
Publishable Summary for 15NRM01 Sulf-Norm

Metrology for Sampling and Conditioning SO₂ Emissions from Stacks

Overview

This project will deliver the pre-normative work without which full implementation of the EU's Industrial Emissions Directive will not be possible negating some of the health and the environmental benefits it is designed to deliver. Furthermore, this project will support CEN/TC 264 "Air Quality" in terms of laying the platform necessary to develop a new Reference Method for regulatory monitoring of Sulfur Dioxide (SO₂) emissions from industrial processes.

Need

There is a need to take continued steps to reduce pollution from industrial process plants to realise both health and associated economic benefits. The recent Industrial Emissions Directive (IED - 2010/75/EU) is bringing in 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 result in a reduction in premature deaths and years of life lost in Europe of 13,000 and 125,000, respectively, and realise associated cost savings of €7 – 28 billion per annum (COM (2007, 843 final)). There are also environmental drivers to reducing pollution as, for example, it was recently shown that the risk of SO₂ acidification of water and soil has been underestimated (www.eea.europa.eu/highlights/europe-still-playing-catch-up).

The seven prior directives that the IED has 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. This issue has been formerly recognised by CEN/TC 264 who have highlighted the following future needs, which are to identify new monitoring requirements of the IED, the assessment of current SRM to meet stricter limit values, and automated methods for measuring emissions (N2204 Future Work Items of CEN/TC 264).

With respect to the current SRM for SO₂ (EN 14791) the original mandated validation work found an associated uncertainty $\pm 1.7 \text{ mg.m}^{-3}$ (95 % confidence), whereas, for example, for Liquefied natural gas (LNG) combustion gas processes the IED now requires $\pm 1.0 \text{ mg.m}^{-3}$ (95 % confidence). There are portable automated measuring systems that in principle could offer improved uncertainties, but in contrast to the current SRM these require the extracted gas stream to be dried - often referred to as 'conditioned'. Some conditioned sampling systems are available, but there is, as yet, insufficient evidence that they can transfer the extracted gas stream without altering the gas causing unacceptable levels of bias in the measurement. Consequently, to move forward metrology support is needed: to determine as a benchmark for comparison the sampling performance of the current SRM; to investigate the 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 SO₂ 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 are:

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) will go beyond the state of the art in terms of providing new performance data at emission concentrations commensurate with the increasingly stringent emission limits coming into force. The outputted data will inform on the limitations of the SRM and future revisions of EN 14791.

Work testing for any sampling biases as a function of apparatus material is of importance as effects that are negligible and not seen at higher emission concentrations may have significant impact at low emission levels. These data will provide the basis for either accepting or rejecting the materials for SO₂ sampling.

Work testing the performance of chiller and permeation based drying technologies will provide new data at emission concentrations commensurate with the increasingly stringent emission limits coming into force. If these data can establish that low concentration SO₂ emissions can be conditioned (dried) in sampling without resulting in unacceptable bias then this will form the basis for portable automated measuring systems to be used in the future facilitating enforcement of ever more stringent emission limits.

Results

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:

A survey of the emissions monitoring community to gather experiences and opinions of the measurement of Sulphur dioxide (SO₂) has been 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 has been analysed and a summary of the results is available from the project website. In addition, a trade journal article has been written and accepted by International Environmental Technology and is due to go to press in December 2018.

Work examining the performance of unconditioned sampling (associated with the SO₂ SRM) has been carried out using the NPL Stack Simulator Facility. 9 stack testing organisations sampled various test matrices generated in the simulator. These data are currently being analysed as part of characterising unconditioned sampling.

Also, to compliment the above an inter-laboratory comparison (ILC) was carried out with respect to the analysis element of the SO₂ SRM. Sulphate samples were despatched to ISO/IEC 17025 accredited chemistry laboratories for quantification. From the data returned it was clear from the dispersion of the results that the true uncertainty of analysis may be greater than is believed in the community. This important conclusion has been written into a peer review paper which has been submitted to the Journal of the Air and Waste Management Association (JA&WMA).

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:

A field trial has been carried out on a 'real' stack in Finland where NDIR analysers were interfaced with the

stack using both chiller and permeation based drier systems. Also, the stack was measured using FTIR and also UV-fluorescence utilising a dilution probe based sampling system. As part of this work sampling apparatus was swapped enabling measurements to be carried out with apparatus based on stainless steel and borosilicate glass. Analysis of the data has shown that neither material leads to any bias in these sampling systems.

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:

In the field trial on a real stack in Finland (described above) measurements were also carried out comparing chiller and permeation based drier technologies. Whilst analysis is still ongoing it was found that across a range of process conditions there was a significant negative bias of chiller based drying when compared to permeation based.

Complementing the above, work has been carried out using the NPL Stack Simulator facility to compare these same technologies under more controlled, laboratory conditions. 9 stack testing organisations sampled various test matrices generated on the simulator using P-AMS systems from a variety of manufacturers. This work was completed recently and analysis of the data is in its initial stages.

Impact

Dissemination highlights have included: trade journal articles published in the Finnish Air Pollution Prevention Society (FAPPS) and accepted for publication by International Environment Technology (IET); multiple oral presentations at well-established emission conferences Air Quality and Emissions (AQE) and International Conference and Exhibition on Emissions Monitoring (CEM), and also beyond Europe at CEM India; oral presentations given at a special EU Joint Research Centre and CEN endorsed workshop on emission test benches (stack simulators); oral presentations to Finnish National Emission Measurement Conference and to UK National Regulator staff; representations to various CEN working groups and national mirror groups, and importantly invited oral presentations given at two annual plenary's of CEN/TC 264 'Air Quality'.

Impact on industrial and other user communities:

Instrumental based monitoring is real-time whereas with the existing SRM for SO₂ 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 SO₂ analysers.

Results to date have been disseminated to this community 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, NO_x, 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.
- An article accepted for publication in the December 2018 issue of the trade journal International Environmental Technology (IET).

Impact on 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 and 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 to date have been disseminated to this community as follows:

- Oral presentation at AQE2017, entitled: *Issues with Monitoring SO₂ Emissions*.
- Oral presentation at CEM India 2017, entitled: *Testing equivalency of alternative methods for monitoring of SO₂ 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, NO_x, TOC and SO₂ 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 SO₂ enabling the use of real-time instrumental techniques capable of increased sensitivities but which rely on conditioned sampling from 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 NH₃, 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 to date 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 and 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 SO₂, the importance of which is further emphasised by the Aphekomp project, which has established a linear relationship between SO₂ 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 SO₂ 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 than previously thought.

List of Publications

There are no publications yet.

Project start date and duration:		01 July 2016 (36 months)
Coordinator: Garry Hensey, National Physical Laboratory Tel: +44 (0)2089436626 E-mail:garry.hensey@npl.co.uk Project website address: http://empir.npl.co.uk/sulf-norm/		
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: