

How do passive diffusion tubes measure NO₂ concentrations?

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As part of the UK Air Quality Strategy, Local Authorities are legally obliged to assess atmospheric NO₂ concentrations (and those of other specified air pollutants). The best method for measuring ambient NO₂ concentrations is the chemiluminescence analyser, providing real-time data at high precision. However, the analysers are expensive and need power and security at the operating site. Local Authorities therefore continue to take advantage of the simplicity and low cost of passive diffusion tubes (PDTs) to assess NO₂ concentrations across a spatial network. This Brief explains how PDTs work and describes some of their limitations.

Principles of PDT methodology

The passive samplers used in the UK are of the tube design first introduced by Palmes *et al.* in 1976 (1) (Figure 1). They consist of 7.1 cm-long acrylic plastic tubes, with an internal cross-section of 0.92 cm², with the NO₂ absorbent triethanolamine [N(CH₂CH₂OH)₃, TEA] coated onto two stainless steel grids in the internal end. TEA is assumed to be 100% efficient at facilitating the 1:1 conversion of NO₂ molecules into nitrite (NO₂⁻)

anions.

Samplers are typically exposed just above adult breathing height, with the open end of the tube facing downward (to avoid rain ingress) for a period of 1-4 weeks. At the end of the exposure the tubes are recapped. The nitrite in the TEA is subsequently extracted in the laboratory into a known volume of water and quantified either directly by ion chromatography or by a colorimetric procedure. The latter involves adding solutions of sulphanilamide and *N*-(1-naphthyl) ethylenediamine (NEDA) to form a pink dye; the absorbance intensity of this dye (measured at a wavelength of 540 nm) is proportional to the nitrite concentration in the extracted solution and hence to the amount of NO₂ captured by the sampler during exposure.

The PDT operates through the diffusion of NO₂ molecules down the concentration gradient set up between the concentration in the ambient air at the mouth of the tube and the TEA absorbent. Assuming zero NO₂ concentration in the air just above the absorbent, the concentration gradient is $-\text{NO}_2]_{\text{av}}/L$, where $[\text{NO}_2]_{\text{av}}$ is the average concentration at the mouth of the tube during exposure and L is the length of the tube. For an exposure duration t , the total amount, Q , of NO₂ collected (as NO₂⁻)

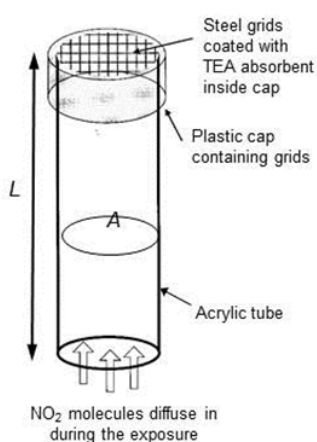


Figure 1: Schematic of a Palmes-type passive diffusion tube, and an example deployment (photo from Gradko International Ltd.).

is given by:

$$Q = [\text{NO}_2]_{\text{av}} ADt/L \quad (\text{eq. 1})$$

where A is the internal cross-sectional area of the tube and D is the diffusion coefficient for NO_2 in air. Rearranging gives the expression for the average NO_2 concentration during exposure as:

$$[\text{NO}_2]_{\text{av}} = QL/ADt \quad (\text{eq. 2})$$

The value of D recommended by the UK working group convened on behalf of Defra to report on harmonisation of NO_2 passive diffusion tube (PDT) procedures is $0.151 \text{ cm}^2 \text{ s}^{-1}$ (2).

Limitations of PDT performance

The inherent simplicity of the PDT method means that its precision and accuracy cannot in general compare with that of a chemiluminescence analyser. A number of factors may influence both precision and accuracy of NO_2 concentrations derived from PDT data (2, 3). Factors that may influence NO_2 PDT performance include the following, at different stages of a PDT measurement:

1. In PDT preparation: the mass of TEA applied to the grid; the choice of solvent (water or acetone) used to apply TEA absorbent to the grids; and whether the TEA is applied by dipping grids in the TEA:solvent solution or by pipetting the solution directly onto the grids.
2. In PDT exposure: humidity and temperature of the ambient environment; air turbulence at the mouth of the tube during exposure (which can shorten the effective diffusion path length, leading to systematic positive bias in the NO_2 concentration); production of additional NO_2 in the tube by reaction of co-diffusing NO and O_3 (a consequence of the opacity of the standard acrylic tubes to NO_2 photolysis wavelengths), again leading to systematic positive bias (4); and degradation of the nitrite-TEA complex during exposure, leading to systematic negative bias.
3. In PDT analysis: the concentration of the colorimetric reagents; and degradation of the dye between its formation and the measurement of its absorption.

The NO_2 PDT harmonisation working group recommended specific protocols regarding many of the above issues (2). For example, absorbent preparation should be done either by dipping grids in 50:50 TEA:acetone solution or by pipetting 50 μL of 20:80 TEA:water solution onto the grids.

Some effects of temperature and relative humidity on PDT performance have been noted but these have been variable and within the general uncertainties in PDT measurements.

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The two major lingering bias concerns for PDTs are the positive biases from within-tube chemical production of additional NO_2 and the effect of air movement across the mouth of the tube causing a shortening of the diffusion path compared with the physical length of the tube.

The magnitude of the former bias depends on the relative amounts of NO , NO_2 , and O_3 in the ambient air and will be greatest when NO and O_3 concentrations are both comparable to NO_2 concentrations. This means that the effect is likely to be most significant in urban background areas, and not at road sides, where O_3 concentrations tend to be low, nor in rural areas, where most NO_x is already in the form of NO_2 .

Average positive biases of the order of 10 to 20% have been reported for PDT exposures in urban background air. The wind-induced bias will clearly be highly dependent on the nature of the deployment site and of the windiness during a given exposure. The use of shelters over the PDT or a coarse mesh across the "open" end of the tube during exposure may be able to mitigate against this positive bias, although further research on this particular issue is necessary.

The EU Directive on air quality (5) recognises the uncertainties in NO_2 passive samplers and designates them as indicative measures of NO_2 with a potential uncertainty of $\pm 30\%$. Overall, however, with careful preparation and analysis, coupled with an appreciation of issues of potential limitation, NO_2 PDTs remain a very useful method for understanding spatial and longer-term trends in ambient NO_2 concentrations.

References

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5. EU Directive on Air Quality, see <http://ec.europa.eu/environment/air/quality/legislation/directive.htm>.