SO$_2$ emission measurement with the European standard reference method, EN 14791, and alternative methods – observations from laboratory and field studies

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ABSTRACT
EN 14791 is a European Standard Reference method for the measurement of SO$_2$ in emissions. This standard is based on a wet-chemical method in which SO$_2$ present in flue gases is absorbed into an absorption solution containing hydrogen peroxide, and analyzed as sulfates after sampling. This study presents the results obtained when three portable automated measuring systems (P-AMS), based on Fourier-transform infrared (FTIR) spectroscopy, non-dispersive infrared (NDIR) and ultraviolet-fluorescence (UV) techniques, were compared to the Standard Reference Method for SO$_2$ (EN 14791) in order to verify whether they could be used as alternative methods (AM) to EN 14791. In the case of FTIR, the measurements were performed from hot and wet gas, without any conditioning. UV-fluorescence analyzers were equipped with dilution probes and one NDIR applied a permeation dryer, whereas the other had a chiller. Tests were carried out at concentration ranges from 0 to 200 mg/m$^3$(n) and from 0 to 800 mg/m$^3$(n) for testing of equivalency according to CEN/TS 14793 using a test bench. Equivalency test criteria were met for all tested P-AMS except for NDIR at the lower range. The SO$_2$ results measured with NDIR and the chiller were lower compared to the set-up with NDIR and permeation. This was most probably due to the chiller causing absorption of SO$_2$ in the condensate. Tests were also carried out at field conditions, measuring the SO$_2$ emissions from a boiler combusting mainly bark. The same phenomena were observed in these tests as during the test bench study, i.e. the measurement set-up with NDIR and the chiller gave the lowest results. These data demonstrated that the tested alternative methods (FTIR, UV-fluorescence, and NDIR) could be used instead of the standard reference method EN 14791, thus providing real-time calibration of automated measuring systems. It must however be emphasized that when measuring water-soluble gases, such as SO$_2$, the choice of suitable conditioning technique is critical in order to minimize losses of the studied component in the condensate.

Implications: Portable automated measuring systems (P-AMS) provide real-time information about emissions and their concentrations, thus offering significant advantages compared to wet-chemical methods. This study presents results which can be used as a validation protocol to show that the tested P-AMS techniques (FTIR, NDIR, UV-fluorescence) could be used instead of EN 14791 (CEN 2017a) as alternative methods (AM), when paying attention to the selection of an appropriate conditioning technique.

Introduction
According to the European Industrial Emissions Directive, IED, 2010/75/EU, (European Union 2010), SO$_2$ emissions must be measured on a continuous basis from Large Combustion Plants as well as from waste incinerators. The continuous measurement of SO$_2$ is based on Automated Measuring Systems (AMS), which are also referred to in many texts as Continuous Emission Measurement Systems, CEMS. The techniques used as AMS for SO$_2$ vary depending on the plant.

The requirements for the measurement uncertainties for AMS are given in IED (as 95% confidence intervals at the emission limit value) and according to IED, the maximum permissible uncertainty as a percentage related to the emission limit value (ELV) for the AMS for SO$_2$ is 20%. This means that the plant operator must show to the local authority that the AMS used to measure SO$_2$ emissions in the plant has a measurement uncertainty which does not exceed this value.

In Europe, quality assurance procedures for Automated Measuring Systems, AMS, must be performed using the principles shown in EN 14181 (CEN 2014) Quality Assurance of Automated Measuring Systems, QA of AMS. This European Standard describes the quality assurance procedures needed to ensure that an AMS is capable of meeting the uncertainty requirements on measured values given by legislation, e.g. EU Directives.
Quality assurance has been divided into four parts in the standard:

- **QAL 1**: Quality check of the measuring procedure = suitability of an AMS for its measuring task (EN ISO 14956)
- **QAL 2**: Quality assurance of installation = calibration and validation of automated measuring systems (AMS) by means of the standard reference method (SRM).
- **QAL 3**: Ongoing quality assurance during operation
- **In addition**, annual control, an Annual Surveillance Test, AST

The tools for how to demonstrate that the AMS fulfills the uncertainty criteria which are set for it in IED are given in QAL2. During QAL2, AMS is calibrated with parallel measurements performed with the standard reference method (SRM) and the variability of the measured values obtained with the AMS is evaluated against the criteria set in IED, the maximum permissible uncertainty.

