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Technical note

Sampling system influence on gaseous air pollution measurements

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ABSTRACT

Efficient sampling systems are key components of ambient air pollution measurement systems used for both regulatory and research purposes. Gaseous sampling systems were tested at 83 monitoring sites incorporating three different sampling system designs. The mean sample collection efficiency was 98% for CO, 99.1% for NO_2, 88.7% for O_3 and 96.7% for SO_2. In most cases, the test uncertainties were greater than the 2% threshold for sample losses allowed by the relevant European Standards. These uncertainties were largely due to repeatability and signal noise within the equipment being tested and the low test gas concentrations required to avoid conditioning the sampling system. There is therefore little scope for improving the test uncertainty. For O_3, test uncertainties and repeatability issues meant that firm conclusions could not be reached. For other pollutants, manifold systems offered no systematic advantages over simple PTFE tubing. PTFE tubes should therefore be favoured in site design, providing sample residence times can be met. The high average sampling efficiencies of PTFE sample tubes combined with the uncertainties inherent in the test procedure suggest that regular testing is not worthwhile for this type of sampling system providing sample lines are regularly changed or cleaned. Where a manifold is used, periodic maintenance should include cleaning, as well as flow and leak tests.

1. Introduction

Operating procedures for ambient air quality measurement tend to focus on the design, testing and calibration of the measurement instruments with less emphasis on sampling systems, despite these being a known source of uncertainty.

Sampling system losses first were quantified across Europe by Payrissat et al. (1997). Using a mobile dilution system they delivered ambient concentrations of NO, NO_2 and SO_2 directly into sampling systems at 34 monitoring sites in 12 European countries and found a mean sample loss of 5% for NO_2 but 20–27% for SO_2, depending on the type of quality system employed at the station. In the UK, Stacey (2004) found that losses depended on sampling system design; losses of 1% were found for a glass manifold, 1.5% for a PTFE tube sampling system and 11.5% for a laminar flow manifold. NO_2 sample losses in California for 2002, 2003, 2004, and 2005 were 1.1%, 0.9%, −0.7%, and −2.1%, respectively, representing 96, 77, 78, and 79 instruments (CARB, 2007).

These results are troubling when compared to CEN Standards (e.g. CEN, 2005 for NO_2) which stipulate sample losses $<2\%$ to achieve overall measurement uncertainties required by European Air Quality Directive 2008/50/EC. This study therefore investigated gaseous sampling system losses at 83 London region sites in a range of locations from kerbside to urban background, with three sampling system designs (see Table in Supplementary material), between January 2007 and October 2010.

1.1. Sampling systems

Sample losses can arise from reactions between gases in the sampled air (Butcher and Ruff, 1971), between gases and particles in the sampled air, between gases and material deposited within the sampling system, and between gases and the sampling system itself (Yamada and Charlson, 1969). Payrissat et al. (1997) attributed losses to dirty sample lines, use of "reactive materials", poor design, and condensation in the sampling system. The reaction between NO and O_3 can be significant, even with a sampling system residence time of ten seconds (Butcher and Ruff, 1971). Sampling system residence time should therefore be minimised. U.S. regulations state that residence time should not exceed 20 s (USEPA, 2011) and European standards limit the combined sampling system and instrument residence time to 5 s.

Additionally, in manifold systems, accumulation of water can cause loss of soluble gases in humid conditions (USEPA, 2005) and, where glass manifolds are exposed to sunlight, reactions can occur

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between NO_2 and O_3, especially when interacting with surface contaminants (Teitz et al., 2009).

Three types of sampling system (see schematic in Supplementary material) were tested in this study:

1. Fluorocarbon manifold (28 sites). Approximately 3 m of 25 mm (ID) fluorocarbon pipe work, with a manifold blower, is connected to each instrument by short PTFE tubing. Residence time <5 s.
2. Glass manifold (10 sites). A 20 mm (ID) PTFE sample inlet is joined to a glass manifold with a manifold blower. 4 mm (ID) PTFE sample tubes, less than 1 m long, connect the manifold to up to four instruments. Residence time <5 s.
3. PTFE sample tubes (45 sites). The tubes are typically between 0.5 and 15 m long but in most cases are less than 5 m. The instrument pump draws air through the tube at 500–800 cc min^{-1}, depending on the instrument. For a typical 5 m sample tube, residence time is 4.7 s at 800 cc min^{-1} flow rate and 7.5 s at 500 cc min^{-1} flow rate.

2. Method

Sampling efficiency tests were carried out by the National Physical Laboratory using an ISO 17025 accredited procedure.

