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MEASURING FIELD CONCENTRATIONS OF NITROGEN DIOXIDE USING DIFFUSION TUBES

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Introduction

Nitrogen dioxide (NO_2) is second only to sulphur dioxide (SO_2) as the most commonly occurring acid pollutant gas found in Britain. It is formed as a result of most industrial processes which emit SO_2 , although at lower concentrations. Another important source of NO_2 is motor vehicles and these account for about 50% of the total formed in Britain. The pollutant arises in the heat of combustion when atmospheric oxygen and nitrogen combine to form nitric oxide (NO). Upon release, NO is oxidised in air to produce NO_2 .

In contrast to SO_2 , few measurements have been made of ambient concentrations of NO_2 except in city centres, where levels were found to be related to density of road traffic (eg. Hickman et al., 1976). Mainly, this is because most investigators considered NO_2 to be an urban pollutant and of little threat to rural environments (see review by Mansfield & Freer-Smith, 1981). However, Martin and Barber (1981) reported concentrations of NO and NO_2 collectively to be in excess of SO_2 at a rural site in England. More recently, in a survey of Wales, we have found monthly mean concentrations of over 25 ppb (parts per billion, by volume) for rural sites remote from any known source of pollution (Ashenden & Bell, 1989).

The use of diffusion tubes for monitoring NO_2 was first introduced by Palmes et al. (1976). They were developed as on-person air samplers, specifically for use in underground mines and emphasis was placed on measuring concentrations up to 5 ppm. Later, they have been used to measure levels of NO_2 in homes to compare

pollutant formation from gas as compared to electric cooking (see Atkins, Healy & Tarrant, 1978). Recently, some studies have used diffusion tubes to monitor field concentrations of NO₂ (eg. Goldsmith, 1986) but large blank values have been recorded for unexposed tubes. It is apparent that standard procedures are required for the use of diffusion tubes to monitor NO₂. We report in detail our own techniques which have been used successfully to generate maps of background levels of NO₂ pollution throughout Wales and result in low (zero) blank values for unexposed tubes.

Construction of tubes

The diffusion tubes comprise 7.2 x 1.12 cm diameter acrylic tubes fitted with one blue and one natural airtight polythene end-cap. They are supplied by Gradco International Limited., Winchester. Before use, the tubes are acid washed (5% hydrochloric acid), thoroughly rinsed with distilled water and dried in an oven at 70°C.

Discs, which fit tightly inside the blue end-caps, are cut from 34 gauge stainless steel woven wire of mesh 0.224 mm. They are acid washed and dried before dipping in 50% v/v triethanolamine (TEA)/acetone solution. Discs are then placed on filter paper to allow the acetone to evaporate and thus leave a fine coating of TEA. Next, three prepared discs are placed inside the blue polythene end caps and these are re-fitted to the diffusion tubes. It is important that prepared discs are placed inside coloured end-

caps rather than natural ones to prevent possible light-induced reactions which may affect pollutant adsorption. Once prepared, the diffusion tubes with both end-caps in place are packed in sealed polythene bags; this effectively ensures that blank tube values remain at under 0.1 ug nitrite, even after 3 months storage.

Sampling procedure

It is essential to ensure that sampling tubes are located away from obvious obstructions which could shield them from air streams from any direction, or trees and hedgerows which could filter pollutants from the air being sampled. We have found 1.5-3 m high wooden stakes, fitted with metal cross-bars supporting spring-clips, ideal for attaching samplers. To avoid any possible influence of vegetation or surface unevenness, tubes are mounted at about 1 m above the vegetation surface.

During sampling, the natural-coloured polythene end-caps are removed and the tubes mounted vertically, with the open end pointing downwards to prevent the entry of rain and dust particles. Duplicate tubes should be a minimum requirement, so that possible damage to the tubes during exposure or in transit to the laboratory will not result in a loss of data, and thus possible faults in analytical techniques will easily be detected. At the end of the sampling period, the open ends are re-sealed with polythene end-caps and the tubes again sealed in polythene bags prior to storing for analysis. Sampling periods of 1-2 weeks have been found

satisfactory for monitoring low, background concentrations of NO_2 .