As a consequence, SRM is a very important component of this quality assurance process. SRM must be validated so that the results are reliable, and the user of SRM must be skilled in using the method.

In Europe, the SRM method for the measurement of SO$_2$ is EN 14791 (Stationary source emissions. Determination of mass concentration of sulfur oxides. Standard reference method). EN 14791 is a method which is based on wet-chemical measurement. The sample is extracted from the stack using a heated probe. After the sample gas has been filtered, it is drawn through impingers which contain hydrogen peroxide as absorption solution. The sulfur dioxide in the sampled gas is absorbed and oxidized to sulfate ion. The mass concentration of sulfate in the absorption solutions is determined using ion chromatography or by titration with a barium perchlorate solution using Thorin as indicator.

The user of this SO$_2$ SRM must demonstrate that the maximum relative expanded uncertainty for this SO$_2$ SRM does not exceed 20% of the daily emission limit value or of the lowest limit value fixed to the plant by the local authorities. This expanded uncertainty is calculated on a dry basis and before correction to the O$_2$ reference concentration, and it is calculated by establishing an uncertainty budget.

However, as SRM for SO$_2$ is used to calibrate AMS for SO$_2$, the expanded uncertainty of this SRM should be lower than 20%, since the uncertainty requirement for automated measuring systems for SO$_2$ given in IED is 20% (given as 95% confidence interval). For example, the measurement uncertainty of AMS for NO$_x$ is also 20% and in comparison, the relative expanded uncertainty of SRM for NO$_x$ should be lower than 10% (according to EN 14792, CEN 2017b). Since the permitted relative expanded uncertainty for SRM SO$_2$ is the same as the permitted uncertainty for AMS, it is obvious that there is a risk of drawing incorrect conclusions when using EN 14791 for the calibration of AMS.

Operating permits for industry are based on “best available techniques”, BAT, which are presented in the BAT reference documents, in so-called BREF documents. The “BAT conclusions” is a document containing the parts of a BAT reference document laying down the conclusions on best available techniques, and BAT conclusions are binding. In many revised BREF documents, new BAT-conclusions pose even lower Emission Limit Values (ELV) for SO$_2$ than earlier limits. For example, in the Final Draft for the BREF document for waste incineration (BAT Final Draft 2018), it is stated that BAT-associated emission limits (BAT-AELs) for SO$_2$ for existing plants are 5–40 mg/m$^3$ (n) as a daily average. If the emission limit value is set as 5 mg/m$^3$, this means that the measurement uncertainty of the AMS measuring SO$_2$ shall not exceed ± 1 mg/m$^3$ (n), since as has been mentioned previously, the requirement for measurement uncertainty for continuous measurement of SO$_2$ is 20%.

Other techniques can also be applied instead of SRM if their equivalency with SRM has been tested and proved to be sufficient. These techniques are called Alternative Methods, AM. The procedure for demonstrating the equivalency of AMS with SRM is given in: EN 14793. Stationary source emissions. Demonstration of equivalence of an alternative method with a reference method (CEN 2017c). At the time when this study was conducted, the document did not yet have the status of a European standard, it was a Technical Specification CEN/TS 14793 (CEN 2005). Therefore, later on in this document reference is made to this Technical Specification.

There are portable automated measuring systems (P-AMS) available on the market that could be used as alternative methods (AM) to the wet-chemical method EN 14791. P-AMS have several advantages over wet-chemical methods. They provide real-time information about the process concentrations, so that plant owners can react immediately if there are any excesses in their emissions. On the other hand, the investment costs for wet-chemical methods are typically lower compared to P-AMS, but their use usually requires more labor and their result gives only an average value of the sampling time. As the sulfate samples are taken to the chemical laboratory to be analyzed after the measurement campaign, it takes several weeks before the results are received.
As part of the EMPIR program, a project called Sulf-Norm was launched in 2016. The overall aim of the Sulf-Norm project is to compare conditioned sampling approaches to the unconditioned sampling approach associated with the incumbent SRM (EN 14791).

