

ATMOSPHERIC CHEMISTRY – NITROGEN DIOXIDE

Version 1.1 (previously AC Protocol, updated Jan 2001)

Aim *To detect and define changes in periodic mean atmospheric concentrations of nitrogen dioxide*

Rationale Natural and man-made sources emit oxides of nitrogen in approximately equal quantities, but, whilst the former tend to have equal world-wide distribution and are relatively constant over time, the latter are concentrated in or around centres of population. Nitric oxide (NO) and nitrogen dioxide (NO₂) are the most important oxides of nitrogen in urban atmospheres and it is NO₂ which has the more significant health and ecosystem effects. Major sources of NO₂ in urban areas result from fuel combustion in motor vehicles, power generation, heating plants and industrial processes, mostly by oxidation of NO emissions from these sources. NO₂ is a respiratory tract irritant, is toxic at high concentrations, and is involved in the formation of photochemical smog and acid rain. It can also cause direct damage to crops and other vegetation, together with SO₂ and ozone (UNEP/WHO 1994). High concentrations of NO₂ can have an indirect effect on ecosystems by providing an increased nitrogen input and this is important in the context of systems with a low natural nitrogen demand. The method selected for measuring nitrogen dioxide uses passive diffusion tubes; this method is well researched and reliable, though variation between individual tubes requires that they are replicated; the method has a low capital cost, requires no on-site power source and is reasonably inexpensive to operate.

The possibility of extending the ECN measurement programme to include other pollutant atmospheric gases, particularly ammonia, sulphur dioxide and ozone, has been considered and is under continuing review. At present, however, there appear to be no acceptably reliable passive methods.

Method

Equipment

The construction of the diffusion tubes is shown in Figure 5. Discs of stainless steel mesh coated with NO₂ absorbent are secured in the upper end of the plastic tube. The 1 cm diameter discs of stainless steel mesh can be purchased ready-cut from the supplier of tubes and caps. Alternatively, ready-made tubes, which include prepared discs, may be purchased from the same source.

Where ready-made tubes and disks are not being used, equipment is prepared as follows. Tubes and caps are placed in a 5% acid wash overnight and then washed in Decon 90 for one hour and rinsed with distilled water. Stainless steel mesh disks should not be placed in acid but are stored overnight in Decon 90 and placed in an ultrasonic bath for 20 minutes; the disks are then rinsed thoroughly with distilled water and placed on filter paper to dry. Forceps should be used when handling the disks. Two dry disks are placed in each cap and 30 µl of a 10% aqueous solution of triethanolamine is pipetted into each cap. A tube is fitted into the coloured cap and the other end of the tube is then sealed with a white cap. The tube is then placed into a Sterilin vial, sealed tightly and placed in a labelled plastic bag. Samples are stored in a refrigerator until they are needed. The diluted absorbent should be made up freshly shortly before use, and clean disks are best stored dry.

Location

Three diffusion tubes are mounted in clips (see Figure 5) which are either fastened to the pole of the bulk precipitation collector (see PC Protocol) or to a post at a height of 1.5 m above ground level. If a meteorological instrument enclosure exists, the post should be sited within the enclosure.

Authors
References

Sampling

The white cap is removed from each tube immediately prior to its deployment and the tubes are placed vertically with their open ends pointing downwards. The tubes are collected after two weeks and the white caps are re-fitted to the tubes before their removal from the post. Three blank tubes are transported to the site but are not exposed on arrival. They should be returned to the laboratory the same day, stored in a refrigerator during the two-week sampling period and analysed with the experimental tubes.

Labelling

Tubes should be labelled as follows:

- the ECN Measurement Code (AN),
- the ECN Site ID Number (eg 04 for Moor House),
- the Location Code (eg 01),
- the individual tube code (E1, E2, or E3 for exposed tubes; B1, B2, or B3 for blank tubes),
- the collection date ('Sampling Date') (eg 01-Jan-1996).

This unique reference MUST accompany the analytical results for transfer to the ECN database.

D. Bojanic, J.K. Adamson, A.P. Rowland and J.M. Sykes

Hargreaves, K.H. 1989. *The development and application of diffusion tubes for air pollution measurement*. PhD thesis. University of Nottingham.

United Nations Environment Programme/World Health Organization. 1994. *GEMS/AIR methodology reviews vol 1: quality assurance in urban air quality monitoring*. Nairobi: UNEP.

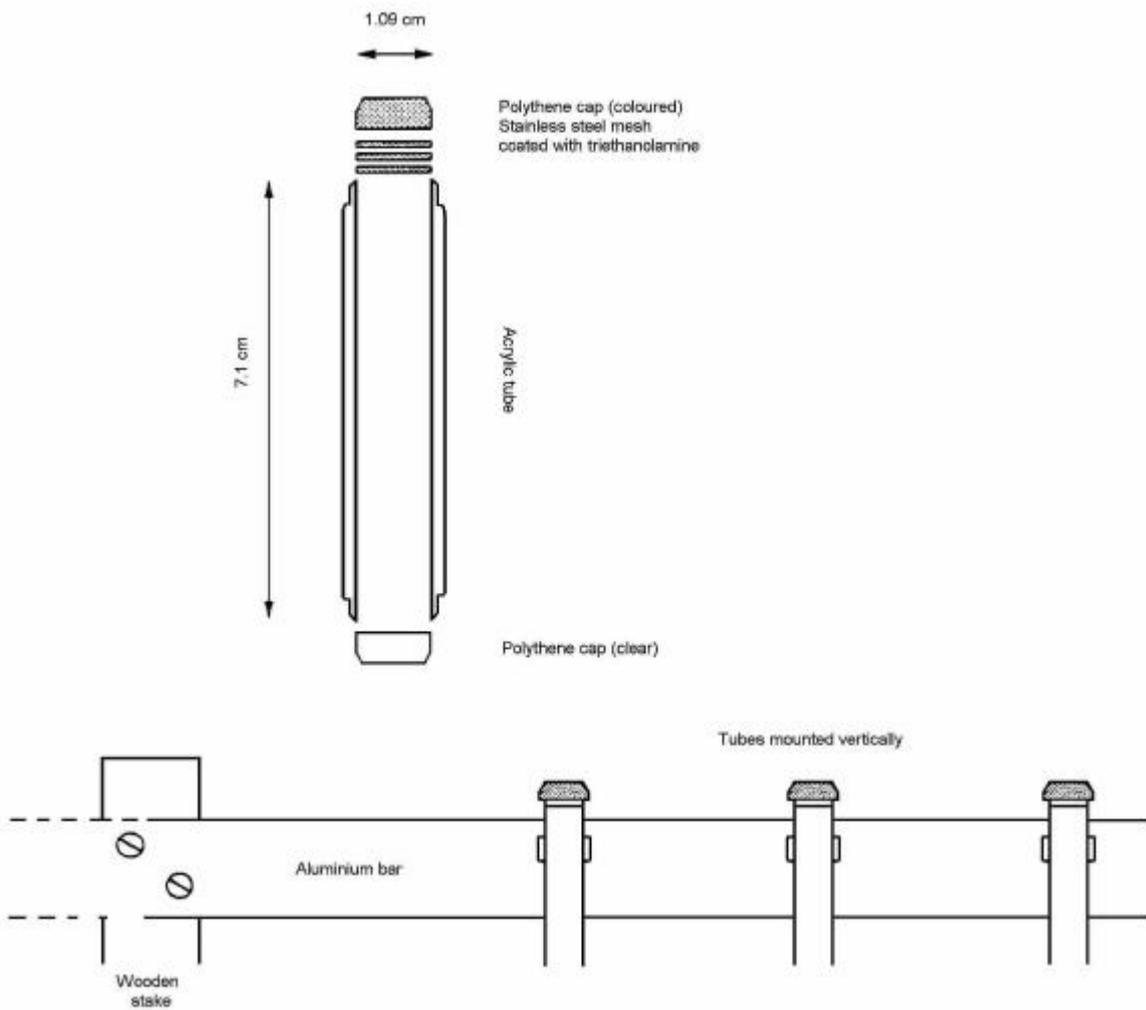


Figure 5. Diffusion tube used for long-term monitoring of nitrogen dioxide and its position in the field

Appendix I. Analytical procedure

Analysis

The absorbent is analysed to give the total NO₂ absorption for the sampling period and this is used to calculate mean NO₂ concentration over the same period.

