Report

Evaluation of Methodologies to Test Losses of Gases to Sampling Systems

Report to Department for Environment, Food and Rural Affairs, Welsh Assembly Government, The Scottish Executive and Department of the Environment in Northern Ireland

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Executive Summary

netcen has undertaken a short study to devise and evaluate methodologies to assess losses of gases to sampling systems.

The study was commissioned by Defra and the Devolved Administrations, to determine whether tests could be undertaken reliably, accurately and cost-effectively in light of proposed performance requirements laid down in future EC Legislation.

The study was undertaken in two stages: to devise a successful methodology under laboratory conditions, and to evaluate this in the field at a number of representative sites.

Earlier studies have shown that significant quantities of nitrogen dioxide and sulphur dioxide can be removed by sampling systems, prior to analysis by the instruments on the site. This could have implications for data quality, as reported concentrations may be substantially lower than under ambient conditions.

Test apparatus was evaluated in the lab, using a clean fluorocarbon manifold system, using NO_2 and SO_2 test gases. Once the parameters for introducing the gases were optimised, losses of less than 1% were observed.

The test system was then taken out to three UK monitoring stations, each with a different sampling methodology, to determine whether the apparatus could be used successfully in the field. For this section of the study, only NO_2 losses were evaluated. The manifolds had been exposed to ambient air for between 3-6 months, and showed losses ranging from less than 1% to nearly 12%.

The study has effectively demonstrated that it is possible to evaluate the performance of sampling systems in the field; reliably, accurately and cost-effectively. This report presents the results of the development work and discusses recommendations for further development to ensure compliance with any future EC Directives.

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1 Introduction

Within the United Kingdom, automated continuous air pollution measurements are made at approximately 120 monitoring stations in the Automatic Urban and Rural monitoring Network (AURN), on behalf of defra and the Devolved Administrations in Wales, Scotland and Northern Ireland. These monitoring stations benefit from a comprehensive programme of quality assurance and control. This programme ensures that the data produced by the analysers are of sufficient quality to be used for public information, research, and determination of compliance with Air Quality Strategies and EC Directives.

However, one aspect of the overall performance of a monitoring station that has not yet been regularly assessed is the ongoing performance of field sampling systems that deliver ambient air to air pollution analysers. It is possible that the sampling systems could remove significant quantities of pollutants from ambient air, before the analysers have a chance to measure them. This could have serious repercussions for data quality, as data that are reported may not accurately represent ambient conditions.

Studies carried out by the European Reference Laboratory of Air Pollution (ERLAP) Joint Research Centre (JRC) and subsequently Netcen and NPL have found that losses of acidic gases eg. NO_2 and SO_2 to the sampling system can be significant, and in some cases up to a third of the gas could be lost prior to analysis.

As part of the proposed CEN methodologies for operating an air pollution analyser, any losses to the sample delivery system must be quantified and minimised, in order for the overall Data Quality Objectives for a pollutant to be achieved.

Netcen has undertaken a programme of tests to investigate the possibility of undertaking reliable, cost effective field testing of sampling systems to ensure compliance with future EC legislation.

This report presents an overview of research undertaken to date, an indication of the likely future legislative requirements, and the results of a feasibility investigation undertaken by Netcen, to devise and field trial sampling system calibration methods.

2 Background

There are two main types of sampling systems used in UK monitoring stations;

- Those that use the analyser to draw air through a narrow fluorocarbon tube which is passed through the monitoring enclosure to the ambient air. Typically this system is used where there are only one or two analysers at a site.
- Those that use a fan to draw ambient air at high speed down a wide manifold tube. The analysers are connected to the end of this manifold using short lengths of narrow fluorocarbon tubing, and this type of system is best suited to multi-pollutant sites.

Information on where these systems are deployed was presented in the Summer 2003 intercalibration report.

The wide tubing used in the second system can be made of a number of materials. Historically, the tubing was constructed from aluminium and coated in PTFE, to render the surfaces inert to gases. Modern systems are constructed from fluorocarbon plastics, borosilicate glass or stainless steel.

A number of initial experiments have already been conducted (firstly by JRC in 1995), which identified that some types of sampling system were more prone to sample losses than others. Specifically, manifold systems that were constructed from PTFE-coated aluminium were found to remove significant quantities of sample gas (up to 33%), compared to either glass or fluorocarbon sampling systems. As a result of these findings, the older PTFE-coated aluminium manifolds in use in the UK were replaced with manifolds constructed from other materials (either fluorocarbon plastics or borosilicate glass).

While the JRC tests were very informative, the equipment required to undertake these tests was expensive and cumbersome (requiring a dedicated 3.5 tonne van to transport it).

For these reasons, smaller and more cost effective alternatives have been investigated by Netcen, to evaluate whether these could offer similar performance to the JRC test apparatus.

The tests will become necessary because future European legislation will require the performance of sampling systems to be evaluated and controlled. The CEN documents for operation of air pollution analysers; ISO14211 (NOx), ISO14212 (SO_2), ISO14626 (CO) and ISO14625 (O_3) all require that no more than 2% of the sample gas is lost to the sampling system. The performance of sampling systems will need to be tested when new sites are installed and a frequency of at least every three years thereafter (if less than 2% sample loss).

As yet, a date for the CEN requirements to become mandatory has not been agreed. However, developing a capability to undertake sampling system performance tests in the UK is a sensible precaution.

3 Evaluation of test systems

With these requirements in mind, Netcen undertook a manifold test development programme. The objective of the study was to evaluate the possibility of undertaking cost effective field tests of manifold systems using "everyday" technology, available off the shelf, and at low cost.

Tests were therefore restricted to two gases, NO_2 and SO_2. While it is possible to produce a test system to generate ozone, it will require purchase of additional apparatus, or modification of current equipment. As a result, testing sampling systems to evaluate losses of ozone was not considered at this stage.

Because of the unreactive nature of CO, any losses of this pollutant to a sampling system are likely to be much lower than any of the other three pollutants.

3.1 LABORATORY TRIALS

A series of laboratory tests were undertaken, to determine whether simple tests could be successful. The apparatus used was therefore basic: a cylinder, tedlar bag and connectors, and some flow measurement equipment. The apparatus is currently assembed as a prototype: if sampling systems are to be tested on a long-term campaign, it would need to be made more robust to survive regular transportation.

The apparatus was connected to a standard wide-bore fluorocarbon manifold and fan, to which a NOx and an SO_2 analyser were connected. Figure 1 below shows the schematic arrangement of the manifold test equipment.