As part of the Sulf-Norm project, tests were carried out for the measurement of SO\textsubscript{2} with different P-AMS and SRM using a test bench and also in field conditions. The techniques that were chosen to be tested were Fourier Transform Infrared (FTIR) spectroscopy, Non-Dispersive Infrared (NDIR) and ultraviolet (UV) fluorescence. In FTIR the measurement is performed from hot and wet gases, so there is no need to have any conditioning unit before the analyzer. The moisture must be removed with a conditioning technique when using NDIR, since this analyzer is not heated. Typically, UV-fluorescence analyzers are used with dilution probes which dilute the flue gas so that the UV-analyzer does not have to be heated. The above-mentioned techniques are widely used in Finland.

This paper focuses on the measurement of SO\textsubscript{2} from stack gases representing two studies:

- testing the equivalency of alternative methods (AM) to the European Standard Reference Method, EN 14791 and
- field measurements of SO\textsubscript{2} with P-AMS and different conditioning techniques

**Testing the equivalency of alternative methods (AM) to EN 14791**

**Experimental**

In the spring of 2017, VTT organized tests of the equivalency of alternative methods for monitoring of SO\textsubscript{2} emissions. The aim of these experiments was to test whether these P-AMS could be used as alternative methods (AM) to determine SO\textsubscript{2} concentrations instead of the existing SRM.

P-AMS that were used in this test were a Fourier Transform Infrared Technique analyzer (FTIR), an ultraviolet (UV)-fluorescence analyzer and a non-dispersive infrared (NDIR) analyzer:

- Fourier-transform Infrared (FTIR) Spectroscopy-analyzer-, Gasmet Dx4000, analysis as hot and wet
- Non-dispersive infrared analyzer (NDIR), Horiba PG-350 with chiller (M&C, model PSS-5)
- Non-dispersive infrared analyzer (NDIR), Horiba PG-250 with permeation dryer (Perma Pure Mini-GASS MG-2812T)
- UV-fluorescence analyzers, Teledyne Monitor Labs ML T100 and Monitor Labs 9850, with dilution probes (EPM, model 300)

Two SRMs were operated in parallel with two AMs, as required under CEN/TS 14793. According to this Technical Specification, checks of repeatability and lack of systematic deviation of the AM are made in the field in comparison with the SRM.

It was decided to carry out these tests at the test bench of VTT, which is shown in Figure 1. The advantages of using this test bench were that it was possible to have variable SO\textsubscript{2} concentrations over a wide concentration range, and that the gas matrix was close to the stack gas concentrations e.g. at power plants.

Exhaust gas was produced with a gasoline engine. SO\textsubscript{2}-concentrations were varied by spiking of SO\textsubscript{2} gas to the exhaust gas flow at final concentrations ranging from 2 to 800 mg/m\textsuperscript{3}(n). Typically, the required monitoring ranges for SO\textsubscript{2} are much lower, for example in waste incineration processes, but the justification for choosing this concentration range (up to 800 mg/m\textsuperscript{3}(n)) was that for example in the European Medium Combustion Plant Directive (MCPD) (European Union 2015), the emission limit value (ELV) for SO\textsubscript{2} for existing combustion plant combusting solid fuels, with a rated thermal input equal to or greater than 1 MW and less than or equal to 5 MW, is 1100 mg/m\textsuperscript{3}(n).

Table 1 presents the stack gas conditions and gas matrix concentrations at the test bench.

A total of 25 samples were taken, as well as field blanks and chemical blanks. According to European standards, it is required to analyze field blanks during...
Tables 2 and 3 provide the statistical tools and different criteria to evaluate the alternative method (AM). This document provides the statistical tools and different criteria to evaluate the alternative method (AM).

### Validation procedure according to CEN/TS 14793

The results were analyzed using the principles given in the document CEN/TS 14793 (Stationary source emission. Intralaboratory validation procedure for an alternative method compared to a reference method). This document provides the statistical tools and different criteria to evaluate the alternative method (AM).