The operator must wear gloves to prevent contact with chemicals or solutions. The diffusion tubes must be rinsed immediately following analysis to reduce the risk of contaminating other handlers.

Reagents

Chemicals - AR Grade
Water - deionised or distilled

Sulphanilamide

HARMFUL IF SWALLOWED. AVOID CONTACT WITH SKIN AND EYES
Dissolve 10 g sulphanilamide in water, add 25 ml concentrated H₃PO₄ and dilute to 500 ml. Store in a refrigerator.

N-1-Naphthylethylene-diamine dihydrochloride (NEDA)

HARMFUL
Dissolve 0.14 g NEDA in water and dilute to 100 ml. Store in a refrigerator.

Reagent Y for samples

Mix 100 ml sulphanilamide, 100 ml water and 10.0 ml NEDA reagent. Prepare on the day of analysis.

Reagent X for standards

Mix 10.0 ml sulphanilamide with 1.0 ml NEDA reagent. Prepare on the day of analysis.

Stock standard A (2500 mg l⁻¹ NO₂)

Dissolve 0.9375 g dried sodium nitrite in water and dilute to 250 ml in a volumetric flask.

Stock standard B (25 mg l⁻¹ NO₂)

Dilute 1.0 ml of stock standard A to 100 ml in a volumetric flask.

Working standards (0.25, 0.75, 1.25 µg ml⁻¹ NO₂)

Prepare fresh daily. Pipette 1.0, 3.0 and 5.0 ml aliquots of standard B to 100 ml in separate volumetric flasks and dilute to volume.

Procedure

1. Standards: pipette 1.0 ml standard or blank into a tube. Add 1.1 ml reagent X. Samples: remove the white cap from the tube and add 2.1 ml reagent Y. Replace caps and shake.
2. Shake sample/standard after 15 and 30 minutes, and then record the absorbance at 542 nm against a water blank.
3. Calculate the weight of nitrite from the calibration curve and report the results, in µg, to three significant figures.
4. Nitrogen dioxide concentration in ppb can be calculated from the diffusion tube exposure time, tube dimensions and the amount of nitrite collected (Hargreaves 1989).

Appendix II. Equipment details

Materials

Discs (1 cm diameter) of stainless steel mesh (9)
Plastic diffusion tubes (3)
Coloured polythene caps (3)
Clear polythene caps (3)

Supplier

Gradko International Ltd
St Martins House
77 Wales Street
Winchester
Hampshire, UK

Specification of results and recording conventions

The measurement variables listed below are those required for each AN sampling location at an ECN Site. Sites submitting data to the ECNCCU should refer to the accompanying Data Transfer documentation for the specification of ECN dataset formats, available on the restricted access Site Managers' extranet. Contact ecncu@ceh.ac.uk if you need access to this documentation.

The first 4 key parameters uniquely identify a sample or recording occasion in space and time, and must be included within all datasets:

- [Site Identification Code](#) (e.g. T05) Unique code for each ECN Site
- [Core Measurement Code](#) (e.g. PC) Unique code for each ECN 'core measurement'
- Location Code (e.g. 01) Each ECN Site allocates its own code to replicate sampling locations for each core measurement (e.g. for different surface water collection points)
- Sampling Date (/time) Date on which sample was collected or data recorded. This will include a time element where sampling is more frequent than daily

ECNCCU 2001

Core measurement: atmospheric chemistry - nitrogen dioxide (AN Protocol)

The following variables are recorded fortnightly for each of three experimental and three blank diffusion tubes.

Variable	Units	Precision of recording
Site Identification Code		
Core Measurement Code		
Location Code		
Setting out date		
Setting out time	GMT 24-h clock	1 min
Sampling date		
Sampling time	GMT 24-h clock	1 min
Tube code	2 character code ¹	
Weight NO ₂ ⁻	µg	3 significant figures

Recording forms

A standard field recording form is available from the CCU. An example is provided in Appendix II.

Note

¹ Experimental tubes should be coded E1, E2, E3, blank tubes B1, B2, B3.