

Technical note

Quantifying the impact of nitric oxide calibration gas mixture oxidation on reported nitrogen dioxide concentrations

Bryan P. Sweeney^{a, *}, Paul G. Quincey^a, David Green^b, Gary W. Fuller^b^a Analytical Science Division, National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK^b Environmental Research Group, King's College London, 150 Stamford Street, London SE1 9NH, UK

H I G H L I G H T S

- Several percent of the NO in site calibration mixtures is often oxidised to NO₂.
- Analysis shows that the effect on reported NO₂ can be a multiple of this percentage.
- Calculations with data from kerbside sites show significant underestimations of NO₂.
- The consequences for regulation and quality assurance procedures are discussed.

A R T I C L E I N F O

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Chemiluminescent analysers for measuring nitric oxide (NO) and nitrogen dioxide (NO₂) in ambient air are generally calibrated with certified gas standard cylinders of NO in nitrogen. Verification of the NO_x and NO amount fractions has been carried out on many such 'on-site' calibration cylinders at air quality monitoring stations. These measurements indicate that significant numbers of these gas mixtures have become somewhat degraded, with several percent of the NO oxidised to NO₂. The effect of not compensating for this degradation on reported concentrations is discussed. If such degradation is not quantified and corrected for, there will be a systematic under-reporting of NO₂ concentrations, which, due to the non-linearity of the effect, could reduce high reported NO₂ concentrations at kerbside sites by around 20%. This could significantly reduce the number of reported exceedances of the NO₂ limit value at such sites, compared to results obtained where there is no degradation of the NO cylinder.

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1. Introduction

Measurements of ambient nitrogen dioxide (NO₂) are routinely carried out across the globe to assess compliance with statutory guidelines and to clarify the human health effects of this pollutant. The most common method of continuously measuring time-resolved NO₂ concentration is by ozone chemiluminescence (CEN, 2012; EPA, 1997). This principle utilises the reaction between ozone, in excess, and nitric oxide (NO) as follows:



A photo-detector is used to detect the emitted photons, which produce a signal proportional to the concentration of NO present.

Nitrogen dioxide, the measurand of interest, is converted to nitric oxide prior to analysis using, typically, a heated (320 °C) molybdenum catalyst. The measurement of NO₂ is therefore carried out in two stages: firstly by allowing the sample to pass via the catalyst, to give a measure of NO_x (ambient NO plus converted NO₂); then, bypassing the catalyst, to give a measure of ambient NO. The NO₂ concentration is then derived as the difference between these two quantities. It is the case that other nitrogen containing species, such as polyacrylonitrile or nitric acid, will also contribute to this difference, but these effects do not affect the points being made in this paper.

Chemiluminescent analysers are most commonly calibrated using compressed gas cylinders, traceable to National Standards, containing nitric oxide in nitrogen, as required in the European standard method EN 14211 and by the US EPA, for example. Each stage of the measurement, total ambient NO_x and ambient NO, is calibrated and scaled separately. To this end, it is essential that both

* Corresponding author.

E-mail address: bryan.sweeney@npl.co.uk (B.P. Sweeney).

the total NO_x and NO concentrations in the calibration standard are known accurately. Although the calibration cylinder is nominally a binary mixture containing solely NO and nitrogen, it is common to find NO_2 at low concentrations in the cylinders. This is likely to result from impurities in the filling gases or from the ingress of air to the system, such as when the pressure regulators are fitted and used. Because of the low amount fractions of NO in the cylinders, typically 450 nmol/mol, even very small quantities of oxygen within the system will convert a measurable proportion of NO to NO_2 .

This technical note describes the results of a series of measurements of on-site calibration standards to show the extent of the NO_2 impurities typically found therein, calculates the (non-linear) effect of such degradation on reported NO_2 results from first principles, and attempts to quantify the likely effects on some ambient data sets when degradation is not accounted for.

2. Methods

2.1. Measurement of impurities found in on-site NO calibration standards

To assess the extent of NO calibration cylinder degradation in an operational air quality network, we have made use of the large amount of data available from our own work in this area. As part of ongoing quality assurance, the National Physical Laboratory (NPL) have carried out a long series of quality assurance audits of approximately 100 continuously operating ambient air monitoring sites, in London and south-east England, at six-monthly intervals. These sites are part of the London Air Quality Network. More details of the Network are available here: <http://www.londonair.org.uk/LondonAir/Default.aspx>. We have no reason to believe that the state of the calibration cylinders on this network is significantly different from that of other monitoring networks.

Transfer standard, nominally 450 nmolNO/mol N_2 , mixtures are taken to each site. These have been certified by dynamic dilution of an NPL-certified 30 $\mu\text{mol/mol}$ NO/ N_2 standard, closely bracketing the concentration of the transfer standard. To account for small drifts in the concentration of the transfer standard during its use, the cylinder is recertified, again by dynamic dilution, following the audit campaign.