CEN/TS 14793 (as well as EN 14793) describes three steps in the validation procedure:

- description of the AM and setting of the field of equivalence (range and type of gas matrix);
- determination of the performance characteristics of the AM and calculation of the overall uncertainty, where appropriate, and checking of compliance of the maximum overall uncertainty allowed for the SRM;
- checking of repeatability and lack of systematic deviation of the AM in the field in comparison with the SRM for the type of matrix defined in the field of equivalence.

Performance characteristics and overall uncertainties were not evaluated during this study; the focus in the laboratory tests was on the test for equivalence. It must be noted, however, that the alternative methods that were tested during these measurements (FTIR, NDIR) have been certified according to EN 15267–3. A UV-fluorescence analyzer (Teledyne) has been certified according to EN 15267 (CEN 2009) as an ambient air analyzer.

Figure 2 shows the concentrations measured with different techniques in the concentration range from 0 to 200 mg/m$^3$(n).

Typically, results of the measurement set-up NDIR and chiller were about 5–30 mg/m$^3$(n) lower than the results given by other methods, the difference being dependent on the concentration level.

As mentioned before, two SRMs were operated in parallel with two AMs in order to be able to carry out testing of systematic deviation and repeatability between AM and SRM.

The maximum allowable repeatability standard deviation $S_{r,limit}$ (see eq (1)) and the reproducibility standard deviation $S_r$ (see eq (2)) expressed as a mass concentration in mg/m$^3$ for the standard reference method are given in EN 14791. They are:

\[
S_{r,limit}(C) = 0.051C + 2.3 \frac{mg}{m^3} \quad (1)
\]

\[
S_r(C) = 0.0678C + 3.47 \frac{mg}{m^3} \quad (2)
\]

where $C$ is the concentration (mg/m$^3$).

The results of these tests of equivalence are shown in Tables 2–7. Results in the concentration range from 0 to 200 mg/m$^3$(n) are shown in Tables 2–4, and the concentration range from 200 to 800 mg/m$^3$(n) in Tables 5–7.

From Tables 2–7, it can be seen that the test criteria are met for all Alternative Methods when the equivalency is tested over the range of 0–800 mg/m$^3$(n). However, when the equivalency is tested only for the lower range, 0–200 mg/m$^3$(n), the NDIR method does not conform to the repeatability criteria. This is due to the lower concentrations that were measured with the NDIR and chiller. It should be noted that according to the type testing certificate for the Horiba NDIR (Certificate of Product Conformity (QAL1) 2018) used in these tests, the use of a permeation dryer is recommended, not of a chiller. Based on earlier studies (Vahlman and Larjava 1990), condensation methods have the tendency to absorb SO$_2$ into the condensate, and their use is thus not recommended if the measured...
Figure 2. SO\textsubscript{2} concentration measured with Standard Reference Method (EN 14791) and with different alternative methods (AM) (NDIR, UV-fluorescence, FTIR), measured range 0–200 mg/m\textsuperscript{3}(n).

Table 2. Test of equivalency for FTIR to EN 14791 (IC-method) across a concentration range of 0–200 mg/m\textsuperscript{3}(n).

| Verification tests                  | Value obtained | Criterion | Conclusion |
|-------------------------------------|----------------|-----------|------------|
| Systematic deviation                |                |           |            |
| -correlation coefficient (r)        | 0.9989         | r ≥ 0.97  | yes        |
| -slope (C\textsubscript{1})         | 1.08           | 0.89 ≤ C\textsubscript{1}≤ 1.11 | yes        |
| -intercept (C\textsubscript{0})     | -5.77          | | |
| Repeatability standard deviation    |                |           |            |
| -SRM                                | 2.05           | ≤ 6.59    | yes        |
| -AM                                 | 1.37           | ≤ 6.59    | yes        |

Table 3. Test of equivalency of UV-Fluorescence (with dilution probe) to EN 14791 (IC-method) across a concentration range of 0–200 mg/m\textsuperscript{3}(n).

| Verification tests                  | Value obtained | Criterion | Conclusion |
|-------------------------------------|----------------|-----------|------------|
| Systematic deviation                |                |           |            |
| -correlation coefficient (r)        | 0.9997         | r ≥ 0.97  | yes        |
| -slope (C\textsubscript{1})         | 0.94           | 0.89 ≤ C\textsubscript{1}≤ 1.11 | yes        |
| -intercept (C\textsubscript{0})     | 3.57           | | |
| Repeatability standard deviation    |                |           |            |
| -SRM                                | 2.05           | ≤ 6.59    | yes        |
| -AM                                 | 1.84           | ≤ 6.59    | yes        |

Table 5. Test of equivalency of FTIR to EN 14791 (IC-method) across a concentration range of 0–800 mg/m\textsuperscript{3}(n).

| Verification tests                  | Value obtained | Criterion | Conclusion |
|-------------------------------------|----------------|-----------|------------|
| Systematic deviation                |                |           |            |
| -correlation coefficient (r)        | 0.9988         | r ≥ 0.97  | yes        |
| -slope (C\textsubscript{1})         | 1.04           | 0.92 ≤ C\textsubscript{1}≤ 1.08 | yes        |
| -intercept (C\textsubscript{0})     | -0.577         | | |
| Repeatability standard deviation    |                |           |            |
| -SRM                                | 6.06           | ≤ 16.31   | yes        |
| -AM                                 | 3.55           | ≤ 16.31   | yes        |

Table 6. Test of equivalency of UV-Fluorescence (with dilution probe) to EN 14791 (IC-method) across a concentration range of 0–800 mg/m\textsuperscript{3}(n).

| Verification tests                  | Value obtained | Criterion | Conclusion |
|-------------------------------------|----------------|-----------|------------|
| Systematic deviation                |                |           |            |
| -correlation coefficient (r)        | 0.9996         | r ≥ 0.97  | yes        |
| -slope (C\textsubscript{1})         | 0.96           | 0.92 ≤ C\textsubscript{1}≤ 1.08 | yes        |
| -intercept (C\textsubscript{0})     | 0.975          | | |
| Repeatability standard deviation    |                |           |            |
| -SRM                                | 6.19           | ≤ 16.94   | yes        |
| -AM                                 | 1.67           | ≤ 16.94   | yes        |

Table 7. Test of equivalency of NDIR-analyzers (with chiller and with permeation dryer) to EN 14791 (IC-method) across a concentration range of 0–800 mg/m\textsuperscript{3}(n).

| Verification tests                  | Value obtained | Criterion | Conclusion |
|-------------------------------------|----------------|-----------|------------|
| Systematic deviation                |                |           |            |
| -correlation coefficient (r)        | 0.9993         | r ≥ 0.97  | yes        |
| -slope (C\textsubscript{1})         | 1.005          | 0.92 ≤ C\textsubscript{1}≤ 1.08 | yes        |
| -intercept (C\textsubscript{0})     | -9.394         | | |
| Repeatability standard deviation    |                |           |            |
| -SRM                                | 6.19           | ≤ 16.90   | yes        |
| -AM                                 | 14.52          | ≤ 16.90   | yes        |
component has high solubility in water, as for example in the case of \( \text{SO}_2 \) and \( \text{NO}_2 \).

It is also seen that the AMs usually seem to have a better repeatability than the wet-chemical based SRM, EN 14791, with the exception of the NDIR-based measurement set-up. This same phenomenon has been observed also in earlier studies (Coleman et al. 2015).

Based on these measurements and their results, the data demonstrated that the tested Alternative Methods (FTIR, UV-fluorescence, and NDIR) could be used instead of the existing wet-chemical SRM to measure \( \text{SO}_2 \), thus providing real-time data on the measured source. It must however be emphasized that when measuring water-soluble gases, such as \( \text{SO}_2 \), the choice of suitable conditioning technique is critical in order to minimize losses of the studied component in the condensate. The measurer must always test the conditioning method that is going to be used in order to ensure that it is fit for its purpose.

Field study at a plant combusting bark

Experimental

Tests were carried out at a plant located in eastern Finland in January 2018. Bark, sludge from wastewater treatment facilities, and sometimes also coal are combusted in this plant. Its thermal power is 160 MW and production of steam 60 kg/sec.

Emission measurements were performed at the measurement platform, which was located at a height of 50 meters. Stack height was 120 meters. As flue gas cleaning system the plant had electrostatic precipitator (ESP). Flue gas temperature was typically around 160°C.

The aim of this field study was to test different conditioning units for portable automated measuring systems for \( \text{SO}_2 \).

Homogeneity of the flue gas was tested before the measurements according to the principles given in EN 15259 (CEN 2008). Flue gas is assumed to be homogeneous for an individual measurand, if the actual value varies only over time but not over the measurement plane.

For the tests of homogeneity, two probes were installed in the flue channel, one for the reference measurement of \( \text{O}_2 \) at a fixed point in the measurement section and the other for the grid measurement of \( \text{O}_2 \). Grid measurement was performed and at the same time measurements at the fixed point and \( \text{O}_2 \) results were recorded. Standard deviation of the grid measurements \( s_{\text{grid}} \) was 0.83 and standard deviation of the reference measurements \( s_{\text{ref}} \) was 0.77. With these values, the calculation for homogeneity was performed and it was ascertained that the flue gas was homogeneous at the measurement plane.

Environmental conditions at the measurement site were typical for Finland during winter. The temperatures were around +1°C, and therefore extra heating was needed to maintain the analyzers at ideal environmental temperatures.

The measurement techniques that were used to measure \( \text{SO}_2 \) emissions were:

- Fourier-transform Infrared (FTIR) Spectroscopy analyzer Gasmet Dx4000, analysis as hot and wet
- Non-dispersive infrared analyzer (NDIR), Horiba PG-350 with chiller (M&C, model PSS-5)
- Non-dispersive infrared analyzer (NDIR), Horiba PG-250 with permeation dryer (Perma Pure Mini-GASS MG-2812T)
- UV-fluorescence analyzer, Teledyne Monitor Labs ML T100, with dilution probe (EPM, model 300)

Sampling was performed using a heated probe and ceramic filter (by Paul Goethe) and the sample gas flow was divided between three analyzers: FTIR, NDIR with chiller and NDIR with permeation dryer. The sample for the UV-fluorescence analyzer was taken with a separate dilution probe.

In Finland, many emission measurement laboratories use dilution probes, and therefore it was decided also to perform the tests with a dilution probe. The dilution probe dilutes the sample gas with dry and clean ambient air and the pollutant concentrations are measured with ambient air analyzers. It must be noted, however, that the diluted result is given as wet, so the user must also know the moisture concentration in order to convert the results to dry concentrations. The UV-fluorescence analyzer had its own dilution probe as a sampling probe.

Since the plant holds a permit as a co-incineration plant, it has an AMS analyzer to measure continuously the following gaseous components: \( \text{NO}_x \), \( \text{SO}_2 \), \( \text{CO} \), TVOC, HCl, and HF. For this purpose, the plant uses an AMS analyzer based on Fourier Transform Infrared Spectroscopy, FTIR, for the measurement of its emissions. This FTIR is manufactured by MKS and its model is MG2030.

The \( \text{SO}_2 \) emission limit value (ELV) for this co-incineration process is 175 mg/m\(^3\)(n) given as a daily average. Typically, however, the concentrations are well below this ELV, average levels being around 10–25 mg/m\(^3\)(n). It was agreed with the plant operators that they would add coal to their process periodically in order to create variable \( \text{SO}_2 \) levels during this test period.
Results

SO\textsubscript{2} concentrations were calculated as 30 min averages, mg/m\textsuperscript{3}(n), given as dry gas.

Variation of SO\textsubscript{2} concentrations during the measurement campaign measured with FTIR technique is presented in Figure 3. In Figure 4 the SO\textsubscript{2} concentrations measured with different analyzers and conditioning techniques are shown.

An example of measured SO\textsubscript{2} concentrations as half-hourly averages, measured with different techniques on 17.1.2018, is shown in Figure 5.

As can be seen from Figures 4 and 5, NDIR with chiller gave remarkably lower results than analyzers with other conditioning techniques. Typically, either FTIR (analysis as hot and wet) or UV-fluorescence with dilution probe gave the highest concentrations, their ratio being dependent on the concentration.

As was mentioned before, ambient temperatures during the measurement campaign were low. Due to the cold temperatures, there were some breaks in the operation of both permeation dryer and chiller, which can be seen from Figure 4. On the other hand, UV-fluorescence with
NDIR with chiller, FTIR and UV-fluorescence with dilution probe had almost identical similar response times, although as can be seen from Figure 5, NDIR with permeation dryer had the slowest response time.

**QAL2 functions**

The calibration functions for the plant’s FTIR (Automated Measuring Systems) according to the QAL2 procedure given in the European standard EN 14181, Quality Assurance of Automated Measuring Systems, were calculated using the results obtained with the studied P-AMS. Plant owners must use only calibrated values when reporting their emissions to the authorities, and therefore use of the correct QAL2 calibration function is important.

Calculated QAL2 calibration functions are shown in Figure 6. In Table 8, in addition to this, also valid calibration ranges as well as results for the variability tests are presented.

As can be seen from Figure 6 and Table 8, there were differences in the calculated calibration functions, as well as in the valid calibration range. However, the AMS passed the variability test with all P-AMS results.

The same phenomena can be seen from the QAL2 calibration functions as was observed during the test bench tests, i.e. that the results of NDIR with chiller are lowest, only about 40% to 50% of the highest measured value during this field study. As a consequence, if the calibration function for AMS would have been calculated using the results of NDIR with chiller, the emissions the plant is reporting to the authorities would have been much lower.

**Figure 5.** SO₂ concentrations measured with FTIR, NDIR with chiller, NDIR with permeation dryer and UV-fluorescence with a dilution probe, 17.1.2018.

**Figure 6.** QAL2 calibration functions (according to EN 14181) for AMS for SO₂, calculated with different measurement set-ups.
lower than if the QAL2 function had been calculated using the results from other P-AMS.

### Conclusion

During the laboratory tests, it was shown that the tested Alternative Methods (FTIR, UV-fluorescence with dilution probe, NDIR with chiller/permeation dryer) all meet the test criteria given in CEN/TS14793 for the range 0–800 mg/m³(n). All other AMs but NDIR also meet the criteria for the lower range, 0–200 mg/m³(n). The reason for NDIR not passing the criteria in the lower range is due to the SO₂ losses in the chiller’s condensate. Thus, most probably if both NDIRs had been equipped with permeation dryers instead of a chiller, they would both have passed these tests for the lower range.

During the field study, the same Alternative Methods were used to measure flue gases from a plant combusting bark. The same phenomena were observed in these tests as in the laboratory tests, meaning that the measurement setup with NDIR and chiller gave the lowest results.

These data demonstrated that the tested alternative techniques (FTIR, UV-fluorescence, and NDIR) could be used instead of the standard reference method EN 14791, which is based on wet-chemical sampling, thus providing real-time calibration of automated measuring systems. It must however be emphasized that when measuring water-soluble gases, such as SO₂, the choice of suitable conditioning technique is critical in order to minimize losses of the studied component in the condensate.

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**Table 8. QAL2-calibration functions, valid calibration ranges and results of variability tests, calculated using the results of different analyzers with different conditioning techniques, 16.-18.1.2018.**

| Analyzer | Calibration function, \( y = a + bx \) (at AMS condition) | Valid range of the calibration function, mg/m³(n) | Variability test, value should be \(< 13.2 \text{ mg/m³(n)}\) | 6% O₂ | 6% O₂ |
|----------|------------------------------------------------------------|--------------------------------------------------|--------------------------------------------------|-------|-------|
| FTIR     | \( y = -1.25 \text{ppm} + 1.66 \times x \)               | 202                                              | 11.2                                             | OK    |       |
| NDIR + permeation | \( y = -0.18 \text{ppm} + 1.28 \times x \) | 158                                              | 12.4                                             | OK    |       |
| NDIR + chiller | \( y = 1.04 \text{ppm} + 0.60 \times x \) | 79                                               | 9.8                                              | OK    |       |
| UV-fluorescence + dilution probe | \( y = 0.49 \text{ppm} + 1.50 \times x \) | 188                                              | 10.6                                             | OK    |       |

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