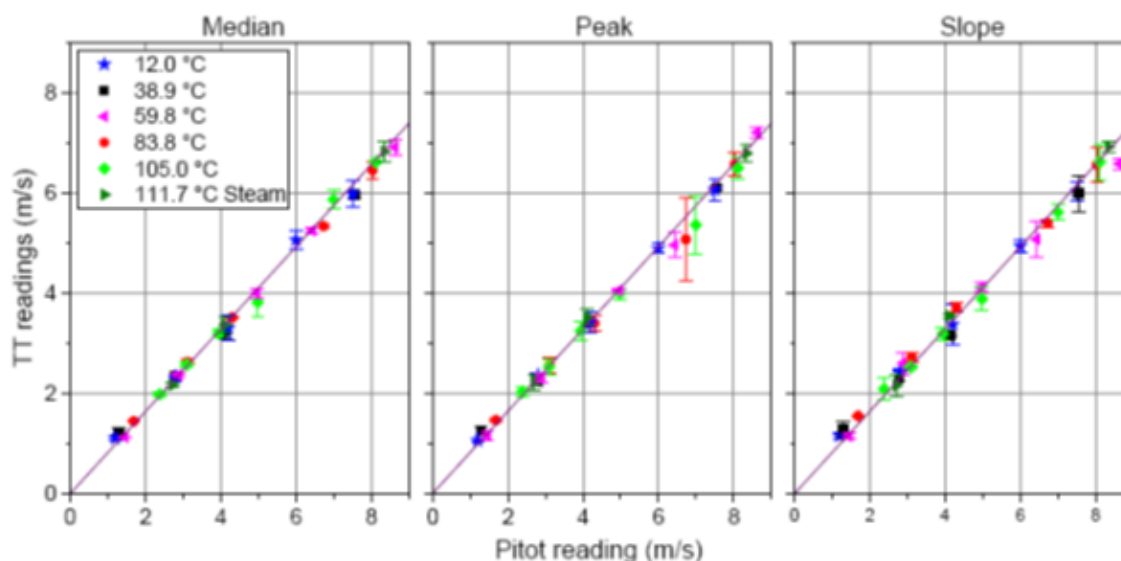

Figure 11: Plot of median (left), peak (centre) and slope (right) from comparisons of Pitot and tracer transit time measurements made at different temperatures, indicating the linearity of results in this range.

This kind of probe, though remaining the best known and used, requires an on-site calibration with a different method, like a spectroscopic one, to be repeated every time modifications occur along the stack ahead of the probe. CNR and ISSI have published a paper based upon these results.

The key outputs of Objective 4 are:
- Modelling alternative reference methods to access their uncertainty contributions
- Modelled and lab-based measurements to assess the uncertainty contribution of flow instability
- Lab based investigation of flow rate uncertainty from tracer based flow measurement techniques
- 5 peer-reviewed publications

This objective was successfully achieved.

5   Impact

Impact on industrial and other user communities

NPL hosted an online stakeholder workshop to engage with industrial and regulatory stakeholders. This was well attended with more than 40 attendees and gave the opportunity to communicate the findings of the whole project directly to the important stakeholders, ensuring maximum impact.

VTT developed an instrument and sampling setup to apportion emission ratios of biomass and fossil fuels from CO_2 isotope analysis. This will enable combustion plants co-firing biomass and fossil fuels to report carbon emissions based on measurement of actual emissions rather than calculated based on fuel usage monitoring, which should lead to improvements in local, regional and national emission inventories. Reducing monitoring

overheads in this way could encourage increasing use of co-firing, reducing the fossil fuel proportion in the fuel mix used at such facilities.

Achievements from this project are likely to lead to new reference methods allowing the setting of emission limits for previously unregulated measurands and the tightening of existing limits where the project has improved uncertainties enough to make lower limits enforceable. This will drive investment in new analytical instrumentation and associated sampling equipment. If the technologies developed in this project can demonstrate the ability to enforce lower emission limits, then it will be very difficult for policy makers to avoid casting future regulation to meet the 2050 target of meeting WHO air quality pollution guidelines. This compliance demand will result in further acquisitions of stack testing instrumentation increasing sales.

Impact on the metrology and scientific communities

The work in this project has highlighted the need for advances in measurement techniques for several measurands in order to meet the measurement challenge of lower emission limit values. Project partners have been developing and validating new techniques and protocols to standardise the measurements to meet this target. This is clearly a good problem to have as it indicates that process operators are lowering their emissions, leading to better air quality and a reduction in negative health effects on the general population.

