FINAL PUBLISHABLE REPORT

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Coordinator: *Garry Hensey, NPL* Tel: +44 (0)208 943 6626 E-mail: garry.hensey@npl.co.uk Project website address: http://empir.npl.co.uk/sulf-norm/			
Chief Stakeholder: *n/a* Tel: n/a E-mail: 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:

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1 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).

2 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.

3 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.

4 Results

4.1 Benchmark sampling performance for processes using existing standard reference method for SO_2 (EN 14791)

Understanding the usage rates of EN 14791, along with the practical concerns of users within the industry is key to understanding performance and how to improve in future. STA led the consortium partners in producing a survey to investigate opinions on monitoring using the standard reference method (SRM) compared with portable instrumental techniques. Prior to this project concerns may have been communicated locally, but no-one had surveyed the whole European measurement community to assess opinions and practical experience of EN 14791. Using contacts from all project partners (NPL, STA, VTT, HLNUG, EA, Uniper, CMI, NAB, Ramboll) led to a broad range of institutions providing responses, covering nine countries across Europe. Most responders were test houses who carry out the monitoring, but many national regulators, industrial operators and instrument manufacturers also contributed to provide a representative cross-section of views.

Concerns about EN 14791 included problems with contamination, quality of the solutions and space/logistical requirements for setting up the sampling trains. In contrast for instrumental techniques issues raised were around cross-interference, sampling system losses and logistical issues with the use and transport of cylinders.

Method preferences varied strongly on national levels, driven by the regulatory environment (e.g. 73% of German respondents who have to use it for QAL2 favour EN 14791, while 66% of UK respondents prefer portable instrumental techniques). Overall 59% of the respondents preferred the use of portable instrumental techniques if given a free choice. However, there must be confidence that the data these techniques provide will be of sufficient quality to meet the requirements of legislation. The highest response relating to portable techniques was around poor data quality due to cross-interference, so clearly this is an area requiring further improvement.

The Environment Agency (EA) of England produced a position paper describing the UK perspective and regulatory approach to specifying requirements for monitoring sulphur dioxide (SO_2). Regulated industrial processes are diverse, with wide variations in emissions profiles and monitoring provisions. The EA's experience is that this situation requires both flexibility and pragmatism when monitoring SO_2. The EA applies a risk-based approach to ensure an appropriate level of quality of emission monitoring. This approach permits monitoring laboratories to use both instrumental techniques and manual methods to measure SO_2, with each being necessary and complementary. No single technique, method or instrument is better than any other, whilst a technique suited to one installation can be less suitable for another.

Instrumental monitoring was initially popular because of its perceived simplicity, advantages and convenience. Achieving the required level of uncertainty requires careful management of the instrumental technique. Audits of both test reports and monitoring laboratories for industrial sites have revealed common problems that can be eliminated by relatively simple improvements.

Although instrumental techniques were initially popular, there has been a resurgence in use of EN 14791. Most monitoring organisations now use both the manual and portable instrumental techniques applied through Alternative Methods (AMs). In the UK, instrumental techniques are most popular for QAL2 and ASTs at waste incinerators, with multicomponent analysers (FTIR) being the preferred technique.

When there was a significant difference in individual reports between periodic monitoring and AMS results, the periodic monitoring results were typically lower than the AMS. On further examination, audits have suggested errors in applying the instrumental methods, which can lead to a negative bias in periodic monitoring results. This difference was thought to be due to losing SO_2 in conditioning systems of portable analysers with chillers.

The EA presented their approach at a Sulf-Norm workshop (13 June 2019). The presentation led to questions about the implementation of CEN/TS 17021, the drafting of which was led by Sulf-Norm under CEN/TC 264/WG 16. It provides QA/QC for portable systems but can't solve fundamental bias in terms of sample loss, only provide a method to test / quantify it. At the workshop it was discussed that national regulators need to decide how this data should be used, then implement this in a formal Method Implementation Document.

