

Outcome of the UK Working Group on Harmonisation of NO₂ Diffusion Tube Methodology





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Diffusion Tubes for Ambient NO₂ Monitoring: Practical Guidance
Practical guidance for Laboratories and Users

Background

- Palmes-type NO₂ diffusion tubes widely used in UK for *indicative* monitoring of NO₂ in context of Local Authority Air Quality Management.
 - *Cheap, convenient, offer good spatial coverage.*
- Many suppliers/analysts (currently around 20), ranging from small Local Authority labs to large commercial suppliers.
- No ISO, UK or (as yet) EU standard method – so variations in:
 - Preparation of tubes (water/acetone as solvent, % of TEA)
 - Exposure procedures
 - Analysis of tubes (*extraction, analytical procedures, preparation of standard solutions, calibration...*)



Inter-laboratory variation in diffusion tube performance

- UK's centralised QA/QC programmes indicated considerable inter-laboratory variation in the results.
- This was also apparent in the results of UK Local Authorities' co-location studies (which are also centrally databased).
- ***Tubes from different labs, exposed at the same site, may give significantly different results!***
- Harmonised method should reduce inter-laboratory variation in results. *But without a standard method, this would not be easy!*

UK Working Group

- In 2006, Defra and Devolved Administrations commissioned a UK Working Group on harmonisation of NO₂ diffusion tube preparation and analysis methods.
- UK Working Group was managed jointly by AEA and Air Quality Consultants Ltd.
- Included laboratories, Local Authorities, experts in the field of diffusive sampling – such as NPL, Univ. of Edinburgh, HSL, Environment Agency and other stakeholders.

Objectives of Working Group

- To harmonise, as far as practicable, the methods used for diffusion tube preparation, use, and analysis.
- To produce **Practical Guidance** harmonising the different steps in the UK diffusion tube methodology.
- This was intended to be based on current knowledge of best practice (both in the UK and Europe).

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Practical Guidance

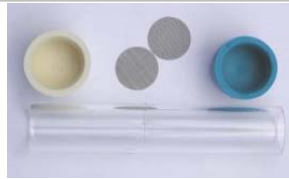
- Practical Guidance was released in Feb 2008
- Available on UK Air Quality Archive at www.airquality.co.uk
- Forms the basis of harmonisation of methods within the UK
- Aimed at suppliers/analysts **and** end-users – in particular, UK Local Authorities using diffusion tubes for Local Air Quality Management
- Does **not** constitute a formal standard method.

The main points covered by the harmonised method, as set out in the Practical Guidance, included the following:



Materials and Reagents

- Specification of tube material (acrylic/polypropylene), end caps and grids.
- Specification of reagents (Analytical Grade), glassware (grade B), and deionised water (18MΩ or purer)
- Calibration of balances and pipettes.
- Guidance on cleaning tube components before re-use



Tube preparation method

- Both the currently most widely-used preparation methods are acceptable:
 - Dipping grids in a 50% TEA in acetone solution
 - Pipetting a 20% TEA/water solution onto the grids.

Field trial (2007) showed no significant difference between the two – inter-lab differences were more significant.

POSTER on this field trial

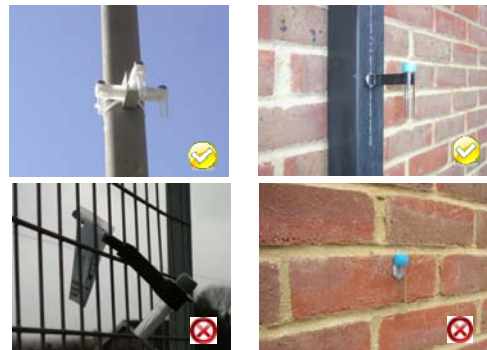
- Details of preparing and applying the TEA solution are given, also of handling and storing the tubes.

Use and siting of diffusion tubes

Guidance includes:

- Macro-scale siting of diffusion tube monitoring sites of different types (roadside, urban background etc)
- Micro-scale siting of tubes
- Fixing of tubes, and how not to...

Use and siting of diffusion tubes



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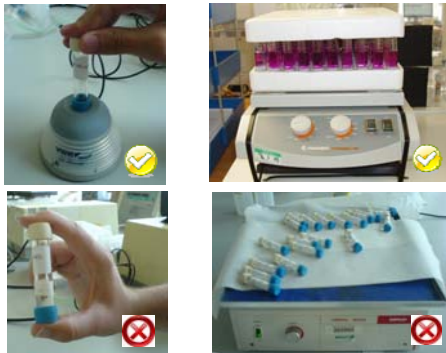
Analysis

- A large section of the Guidance is devoted to analytical methods
- This is an area where there were large differences between labs
- Some important aspects are...

