*Chapter 4*

# Measurement methods and UK monitoring networks for $NO_2$

## Key points

- Several techniques are available to measure $NO_2$ concentrations in the atmosphere.
- The chemiluminescent analyser is widely used for continuous monitoring of $NO_2$ concentrations in the UK. It is the reference method specified in the EU First Air Quality Daughter Directive and is based on the chemiluminescent reaction between NO and $O_3$.
- Other methods of measurement, such as diffusion tube samplers, electrochemical sensors, thick film sensors and open path optical methods are also available, and can provide useful data in many circumstances and for different applications. However, the data from these other measurement techniques may not be directly comparable with the chemiluminescent reference method for a number of reasons.
- Monitoring of $NO_2$ concentrations using the chemiluminescent analyser is carried out on a national scale, on behalf of Defra and the Devolved Administrations, and at a regional or sector-specific scale, on behalf of local authorities, the Highways Agency, the power generation industries, and other organisations. These networks are subject to rigorous quality assurance and quality control procedures, which ensure the reliability of the data.
- Data from 212 chemiluminescent monitoring sites, including kerbside, roadside, urban background, industrial and rural locations, have been considered in this report. A number of these sites have co-located $O_3$ analysers.
- A CEN standard for making $NO_2$ measurements using chemiluminescent analysers is being drafted. This will provide performance specifications for instruments, and operational procedures, to ensure that data meet the uncertainty requirements of the EU First Daughter Directive.

## 4.1 Introduction

**374.** There are a variety of monitoring methods available for the measurement of ambient $NO_2$ concentrations. These include:

- Chemiluminescent analysers
- Diffusive samplers
- Electrochemical sensors
- Thick film sensors
- Differential optical absorption spectroscopy (DOAS).

The various advantages and disadvantages of each of these methods are summarised in Table 4.1.

**375.** Whilst a number of wet chemical methods have also been developed, these are no longer widely used, and have been almost entirely replaced by the techniques described above. Fourier-transform infrared (FTIR) samplers are also available for $NO_2$ measurements, although their use has, to date, largely been restricted to the laboratory and to emissions testing.

**Table 4.1** Summary of advantages and disadvantages of $NO_2$ measurement methods.

| Technique | Advantages | Disadvantages |
|---|---|---|
| Chemiluminescence[a] | The reference method specified in the EU First Daughter Directive.<br>Lower detection limit of ~ 1 µg $m^{-3}$.<br>Provides real-time data with short time resolution (<1hr) that can be used for public information. | Relatively high capital cost.<br>High operating costs. |
| Diffusion tubes | Low capital and operating costs.<br>Possible to carry out surveys over wide geographical areas to provide information of the spatial distribution of $NO_2$ concentrations.<br>Require no power supply, and minimal training of site staff. Site calibrations are not required.<br>Lower detection limit of ~2-3 µg $m^{-3}$ for a 4 week exposure period. | Only provide concentrations averaged over the exposure period (typically 4 weeks).<br>Accuracy of the method, and bias relative to the reference sampler, is dependent upon the method of tube preparation and the laboratory completing the analysis. Results need to be 'bias-corrected' before comparison with limit values and objectives. |
| Electrochemical Sensors[a] | Portable samplers that can be easily deployed in the field. | Lower detection limit of some samplers (~200 µg $m^{-3}$) makes then unsuitable for ambient monitoring. |
| Thick-film sensors[a] | Portable samplers that can be easily deployed in the field.<br>Potential to measure a number of pollutants simultaneously.<br>Provides real-time data with short time resolution (<1 hr) that can be used for public information.<br>Lower detection limit of ~4 µg $m^3$. | At this time, the sensor for $NO_2$ has not been commercially released. Only measurements of $NO_x$ may currently be carried out. |
| DOAS[a] | Concentration integrated over the length of the light path. Gives an 'average' concentration that can be useful to assess public exposure.<br>Potential to measure a number of pollutants simultaneously.<br>No inlet manifold required.<br>Provides real-time data with short time resolution (<1 hr) that can be used for public information.<br>Lower detection limit of ~ 1 µg $m^{-3}$. | The integrated measurement cannot be directly compared with the EU limit values or the air quality objectives (which are set for a single point measurement).<br>Relatively high capital cost.<br>Unfavourable weather conditions, such as fog or snow, can affect the instrument performance. |

[a] Methods require regular calibration

## 4.2 Chemiluminescent analysers

**376.** The chemiluminescent analyser is widely used for continuous monitoring of $NO_2$ concentrations in the UK, and throughout the World. It is the reference method specified in the EU First Air Quality Daughter Directive. A typical specification is provided below.

- Lower Detection Limit: < 2 mg $m^{-3}$
- Precision: <1% (Full Scale)
- Linearity error: <2%
- 95% response time: <180 seconds (a typical specification is 20 seconds lag + 60 seconds rise to full scale)

**377.** Chemiluminescence describes the process of fluorescence resulting from a chemical reaction. The chemiluminescent sampler for the measurement of $NO_2$ relies on the reaction of NO with $O_3$ to produce an 'excited' form of $NO_2$. As the excited molecule returns to its ground state, fluorescent radiation is emitted, the intensity of which is proportional to the concentration of NO. This is expressed by the following reactions:

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO_2^* \rightarrow NO_2 + hv$$

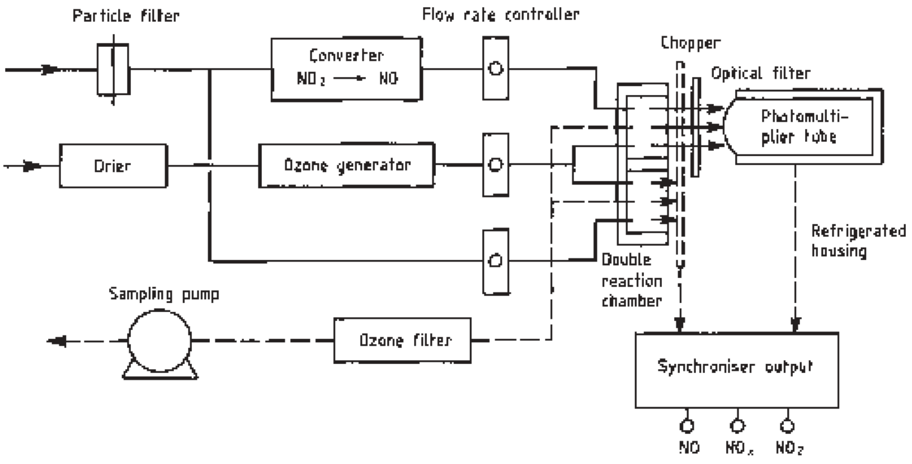
Where *hv* represents the emitted radiation.

**378.** It is important to note that chemiluminescent analysers do not directly measure concentrations of $NO_2$. This is achieved by reducing the $NO_2$ component of the ambient air sample to NO (in a $NO_2$-to-NO converter[1]), which gives the concentration of total $NO_x$ and then subtracting NO:

$$NO_2 = NO_x - NO$$

It is therefore necessary for the analyser to make two independent measurements, of NO and $NO_x$ ($NO+NO_2$). Within some analyser types, this is achieved by having a dual-chamber configuration that measures $NO_x$ and NO simultaneously in individual reaction chambers. A typical dual-chamber configuration is shown in Figure 4.1. Some dual-chamber instruments have dual detectors and some have only a single detector.

**Figure 4.1** Schematic diagram of a dual-chamber $NO_x$ analyser.



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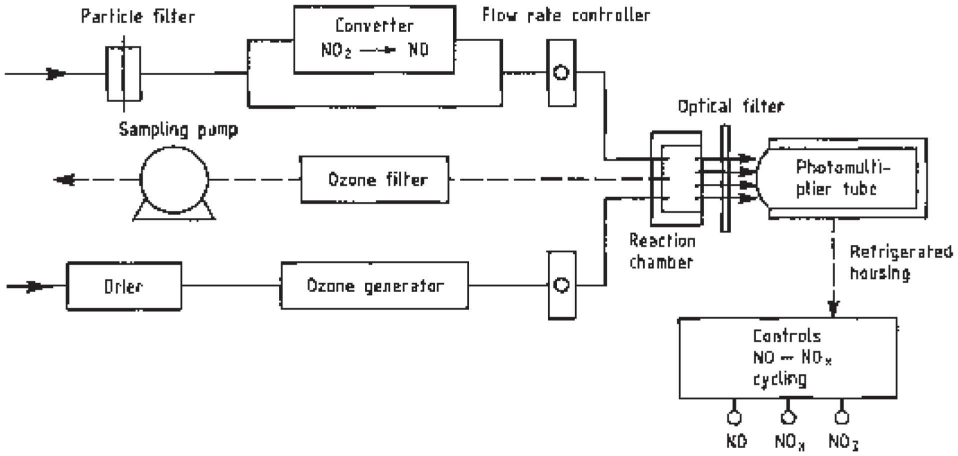
[1] Typically, these converters are comprised of a high-temperature (≈350ºC) molybdenum catalyst cell, although low-temperature converters (≈200ºC) are now also available.

**379.** In recent years, many manufacturers have moved to the production of single-chamber instruments, mainly to save on the costs of plumbing and electronics. In this case, the measurements of $NO_x$ and $NO_2$ must be made sequentially, by switching the air sample either directly to the reaction chamber or via the $NO_2$-to-NO converter. A typical single-chamber configuration is shown in Figure 4.2.

**Figure 4.2** Schematic diagram of a single-chamber $NO_x$ analyser.



## 4.2.1 Single- vs dual-chamber analysers

**380.** In the majority of cases, single-chamber instruments perform without difficulty. To overcome problems that may occur at sites where the $NO_x$ and NO concentrations fluctuate rapidly, for example at kerbside or roadside sites, manufacturers have devised a number of solutions. These mostly involve increased cycle frequency, or the introduction of delay loops (see below). Experience to date within the operation of the UK national networks has not indicated concerns regarding the performance of single-chamber instruments at roadside and kerbside sites. However, at the London Marylebone Road kerbside, which represents an extreme monitoring environment, a dual-chamber sampler is installed. Care in the installation and configuration of single-chamber instruments at roadside and kerbside sites is recognised as an important aspect of site commissioning.

**381.** There is a paucity of peer-reviewed studies comparing the performance of single- and dual-chamber samplers and reliance has largely been based on manufacturers' reports. There is a need for more independent research in this area. The new CEN standard for chemiluminescent analysers (see Section 4.10) will introduce a specific test to evaluate the ability of analysers to respond correctly under conditions of rapidly changing concentrations. This will provide a valuable benchmark against which to assess all analysers in future.

## 4.2.2 Increased cycle frequency

**382.** Single-chamber chemiluminescence analysers are typically set to operate with 15-second cycle times i.e. the switching between the $NO_x$ and NO measurement takes place every 15 seconds. In environments where the $NO_x$ concentration is expected to fluctuate on a shorter timescale than this, then the cycle time can be reduced to 3 or 4 seconds. An investigation into this approach was performed at a kerbside location in Oxford for a 3-month period in 1996, when a single-chamber and a dual-chamber instrument were operated in parallel. The single-chamber instrument was modified to allow operation at high switching speeds by reducing the cycle time to 3 seconds per mode, increasing the response time of the input amplifier, adjusting the final signal processing, and fitting a reservoir volume to the sample inlet to reduce gas transients to within the overall cycle time of 6 seconds. The single-chamber instrument showed no negative $NO_2$ 15-minute averages, which would appear if rapid fluctuations were a significant problem, and good long-term agreement with the dual-chamber instrument.

**383.** More recently, single-chamber analysers have been developed with low-temperature NO-to-$NO_2$ converters and fast-response photodiode detectors. The system allows switching between the $NO_x$ and NO channels at 0.5 second intervals, and provides a virtually concurrent analysis.

### 4.2.3 Delay loops

**384.** An alternative approach to increased cycle frequency has been the introduction of a delay loop into the sample stream. This effectively allows the instrument to sample $NO_x$ and NO simultaneously, but to measure them sequentially. Both the $NO_x$ and NO sample streams are collected at the same time. Whilst $NO_x$ is measured, the NO sample stream is sent round a precise volume loop, delaying its arrival at the reaction chamber until the $NO_x$ cycle is completed. Typical cycle times of 4 seconds are used.

### 4.2.4 Interferences

**385.** An assessment of overall uncertainty budgets, including interferences, has been reported (Gerboles *et al.,* 2002). Two forms of interference may occur in the chemiluminescent sampler; a reduction in the chemiluminescence intensity by quenching in the reaction chamber and, bias due to conversion of various N-species to NO taking place in the $NO_2$-to-NO converter. Whilst a variety of compounds (including $H_2O$, $O_2$, $CO_2$, CO, Ar and $H_2$) may give rise to quenching effects, Gerboles *et al* concluded that only water vapour is likely to give rise to significant effects. The installation of permeation driers at the sample inlet should prevent such problems occurring and are a common feature of most modern samplers.