Stack testing organisations are required to take part in proficiency testing (PT) schemes to demonstrate to the competent authority they are capable to carry out the necessary measurements in an accurate manner. There are long running ISO 17043 accredited PT schemes run by HLNUG (Germany) and NPL (UK). These provide a record of proficiency across the industry, which can be interpreted as an indication of the ability to meet uncertainties required for increasingly stringent emission limit values (ELV) being introduced in new BREF (best available technique reference) documents for Waste Incineration.

The combined NPL/HLNUG dataset, with ~2800 participant results from 2003-2018, is an important potential source of historical data for such comparisons and would not have produced such significant results without the combined data from both schemes. During PT schemes z-scores are used to normalise results, such that a z-score of ±2 is an acceptable result and a result greater than ±3 is a failure. To compare results over the two schemes and over time the results here have been renormalized by NPL with a standard target deviation of 2.5 $mg.m^{-3}$. The new performance scores will indicate the required uncertainty is achieved for <±4 for current ELV for waste incineration or <±0.8 for an ELV of 10 $mg.m^{-3}$ which is the proposed tighter limit (Table 1).

Table 1: Required uncertainty and normalised score limits for different waste incinerator ELV

	SO_2	Proposed stricter ELV
Normalised deviation / mg m_0^{-3}	2.5	2.5
Waste incinerator ELV / mg m_0^{-3}	50	10
Req. U_{95} / % of ELV	20	20
Req. U_{95} / mg m_0^{-3}	10	2
Req. U_{95} / normalised-score	4.0	0.8

In Germany the competent authority requires the use of the SRM (EN 14791), with the results indicating that the required uncertainty is widely achieved for the current ELV (Figure 1). However, with the stricter limit value a significant number of results would no longer be meeting the required uncertainty. This demonstrates that the current SRM is not capable of routinely meeting the uncertainty requirements specified in the IED (i.e. <20% of ELV) if the ELV reduces to the proposed level.

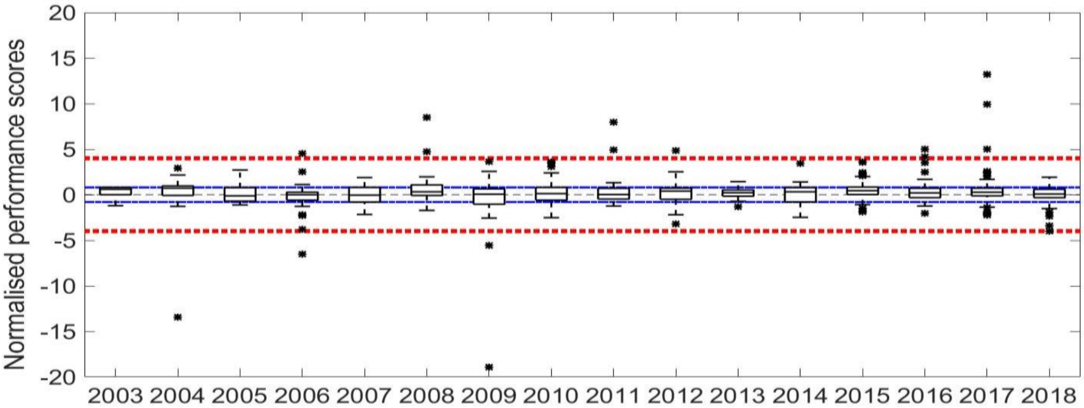

Figure 1: Results for the HLNUG PT scheme using EN 14791. The wider broken lines (red) indicate the required uncertainty limit for 50mg.m^{-3} ELV and the narrower dot-dashed lines (blue) apply to 10mg.m^{-3} ELV.

NPL carried out laboratory tests with three sets of impingers with different set ups to benchmark the SRM. For one set the heated gas line was directly connected to the impinger glassware, while the second was the full Standard Reference Method set-up as determined in EN 14791 with nozzle, probe, filter box and glassware and the final set had the heated gas line directly connected to the mini-impingers. The results indicate that there is no observable trend in the effect of unconditioned sampling with impinger trains and demonstrates that there is no difference between the performance of full-size impingers and mini-impingers.