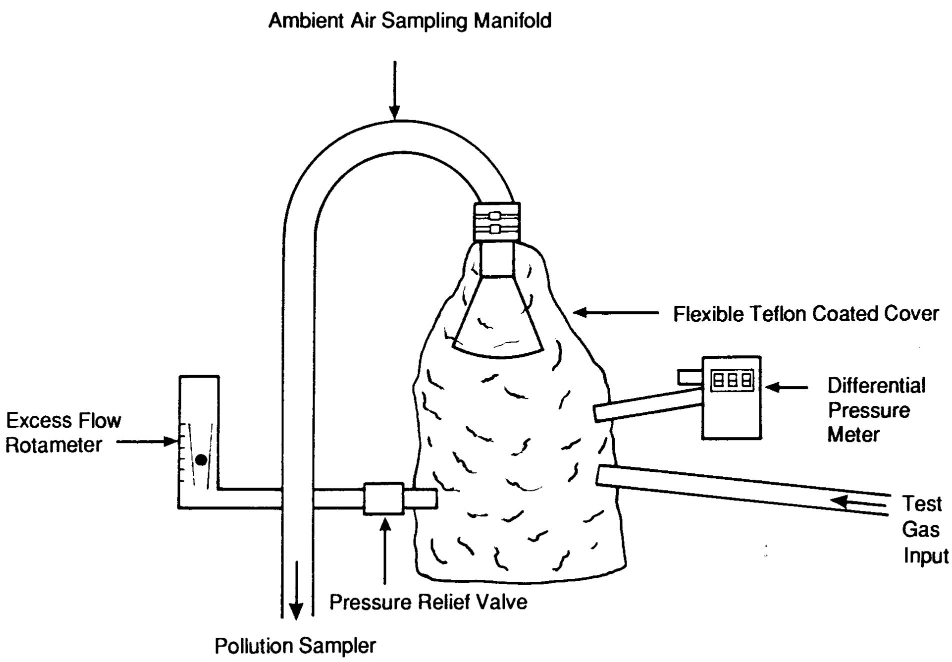

Figure 1 – Schematic diagram of test apparatus

The test programme was undertaken as follows:

The analysers were first calibrated as normal, using the test gas cylinder. These results were then used to compare against the other tests.

The analysers were then calibrated with gas passing through the tedlar bag only, to evaluate any loss of gas to the bag.

A series of different parameters were then applied to determine the most appropriate method to use to evaluate sample losses.

A typical manifold system in the UK has an air flow rate of between 2 – 5 litres per minute through it, and a differential pressure from ambient conditions of between 0.2 and 0.4 inches of water. The tests were set up to mimic these conditions as closely as possible.

A series of initial tests were undertaken on the SO_2 analyser at a range of flow rates, with the fan on, off and disconnected, as shown in Table 1 below:

Table 1 – Assessment of manifold performance under varying conditions

Calibration Parameters	SO_2 response, ppb
Fan off	
Flow set to 2.0 m/s	403
Flow set to 3.0 m/s	448
Flow set to 4.0 m/s	537
Flow set to 5.0 m/s	671
Fan disconnected	
Flow set to 2.0 m/s	404
Flow set to 3.0 m/s	451
Flow set to 4.0 m/s	549
Flow set to 5.0 m/s	680
Fan on	
Differential pressure set to 0.20 in H_2O	420
Differential pressure set to 0.25 in H_2O	422
Differential pressure set to 0.30 in H_2O	422
Differential pressure set to 0.35 in H_2O	424
Differential pressure set to 0.40 in H_2O	422

It was seen that the SO_2 analyser exhibited considerable response sensitivity as a function of the applied flow rate through the manifold, when the fan was turned off or disconnected. The experimentation above showed that this effect was minimised by leaving the manifold system running in normal operation and adjusting the output from the cylinder to match the “normal” differential pressure of the manifold system. This is contrary to the recommendation in the CEN Standards, which is to switch off the manifold fan during testing.

The CEN recommended method for calculating sample collection efficiency is presented in Annex 1.

Tables 2 and 3 below present the results using the flow optimised parameters.

Table 2 – Laboratory losses of SO_2 to manifold system

	Direct analyser calibration, ppb	Calibration through Tedlar Bag, ppb	Calibration through complete manifold, ppb	Manifold loss compared to Tedlar bag, %	Sampling system collection efficiency, %
SO_2 analyser	453.4	422.8	421.9	0.2	99.8

Table 3 – Laboratory losses of NO_2 to manifold system

	Direct analyser calibration, ppb		Calibration through Tedlar Bag, ppb		Calibration through complete manifold, ppb		Manifold loss compared to Tedlar bag, %		Sampling system collection efficiency, %
	NOx	NO	NOx	NO	NOx	NO	NOx	NO	NOx
NOx Analyser	199.6	0.9	188.7	1.7	187.9	1.9	0.4	-	99.6

Results obtained in the lab comparing the results through the tedlar bag with a clean manifold were encouraging and close to the repeatability limits of the analysers under test. However, the method is very wasteful of gas: one cylinder is good for only 1-2 tests.

