Publishable Summary for 15NRM01 Sulf-Norm
Metrology for sampling and conditioning SO_2 emissions from stacks

Overview

The EU's Industrial Emissions Directive introduced tighter controls on emissions of SO_2, requiring further research on measurement capability to ensure that it was possible to fully implement and enforce it. This project has delivered pre-normative work to assess current testing capability, benchmarking of the existing standard reference method and alternative methods using automated measurement systems and investigated the efficiency of different sampling and conditioning systems. Without this work full implementation of the EU's Industrial Emissions Directive would not have been possible, negating some of the health and the environmental benefits it was designed to deliver. The project has supported CEN/TC 264 "Air Quality" in developing CEN/TS 17021, a new Reference Method for regulatory monitoring of Sulfur Dioxide (SO_2) emissions from industrial processes using portable automated measurement systems (P-AMS).

Need

Prior to the project there was a need to take continued steps to reduce pollution from industrial process plants to realise health and associated economic benefits. The Industrial Emissions Directive (IED - 2010/75/EU) has introduced increasingly stringent emission limits for a range of pollutants to meet these aims. The European Commission estimates that, if this directive can be successfully enforced, it will reduce premature deaths and years of life lost in Europe by 13,000 and 125,000, respectively, and realise associated cost savings of €7 – 28 billion per annum (COM (2007, 843 final)). There were also environmental drivers as it was shown that the risk of SO_2 acidification of water and soil had been underestimated (www.eea.europa.eu/highlights/europe-still-playing-catch-up).

Seven prior directives that the IED replaced were enforced through a series of Standard Reference Methods (SRMs) produced by CEN under mandate from the European Commission. These methods being either directly passed into, or referred to, in member state legislation, i.e. such CEN standards have special standing. With the decreased emission limits coming into force under the IED it is becoming clear that these SRMs may no longer be fit for purpose on all industrial processes. Prior to the project the issue had been formerly recognised by CEN/TC 264 who highlighted the need to identify new monitoring requirements of the IED, assessment of the current SRM to meet stricter limit values and automated methods for measuring.

With respect to the current SRM for SO_2 (EN 14791) the original mandated validation work found an associated uncertainty ±1.7 $mg.m^{-3}$ (95 % confidence), whereas, for example, for Liquefied natural gas (LNG) combustion gas processes the IED now requires ±1.0 $mg.m^{-3}$ (95 % confidence). Portable automated measuring system (P-AMS) that in principle could offer improved uncertainties were available, but in contrast to the current SRM, these required the extracted gas stream to be dried - often referred to as 'conditioned'. Some conditioned sampling systems were available, but there was insufficient evidence that they can function without altering the composition of the gas causing unacceptable levels of bias in the measurement. Metrology support was required: to determine as a benchmark for comparison the sampling performance of the current SRM; to investigate potential bias of different materials for sampling apparatus; to evaluate drying approaches based on chilling and permeation principles; to contribute to efforts at CEN in standardising SO_2 measurement via a conditioned sampling approach.

Objectives

The overall aim of the project is to compare conditioned sampling approaches to the unconditioned sampling approach associated with the incumbent SRM (EN 14791). There is currently insufficient evidence that proposed conditioned sampling approaches are able to transfer extracted gas streams without physical and chemical changes occurring resulting in unacceptable levels of bias. If P-AMS systems are to be used and standardised at CEN and their potential realised it, must first be demonstrated that conditioned sampling can be carried out compliant with current and future uncertainty requirements.

The specific objectives of this project were:

1. To determine a benchmark sampling performance for a range of industrial processes that use the existing Standard Reference Method for SO2 (EN 14791). This will include a critique of the impact of the findings on the capability for enforcing decreased emission limits under the Industrial Emissions Directive;
2. To investigate appropriate materials (e.g. stainless steel, borosilicate glass, ceramic) for conditioned sampling for use with different stack gas matrices i.e. in order to avoid sample alteration e.g. due to catalysing surface reactions. The stability of sampled gaseous components will be investigated in order to determine the consequences of short term affects;
3. To evaluate the performance of chiller versus permeation based drying technologies for conditioned sampling to determine which processes are at risk of sample bias. The mechanism of sample bias shall also be determined;
4. To contribute to a future revision of EN 14791 by providing the data, methods and recommendations, which are necessary for the standardisation of SO2 sampling, to CEN / TC 264. Outputs will be communicated through a variety of media to the standards community and to end users;
5. To contribute to the production of CEN Technical Specification SO2 being drafted by CEN / TC 264 / WG16 and data to move standard closer towards EN status.

Progress beyond the state of the art

Work testing the sampling of the SRM (EN 14791) has gone beyond the state of the art in terms of providing new performance data at concentrations commensurate with the increasingly stringent emission limits coming into force. The data has informed on the limitations of the SRM, both in terms of detection limits and achievable uncertainty levels, which will inform and guide future revisions of EN 14791.

Prior to the start of the project there was knowledge that apparatus material would influence results, but no quantifiable evidence to demonstrate the scale of the issue. The work testing for any sampling biases as a function of apparatus material in this project is of importance as effects that are negligible and not seen at higher emission concentrations may have significant impact at the lower emission levels required by the Industrial Emissions Directive. The project data has confirmed the scale of these effects will be significant at lower emission limits and provides a basis for future decisions on the materials required for SO_2 sampling applications.

Prior to the start of the project it was widely acknowledged that there were issues with sample losses due to sample conditioning systems, but this had not been quantifiably demonstrated. Work testing the performance of chiller and permeation based drying technologies has provided new data at emission concentrations commensurate with the increasingly stringent emission limits coming into force. This data has established that some conditioning systems, particularly chillers that had been widely used before the project, can result in unacceptable bias when measuring low concentration SO_2 emissions. The results have also indicated that some P-AMS are capable of sampling without resulting in unacceptable bias, so this will form the basis for these P-AMS to be used in the future, facilitating enforcement of ever more stringent emission limits.

Results

Determining a benchmark sampling performance for a range of industrial processes that used the existing standard reference method for SO_2 (EN 14791). This included a critique of the impact of the findings on the capability for enforcing decreased emission limits under the Industrial Emissions Directive:

A survey of the emissions monitoring community to gather experiences and opinions of the measurement of Sulphur dioxide (SO_2) was carried out. There were 57 respondents across Belgium, Denmark, Estonia, Finland, France, Germany, Italy, Sweden and the UK. The respondents included test laboratories, process plant operators, national regulators, accreditation bodies and providers of proficiency testing schemes. The data was analysed, and a summary of the results is available from the project website (http://empir.npl.co.uk/sulf-norm/). In addition, a trade journal article (SO2 Emissions Monitoring: European Survey of Opinions on Monitoring using the SRM (EN 14791) or Portable Instrumental Techniques) was written and published by International Environmental Technology in December 2018.

In addition to this the regulator for England produced a position paper to provide a different insight into the implementation of EN 14791. This identified that while uptake of instrumental techniques was initially high, for some types of application EN 14791 has returned to being the dominant method. Auditing and report reviewing has shown a tendency for instrumental techniques to read up to 10% lower than the AMS, something that has been attributed to sampling losses caused by the conditioning systems. Therefore, the regulator is considering releasing guidance for the technical specification (TS) for SO_2 measurement by instrumental techniques,