**386.** The conversion of a number of additional oxidised nitrogen species to NO has been reported to occur with high efficiency, under the conditions in the $NO_2$-to-NO converter (for example, Winer *et al*., 1974; Grosjean and Harrison, 1985). These species include $HNO_3$, HONO, peroxyacetyl nitrate (PAN) and alkyl nitrates, which therefore potentially make some contribution to the apparent $NO_2$ signal. As described further in Section 3.3.2, only PAN and HONO are believed to contribute significant interference at ambient concentrations observed in the UK. For high temperature converters, these interferences are likely to account for ≤ 2% and ≤ 5% of the $NO_2$ signal, respectively, under typical urban background conditions, although larger contributions potentially occur under certain conditions.

## 4.3 Diffusive samplers

**387.** Passive diffusive samplers for $NO_2$ are simple and inexpensive devices that have been used over many years for the measurement of ambient $NO_2$ concentrations. The samplers widely used in the UK are based on the design introduced by Palmes (Palmes *et al.,* 1976) and are comprised of an acrylic tube that can be sealed at both ends. One end of the tube contains stainless steel grids coated with triethanolamine (TEA) that adsorbs $NO_2$ to produce a nitrite salt that is subsequently determined by colorimetry (analysis by ion chromatography has also been used (Gair *et al.,* 1991) to improve the detection limit for monitoring in remote rural areas). Exposure commences when the inlet cap is removed, which sets up a concentration gradient within the tube, such that molecular diffusion occurs towards the TEA-coated grid. The rate of diffusion occurs according to Fick's Law:

$$F = -D\frac{dC}{dZ}$$

Where F is the molar flux (mol $cm^{-2}$ $s^{-1}$), D is the diffusion coefficient ($cm^2$ $s^{-1}$), C is the concentration (mol $cm^{-3}$) and Z is the diffusion path coordinate (cm).

**388.** After the period of exposure (t), the total quantity of gas transferred along the tube (Q) is determined by chemical analysis. Since the rate of gas transfer is governed by the tube geometry (length (l) and internal area ($\Pi r^2$)), and the gas concentration at the closed, absorber, end of the tube is zero, the average gas concentration, C, at the open end of the tube during the exposure can be calculated from:

$$C = \frac{Ql}{D\pi r^2 t}$$

**389.** Whilst Palmes tubes are used almost exclusively in the UK, other passive diffusion samplers have been developed in other countries. These include the Passam sampler (Switzerland), Analyst (Italy), IVL (Sweden), and Radiello (Italy).

**390.** It is important to note that there are a number of different tube preparation methods in use, which may have a significant effect on the performance of the method. The difference principally relates to the way in which the metal grids are coated with the TEA solution. The methods currently in common use are based on 50% TEA in acetone, 50% TEA in water, and 20% TEA in water, with a few laboratories using 10% TEA in water.

### 4.3.1 Performance of diffusion tubes

**391.** A number of studies have examined the performance of diffusion tubes, since their first application to ambient sampling in the early 1980s. Most have involved exposing tubes alongside chemiluminescence monitors. Several factors, listed below, have been identified that appear to affect tube performance, although the findings are often confusing and contradictory.

- the laboratory preparing and analysing the tubes
- the exposure interval – weekly, fortnightly or monthly
- the time of year
- the exposure setting – sheltered or exposed
- the exposure location – roadside or background
- the tube preparation method
- the exposure concentration and $NO_2/NO_x$ ratio.

**392.** A number of mechanisms have been identified to explain some of the observations. This section identifies those factors that clearly influence tube performance. It is based on a more detailed, but not exhaustive, review presented in Appendix 2. It is important to note that the majority of $NO_2$ data used in compiling this report are derived from continuous analysers, rather than diffusion tubes, although the latter remain important for general assessment of $NO_2$ air quality.

**393.** It is clear that attempts to identify and/or quantify the influence of a given factor may be confounded by the influence of other factors. For example, the statement commonly made that diffusion tubes tend to over-estimate $NO_2$ concentrations, for example, Heal *et al.* (1999), Heal *et al.* (2000), Kirby *et al.* (2001) and Bush *et al.* (2001), applies to specific circumstances. In practice there are circumstances when diffusion tubes can systematically over-estimate or under-estimate concentrations.

**394.** The key factor influencing the performance of diffusion tubes is the laboratory carrying out the preparation and analysis. For instance, in a recent comparison of 7 laboratories, using one tube preparation method, 50% TEA in acetone, with tubes exposed for a month at a time, the annual mean bias (as quantified against collocated chemiluminescence analysers) ranged from +20% to -26% from one laboratory to another. The reason for the differences between the laboratories is currently not understood. Variability in performance may also be related to the tube preparation method, in particular the method of preparation of the adsorbent coating on the grids. Four TEA/solvent preparations are currently used in the UK: 50% TEA in acetone, 50% TEA in water, 20% TEA in water, and 10% TEA in water. Preparation methods also differ in whether grids are coated in advance of tube assembly by dipping into TEA/solvent mixtures, or whether an aliquot of TEA/solvent is pipetted onto grids after the tubes have been assembled. Various studies have examined whether preparation method affects performance but, as yet, no consistent pattern has emerged.

**395.** Diffusion tube performance is clearly influenced by the exposure interval, which ranges from 1 week to 1 month, with tubes exposed for longer intervals producing lower concentrations. Although no convincing mechanism has been put forward to account for lower measured concentrations, a light-dependent loss of nitrite from the adsorbent, or a temperature dependency in the diffusion coefficient that is not allowed for, have been postulated. Time of year also influences performance, with TEA-in-water tubes showing higher concentrations in the August to November period. This seasonal pattern is not seen in results for tubes prepared with TEA-in-acetone. There is currently no explanation for this pattern.

**396.** There is some evidence that the exposure setting may influence concentrations, with greater uptake in more exposed locations. The explanatory mechanism is believed to be a shortening of the effective diffusion length as a result of wind induced turbulence at the tube entrance.

**397.** There is some evidence that tube performance is affected by ambient concentrations of $NO_2$, $NO_x$ and $O_3$ at the exposure site. The postulated mechanism is that a greater uptake of $NO_2$ arises from production of additional $NO_2$ along the diffusion path within the tube because of reaction between co-diffusing NO and $O_3$ and a disruption of the photochemical equilibrium between $NO_2$ – NO – $O_3$ (see Section 3.2.1). (The photolytic component is switched off within the tube). Evidence for any systematic difference in diffusion tube performance between roadside and background location is equivocal and will be related to the above mechanism. Clearly, any relationship between diffusion tube performance and ambient concentrations is complex and may be masked by effect on performance arising from preparation method, exposure interval, etc.

**398.** Defra has recently initiated an annual intercomparison exercise for diffusion tubes. This will involve exposure of triplicate tubes, from the full range of laboratories supplying and analysing tubes in the UK, alongside a chemiluminescence monitor at a background location at Leigh, in Greater Manchester. Unlike previous such studies, this scheme will run using monthly exposures for a full year (although some smaller laboratories have opted to participate on a quarterly basis). It will provide useful additional information on tube performance.

