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Regulatory position paper on sulphur dioxide monitoring, comparing portable-instrumental techniques with manual methods

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Summary

This position paper describes the UK perspective and in particular, the Environment Agency's (EA) approach to specifying requirements for monitoring sulphur dioxide (SO_2), describing the EA's experiences with both instrumental and manual methods.

Many industrial processes have emission limit values for SO_2. These 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, in order to apply a risk-based approach and to ensure an appropriate level of quality of monitoring.

Practically, this means achieving a measurement uncertainty that takes into account the environmental risks posed by the industrial process and the regulatory requirements. Using either manual or instrumental methods for SO_2 monitoring provides this flexibility and pragmatism. Therefore the Environment Agency has always permitted test laboratories to use both types of technique to measure SO_2, with the caveat that the test laboratories must be accredited to ISO/IEC 17025 and the applicable Monitoring Certification Scheme (MCERTS) performance standards, with appropriate monitoring standards and methods in their scope of accreditation.

When examining the QAL2 and Annual Surveillance Test (AST) reports required by EN 14181, as well as periodic compliance-reports, there is a clear preference amongst test laboratories for instrumental methods, rather than using the wet-chemistry manual-method.

The EA's strategy has been to require international and national standards for monitoring, using a hierarchy of standards that the European Commission now considers as Best Available Techniques (BAT) for monitoring. In addition to specifying standards for monitoring and quality assurance, the EA also routinely audits test laboratories using two types of audits. These are: unannounced field-audits, similar to those used by national accreditation bodies, and; desktop audits of monitoring reports, specifically those for the periodic compliance-monitoring of SO_2 emissions as required by a permit, and QAL2/AST reports required by EN 14181.

Our main findings are as follows:

- Instrumental techniques and manual methods for monitoring SO_2 are both necessary and complementary. No single technique, method or instrument is better than any other, whilst a technique suited to one installation can be inconvenient for another.
- Instrumental monitoring was initially popular in the UK, as well as some other EU Member States, because of its perceived simplicity, advantages and convenience. That said, achieving the required level of uncertainty requires careful management of the technique, whilst audits of both test reports and test laboratories in the field reveals common problems that can be easily eliminated.
- Although instrumental techniques were initially very popular, there has been a resurgence in the use of the manual, wet-chemistry Standard Reference Method (SRM), EN 14791. As a result, most test laboratories use both the SRM and portable instrumental-techniques applied through Alternative Methods (AMs). That said, instrumental methods are by far the most popular.
- An analysis of audits of QAL2 and AST reports indicates that there was not a significant difference between the permanently-installed Automated Measurement Systems (AMS) results; and those from the SRM or AMs. The latter are the EA's methods described in Technical Guidance Note (TGN) M21 (Typically NDIR or UV-based portable instrumental-techniques) and TGN M22 (FTIR-based portable instrumental-technique). In approximately half the results, the AMS results were higher whereas this was reversed in the other half of the examples. The SRM results were higher as an average by approximately 10% across all sites, but this difference was not statistically significant.

1. The Environment Agency's strategy for monitoring, when applied to measurements of SO_2

1.1 The Environment Agency's position on monitoring

There are two facets of the EA's strategy for monitoring that are relevant to the SULF NORM project. Firstly, the EA sees a strong benefit in portable instrumental-techniques for periodic monitoring, such as real-time readings and the ability to characterise short-term variations in SO_2 concentrations relative to changes in the industrial process. Secondly, the EA has always specified the standards hierarchy for monitoring, i.e. to use CEN standards where these are available and suitable, and then ISO, national, and other native national or international standards. The latter could include VDI and USEPA methods for monitoring, as well as the Environment Agency's TGN M21 and TGN M22.

The EA has applied these standards through permit conditions and through MCERTS, which uses a framework of accreditation standards, standards for monitoring, and supplementary specifications to provide quality assurance and control. Additionally, if there were gaps in any standards – such as personnel certification for the competency of test-laboratory staff performing emissions - then the EA developed and applied specific MCERTS standards until EN standards become available.

Before CEN published the manual, wet-chemistry method EN 14791 for SO_2 monitoring, test laboratories in the UK used the following two standard methods:

- ISO 7935 as a basis for a method employing a portable instrumental-technique. This ISO standard describes performance requirements for an instrumental system, together with requirements for use and quality assurance/quality control (QA/QC). The QA/QC requirements within ISO 7935 include functional tests and drift requirements.

  The scope of ISO 7935 can be applied to both permanently-installed AMS and portable instrument-techniques. When CEN published EN 15267-3, this conflicted with several parts of ISO 7935; therefore EN 15267-3 superseded ISO 7935.

- ISO 7934 as a wet chemistry method. This is very similar in principle to EN 14791 and was therefore superseded by the CEN standard.

EN 14791 was clearly a direct replacement for ISO 7934, whilst this standard is still current in countries which are not members of CEN. However, although EN 15267-3 superseded ISO 7935, the ISO standard had a wider scope. In simple terms, EN 15267-3 specifies performance characteristics and test procedures for AMS, although before the development of EN 15267-4, it was adapted for testing portable instrumental-techniques. ISO 7935, on the other hand, includes performance characteristics and test requirements for instruments that measure SO_2, but additionally includes procedural requirements for use, together with associated provisions for QA/QC.

In other words, ISO 7935 readily provided a strong foundation for an AM using portable instrumental-techniques, whereas EN 15267-3 does not. This left a gap in available standards for the periodic monitoring of stack emissions using a portable instrumental-technique. Therefore the EA worked with an industry trade-association, the Source Test Association (STA, www.s-t-a.org), to develop and produce an instrument-based AM for SO_2, TGN M21. The STA's members include test laboratories, process operators and instrument manufacturers. TGN M21 is now one the EA's two AMs for the periodic monitoring of SO_2 using portable instrumental-techniques.

Additionally, in England and in other countries which apply the MCERTS standards, test laboratories using FTIR-based systems are required to apply TGN M22, which is now the EA's prescribed AM for periodic monitoring using transportable FTIR.

When comparing TGN M21 and TGN M22, the former standard is specifically for monitoring SO_2, whereas TGN M22 applies to SO_2 and any other determinands that an FTIR can measure, as long as the measurements meet the performance requirements specified in TGN M22.

The scope of the TGN M21 is not restricted to any particular instrumental-technique as TGN M21 specifies performance characteristics and QA/QC requirements for any instrumental-technique that the test laboratory chooses to use and that is capable of meeting the performance requirements. For example, common techniques for SO_2 include NDIR and UV-based systems. If a test laboratory chooses to use a FTIR-based instrumental-system and apply TGN M21, then the test laboratory must also apply the QA/QC requirements of the ASTM or the applicable USEPA methods for FTIR, e.g. USEPA Method 320.

Similarly, EN/TS 17021 includes provisions for all instrumental-techniques that meet the performance requirements. If a test laboratory uses FTIR-based systems, then the laboratory must also satisfy the QA/QC requirements of the CEN TS which is being developed by CEN TC 264 WG26.

1.3 Terminology

It is worth noting that different standards and methods use varying terminology, depending on their scope. For example, a *portable instrumental-technique* is equivalent to the term *Portable Automated Measuring System* (P-AMS), used in EN 15267-4. Additionally, the term *permanently-installed instrumental-techniques* and *Continuous Emissions Monitoring Systems* (CEMs) are equivalent to the term Automated Measuring System (AMS), EN 15267-4 and EN 15267-3 provide for type-testing and certification for P-AMS and AMS, respectively.

For example, in the case of P-AMS for carbon monoxide (CO), EN 15267-4 specifies performance requirements and test procedures used for type-testing and certification of the P-AMS. Following this, if an instrument meets the performance requirements in EN 15267-4, then the SRM for CO, EN 15058, provides for the ongoing QA/QC throughout the operational lifetime of a P-AMS for CO. EN 15058 specifies functional tests that a test laboratory must perform during each measurement campaign and also at specified intervals such as annually, in order to give confidence that the P-AMS is performing to the tolerances specified on its type-testing certificate.

In the case of SO_2 monitoring, the scope of EN15267-4 would apply to techniques such as NDIR, UV-based systems and FTIR used as P-AMS, whilst ongoing QA/QC would then be carried out under EN/TS 17021, TGN M21 or TGN M22 as appropriate. Similarly, an AMS for SO_2 AMS would be tested and validated under EN 15267-3; following this, the ongoing QA/QC would be performed according to EN 14181, together with either the SRM for SO_2, or an accredited AM.

1.4 Application through permits according to Article 14 of the Industrial Emissions Directive (2010/75/EU)

All permits for installations in England regulated under the Industrial Emissions Directive (IED) state that monitoring must be MCERTS accredited or certified where applicable. Therefore for test laboratories measuring SO_2 with instrumental methods, this means that the test laboratories' scope of accreditation must include the following:

- Accreditation to EN ISO/IEC 17025, EN ISO/TS 15675, EN 15259 and the MCERTS performance standards for manual stack-emissions monitoring for test laboratories and personnel.
- TGN M21 and/or TGN M22 must be within the scope of accreditation.
- Portable instrumental-techniques must be certified to at least Annex F of the MCERTS performance standards for continuous emission monitoring systems, or to all the requirements for permanently installed AMS (i.e. meet the requirements of EN

15267-3). In the next two years, the MCERTS performance standards will be revised to provide for the requirements of EN 15267-4, which refers to portable instrumental-techniques as Portable-AMS.

1.5 TGN M21 for monitoring SO_2 using instrumental methods

TGN M21 is very similar to the instrumental SRMs such as EN 15058, produced by CEN TC 264 WG16. TGN M21 itself is based on EN 15058 for measuring carbon monoxide. As such, it includes performance specifications for the transportable AMS used in TGN M21, procedures for performing the measurements, provisions for quality assurance and quality control, and an uncertainty budget.

TGN M21 does not specify any particular type of technique for the transportable AMS, but instead specifies performance requirements for the complete transportable AMS. Therefore although test laboratories typically use NDIR-based instruments when using TGN M21, there are some test laboratories which use NDUV-based transportable AMS.

TGN M21 has been accepted by the EA as equivalent to EN 14791 on the basis of test data acquired in accordance with the Technical Specification for equivalency of AMs current at the time, CEN/TS 14793.

2. Experiences with TGN M21

When TGN M21 was published, test laboratories rapidly adopted it, such that it became the dominant method for SO_2 monitoring. Also, as a growing number of test laboratories were purchasing and using transportable FTIR, the EA, STA and National Physical Laboratory collectively produced TGN M22 to specify performance requirements for the FTIR, together with procedures for monitoring, and quality assurance/control. Today, test laboratories commonly use all three methods, i.e. TGN M21, TGN M22 and EN 14791 for measuring SO_2.

2.1 Results of field audits of test laboratories

Every MCERTS-accredited test laboratory must have at least one audit by the United Kingdom Accreditation Service (UKAS) annually. Additionally, the EA performs unannounced audits too. As these audits can happen anywhere at any time, the EA has found that these additional audits help to maintain the quality of the monitoring.

Regarding typical non-compliances, the most common of those found has been that test laboratories use an inappropriate concentration of span gas during the QA/QC checks of the transportable AMS. However, one test laboratory began to routinely use a gas blender so that the span gas was always at the appropriate concentration. Therefore the EA recommends that test laboratories should also use a gas blender for span checks.

Another observation is that according to TGN M21, test laboratories typically use a dry gas when calibrating the AMS and when performing span checks. Although a wet gas is not required, it can improve the quality of the calibration when there are potential losses in the sampling system. This can result in a negative bias and this will be explored in the final sub-section.

Based on test reports for routine periodic monitoring and for QAL2/AST exercises, a quick scan of the data, coupled with simple statistical-tests, suggests that test laboratories can usually meet the uncertainty requirements specified by legislation. This is reflected, for example, in both the data and the graphs of the AMS results versus test-laboratory measurements. Work elsewhere under SULF NORM is examining proficiency testing-data to better understand the 'real-world' capabilities of EN 14791 and TGN M21; therefore it is recommended that further work explores this correlation further, and quantifies the uncertainties of the SRM and EN/TS 17021.

2.2 Audits of QAL2/AST reports

The Environment Agency examined QAL2 and AST reports for the past two years. Within these reports, test laboratories predominantly used instrumental methods, i.e. FTIR, NDIR and NDUV.

Regardless of the instrumental technique used, the average test laboratory results were slightly higher than those of the AMS, but not significantly so; the overall average was 10% higher for the SRM results when considered as a group, but the difference was not significant. In half of the reports examined, the AMS results were higher than those of the SRMs and lower in the remaining reports.

That said, when there has been a significant difference in individual reports, the SRM results are typically lower than those of the AMS. On a further examination, audits have suggested errors in applying the instrumental methods, which in turn can lead to a negative bias in the SRM readings.

3. Recommendations

- Test laboratories should use gas blenders when performing calibration and span checks, in order to produce the ideal concentrations of test gases. Additionally, the benefits of using moistened test-gases needs consideration.
- The SULF NORM project team should perform a comparison of span checks through the sampling system of a transportable AMS, using both dry gas and wet gas, in order to determine whether there are losses of SO_2 in the sampling system when the test gas is in the presence of moisture.
- The SULF NORM project team should determine whether spiking with SO_2 during measurements has an effect on the calibration of the transportable AMS.
- The SULF NORM project team should determine the uncertainties of the portable-instrumental techniques when using EN/TS 17021, and compare these with those of the SRM EN 14791, in order to determine whether there is a robust correlation between the SRM and AM.

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