Laboratory analysis

Nitrogen dioxide is determined colorimetrically as NO_2^- . A mixed reagent is prepared consisting of one part distilled water: one part sulphanilamide reagent (2g sulphanilamide + 5 ml concentrated ortho-phosphoric acid diluted to 100 ml with distilled water): one tenth part N-1-naphthyl-ethylene-diamine-dihydrochloride (NEDA) reagent (70 mg NEDA in 50 ml distilled water). A 2.1 ml aliquot of the mixed reagent is added directly to each sample tube at the opposite end to the mesh collectors; the tubes are then re-sealed and agitated. After 10 minutes they are shaken again and then left for a further 10 minutes for the reaction to proceed. It should be noted that addition of the reagents separately may cause the formation of unstable compounds and affect the reproducibility of results.

The nitrite ion is released from the mesh collectors in solution and diazotizes the sulphanilamide. The salt formed becomes coupled with NEDA and a purple-red azo dye is produced whose absorbance is measured at 520 nm using a spectrophotometer previously calibrated with known concentrations of NO_2^- .

Calculations

The theoretical basis for the diffusion tube method of sampling depends on Fick's first law. The equation to describe

unidirectional diffusion of a gas 'a' through a mixture of gases 'a' and 'b' under conditions of constant temperature is

$$F_a = - D_{2ab} \frac{dc_a}{dz}$$

where

- F = flux of a (moles.cm⁻².sec⁻¹)
- D_{ab} = diffusion coefficient of 'a' through 'b' (cm².sec⁻¹)
- C_a = concentration of 'a' in 'b' (moles.cm⁻³)
- z = distance measured in the direction of diffusion (cm).

The flux is negative because it is in the direction of decreasing concentration.

For a tube of length 7.2 cm and cross-section area of 0.99 cm² and a concentration gradient between its end (C₁ - C₂ moles.cm⁻³) the equation becomes:

$$Q_a = F_a \cdot 0.99t = \frac{-D_{ab} (C_1 - C_2) \cdot 0.99t}{7.2}$$

where Q_a = the quantity of gas 'a' transferred in t seconds. Then if the concentration at one end of the tube is maintained at zero by an efficient absorbant (ie. TEA):

$$Q_a = \frac{-D_{ab} C_1 \cdot 0.99t}{7.2}$$

By substituting a diffusion coefficient for NO₂ in air of 0.154 cm³.sec⁻¹ (see Palmes et al., 1976), letting

$C_1 = 1 \text{ ppm} = 0.0416 \times 10^{-9} \text{ g.moles NO}_2 \text{ cm}^{-3}$ (at STP) and

$t = 1 \text{ h} = 3600 \text{ seconds:}$

$$Q_a = \frac{0.154 \times 0.0416 \times 10^{-9} \times 0.99 \times 3600}{7.2}$$

Thus $Q_a = 3.139 \times 10^{-9} \text{ g.moles.ppm}^{-1} \cdot \text{h}^{-1}$.

The chemical analysis determines the quantity of NO_2^- in ug.

Now 1	nanomole NO_2	=	$46 \times 10^{-9} \text{ g}$
	3.139 nanomoles	=	$46 \times 3.139 \times 10^{-9} \text{ g}$
		=	0.144 ug

Hence $Q = 0.138 \text{ ugNO}_2 \cdot \text{ppm}^{-1} \cdot \text{h}^{-1}$

$$= \frac{1000 \times 1}{0.138} \text{ ug NO}_2 \cdot \text{ppb}^{-1} \cdot \text{h}^{-1}$$

$$= 7246.38 \times 1 \text{ ug NO}_2 \cdot \text{ppb}^{-1} \cdot \text{h}^{-1}$$

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Thus to determine concentration of NO_2 in air during a known period of sampling in which x ug NO_2 have been collected:

$$\text{ppb NO}_2 = \frac{7246.38 \times x}{\text{hours}}$$

hours

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