CEN/TS 17021:2017, partly based on the findings of the Sulf-Norm project. Such guidance could be considered when revising the TS for consideration as a future standard.
NPL and HLNUG carried out analysis of proficiency testing (PT) results from the UK and Germany over the last 15 years. Results for the HLNUG scheme, where EN 14791 is routinely used, demonstrate that performance meets the uncertainty standards currently required under the IED. Proposed tighter emission limit values (ELVs) in the new best available technique reference document (BREF) for waste incineration plants would prevent the current SRM from routinely meeting the IED uncertainty standards based on current performance.
NPL laboratory tests investigated the effect of different measurement equipment when implementing EN 14791, in particular the use of mini-impingers. The results demonstrated that there was no systematic bias in the measurements at a variety of SO_2 concentrations.
VTT also carried out laboratory testing with their diesel test bench to access performance of EN 14791 against an FTIR instrument and the calculated SO_2 levels based on the inputs. Initial results indicated that EN 14791 was under reading at high concentrations, something that was later identified as being due to insufficient rinsing of the sample probes. This demonstrates that EN 14791 is not immune to the possibility of sampling losses if correct procedures are not completely implemented. For one test with a dry, high SO_2 concentration gas matrix, the impinger solution was split and sent to two independent testing laboratories for analysis. Both laboratories returned results indicating recovery rates below 90%, again highlighting a potential under-reading issue with EN 14791 for measuring high SO_2 concentrations.
This range of activities have demonstrated the qualities and limitations of the SRM described in EN 14791. The regulator paper and stakeholder survey have provided different viewpoints on the usage of the standard and potential issues that exist with it. The historical PT data illustrate the difficulty with meeting uncertainty requirements based on percentage of the ELV. The project results demonstrate that as limit values fall the ability of current methods, including EN 14791, to meet the IED uncertainty requirements will continue to suffer.
The objective has been successfully completed, quantifying sampling performance of the SRM and it's suitability for more stringent future emission limits.

Investigating appropriate materials (e.g. stainless steel, borosilicate glass, ceramic) for conditioned sampling for use with different stack gas matrices i.e in order to avoid sample alteration e.g due to catalysing surface reactions. The stability of sampled gaseous components was investigated to determine the consequences of short term effects:
Field testing with different probe materials has demonstrated an offset in measurement, with stainless steel probes presenting lower loss rates than glass probes. The difference is small so would only become significant when measuring low concentrations (<10 $mg.m^{-3}$) of SO_2, however this is the level of the proposed new ELV for waste incineration, so is likely to become more important in the near future. Identifying the issue will support efforts to standardise towards more specific equipment to prevent the problem in future. For now, these findings demonstrate how to allow for this material uncertainty when assessing current measurement uncertainties. Ceramic was not tested, but this was not widely used, compared to stainless steel and borosilicate glass, within the emission monitoring community.
SO_2 is lost when water condenses so CMI carried out modelling work to investigate losses in typical sample conditioning systems (permeation drier unit). This demonstrated the mechanism occurring and quantified the rate at which losses occur in such systems.
This objective was only partially completed, but work has focussed on the most widely used materials to ensure that the impact from the objective was still achieved.

Evaluating the performance of chillers versus permeation based drying techniques for conditioned sampling, determining which processes were at risk of sample bias. The mechanism of sample bias was also determined:
VTT, NAB and Ramboll carried out laboratory and field based parallel testing with the SRM and several alternative methods for SO_2 measurement according to EN 14793, in order to demonstrate the equivalence of these techniques. Fourier transform infrared spectroscopy (FTIR), UV fluorescence with dilution probe and Non-dispersive infrared (NDIR) with permeation dryer all successfully passed the equivalency testing and have since been approved by the national regulator for use in Finland. NDIR with chiller conditioning systems were found to present a high degree of SO_2 loss compared to the other methods over 0-200 $mg.m^{-3}$ range, so cannot be used as an alternative method in Finland. Since this testing requires parallel measurement with two sets of each technique (ten in total with the SRM) it would not have been possible without the collaboration in this project.
CMI used mathematical modelling to investigate the rate of SO_2 losses occurring due to being dissolved in the

liquid water droplets and water film within the dryer. The work demonstrated that diffusion into water films within the dryer was the major source of SO_2 loss since droplet accretion occurred too slowly. Slower input gas velocity was demonstrated to increase SO_2 loss rates from permeation dryers, since the gas had more time in contact with the liquid film within the dryer. NPL and VTT supplied information about typical concentrations and flow rates to ensure that the CMI modelling would be relevant to real world equipment.
NPL laboratory tests compared three sets of EN 14791 kit ran in parallel to investigate the effect of different conditioning systems. The results showed no significant difference between impingers with method 5 kit and mini-impingers with method 6 kit. Adding chiller or permeation dryer systems also did not affect the measurements when the gas stream is dry, demonstrating that any effect is due to the active removal of water containing dissolved SO_2. The mean deviation in chiller results was -12.3% compared to EN 14791, while permeation dryers mean deviation was -5.7%. These results support the findings of the VTT/NAB/Ramboll testing (-11.8% chiller mean deviation), increasing confidence that chiller systems lead to more significant SO_2 sampling losses.
This objective has been completed successfully, demonstrating quantifiably the level of bias produced by different sample conditioning systems.