The VTT test bench facility uses a 1.6MW diesel engine to generate emissions to be measured. By varying fuel sulphur content and load on the engine, the facility can generate a range of potential SO_2 concentrations. Measurements were made at two engine load levels and three different fuel sulphur contents, with expected SO_2 concentrations calculated from stoichiometric combustion calculations. Measurements were also made with a Gasmet Dx4000 FTIR instrument to give another comparison of the SRM performance. SRM measurements were made with a single sampling train.

At lower concentrations (<100ppm) the SRM agreed well with the calculation-based approach, but at higher concentrations the performance worsened, typically resulting in measurements far lower than the FTIR. Checks indicate that rinsing of the sampling line was not efficient enough at high SO_2 concentrations, so sulphate was lost in the sampling line leading to low reported values.

A further laboratory test at VTT involved measurement of a dry gas mixture of 1280 mg.m^{-3} SO_2 in nitrogen which was produced by thermal mass flow meters. This was sampled according to EN 14791, before the absorption fluid was split and sent to two independent laboratories. The results indicated recovery rates of 82% and 89% which demonstrates that the SRM will under-read at high concentrations.

The results of the test bench trials were analysed according to CEN/TS 14793, which sets out the tests required to demonstrate equivalency of a measurement technique with the reference method.

Uniper have identified a potential issue with current assessment of positional uncertainty relating to reference methods. Based on a one-off flue gas concentration grid traverse, EN15259 allows reference method sampling from a single point when the stack is deemed to be ‘homogeneous’. There is a residual concentration distribution across the stack which may be significant due to the nature of the homogeneity test in EN15259. This can then impose a significant systematic bias when the QAL2 calibration is applied to the AMS.

The residual positional standard uncertainty, s_{pos}, for 13 coal fired boiler units fitted with wet flue gas desulphurisation (FGD) units where all of the cases passed the EN15259 homogeneity test were used. 9 other compliant units with even higher positional uncertainties have been excluded due to either low absolute SO_2 concentrations (< 40 mg/m^3), combined high temporal and spatial process variations or non-ideal sampling location, i.e. closer than usual to the FGD outlet, causing unexpectedly high spatial variations.

Since it is not always possible to evaluate s_{pos}, an alternative approach was developed to correct the grid concentration points to account for temporal concentration and oxygen variations, as measured at a fixed reference point, giving $s_{grid,t}$. When it is possible to evaluate s_{pos}, there is generally good agreement between the two quantities, with $s_{grid,t}$ generally more conservative (lower) than s_{pos}.

For SO_2 monitoring within this plant configuration, the relative standard uncertainty relating to a single point SRM implementation is circa 5% which is similar in magnitude to both the SRM method uncertainty and the sampling losses associated with chillers. This is a significant issue, requiring further investigation, that needs to be taken into account in method validation studies. EN15259 needs to be improved with regards to: statistical testing of homogeneity; assessment of residual uncertainty and recommended sampling strategies.

Summary of key outputs and conclusions

The survey found a fairly even split of preferences for EN 14791 (41%) and instrumental techniques (59%), although this varied far more on national levels. Data quality was the major concern, particularly regarding cross-interference found with instrumental techniques. A report was produced and the results were also published in a suitable trade journal (*International Environment Technology*), ensuring that the findings are communicated to the broadest audience possible within the sector.

The regulator position paper provides a different insight into the implementation of EN 14791. The EA has 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. EA are considering releasing guidance for the technical specification for SO_2 measurement by instrumental techniques, CEN/TS 17021:2017, partly based on the finding 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 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 ELVs in the new 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.

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 range of activities have demonstrated the qualities and limitations of the SRM described in EN 14791, meeting the objective. The regulator paper and stakeholder survey have provided different viewpoints on the usage of the standard and highlighted potential issues that exist with it. The historical PT data illustrate the difficulty with meeting uncertainty requirements based on percentage of the ELV. As limit values fall the ability of current methods, including EN 14791, to meet the IED uncertainty requirements will continue to suffer. This objective has been successfully completed.

4.2 Materials for conditioned sample systems and sample stability

Materials used in sampling and conditioning systems can affect the measured values due to the reactivity of SO_2. Understanding which materials are particularly susceptible to these sorts of reaction and to what extent is therefore very important when assessing measurement uncertainty. SO_2 can be lost when water condenses forming water droplets and/or liquid films in the equipment. In general, this effect is limited by keeping sample lines and equipment above the condensation point of water, except in conditioning systems which there to remove the water for dry analysis techniques.