**399.** The precision of diffusion tube samplers, as determined by the standard deviation of results from groups of 6 tubes exposed simultaneously as part of the UK $NO_2$ Diffusion Tube Network Annual Intercomparison (AEA Technology, 2002), has been found to be below 6 μg $m^{-3}$ in most cases

### 4.3.2 Recommendations for use of diffusion tubes

**400.** The analysis of factors influencing diffusion tube performance identifies a range of factors that seem to be related to tube performance: the laboratory preparing and analysing the tubes; the exposure interval; the time of year; the relationship between NO, $NO_2$ and $O_3$ at the exposure site; possibly a difference between exposed and more sheltered settings; and the method of tube preparation. Because there are so many factors affecting tube performance, it is crucial for any particular survey that:

- the variables that can be controlled are held constant, especially laboratory, tube preparation method and exposure interval;
- the performance of the tubes is determined specifically for the fixed set of variables being used, and the results adjusted for any bias identified.

**401.** Diffusion tube measurements would benefit from specific, validated procedures for their implementation. The preferred route would be for these to emerge through the work of the European standardisation body, CEN, mentioned further in Sections 4.8.3 and 4.10. If this does not happen in the near future, the UK should consider adopting a national standardised method.

**402.** As the principal value of diffusion tubes is to measure annual mean concentrations, the assessment of tube performance should be determined over a full year, with a minimum of 9 months collocation data being necessary to give a reasonable estimate of annual performance (Laxen & Wilson, 2002). It seems reasonable to conclude, on the evidence available, that when used in an appropriate way, as described above, diffusion tubes should be capable of measuring the annual mean concentration to within ±20% (95% confidence interval).

## 4.4 Electrochemical cells

**403.** There are a variety of portable samplers available, based on the use of electrochemical cells. In its simplest form, the principal of operation depends on the electrochemical reduction of $NO_2$ between two electrodes immersed in an electrolyte reservoir. $NO_2$ present in the sample air passes through a capillary diffusion barrier into the reaction cell, where it is reduced at the electrode. The migration of electrons produced by the reaction results in a net current flow, which is proportional to the $NO_2$ concentration.

**404.** Whilst these types of samplers continue to be widely used for the assessment of occupational exposure, their application to ambient monitoring is limited due to the high limit of detection of the electrochemical sensor. As an example, the stated lower limit of detection for $NO_2$ quoted for one commercially available electrochemical analyser is 200 $\mu g\ m^{-3}$.

**405.** There is evidence that some or all varieties of electrochemical cell intended to measure $NO_2$ actually measure a combination of $NO_2$ and $O_3$. This may be useful at certain times in some environments, for example at city centre roadside locations where $NO_2$ concentrations are often higher than $O_3$. Elsewhere, interpretation of the data can be difficult.

**406.** A growing application of analysers based on electrochemical cells is as part of urban traffic control systems or urban traffic management and control systems. Because of the problems with $NO_2$ measurement by electrochemical cells, the air quality data used in these situations tends to focus on CO, not $NO_2$, as an indicator of levels of traffic pollution, since CO is easily measured by electrochemical cells (Ropkins *et al.,* 2000).

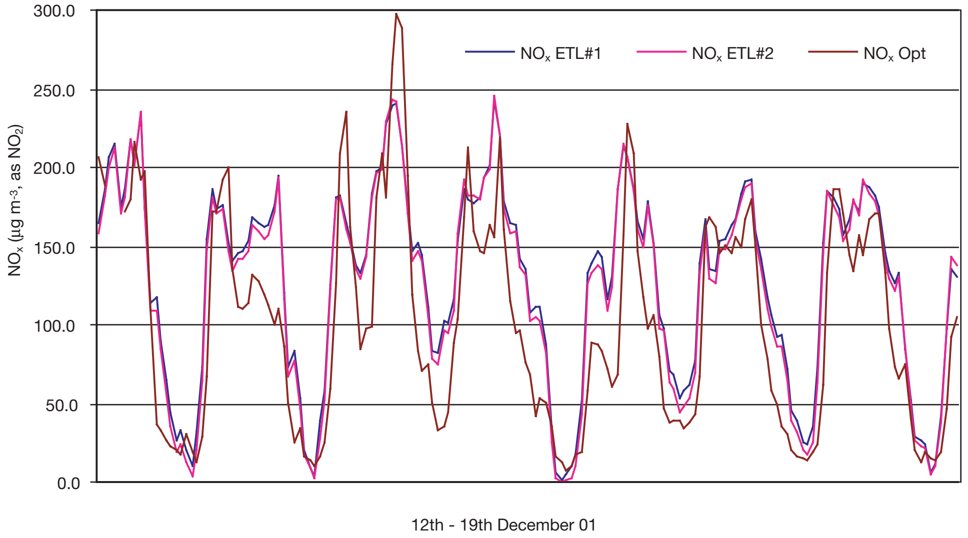
## 4.5 Thick film sensors

**407.** The development of solid-state thick film gas sensors based on semi-conducting oxides has provided a new range of samplers for environmental monitoring (Carotta *et al.,* 2000). These sensors are constructed from nano-structured semi-conducting metal oxides, which are maintained at an operating temperature of between 250 and 400°C. As current is passed through the sensor, an electrical response is produced in proportion to a specific gas concentration.

**408.** Currently, these thick film sensors have been produced for a range of common pollutants, including CO, $O_3$, NO and $NO_2$, and commercially available instruments are becoming available. Whilst the $NO_2$ sensor is still undergoing development, a thick film $NO_x$ sensor has been trialed in the UK and shown to demonstrate reasonable comparison with a co-located chemiluminescent analyser (see Figure 4.3).

**409.** Whilst is it not envisaged that these samplers will replace the chemiluminescent method, they offer a number of potential benefits, such as use in screening surveys in urban locations, the identification of pollution 'hot spots'; and mobile monitoring in buses and cars etc.

**Figure 4.3** Comparison of co-located thick film sensors and chemiluminescence analyser at a roadside site (12-19 December 2001). $NO_x$ETL#1 and $NO_x$ETL#2 are thick film sensors and $NO_x$Opt is a chemiluminescent analyser.



## 4.6 Differential optical absorption spectroscopy (DOAS)

**410.** DOAS is a technique that can be used for the measurement of a wide range of air pollution species. In the usual configuration, light (visible, non-laser light) from a light source passes through a fixed path in the atmosphere, typically 100 – 1000 m in length. At the end of this path, the light received is analysed in an opto-analyser system. The amount of a specific gaseous substance in the atmosphere follows the principle of the Beer Lambert Law:

$$I_1 = I_0 e^{-\alpha LC}$$

where: $I_1$ is the light intensity after absorption, $I_0$ is the light intensity before absorption, $\alpha$ is the absorption co-efficient at the selected wavelength, L is the optical path length and C is the concentration of the gaseous substance.