Impact
Project partners have produced two peer reviewed open access scientific publications, presented ten conference presentations and/or posters, spoken at eight external events to interested stakeholders and published two trade journal articles.

VTT and NAB held a seminar for Finnish and Estonian stakeholders to demonstrate the findings of the project.

NPL produced a spreadsheet template for uncertainty assessment for use with CEN/TS 17021, along with a training video to ensure stakeholders would know how to use it.

Uniper identified a potentially significant source of error related to positional uncertainty in the reference method. A homogenous stack will still have residual variation across the profile, which is a source of systematic bias in the calibration. The scale can vary each time the reference method is deployed if careful attention is not paid to probe angle and depth within the stack, leading to significant potential errors ~5%. This will need to be addressed, otherwise CEN/TS 17021 will not be able to meet the uncertainty requirements for measuring SO_2 from stacks.

Partners contributed to ten national or European standard committees to ensure the project finding were disseminated to the standardisation community.

Impact on industrial and other user communities
Instrumental based monitoring is real-time whereas with the existing SRM for SO_2 often it takes several weeks before the data are available. Consequently, if the community moves towards an instrumental approach it will potentially reduce periods of inaccurate emission reporting which is not only desirable from the perspective of a national regulator but also for the operator as by resolving issues more quickly they can demonstrate their commitment to environmental protection. Furthermore, as instrumental systems are automated there are potential savings for accredited stack testing organisations in terms of reduced staff time costs.

Instrument manufacturers also stand to benefit as once conditioned sampling has been validated and standardised it will make it possible for national regulators to accept such an approach significantly boosting the market for portable SO_2 analysers.

Results that have been disseminated to this community are as follows:

- 2 oral presentations given to national regulators and Environment Agency for England regulatory staff.
- Oral presentation at the Source Testing Association Technical Transfer Seminar - The new SRMs and incoming Particulate standards and Flow Measurements including Calculations, entitled: *Summary of the Changes to the Updated SRM Standards for SO2, NOx, O2, H2O and CO.*
- Oral presentations at two consecutive Finnish National Emission Measurement Conferences, entitled: *Sulf-Norm Project Update.*
- Article published in the Finnish Air Pollution Prevention Society (FAPPS) trade journal.
- Article published in the December 2018 issue of the trade journal International Environmental Technology (IET).

Impact on the metrology and scientific communities

For an organisation to maintain their accreditation it is a requirement to take part in a proficiency testing scheme if an appropriate scheme exists. In recent years schemes have emerged based on stack simulation facilities (pilot plant scale facilities) with some based at National Metrology Institutes. This project will characterise conditioned sampling enabling proficiency testing scheme providers to set pass / fail criteria at appropriate levels (often a performance score of satisfactory, questionable, or unsatisfactory is awarded). This is significant as repeated poor performance can lead to an organisation's accreditation being suspended, hence, the work under this project is important as it will help ensure that performance expectations are set appropriately.

Results have been disseminated to this community as follows:

- Oral presentation at AQE2017, entitled: *Issues with Monitoring SO_2 Emissions.*
- Oral presentation at CEM India 2017, entitled: *Testing equivalency of alternative methods for monitoring of SO_2 emissions.*
- Oral presentation at CEM India 2017, entitled: *Improving the measurement of stack emissions – an update on standardisation and research activities in Europe.*
- Oral presentation at CEM2018, entitled: *The Last Decades Performance for Emissions Measurements of CO, NOx, TOC and SO_2 Assessed via Combining UK and German Proficiency Testing Data from Stack Simulator Facilities.*

Impact on relevant standards

This project is carrying out pre-normative work and hence is very much geared towards achieving high impact in the standardisation community. The first target is to determine the limitations of the unconditioned sampling of the SRM to understand issues with respect to enforcement of the increasingly stringent emission limits under the Industrial Emissions Directive. The second target is to facilitate the production of a CEN Technical Specification standard for SO_2 enabling the use of real-time instrumental techniques capable of increased sensitivities, but which rely on conditioned sampling form the stack.