VTT carried out laboratory-based testing with probe assemblies made of different materials (e.g. stainless steel, borosilicate glass, ceramic) and attached to identical Fourier Transform Infrared (FTIR) instruments. The first was a metal (stainless steel) probe and sampling system, while the other was a glass probe with a PTFE tube connecting it to the FTIR. There were thirteen sets of paired measurements made over two days of testing.

The instrument with a glass probe produced consistently lower results (~3 $mg.m^{-3}$), with a t-test demonstrating that there was a significant difference between the paired measurements with the different probes. However due to the small sample size confidence in this conclusion will be limited without further testing.

The absolute scale of the offset is consistent at all concentrations. Since uncertainty in reported emissions is stated as a percentage of the measurand, at higher concentrations probe material becomes a less significant issue. However, with SO_2 ELV falling, probe material may become a more significant issue in the coming years.

Since most P-AMSs are able to measure only filtered and dried stack gas and sulfur dioxide is soluble in water, the amount of SO_2 removed from stack air during process of drying needs to be described. CMI used computational fluid dynamics (CFD) modelling to investigate this effect.

Two basic phenomena need to be taken into account in modelling removal of gaseous substances during the drying process. Since the gas is dissolved in liquid water condensing in the dryer, the condensation processes need to be described quantitatively in dependence on the physical and geometrical conditions. Once the microscopic liquid phase of water occurs in the dryer (in the form of water film or water droplets), the transfer of gaseous soluble species into water is driven by diffusion processes simultaneously with the ongoing condensation of water. Thus, the condensation and diffusion are the key physical phenomena required. Models of droplet growth and liquid film formation during condensation have been modelled on the basis of theoretical as well as experimental findings published in literature.

It was found that although the maximal concentration of SO_2 in water droplet can be reached in time less than 0.1s, the droplet growth is slow (about 100s is needed to double the initial diameter of the droplet). Thus, for the total amount of SO_2 dissolved the formation of liquid film is more important. The classical Nusselt formula has been used for estimation of liquid film thickness.

Molecular transport of condensable SO_2 has been discussed with regards to the molecular processes on the gas-liquid interface as well as with regards to chemical processes inside liquid. The governing equations of diffusion processes have been summarized and the significant boundary conditions defined using Henry's Law, constant and mass accommodation coefficient. The concentrations of SO_2 dissolved in one droplet by diffusion have been mathematically modelled simultaneously with modelling droplet growth. The average concentration of SO_2 in the gas flow leaving the dryer has been simulated for stagnant film thickness as well as for droplets using a diffusion model and chemical reactions connected with dissolution of SO_2 in water. Both cases have been implemented and simulated in finite element model (FEM) tool COMSOL Multiphysics®.

Several simulations have been done for different gas velocities and different initial SO_2 concentration in the gas entering the dryer. The resulting dependencies show that the SO_2 loses increase with decreasing gas velocity and decreasing SO_2 concentration in gas phase. The loses increase only slightly for lower inlet concentrations, while the dependence on the gas velocity is much more significant. This result is related to the fact, that in case of low gas velocity the dissolving species have more time to diffuse into the water film. Finally, from the comparison of resulting SO_2 concentrations at the inlet to the dryer and the final concentrations at the outlet from the dryer it follows that the SO_2 loses are significant for the measurements using P-AMSs. However, for quantitative results more detailed numerical analysis and comparison with experimental findings should be done.

Summary of key outputs and conclusions

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, the findings demonstrate how to allow for this material uncertainty when assessing current measurement uncertainties. Ceramic probes were not tested as initially intended, but these are not widely used so their omission will not limit the impact of this objective.

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.

The project has demonstrated and quantified the effects of different sample conditioning systems, improving understanding of the issues surrounding their use. Even though ceramic probes were not tested as originally intended, the objective has been achieved, greatly improving understanding of the issue.