The project has focused on field measurement issues including field validation of flow modelling work, testing NH_3 and formaldehyde measurement protocols on stack simulator facilities, investigating the limitations of the dust SRM and developing and testing the dilution chamber approach for residential scale biomass emissions sampling. This direct knowledge of real-world measurement challenges allows the metrology community to develop better instruments and methods for future use in the field.

The peer-reviewed papers that have come out of the project have significantly advanced the evidence base in the scientific literature in this field, especially since they are open access and available to the community. In the past, testing of alternative methods that were not approved would not be recorded. Failing to record these unsuccessful test campaigns leads to the reasons for rejection being lost, which could potentially lead to wasted effort repeating these tests. This evidence will benefit the community going forward.

Impact on relevant standards

Work by NPL and INERIS contributed to a draft standard for the determination of formaldehyde in ducts and stacks which is under preparation by WG40 of CEN/TC 264. Additionally, the protocols developed for HF and NH_3 have also fed into CEN/TC 264/WG 3 and ISO/TC 146/SC 1/WG 33 respectively.

INERIS, RISE, ENEA, ISSI and DTI developed protocols for measuring SVOC, PAHs or condensable PM generated from small scale biomass. These protocols are now being put forward for adoption as new standards under CEN/TC 295.

Longer-term economic, social and environmental impacts

Better monitoring techniques with lower uncertainties allow lower emission limits to be set and enforced, leading to improved air quality, which in turn is beneficial for human health and the environment. The European Commission stated that successful implementation of the Industrial Emission Directive would lead to a reduction in premature deaths / years of life lost in Europe of 13000 and 125000 respectively. This would save the EU €7 – 28 billion per annum.

The Clean Air Policy Package for Europe, which includes the Medium Combustion Plant Directive, is expected to avoid 58000 premature deaths per annum by 2030. This package is expected to save €40-140 billion per annum, compared with an implementation cost of €3.4 billion by 2030, while creating an estimated 100000 jobs. Emission reductions are also expected to lead to increased crop yields equivalent to €230 million of product.

The Eco-design Directive is expected to lead to emission reductions of 37kt of PM and 19kt of OGC per annum by 2030, significantly improving urban air quality. This directive is expected to lead to savings equivalent to 12 % of EU electricity consumption and a reduction of dependency on energy imports of 23 % and 37 % for natural gas and coal, respectively.

6   List of publications

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2. T. O. M. Smith (2018), Modelling a quality assurance standard for emission monitoring in order to assess overall uncertainty. In: A. B. Forbes, N. F. Zhang, A. Chunovkina, S. Eichstädt, F. Pavese (eds.), Advanced Mathematical and Computational Tools in Metrology and Testing XI. Series on Advances in Mathematics for Applied Sciences, Vol. 89, Pg. 341-348. https://doi.org/10.1142/9789813274303_0034

3. Z. Qu, O. Werhahn, V. Ebert (2018), The thermal boundary layer effects on line-of-sight TDLAS gas concentration measurements. Applied Spectroscopy, Vol. 72 (6), Pg. 853-862. https://doi.org/10.7795/EMPIR.16ENV08.JA.20200130

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9. F. D'Amato, S. Viciani, A. Montori, M. Barucci, C. Morreale, S. Bertagna, G. Migiavacca (2020), Spectroscopic Techniques versus Pitot Tube for the Measurement of Flow Velocity in Narrow Ducts. Sensors, Vol. 20 (24):7349. https://doi.org/10.3390/s20247349

10. Z. Qu, J. Nwaboh, O. Werhahn, V. Ebert (2021), Towards a dTDLAS-Based Spectrometer for Absolute HCl Measurements in Combustion Flue Gases and a Better Evaluation of Thermal Boundary Layer Effects. Flow, Turbulence and Combustion, Vol. 106, Pg. 533-546. https://doi.org/10.1007/s10494-020-00216-z

11. Z. Qu, J. Nwaboh, O. Werhahn, V. Ebert (2020), Effects of the spatial heterogeneity of gas matrix and thermal boundary layers on absolute TDLAS HCl measurements in hot flue gases. Physikalisch-Technische Bundesanstalt (PTB). https://doi.org/10.7795/810.20200309

12. J. Meléndez, G. Guarnizo (2021), Fast Quantification of Air Pollutants by Mid-Infrared Hyperspectral Imaging and Principal Component Analysis. Sensors, Vol. 21 (6):2092. https://doi.org/10.3390/s21062092

13. Z. Qu, J. Nwaboh, G. Li, O. Werhahn, V. Ebert (2021), Measurements of N_2, CO_2, Ar, O_2 and Air Pressure Broadening Coefficients of the HCl P(5) Line in the 1–0 Band Using an Interband Cascade Laser Applied Sciences, Vol. 11 (11), 5190. https://doi.org/10.3390/app11115190

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7 Contact details

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