Analysis

- Calibrating the spectrophotometer/colorimeter
 - Purchase/preparation *and testing* of standard solution.
 - Preparation of reagents, storage & shelf-life
 - Extracting the absorbed nitrite from the exposed tubes
- Lab-based trials with Oxford Brookes University showed it is more efficient to use a vibrating tray or vortex mixer: minimum times & settings are specified.*

Analysis



Analysis

- Calculating the mass of nitrite on the tube – and the ambient concentration (e.g. value of D)
- Dealing with samples that are found to be above the calibrated range
- Problems and troubleshooting
- Role of laboratory blanks and travel blanks: *guidance is that travel blanks should not be routinely subtracted.*

Data Handling & Interpretation

- Calculating precision and accuracy, bias adjustment
- Identifying outliers
- Guidance on when to reject a tube result

Implementation

- Practical Guidance released to labs and users in Feb 2008
- Not realistic for all labs to implement it at exactly the same time, due to considerations such as the timing of their annual UKAS assessment visit (UK accreditation).
- Labs were requested to implement the Guidance by 1st Jan 2009.
- Generally a very positive response!

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How will we know if it's working?

- We would expect to see improved inter-laboratory agreement demonstrated in results of -
 - Workplace Analysis Scheme for Proficiency (quarterly independent proficiency testing scheme, operated by UK Health & Safety Laboratory)
 - Ongoing Field Intercomparison at Marylebone Road (London) (monthly co-location study operated by HSL and AEA)
 - Database of LA's co-location studies for 2009 (2009 data will be available in 2010)
- Not enough data yet - will analyse these datasets later in the year.

Field investigation of inter-laboratory variation 2009

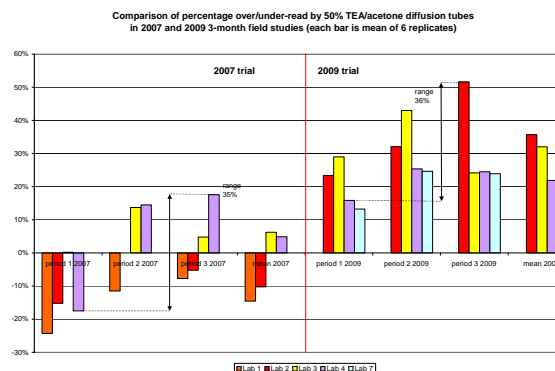
- Meanwhile, earlier this year a **short-term, small-scale** field trial of inter-laboratory variation was undertaken.
- Same procedure as 3-month trial carried out in 2007 to evaluate 5 diffusion tube preparation methods – co-location with automatic analyser.
- but included only the 2 preparation methods permitted in the Harmonised Method, i.e.
 - 50% TEA/acetone, grids dipped
 - 20% TEA/water, solution pipetted.

Field investigation of inter-laboratory variation 2009

- 3 x 4-week periods over Apr – Jul 2009 (same exposure periods & time of year as 2007 study)
- Same site as 2007 study - London Teddington (tubes changed by National Physical Laboratory)
- Used 7 of the 8 original trial participants (one no longer analyses tubes).
- 6 replicate tubes from each participant per period.

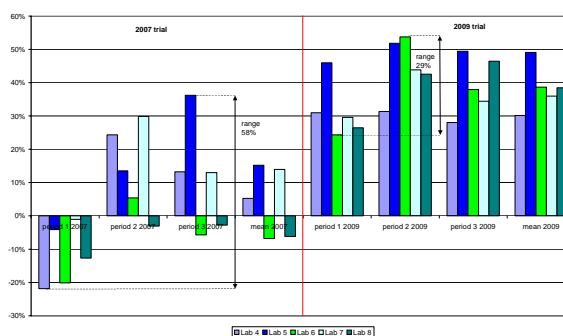


50% TEA/acetone method



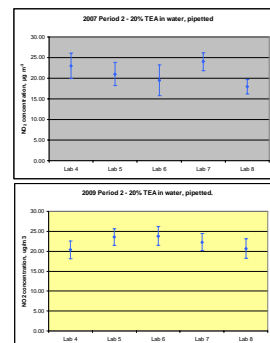
20% TEA/water method

Comparison of percentage over/under-read by 20% TEA/water diffusion tubes in 2007 and 2009 3-month field studies (each bar is mean of 6 replicates)



Agreement between laboratories

- Appears to be better agreement between laboratories
- Fewer cases where 2 labs using same preparation method got significantly different results (based on 2 SD of the mean of the 6 replicates). Only 1 (marginal) case in 2009.
- example shown here.



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2009 Field Trial - Initial results

- Tubes in 2009 study gave higher results: all over-estimated. However, overestimation is expected for Palmes tubes, due to wind and UV effects. Underestimation is often a symptom of inefficient extraction.
- For tubes prepared by the 20% TEA/water method, "bias" less variable in 2009 compared with 2007 study.
- Some evidence of better agreement between labs, particularly for 20% TEA/water method.

Acknowledgements

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Thank you

Any questions?

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