These results suggested that it is possible to evaluate the performance of sample inlet systems in the field. The next stage in the evaluation was to determine the effectiveness of the apparatus with "real world" sampling systems.

3.2 FIELD TRIALS

A number of tests were undertaken on sampling systems at monitoring stations. In the first instance, tests have been undertaken using an NO_2 cylinder, purely to determine the feasibility of the tests. Manifold performance was evaluated on the following sites:

- A dirty glass manifold and fan at Aberdeen (six months since cleaning),
- A dirty fluorocarbon manifold and fan at Harwell (three months since cleaning),
- A dirty narrow tube system at Walsall Alumwell (six months since cleaning).

The tests on the manifold systems were undertaken in exactly the same way as the lab trials; ie

- calibration of the analyser as normal
- calibration of the analyser through the tedlar bag
- calibration of the analyser through the manifold by adjusting the cylinder flow to match the “normal” differential pressure in the manifold

For the narrow tube system at Walsall Alumwell, calibration gas was introduced directly into the dirty tube as well as into the analyser via clean tubing. There was no need to use a tedlar bag to fit around the inlet.

The table below presents the results of the tests:

Table 4 – Results of manifold tests in the field

	Direct analyser calibration, ppb		Calibration through Tedlar bag only, ppb		Calibration through complete manifold, ppb		Manifold loss compared to Tedlar bag, %	
	NOx	NO	NOx	NO	NOx	NO	NOx	NO
Aberdeen 14 Jan 04	274.1	6.9	259.9	4.9	257.7	16.7	0.8	-
Walsall Alumwell 22 Mar 04	472.2	4.2	-	-	465.3	8.7	1.5	-
Harwell, 13 May 04	185.3	5.0	176.2	4.0	155.9	4.0	11.5	-

As the Walsall Alumwell site sampling system is a single narrow tube to ambient, the Tedlar bag was not required: The calibration cylinder was attached directly to the end of this tube, via an excess flow meter.

A number of observations can be made from Table 4:

1. Loss of calibration gases to the tedlar bag is in the order of 5 to 6%. This was also seen in the Lab tests. This will be accounted for before any evaluation of sample inlet performance is made.
2. The smallest loss of calibration gas was seen with a glass sampling system. Less than 1% of the sample was lost at Aberdeen, even when the sampling system had been exposed to six months of ambient air.
3. The largest loss of calibration gas was seen with a wide-bore fluorocarbon plastic sampling system. 11.5% of the calibration gas was lost at Harwell, even though the sampling system had been cleaned three months earlier.
4. The single narrow bore fluorocarbon tube system at Walsall Alumwell performed well, losing less than 1.5% of the calibration gas, even after six months of exposure to ambient air.

The poor performance of the wide-bore fluorocarbon manifold at Harwell is concerning. Further investigation of the sample losses at this site and others where this type of manifold is used will need to be made, to see if this observation is repeated.

These trials have clearly demonstrated that it is possible to evaluate sampling losses of NO_2 in the field reliably, accurately and cost-effectively. Further work will be required to assess the performance of sampling systems for other pollutants (eg SO_2, O_3), and to make the test equipment more robust for transportation

4 Conclusions and Recommendations

Netcen has undertaken a series of laboratory and field based trials, to determine whether cost effective methods of calibrating site sampling systems can be devised.

The study was undertaken in preparation for likely future requirements of EU legislation, regulating the performance characteristics of sampling systems.

Trials have been undertaken under laboratory and field conditions, to evaluate the feasibility of performing reliable and cost-effective assessments of sampling system performance. These trials have been performed for NO_2 and SO_2 under Laboratory conditions, and for NO_2 in the field on the main types of sampling systems used in the UK.

The trials have demonstrated that it is possible to undertake tests of sampling systems using gas cylinders. It is intended that these tests can be undertaken to provide results with sufficient accuracy to satisfy the requirements of future legislation.