4.3 Relative performance and sample bias of alternative drying technologies for conditioned sampling

Using the NPL/HLNUG database of PT scheme results described in section 4.1 above, results from using conditioned (e.g. NDIR) and non-conditioned (e.g. FTIR) measurements can be used to identify potential bias caused by the sampling systems. In general, only the type of instrument used is recorded when the results were submitted, with no information on the specific type of conditioning system (i.e. permeation drier or chiller). In Germany FTIR is rarely used, so all portable automated measurement systems (P-AMS) operate with conditioning systems, although the HLNUG test facility operates at ambient humidity (effectively dry) so you would not expect significant losses of SO_2 in solution. The performance over time shows P-AMS have consistently met the uncertainty requirement for the current IED ELV, but would struggle at the 10$mg.m^{-3}$ ELV. There is no significant bias in the results that could indicate a problem with the sample conditioning systems, but this could be influenced by the dry sampling medium.

In the UK the competent authority has approved a method for using FTIR for stack monitoring (TGN M22), so a comparison can be made between the unconditioned FTIR and other P-AMS requiring a conditioning system. The NPL stack simulator facility operates hot and wet, mimicking conditions in a real stack. Alongside the stack simulator PT scheme NPL runs a cylinder scheme where participants measure certified cylinders directly, without the sampling system. This provides a test of the calibration of the analyser so can eliminate that source of error if a bias is detected. FTIR is not very widely used so PT sample sizes are small, but any skew in the results seems to be explained by poor calibration in the cylinder scheme results.

In contrast with the FTIR, the conditioned P-AMS have more consistent results in the cylinder scheme, demonstrating no problems with the calibration. There is a pronounced negative bias in the measurements on the stack simulator, with only 2010 skewed positively. The consistent negative bias in the majority of years on the simulator scheme must come from the sample and conditioning systems (Figure 2).

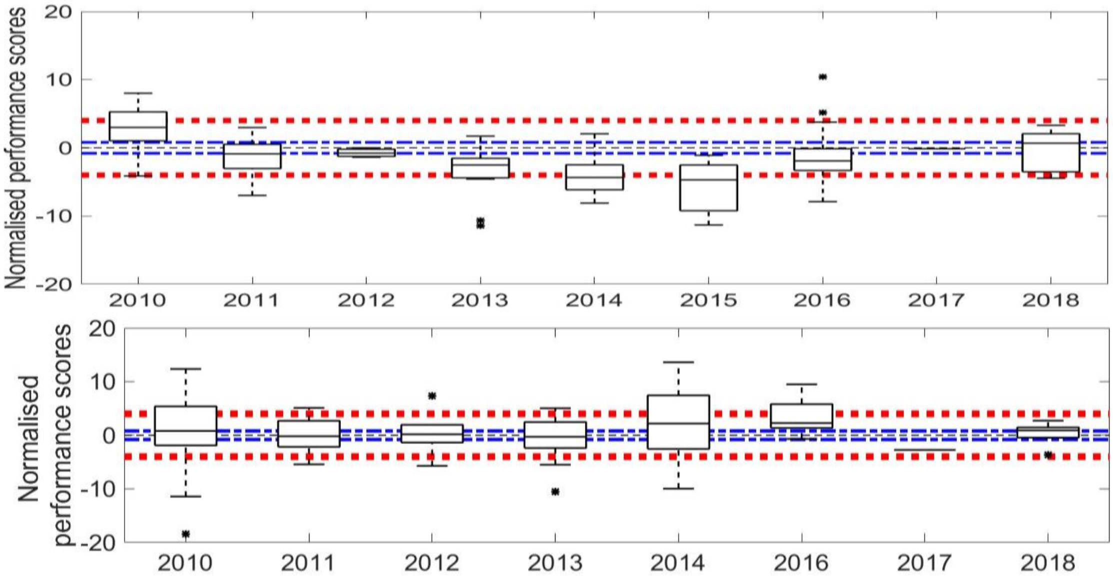

Figure 2: NPL PT scheme results for conditioned P-AMS measurements in the Stack simulator (Top) and Cylinder scheme (Bottom). The wider broken lines (red) indicate the required uncertainty limit for a 50mg.m^{-3} ELV while the narrower dot-dashed lines (blue) are for a 10mg.m^{-3} ELV.

UNIPER provided calibration function data from large combustion plants that require continuous monitoring under the IED. The permanent AMS systems and associated conditioning systems vary across the different plants, so NPL and UNIPER analysed the calibration functions produced when using specific reference methods to investigate the potential impact of different conditioning systems. All the QAL2 testing was carried out using P-AMS with extractive chiller as the reference method. Where the plant AMS also used a chiller (28 QAL2 tests) there was no average offset in the slope of the calibration function. With a permeation dryer system on the plant instrument (19 QAL2 tests) there was an average of 4% offset in the slope for the resulting calibration function. The average slope offset in the calibration for in-situ (un-conditioned) measuring AMS (18 QAL2 tests) was 1%, but there were two different AMS manufacturers which had offsets which cancelled each other out (10 tests with average offset of -2% and 8 tests with average offset of +5%). Clearly there is significant variation between different conditioning systems, but in general the calibration offset produced by the conditioning systems in this dataset is less than ±5%.

The conditioning system losses are just one part of the uncertainty assessment for the overall measurement of emissions. Operators are required to report their annual mass emissions which are usually measured with two AMS systems, one to measure the concentration and the other for flow rate. Propagation of uncertainty is not straight forward so translating the error from a conditioning system into an uncertainty on the annual mass emissions is a complex task.

NPL have created a Monte-Carlo simulation (MCS) model of AMS systems operating on a plant following the quality assurance regime laid out in EN 14181. The model repeatedly samples the probability density function (pdf) for each source of uncertainty in the process, producing a pdf for the annual mass emission, indicating the likely result and the uncertainty. By varying individual uncertainty sources within the model, it is possible to investigate the sensitivity of annual mass emissions to specific factors. The model investigated the effect of sample conditioning losses on the AMS and the reference method, with all other error sources set to zero.

If the sample losses are only occurring on the AMS then this will be completely calibrated out, although there will still be some affect if humidity in the stack varies between the calibration and the normal measurements, although this is minor (<0.005%). Sample system losses on the reference method are a far more significant issue as they will apply an offset error to each individual measurement made with the calibration function. In this case the calibration function will end up “correcting” the AMS with the sample loss error resulting in systematically incorrect reported emissions. The model indicates a sensitivity of ~83%, so a 5% sample loss rate on the reference method would lead to an error in the annual mass emissions of just over 4%. This demonstrates that attention needs to be paid to reference method sampling system losses to avoid significant uncertainty in the reported annual mass emissions.

VTT, NAB and Ramboll have carried out test bench trial comparing unconditioned and conditioned sampling for SO_2. The data set has been analysed to see if the results given by instrumental techniques are equivalent to SRM according to the procedure in EN 14793. P-AMS gave equivalent results to SRM and therefore, this data was used as a validation protocol to the Finnish authorities to show that these alternative methods (AMs) can be used in Finland instead of EN 14791. Tested P-AMS were UV-fluorescence with dilution probe, NDIR with chiller, NDIR with permeation dryer and FTIR which measures hot and wet with no conditioning system. At the lower concentration range, however, it was noticed that the combination of chiller and NDIR had sampling losses and therefore, this combination is not allowed to be used in Finland.

VTT carried out field testing at a combustion plant in Finland fuelled by bark, sludge from wastewater treatment and occasionally coal. Measurements were carried out in January 2018 when ambient conditions were around +1 °C, therefore additional heating was required to maintain the analysers at optimal temperatures. Parallel measurement of SO_2 emissions were made with FTIR (Gasmet Dx4000), NDIR with chiller (Horiba PG-350), NDIR with permeation dryer (Horiba PG-250) and UV-fluorescence with dilution probe (Teledyne T100). The FTIR and both NDIR instruments shared a probe before the gas flow was split between them, while the UV-fluorescence analyser used a separate dilution probe. The plant has a daily average ELV of 175 mg.m^{-3}, however typical emissions are around 10-25 mg.m^{-3}, so coal was used to create more variable SO_2 levels during the test period. Reported values are calculated as 30-minute averages in mg.m^{-3} dry (Figure 3).