As part of the audit procedure, the NO and NO_2 content of the on-site calibration gas standards is measured using the chemiluminescent analyser at the site, as calibrated with the transfer standard cylinders. All measurements, including the certification of the transfer and on-site standards, are ISO 17025 accredited and are directly traceable to NPL primary standards. Although the associated best measurement capability for the concentrations of NO and NO_2 quoted for such measurements is $\pm 4\%$ ($k = 2$), we estimate that for the NO_2/NO ratio measurement, required for this work, the uncertainty is around $\pm 1.7\%$ ($k = 2$). This reduction in uncertainty is possible as we are considering a measured ratio, thus the uncertainties in concentration and drift in the transfer standard become irrelevant. The uncertainties in the ratio are derived primarily from random components, largely dominated by analyser noise and repeatability effects. The audit procedure also includes, amongst other things, measurement of analyser converter efficiency, and the determination of uncertainty components due to repeatability and the lack of fit of the calibration points to a straight line.

The principles of how the calibration process is used to scale reported data are very simple, but for clarity are set out here.

Following a two point calibration of the analyser with the calibration standard, NO_x data are linearly scaled as follows:

A scaling factor, $F[\text{NO}_x]$, is defined where $F[\text{NO}_x] = C/(R[\text{NO}_x] - Z$

$[\text{NO}_x])$, and

C = certified NO_x amount fraction of the calibration standard in nmol/mol

$R[\text{NO}_x]$ = analyser raw response, on the NO_x channel, when sampling the calibration gas standard

$Z[\text{NO}_x]$ = analyser raw response, on the NO_x channel, when sampling pollutant-free air ('zero air')

An analogous calibration factor for the NO channel is also defined, using the instrument responses from the NO channel, and the certified NO amount fraction of the calibration standard.

Scaled amount fraction data, $\text{NO}_x(\text{nmol/mol})$, are then derived from raw analyser outputs, $A[\text{NO}_x]$, using:

$$\text{NO}_x(\text{nmol/mol}) = F[\text{NO}_x] \times (A[\text{NO}_x] - Z[\text{NO}_x])$$

A similar calculation is carried out to scale NO data.

Nitrogen dioxide data, generally the species of interest, are then derived by difference, i.e.

$$\text{NO}_2(\text{nmol/mol}) = \text{NO}_x(\text{nmol/mol}) - \text{NO}(\text{nmol/mol})$$

3. Results

3.1. Measured occurrence of NO_2 impurities in on-site calibration standards

Of the 1008 cylinder re-certifications carried out by NPL between January 2009 and January 2014, it was found that on 205 occasions (20%) the NO amount fraction was less than the NO_x amount fraction (taken to be the sum of NO and NO_2) by greater than 3%. (Small downward drifts in the NO_x amount fraction, of the order of 1% per year, are also frequently observed; such drifts, where the NO_x/NO ratio remains constant, are easily corrected for. It is the occurrence of NO_2 impurities within the cylinders which is the focus of this Note). No attempt has been made correlate the observed degradation of these mixture with the manufacturer (approximately 80% Air Liquide and 20% BOC), the cylinder size (10 L or 40 L water capacity), the composition of the mixture contained, (typically 450 nmol of NO_x per mole of nitrogen), or the age of the on-site cylinder (which can be up to about 5 years, dependent on gas usage and the level of drifts or impurities observed at

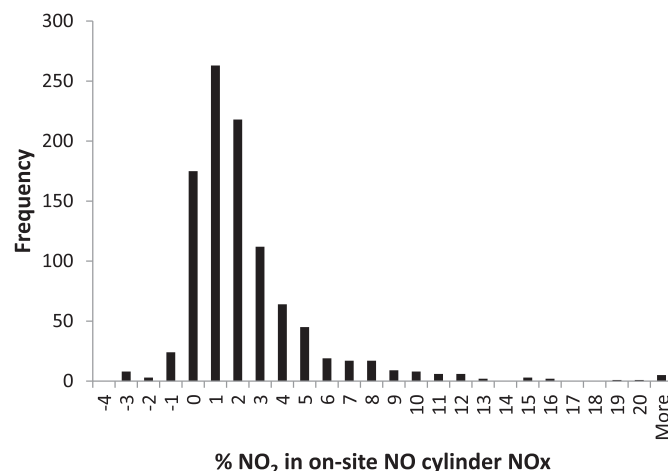


Fig. 1. Histogram showing the amount of NO_2 , as a percentage of the total NO_x , found in on-site calibration cylinders.

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