The test undertaken at Harwell showed that the wide-bore fluorocarbon manifold used there remove significant quantities of sample gas. Netcen will undertake repeat tests at this site to evaluate the reliability of this result.

Losses of carbon monoxide and ozone to sampling systems has not yet been determined. CO is unlikely to be lost in substantial quantities, but development of an ozone assessment capability is required.

For routine testing of sampling systems to be undertaken, the apparatus will need to be made more robust.

The requirements of the CEN documents are that every site sampling system must be tested at site commencement and every three years, and that sample loss must be less than 2% for each pollutant. As there are currently 120 sites in the AURN, this means that at least 40 systems will need to be tested each year to ensure compliance, once the legislation is enacted.

A decision will need to be made regarding the timing of the tests. Clearly, a manifold that has just been cleaned and serviced should show smaller sample losses to one that has been exposed to ambient air for six months. One result would provide a measure of likely best performance, the other a worst case assessment.

However, the additional calibration cylinders required to undertake the tests may mean that it is not always possible to undertake these evaluations at the same time as the network intercalibration visits. This will be especially true for the sites that are long distances from Oxfordshire (eg Scotland, Northern Ireland), where field teams are away from the office for up to three weeks at a time. For these locations, it is likely that specific visits will need to be made.

Netcen suggest the following to progress the development of the sampling system testing capability:

- Reassessment of the sampling systems already tested, to evaluate the repeatability of the technique
- Field assessment of sampling systems for losses of SO_2
- Field assessment of sampling systems for losses of CO
- Development of a methodology to assess losses of O_3
- Ruggedisation of the system for routine field use

Clearly, if the CEN requirements are adopted, a schedule of calibrations will need to be devised. To pre-empt this, it is suggested that manifolds are tested as part of new site commissioning audits and that approximately 20 site sampling systems are assessed during every network intercalibration exercise in future.

Annex 1 –
CEN manifold requirements

The following text is an excerpt from prEN 14211:2002, published in October 2002.

Procedure for testing the sample collection efficiency of the sampling system

The flow rate of the test gas in the sampling system should be such that the residence time is greater than or equal to that found under normal operating conditions. Typical manifold systems (diameter ~30 mm, length 2 m) have a volume of ~2 l and shall have a maximum residence time of 5 s. Therefore, where they are used, sufficient flow of test gas shall be supplied to the manifold to meet these conditions. If a test gas flow of 40 l per min is used, then a residence time of 3 s is obtained. As this is well below the normal manifold flow rate, it will give a worst-case scenario.

Test gas for NO analysers is provided by either dynamic dilution of single or multicomponent cylinders, or from gas cylinders without dilution. Zero-grade air, or better, should be used as a diluent/balance gas for these cylinders.

The results from the tests are in the form of ratio measurement and therefore the correct calibration of the analysers is not necessary, nor is the exact concentration of the test gas. The concentration of the test gas shall, however, be stable.

During testing, the analyser output shall be collected through the data collection system at the monitoring site and the normal site operating procedures followed.

Testing comprises three measurements of the test gas, direct sampling of test gas, sampling of test gas from the delivery system that fits over the inlet to the site manifold, and sampling of test gas from the site manifold. The tests should be performed with the manifold blower switched off. Data averaged over period of 10 min is recorded for each stage of the test.

Sample system collection efficiency, E_{s}s, is then calculated as follows:

$$E_s = \left(1 - \frac{R_d - R_m}{R_d}\right) \times 100 \qquad (31)$$

where:

E_{ss} is the sample system collection efficiency

R_d is the mean analyser response to the test gas directly sampled by the analyser;

R_m is the mean analyser response to the test gas via the sample manifold.

Action criteria:
Frequency of test: at least every three years; if > 2 % sample loss.

Appropriate action:
Clean/replace/repair manifold as necessary and re-test.