Typically, FTIR (sampling hot and wet) or UV-fluorescence with dilution probe gave the highest values (i.e. lowest sampling losses), while NDIR with chiller was consistently lower than all other approaches indicating high sample losses from the chiller. The response times were similar except for the permeation dryer which was slower, indicating a long residence time within the conditioning system. QAL2 calibration functions generated from the different P-AMS varied, with the NDIR and chiller system providing calibrated values that are only around 50% of the highest calibration function at the top of the range. This supports the findings in the laboratory testing with NDIR and chiller producing high sample losses.

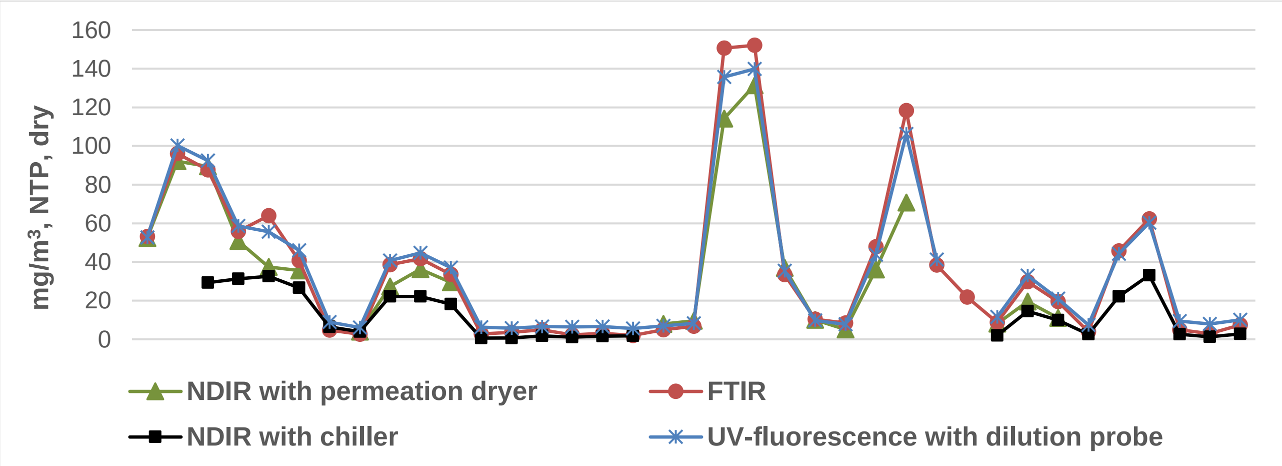

Figure 3: Half-hourly average SO_2 concentrations measured with different instrumental techniques, 16-18th January 2018.

A peer review article on the sampling performance of P-AMS with different conditioning techniques based on both field trials was published in JA&WMA in 2019.

NPL carried out laboratory testing of parallel EN 14791 equipment with the addition of conditioning systems to investigate their effects on SO_2 measurement. By controlling the gas concentrations, moisture levels and gas line temperatures, three separate sample trains were set up and run in parallel allowing direct comparison of the methods in question. Figure 4 shows the test bench arrangement, with the feed from two Mass Flow Controllers (MFC) dividing three ways at the Swagelok interface.