**411.** In commercial analysers, sophisticated signal processing is undertaken to account for interfering species and variability in atmospheric optical transmission conditions.

**412.** Many species can be measured by the DOAS technique, but the most common configuration for ambient air monitoring is to measure $NO_2$, $SO_2$, $O_3$ and benzene. NO can be measured, but requires a different lamp type. At least one commercial DOAS instrument has EPA approval for the measurement of $NO_2$ (and $SO_2$ and $O_3$) provided certain operational and calibration requirements are followed.

**413.** Many intercomparison studies have demonstrated that DOAS can provide comparable $NO_2$ data to chemiluminescent point analysers, within the constraint that the DOAS analyser is averaging concentration measurements along the path length of measurement, rather than measuring at a single point.

**414.** As with all air pollution analysers DOAS instruments require regular calibration and other QA/QC checks to ensure reliable, high quality data.

## 4.7 The UK monitoring networks

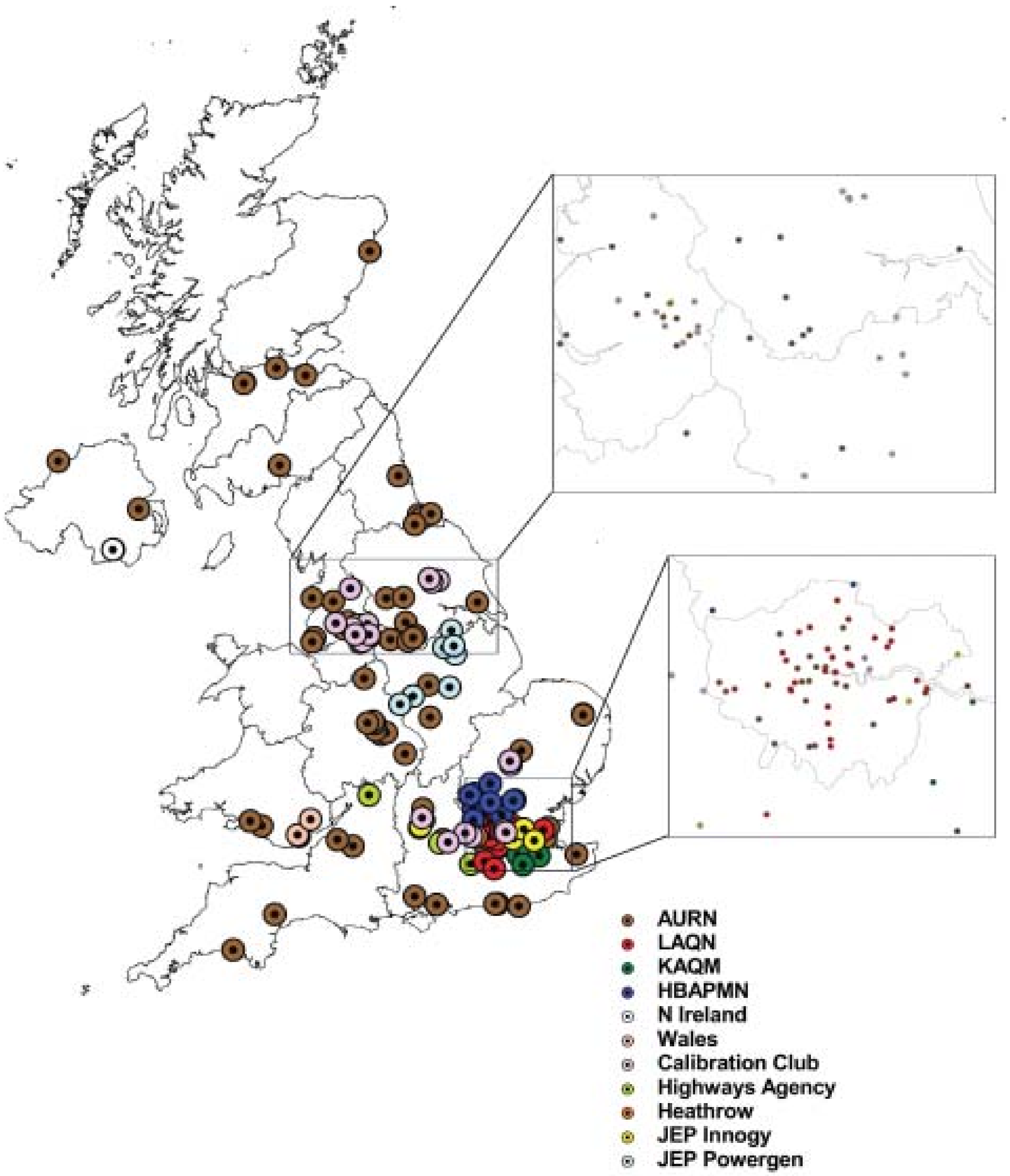
**415.** Monitoring of $NO_2$ concentrations is carried out at both a national and regional scale using both chemiluminescence and diffusion tube samplers. These networks are described in the following sections.

### 4.7.1 Automatic monitoring networks

**416.** Automatic networks are operated at both the national level, on behalf of Defra and the Devolved Administrations, and on a regional or sector-specific level, on behalf of local authorities, the Highways Agency, the power generation industries and other organisations.

**417.** The locations of all sites which have provided $NO_2$ data for this study, for 2001, are shown in Figure 4.4.

**Figure 4.4** Location of NO$_2$ monitoring sites (2001) used in this study.



**418.** The structures of the various monitoring networks are summarised in Table 4.2.

**Table 4.2** Summary of automatic $NO_2$ monitoring networks

[Note – this table summarises information for the $NO_2$ monitoring networks used in this report – it is not a complete list of all networks in the UK]

| Network responsibility | Management unit | QA/QC responsibility | Number of $NO_x$ monitoring locations |
|---|---|---|---|
| UK Networks | | | |
| ● AURN[1] | Casella Stanger | netcen | 85 |
| ● LAQN[2] | Kings College ERG | netcen | 15 |
| Regional Networks | | | |
| ● LAQN[2] | Kings College ERG | NPL/ERG | 54 |
| ● KAQM[3] | Kings College ERG | NPL/ERG | 15 |
| ● HBAPMN[4] | Kings College ERG | NPL/ERG | 13 |
| ● N. Ireland | netcen (from 01/03/02) | netcen (from 01/03/02) | 2 |
| ● Wales | LA or Powergen[5] | LA or Powergen[5] | 3 |
| Other Networks | | | |
| ● Calibration Club | netcen | netcen | 23 |
| ● Highways Agency | TRL | TRL | 5 |
| ● Heathrow Airport[6] | netcen | netcen | 1 |
| ● JEP/Innogy | Casella Stanger | Casella Stanger | 7 |
| | PowerTechnology | | 8 |
| ● JEP/Powergen[5] | | PowerTechnology | |