The testing method was specifically designed for field testing at existing air quality monitoring sites. In contrast to Payrissat et al. (1997), it was not possible to use a dedicated vehicle based test laboratory due to accessibility restrictions at many of the sites in this study.

A dynamic dilution system and a temperature controlled (50 °C) O_3 generator produced concentrations of NO_2, O_3, SO_2 and CO at a flow rate close to 30 l min^{-1}. Varying concentrations of O_3 were produced by an O_3 generator. Mass flow controllers were allowed to stabilise for approximately one hour and gas supplies were switched on for ten minutes prior to each test.

Test concentrations were chosen to avoid conditioning the sampling system and to be close to the EU Limit Values; 45–151 ppb for NO_2, 69–137 ppb for O_3, 85–197 ppb for SO_2 and 10–21 ppm for CO.

No assumptions were made concerning the test concentration; sampling efficiency was derived from the ratio of the concentration measured through a clean system to the concentration measured through the sampling system under test.

There were two types of testing procedure:

a. For sample manifolds, the dilution system was output directly into the sampling system for 10–12 min, ensuring that test gases did not come into contact with the outer surfaces of the manifold inlet. The manifold blower was switched off to ensure that the sampling system flow rate was within the maximum output from the dilution system. This reflects the constraints of the maximum flow rate that could be created in portable field test equipment and prevented excessive use of the test gas.

It is acknowledged that this will have caused higher than normal manifold residence time which may extenuate losses beyond those in normal use. However, the test was designed with the primary purpose of detecting problems and determining their maximum likely impacts on measured data rather than to provide factors to correct for losses.

The short sample residence time in manifold systems, which complies with CEN requirements of less than 5 s, makes interactions between NO and O_3 very minor and these gases could therefore be tested singularly rather than as a mixture.

b. For PTFE sample tubing, the dilution system output was connected directly to the ambient end of the tubing for 10–12 min with an excess flow of around 3 l min^{-1}.

The expanded test uncertainty (coverage factor $k = 2$, $\sim 2\sigma$) was calculated including the uncertainty from the short-term stability of the dilution system and the instrument under test.

3. Results and discussion

3.1. Results by pollutant

Sampling efficiencies have been expressed as a percentage, assuming the losses to be a first order process; in line with European (CEN) Standards and existing literature. Further testing would be required to determine the relationship between sampling efficiency and concentration. However, such testing would be limited at high concentrations by the need to avoid conditioning the sampling system and at low concentrations instrument noise and uncertainty would become a limiting factor.

The number of tests, mean and standard deviation for each pollutant and sampling system type are shown in Table 1. Fig. 1 shows the sampling efficiency and expanded uncertainty of each test. The expanded uncertainties were 2–3% for CO, 4–13% for NO_2, 3–13% for O_3, and 3–9% for SO_2. The expanded uncertainties for CO were lower than for other pollutants due to better linearity and repeatability for CO instruments compared to the other gas instruments tested. Sites which fell below the 98% sampling efficiency required by the CEN Standards, after accounting for test uncertainties, are discussed in Sections 3.1.1–3.1.4.

Table 1
Mean sampling efficiency (%) grouped by sampling system type. μ = mean efficiency, n = number of tests, std(X) = standard deviation, Q_n = quartiles, with Q_2 = median, χ^2 = chi-squared, p = probability.

	Fluorocarbon manifold	Glass manifold	PTFE sample tubes	Kruskal–Wallis		
				χ^2	n	p
NO_2						
μ	98.4	99.0	99.5	1.5	82	0.48
n	28	9	45			
std(X)	4.1	2.2	2.8			
Q_1	97.8	98.0	98.0			
Q_2	99.0	99.0	100.0			
Q_3	100.3	100.0	102.0			
O_3						
μ	74.8	97.0	95.7	2.7	17	0.27
n	6	5	6			
std(X)	23.7	2.3	4.1			
Q_1	59.0	95.0	92.5			
Q_2	77.5	98.0	97.5			
Q_3	94.5	99.0	98.8			
SO_2						
μ	93.7	98.2	98.3	0.65	18	0.74
n	6	5	7			
std(X)	10.7	2.3	2.7			
Q_1	87.0	96.0	97.0			
Q_2	96.5	98.0	97.0			
Q_3	99.3	100.0	98.5			
CO						
μ	93.5	99.7	98.8	0.2	10	0.92
n	2	3	5			
std(X)	10.6	0.6	1.9			
Q_1	89.8	99.5	98.0			
Q_2	93.5	100.0	99.0			
Q_3	97.3	100.0	100.0			
Kruskal–Wallis						
χ^2	7.5	4.2	8.0	1.8	127	0.41
n	42	22	63			
p	0.06	0.25	0.05			