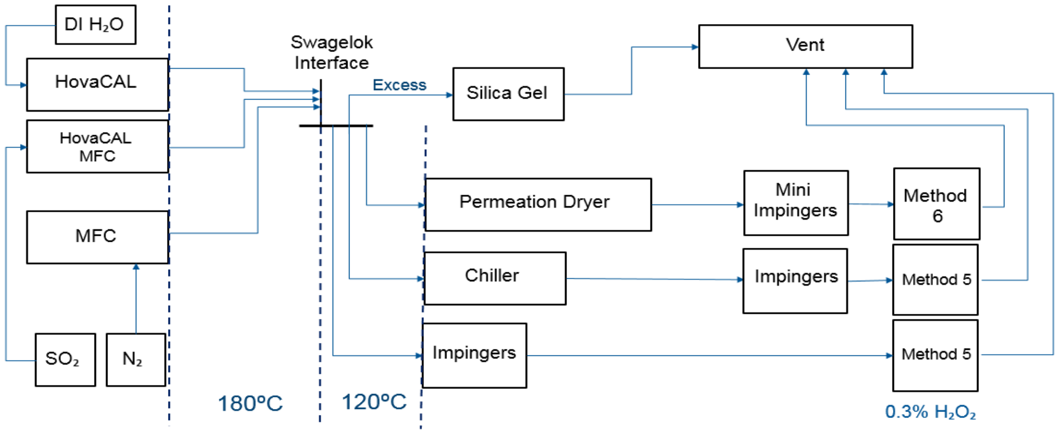

Figure 4: Schematic of controlled test conditions in laboratory

The three sample lines allowed the chiller system, permeation dryer and wet impinger sampling methods to run simultaneously under identical sampling conditions. Each test ran for 30 minutes, with the lowest concentrations run for 60 minutes. The permeation dryer in the majority of tests was the Horiba PS100-E, although some extra sampling was also performed in order to test the efficiency of the PermaPure drying system against the chiller system. The final sample train was run straight into the impingers without any conditioning after the heated line.

Due to the flow requirements of the permeation dryer being 2l/min this had to be run with mini-impingers and a Method 6 rather than the usual full size impingers. The chiller system and impinger system ran with full size impingers and Method 5. Additional test runs were included to ensure that this difference did not introduce a separate bias to the experiment.

Moisture content was controlled by a HovaCAL system with percentage concentration ranging from 0-12%, while the SO_2 concentration was blended to between 2-35mg.m^{-3} using certified cylinders. Gas line temperatures were maintained at 180°C to the Swagelok interface and 120°C from this interface to the conditioning system or impingers. This is because the permeation dryer has lower temperature requirements (maximum 120°C), but this is still above the dew point so no SO_2 was lost to condensation at this point in the system. Between each test the system was purged with nitrogen to ensure no SO_2 remained in the gas lines.

Fresh solution of 0.3% H_2O_2 was made up each morning according to EN 14791 section 6.1.4. 500ml of this solution was added to the full size impingers while 20ml was added to the small ones. Following sampling this was then collected by an experienced Level 1 MCERTs technician and sent to NPL's internal laboratory for analysis of sulphates under EN 14791.

Tests were run without conditioning systems to all three sets of impingers, demonstrating that there was no difference in performance of the full size and mini-impingers. Tests with the chiller and permeation dryer in place but a dry gas stream, demonstrated that with no moisture the conditioning systems do not influence the measurements, i.e. any influence comes from removal of water, not just passing through conditioning systems.

Wet and dry runs at the same SO_2 concentrations were carried out back-to-back for three different concentrations to test for evidence of bias between the systems. The chiller tests show greater variation between wet and dry runs. Over all runs with concentration > 9 mg.m^{-3} the chiller had an average deviation of -12.3% compared to EN 14791, while the average deviation for the permeation dryer was -5.7%. When the same calculation was done with the VTT laboratory test results it produced -11.8% deviation for the chiller and +2.5% deviation for the permeation dryer. The results for the chiller are very similar in both the NPL and VTT testing, so we can be confident that the chiller is a significant source of sampling losses.

During two dryer blank tests only N_2 was run through the sampling system, with the chiller and permeation dryer connected to their normal sample trains. The chiller and impinger trains display similar results close to zero, however the results from the permeation dryer are noticeably higher. This could be due to a 'memory effect' occurring within the adsorbant membrane of the permeation dryer. The tests immediately prior were tests which included high concentrations of SO_2. Although the system was purged between tests, it could be the case that some SO_2 remained within the permeation dryer, so this system may require longer purge times to ensure that zero tests produce an accurate result. This fits with the findings of the VTT testing showing a longer response time for permeation dryer systems.

Summary of key outputs and conclusions

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. FTIR, UV fluorescence with dilution probe and 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.

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 successfully completed, with experimental results quantifying the effect of alternative drying systems for conditioned sampling.

5 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.

6 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

7 Contact details

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