1 Automatic Urban and Rural Network

2 London Air Quality Network. A number of sites in this Network have been affiliated into the national networks

3 Kent Air Quality Network

4 Hertfordshire and Bedfordshire Air Pollution Monitoring Network

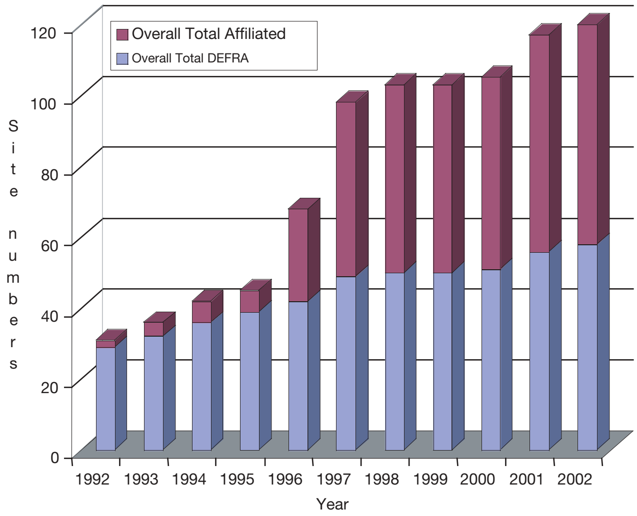
5 The Powergen, Sealand, Deeside site is also part of the Wales network

6 The Heathrow Airport site is also part of the LAQN

### *4.7.1.1 UK networks*

**419.** The UK networks are comprised of monitoring sites within both the Automatic Urban and Rural Network (AURN) and the London Air Quality Network (LAQN). The AURN contains a number of monitoring sites that are directly funded by Defra and the Devolved Administrations, together with additional sites that are owned and operated by other organisations (mainly local authorities) and which have been affiliated into the network. The LAQN consists solely of affiliated local authority monitoring sites. The national networks have expanded significantly over the past 8 years, most recently in order to meet the requirements of the First Daughter Directive (see Figure 4.5). Thus, whilst some sites have been operating for 10 years or more, and can provide invaluable information on long-term trends over this period, data are limited to a considerably shorter period at the majority of monitoring sites.

**Figure 4.5** Number of monitoring sites in the UK National monitoring network.



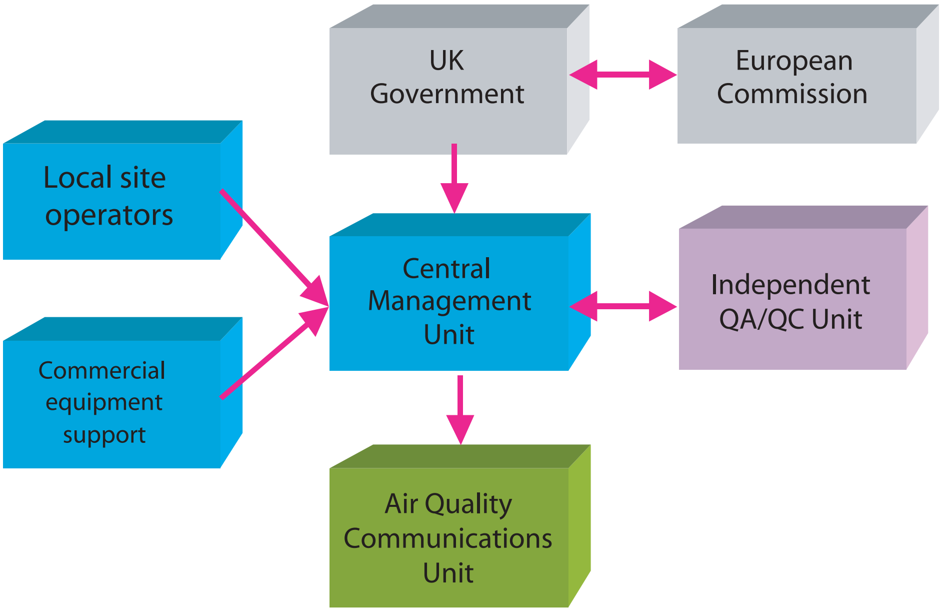
**420.** Monitoring stations are classified according to their location; a summary of the $NO_x$ monitoring sites is provided in Table 4.3. Details of the site type definitions used in the UK are provided in Appendix 3. Further details on the national monitoring network sites, and measurement data, can be found at www.airquality.co.uk.

**Table 4.3** Summary of $NO_x$ monitoring stations in the UK national networks (number of sites with co-located $O_3$ analysers shown in parentheses).

| Site Type | AURN | LAQN |
|---|---|---|
| Kerbside | 1 (1) | 2 (1) |
| Roadside | 15 (2) | 5 (0) |
| Urban Background | 29 (18) | 6 (6) |
| Urban Centre | 23 (23) | — |
| Suburban | 5 (4) | — |
| Industrial | 5 (2) | — |
| Rural | 7 (7) | — |
| **TOTAL** | **85 (56)** | **13 (7)** |

**421.** The basic operating structure of the AURN and LAQN sites in the national networks is identical, and is represented in Figure 4.6. Data are collected from the network sites on an hourly basis and, after initial validation, are disseminated to public and the media via the Air Quality Communications Unit.

**Figure 4.6** Outline structure of the National Air Quality Monitoring Networks.



### *4.7.1.2 Regional networks*

**422.** Regional networks are operated or co-ordinated by Kings' College ERG, DoE Northern Ireland and the Welsh Assembly Government, on behalf of local authorities. The operation of the ERG networks mirrors that of the national networks, with routine data polling and validation, and subsequent QA/QC to provide ratified datasets. A summary of the site types within these networks is provided in Table 4.4.

**Table 4.4** Summary of $NO_x$ monitoring stations in other UK networks.

| Site Type | LAQN[a] | KAQN | HABAPMN | N. Ireland | Wales |
|---|---|---|---|---|---|
| Kerbside | 1 | – | – | – | – |
| Roadside | 32 | 7 | 4 | 1 | 1 |
| Urban Background | 14 | 4 | 9 | 1 | 1 |
| Urban Centre | – | – | – | – | – |
| Suburban | 7 | 1 | – | – | – |
| Industrial | – | 1 | – | – | 1[b] |
| Rural | – | 2 | – | – | – |
| TOTAL | 54 | 15 | 13 | 2 | 3 |

a These sites not part of the UK network (Table 4.3)
b Also part of the JEP Powergen network (Table 4.5)

#### *4.7.1.3 Other networks*

**423.** Some Local Authority monitoring stations, throughout the UK, are part of the Calibration Club network within which data handling and data QA/QC are undertaken centrally by netcen, on behalf of the individual authorities.

**424.** Other monitoring networks are orientated towards monitoring air quality close to particular emission sources. Examples of such monitoring networks used in this report are those operated by the power generators, Heathrow Airport Ltd and the Highways Agency (monitoring sites close to very busy roads). As with national and regional networks, these other networks have recognised procedures for data quality assurance. A summary of the site types within these other networks is given in Table 4.5.

**Table 4.5** Summary of $NO_x$ monitoring stations in other UK networks.

| Site Type | Calibration Club | Highways Agency | Heathrow Airport Ltd | JEP/ Innogy | JEP/ Powergen |
|---|---|---|---|---|---|
| Kerbside | – | – | – | – | – |
| Roadside | 9 | 2 | – | – | – |
| Urban Background | 11 | – | – | – | – |
| Urban Centre | 1 | – | – | – | – |
| Suburban | – | – | – | – | – |
| Industrial | – | – | – | – | 1[b] |
| Rural | 2 | – | | 7 | 7 |
| Special | | | | | |
| rural kerbside | – | 2 | – | – | |
| suburban roadside | – | 1 | – | – | – |
| airport | – | – | 1[a] | – | – |
| **TOTAL** | **23** | **5** | **1** | **7** | **8** |

a also part of the LAQN (Table 4.4)
b also part of the Wales network (Table 4.4)

## 4.7.2 The UK $NO_2$ diffusion tube network

**425.** The Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations fund a large-scale survey of $NO_2$ concentrations throughout the UK, using passive diffusion tubes operated by local authorities. The principal aims of this survey are to:

- Identify high concentrations of $NO_2$ that may warrant more detailed investigation;
- Determine the spatial variation of $NO_2$ concentrations in the UK;
- Determine trends in $NO_2$ concentrations over a number of years.

**426.** The survey commenced in 1993 and currently comprises over 1300 sites operated by more than 300 local authorities. Up to December 2000, each authority operated 4 sites, including one kerbside location (1 to 5 metres from a busy road), one intermediate site (20 to 30 metres away from a busy road) and two background sites (in residential areas, and more than 50 metres from a busy road). From January 2001, sampling at intermediate sites has been discontinued and kerbside sites have been renamed as roadside sites to be consistent with the site classification system used for automatic monitoring. Hence, since January 2000, most authorities now operate 2 roadside sites and 2 urban background sites.

**427.** Tubes are supplied and analysed by a variety of analytical laboratories, and exposed over 4 or 5 week periods. Data are collated and processed centrally by netcen. Detailed information on the monitoring sites and measured data can be found at www.airquality.co.uk. Annual network reports are published (Loader *et al*., 2002) and a 5-year summary has been prepared (Stevenson, 2001).

## 4.8 Measurement uncertainty

### 4.8.1 The uncertainty of measurements – general principles

**428.** No measurement is exact, however sophisticated the method used. A measurement can only determine that the measured quantity lies within a certain range, and when interpreting data it can be as important to know the size of this range as it is to know the values of the data. This range is called the uncertainty of the measurement, and it is typically expressed as the range within which the true value is likely to lie with a probability of 95%.

**429.** Historically, uncertainties have been determined by different groups of scientists in quite different ways, so that the results are not necessarily comparable. Since 1993 there has been wide agreement to follow the principles of the ISO Guide to the Uncertainty of Measurement (ISO, 1993). In formal terms this requires an evaluation of all the factors linking the measurement to the definition of the units in which it is expressed[2].

**430.** The field of air quality in Europe has needed to take a close look at measurement uncertainties, because the Air Quality Directives specify an upper limit for the uncertainty with which different types of measurements must be made. This has resulted in a Report by CEN (the European Centre for Standardisation) entitled: ‘Air quality – approach to uncertainty estimation for ambient air reference measurement methods’ (CEN, 2002). This provides a common approach to determining measurement uncertainty for all pollutants, using various relevant measurement techniques such as automatic analysis, or manual sampling (pumped or diffusive) with subsequent laboratory analysis. The uncertainty limits for $NO_x$ and $NO_2$, as specified in the EU Directive 1999/30/EC are listed in Table 4.6.

**Table 4.6** Measurement uncertainty objectives for $NO_x$ and $NO_2$ given in EU Directive 1999/30/EC.

| | **Uncertainty (listed as accuracy in the Directive)** |
|---|---|
| Continuous Measurement (for example, chemiluminescent analyser) | 15% |
| Indicative Measurement (for example, diffusion tubes) | 25% |

Note: The percentages given in the table are for individual measurements averaged over the period considered by the limit value, at concentrations close to the limit value, for a 95% confidence interval.

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[2] To take a simple example, we might find that using a metre ruler allowed us to measure consistently to the nearest 0.5 mm. However, the GUM approach also requires us to compare our ruler at regular intervals with the definition of the metre – in practice using another ruler that has ultimately been calibrated against a national standard – and to evaluate how our ruler may change in length between calibrations, for example with changes in temperature, in order to assign the correct uncertainty. 0.5 mm is a measure of the repeatability of the measurement, while the uncertainty requires the other factors to be taken into account as well.

### 4.8.2 The uncertainty of chemiluminescence measurements

**431.** CEN has produced a draft standard (CEN, 2003a) setting out how National Networks should operate chemiluminescent analysers in order to meet the required uncertainty of ±15% (at the 95% confidence level). This includes a set of performance characteristics against which analysers need to be assessed for official approval, and activities required for ongoing QA/QC. Although the situation is not entirely clear (for example, no analysers commonly used in the UK have been put through a complete set of performance tests), it is likely that the great majority of UK National Network measurements will meet the uncertainty requirement.

**432.** Uncertainty in measurements with chemiluminescent analysers can arise from many factors relating to the instrument and to its operation and calibration. For example:

Instrument:

- linearity;
- repeatability;
- drift in zero and span;
- dependence on sampling pressure, air temperature, sample gas temperature, voltage;
- averaging error;
- interferences;
- converter efficiency.

Instrument calibration:

- uncertainty in calibration gas concentration;
- incorrect procedure for calibration.

Instrument operation:

- losses in sample line;
- operation outside of specified temperature, line voltage etc.

**433.** Careful testing of analyser performance and close control of calibration and operational conditions is required to ensure minimum data uncertainty.