However, in addition this project will also have broader impact at CEN and ISO with respect to working groups developing standards describing reference methods for HCl by instrumental techniques and NH_3, where conditioned sampling will also be considered. Also, very closely linked to this project is a new working group being created by CEN tasked with standardising proficiency testing based on stack simulator facilities. This project will have representation on this group and outputs from this project will be used to influence the production of this standard.

Results have been disseminated to this community as follows:

- Oral presentations reporting on project progress given at both the 2017 (Helsinki) and 2018 (Seville) annual plenary meetings of CEN/TC 264 'Air Quality'.
- 2 oral presentations given to the Finnish Standards Association mirror group to CEN/TC 264 'Air Quality'.
- 3 oral presentations given at the EC Joint Research Centre (JRC) / CEN Workshop on Emission Test Benches.
- Attendance and dissemination via oral presentation and reports at multiple meetings of CEN/TC 264/WG 45 *Emissions – Test Benches*, attendance at CEN/TC 264/WG 3 *Emissions – HCl manual method*, and also at various national mirror groups to CEN/TC 264.

Outputs from this project will be used both to inform on future revisions of EN 14791 and also to lay the foundations necessary to move the emissions monitoring community towards measurements using portable automated measuring systems, facilitating enforcement of increasingly stringent emission limits.

Longer-term economic, social and environmental impacts

Social: As reported by the European Commission in Towards an Improved Policy on Industrial Emissions (COM (2007), 843 final) successful implementation of the Industrial Emissions Directive will lead to a reduction

in premature deaths / years of life lost in Europe of 13,000 and 125,000 respectively. A key element in achieving this significant impact is achieving the targeted lower emissions of SO_2, the importance of which is further emphasised by the Aphekom project, which has established a linear relationship between SO_2 air pollution and mortality. In terms of the global significance, the World Health Organisation estimates that there are currently 235 million asthma sufferers and furthermore, that this is now the most chronic disease amongst children.

Economic: Overall the economic cost of EU air pollution is in the region of €102 – 169 billion highlighting the financial consequences associated with not taking mitigating steps]. Towards reducing this cost, the European Commission have estimated that successful implementation of the Industrial Emissions Directive will contribute savings of €7 – 28 billion per annum.

Environmental: A key impact associated with SO_2 is acidification of water and soil and despite marked progress since the 1990's, significant risks still remain. This is partly because improvements in methodology to determine risk have shown that previously the risk was underestimated. Consequently, work enabling further reductions in SO2 emissions is now even more important the previously thought.

List of publications

1 Tuula Pellikka, Tuula Kajolinna & Miia Perälä (2019) SO2 emission measurement with the European standard reference method, EN 14791, and alternative methods – observations from laboratory and field studies, Journal of the Air & Waste Management Association, 69:9, 1122-1131.[Online] Available: https://doi.org/10.1080/10962247.2019.1640809

2 Marc D. Coleman, Matthew Ellison, Rod A. Robinson, Tom D. Gardiner & Thomas O. M. Smith (2019) Uncertainty requirements of the European Union's Industrial Emissions Directive for monitoring sulfur dioxide emissions: Implications from a blind comparison of sulfate measurements by accredited laboratories, Journal of the Air & Waste Management Association, 69:9, 1070-1078 [Online] Available: https://doi.org/10.1080/10962247.2019.1604449

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Chief Stakeholder Organisation: n/a	Chief Stakeholder Contact: n/a	
Internal Funded Partners: 1. NPL, United Kingdom 2. CMI, Czech Republic 3. VTT, Finland	External Funded Partners: 4. EA, United Kingdom 5. HLNUG, Germany 6. NAB, Finland 7. Ramboll, Finland 8. STA, United Kingdom 9. Uniper, United Kingdom	Unfunded Partners: