An investigation into the use of EN 14791 for the determination of mass concentration of sulphur dioxide in stack emissions

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1. Introduction

BS EN 14791[1] is the European standard reference method for the measurement of SO_2 concentrations in stacks gases.

The standard is used for periodic regulatory compliance monitoring and for calibration of continuous emissions monitoring systems (CEMs).

Several monitoring organisations have raised concerns about the use of this method. In particular the repeatability of the method. An investigation was carried out to determine the reason why the repeatability of the standard may be poor and to see what measures could be put in place to improve it.

2. Measurement principle of BS EN 14791

The standard requires a representative sample of stack gas to be extracted from a stack using a heated temperature controlled probe. The sample is filtered and drawn through absorbers for a specified time at a controlled flow rate. The absorbers contain H_2O_2 (usually 0.3%) absorber solution. The SO_2 in the sampled gas is absorbed in the solution and becomes sulphate ions. The mass concentration of sulphate in the absorber solutions is determined using ion chromatography.

BS EN 14791 has several quality assurance (QA) criteria that must be met in order to comply with the standard. A key QA criterion is placed on the efficiency of the absorber solution. The standard specifies that two absorbers containing solutions are placed in parallel. The absorber efficiency of the first absorber must be better than 95% (i.e. a minimum of 95% of the sulphate solution must be in the first absorber and a maximum of 5% must be in the second). Its good practice for the absorber efficiency to be checked for each test carried out.

3. Scope of investigation into BS EN 14791

Stack emission monitoring organisations have raised concerns about obtaining repeatable measurements using BS EN 14791.

For example, one testing laboratory carried out identical tests but found that the capture efficiency on one measurement was acceptable but on the other it did not meet the criteria.

The Source Testing Association (STA) carried out a desk based study into the use of BS EN 14793.

During the study a number of laboratories that had MCERTS accreditation for BS EN 14791 were contacted to find out their experiences of using the standard.

Also, several analytical laboratories that carry out analysis of samples, collected using BS EN 14791, were contacted.

Besides contacting UK based companies, a French testing laboratory (INERIS) was also contacted. This laboratory was contacted because it was involved in interlaboratory tests of the analysis part of BS EN14791.

The information collected from the laboratories was used to investigate the application of BS EN 14791, to re-enforce good practice and suggest improvements to the standard.

4. List of laboratories contacted during the investigation

The following testing laboratories were contacted during the investigation:

- Aspen Environmental
- Bureau Veritas
- CES Environmental Instruments
- Cirrus Environmental Solutions
- Corus Research, Development & Technology
- Emco Air Quality Consultants
- ESP Environmental
- Northumbrian Water (AES)
- RPS Consultants
- REC
- Environmental Evaluation
- Alcontrol
- Scientifics

Throughout this report laboratories that carry out sampling are referred to as testing laboratories. The laboratories that analyse the samples are referred to as analytical laboratories.

5. Measurement uncertainty for analysis of sulphate

One of the possible causes of not being able to meet the capture efficiency may be due to problems with the analysis of samples and application of the associated measurement uncertainty.

A test laboratory provided the following example

- a test may have 94% sulphate in the first absorber and 6% in the second, which means the test is invalid. However, by applying an uncertainty for the analysis, the capture efficiency may be in range of 91.9 - 95.6%, which means the absorber efficiency ranges between a valid and invalid result.

The measurement uncertainties provided by four UK analytical laboratories, for the analysis of sulphate, varied from 5 to 13%. Table 1 shows the measurement uncertainties for these laboratories. All the laboratories held UKAS accreditation for the analysis according to BS EN 14791.

Table 1: Measurement uncertainty for sulphate analysis

UKAS accredited UK analytical laboratory	Uncertainty %
Laboratory W	7
Laboratory X	13
Laboratory Y	5
Laboratory Z	5

INERIS provided information on a French intralaboratory test. It had 18 participants who were required to analyse two samples with different sulphate concentrations. Table 2 shows a summary of the results of these tests.

Table 2 Results of French intralaboratory tests

Sulphate concentration (mg/l)	Measurement uncertainty (%)
6	15
30	8

As expected the solution with the higher concentration of sulphate has a lower measurement uncertainty. The measurement uncertainty is similar to that reported by UK laboratories.

6. Contamination of analysis

Evidence was provided by a test laboratory that contamination may occur during the analysis of absorber solutions, when sampling stack gas emissions with SO_2 concentrations of several hundred mg/m^3.

A test laboratory provided the following information:

- the first absorber had a SO_2 concentration of 3000 mg/l. The blank for the test failed the criteria for a blank (i.e. less than 10% of the ELV). The blank was reanalysed, which gave a result of <0.1 mg/l. It became apparent that the failed blank was analysed after the first absorber solution had been analysed. The analytical laboratory believed this could have caused contamination of the blank sample.

It is possible that similar cross contamination could occur when analysing the second absorber after the first absorber. This could affect the capture efficiency.

7. Reliability of analytical results

As part of a previous Environment Agency project[2] a testing laboratory took a series of sulphate samples and split each sample in half. Two UKAS accredited analytical laboratories analysed one half of the sample each. Table 4 shows the results of this trial. The trial showed an average difference of 15% between the results from the two laboratories.

Table 4 Results of split absorber solutions

Lab 1 result	Lab 2 result	% difference
166	163	1.8
173	149	13.9
292	241	17.5
307	251	18.2
3.4	2.8	17.6
3.2	2.7	15.6
28	22	21.4
27	22	18.5
Average % difference		**15.6**

8. Types of sample trains used

BS EN 14791 recommends that absorbers of typically less than 250 ml volume are used. It also recommends a stack gas flow rate of 2 – 3 litres / minute through the absorbers.

A review of how testing laboratories apply BS EN 14791 in the UK highlighted that two different approaches were used. These approaches are based on the following different types of sample train:

- mini-sample train
- US EPA method

The mini-sample train is based on the requirements specified in BS EN 14891, as it typically uses 250 ml absorbers and extracts stack gas at 2 – 3 litres / minute.

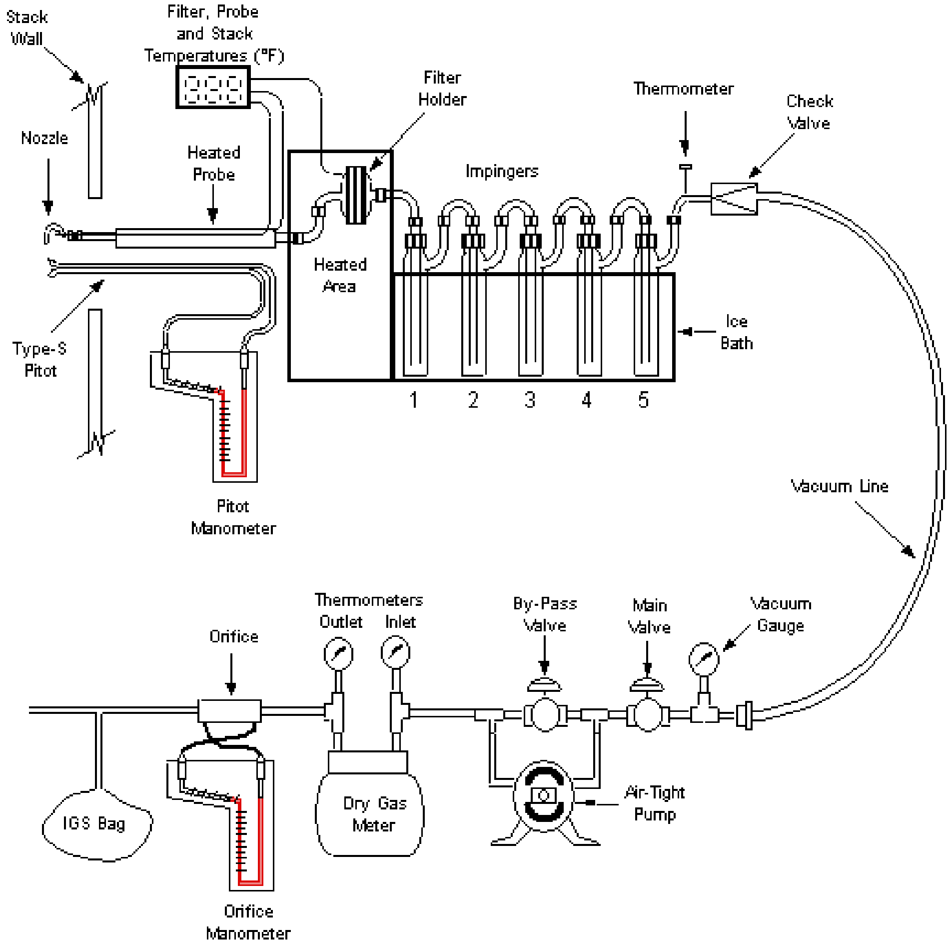
The US EPA equipment uses a full size “method 5 style” particulate train. The stack gas is extracted through 1000 ml absorbers at a typical flow rate of 20 litres / minute. To compensate for the greater volume of stack gas sampled a larger volume of absorber solution is used.

Testing laboratories believe both approaches are acceptable provided the absorber capture efficiency is met.

9. Addition of a third absorber

BS EN 14791 specifies the use of two absorbers in series. However, to help ensure the absorber capture efficiency is met a third absorber can be added to the series of absorbers. If a third absorber is used the first two are combined and compared to the third. The third must have less than 5% of the total sulphate.

Figure 1 shows a typical sample train with an additional absorber added.



Key
Absorbers 1,2 and 3 H_2O_2 solution
Absorber 4 empty
Absorber 5 Silica gel

Figure 1: example sample train for BS EN 14791, with an additional absorber

10. Tests to ensure consistent results

A testing laboratory reported that after carrying out in-house testing they found that absorber solutions deteriorated after two weeks. It did not have an effect on the absorber collection efficiency but it did result in lower concentrations than expected. As a result, the test laboratory make-up the absorber solution on the same day as the test.

They also found using ice to keep the absorbers below 20^{o}C helped ensured consistent analysis results.

11. Conclusions

The report shows the following:

- measurement uncertainties for sulphate analysis are between 5 – 13%.
- the measurement uncertainty can affect the capture efficiency.
- contamination between samples during the analysis can occur.
- analysis of identical sulphate samples varies by 15%.
- two types of sample trains are commonly used, one with a high flow rate (typically 20 litres / minute) and one with a low flow rate (typically 2 – 3 litres / minute).
- keeping the absorber temperature below 20°C helps ensure the absorber efficiency is met.
- the addition of a third absorber containing absorber solution helps ensure the absorber efficiency is met.
- the absorber solution should not be kept for more than two weeks prior to use.

12. Recommendations

A further investigation into anomalies with the analysis of sulphate should be carried out. In order to progress this a meeting has been arranged between the Environment Agency, STA,UKAS and several analytical laboratories.

A Method Implementation Document should be produced to help ensure that BS EN 14791 is implemented consistently by MCERTS accredited monitoring organisations. It should:

- allow the analytical measurement uncertainty to be applied when calculating the absorber capture efficiency.
- allow the use of sample trains with relatively high flow rates (typically 20 litre / minute), provided its demonstrated that the absorber efficiency is met
- ensure the absorbers are kept below 20°C.
- allow the addition of a third absorber containing absorber solution.
- specify that the absorber solution is used within one week of being prepared.

13. Feedback on this report

If you have any comments on this report please contact Rupert Standring at rupert.standring@environment-agency.gov.uk

14. Bibliography

1. BS EN 14791 EN 14791:2005 – Stationary source emissions - determination of mass concentration of sulphur dioxide – Reference method.

2. Validation of an Alternative Method for the measurement of SO_2 emissions using instrumental methods, National Physical Laboratory, June 2008.