### 4.8.3 The uncertainty of diffusively sampled measurements

**434.** Although the procedure for calculating the uncertainty of measurements made with diffusive samplers is given within CR 14377 (CEN, 2002), there are as yet no clear results for $NO_2$ samplers. Properly conducted diffusive measurements of benzene have been found to have uncertainties of around 20 to 25%, but the physical mechanisms for absorbing and analysing hydrocarbons with diffusive samplers are much simpler than those for $NO_2$. There is a CEN Working Group looking at diffusive samplers for $NO_2$ measurement. Samplers of several different designs used across Europe – the Palmes tube used in the UK Diffusion Tube Network, Passam (Swiss), Analyst (Italian), IVL (Swedish), and Radiello (Italian) – have been exposed simultaneously alongside automatic analysers. The results give an indication of the variability within individual samplers of the same design, analysed at the same laboratory, and between different designs of sampler, but the study so far is limited in scale and the results are not published.

**435.** The recent analysis of collocation studies carried out by local authorities throughout the UK has demonstrated that the annual mean concentrations for 50% TEA-in-acetone diffusion tubes, when adjusted for bias, have an uncertainty of ± 20% (at the 95% confidence level). The uncertainty was greater for tubes prepared with 50% TEA-in-water.

## 4.9 QA/QC of $NO_2$ air quality monitoring data

### 4.9.1 Introduction

**436.** In order to make a reliable assessment of air quality from measurement data, it is essential that the data are of sufficient quality. The overall aim of any quality assurance programmes should be to ensure that the measurement data fulfil the aims and objectives of the monitoring programme.

**437.** In this report, data from several monitoring networks are utilised. The aims and objectives of these networks may differ slightly, but the following general objectives will apply in most cases:

- meeting statutory requirements;
- providing necessary information on air quality for the public, regulators and/or the scientific community;
- providing information for local authority air quality review and assessment;
- identifying long term trends on air pollutant concentrations;
- assessment of policy effectiveness.

**438.** ***Quality assurance*** refers to the overall management of the process involved in obtaining the data; whilst ***quality control*** refers to the activities undertaken to check and optimise data accuracy and precision after collection. Hence, quality assurance relates to the measurement **process**, whilst quality control is concerned primarily with **outputs**.

**439.** This section will summarise QA/QC activities in relation to both the automatic $NO_2$ monitoring data and the diffusion tube data presented in this report.

### 4.9.2 QA/QC activities for automatic air monitoring networks

**440.** There will, inevitably, be differences in the detailed QA/QC activities undertaken in each network supplying data for this report. However, this section provides a general overview of activities which will be applied to all networks, perhaps to a greater or lesser extent, depending on the specific objective of the monitoring undertaken.

**441.** Quality assurance activities include:

- network design;
- station siting;
- instrument selection;
- instrument calibration;
- instrument service and repair;
- operations manual;
- operator training;
- correct operation of the on-site equipment.

**442.** Quality control activities include:

- information management;
- data ratification;
- quality circle review and feedback.

**443.** It is important that all factors that may affect the quality of the data are considered. For example, the sample inlet line to the gas monitor needs to be inert and have no, or negligible, effect on the gases monitored. The sample line needs to be carefully designed, cleaned and maintained and regularly tested for its integrity.

## 4.9.3 Quality assurance

**444.** The design of the Automatic Monitoring Network and information on general station siting is provided in the Automatic Urban Monitoring Network Site Operator's Manual (http://www.aeat.co.uk/netcen/airqual/reports/lsoman/lsoman.html) (AEA Technology, 1998). In recent years, some new sites have been added to ensure that the network conforms to the network design and monitoring criteria specified in the Air Quality Framework Directive and subsequent Daughter Directives (96/62/EC, 1999/30/EC, 2000/69/EC). A classification system for UK air quality monitoring site locations has been devised and is presented in Appendix 3. The locations of all monitoring sites used in this report have been classified according to this system.

**445.** The Site Operator's Manual provides information on the procedures adopted in the network for instrument service and repair and general background information about the network. All site operators have a copy of the manual and are trained by the network QA/QC Unit on all of the network operation procedures.

### *4.9.3.1 Instrument selection*

**446.** All of the automatic $NO_2$ data presented in this report have been obtained from chemiluminescent analysers. This is the EU reference method of measurements and described in Section 4.2 of this report. Provided that the operational and QA/QC requirements discussed in this section are followed, measurements from chemiluminescent analysers will be robust and reliable.

### *4.9.3.2 Calibration*

**447.** In the national network and in the majority of local networks a 3-stage approach to calibration is adopted:

- daily span and zero check with the analysers internal gas source (permeation tube for $NO_2$ analysers)
- weekly or fortnightly manual calibration with certified calibration gas cylinder
- 6-monthly site audit check with an independent gas standard to check the calibration of the analyser and the stability of the on-site gas calibration cylinder.

**448.** The daily autocalibration is used only to identify rapidly any possible analyser faults that may require attention. The gas from internal permeation devices is not considered sufficiently stable or reliable to be considered as a calibration source.

**449.** The weekly or fortnightly manual calibrations with accredited gas standards provide the main calibration data to scale the analyser output to correct concentration units for the gas species being monitored. Detailed records are kept for all calibrations undertaken and, during the calibration visits, any consumables (such as filters etc.) are replaced and the general fabric of the site inspected.

**450.** A major tool for quality assurance checking in the national networks is the detailed site, instrument, calibration gas and operator audit carried out at 6-monthly intervals. A single independent body visits every site in the network to undertake a full site check. All analysers on site are checked; in relation to the $NO_2$ analyser, the following checks are undertaken:

- linearity;
- noise;
- response time;
- leaks and flow check;
- converter efficiency;
- analyser calibration.

**451.** The sample inlet and manifold system and the on-site gas calibration standards are also checked to ensure correct operation of the full measurement system. The bodies undertaking these tests have the appropriate UKAS accreditation and a UKAS certificate of calibration is produced documenting the results of the checks.

**452.** These quality assurance tasks ensure, as far as possible, that data collected from the analysers are correct and accurate at the time of collection. However, there may be faults and problems that only become apparent when a large time series of data or calibrations are examined together. The Quality Control system therefore provides a further check on the data.

### 4.9.4 Quality control

**453.** Quality control of air pollution data is the process of checking, accepting, rejecting or adjusting the data, on the basis of all available information. This operation is usually referred to as data ratification and is generally carried out on 3 or 6-month data blocks, or annually, so that a reasonable amount of data and several calibrations are available to assess consistency and long-term performance. The ratification procedure consists of collating all of the available data, calibration records, service records and any other information relevant to the analyser or site operation. All of this information, together with meteorological data and information from other analysers or other sites, may be used in the ratification process. An important principle of the data ratification procedures is that data are always retained unless there is a specific reason for rejection.

**454.** The final task of ratification, within the national automatic network, is to hold a quality circle to identify any generic issues arising from the data ratification process and to use these as a basis for recommendations to improve network performance.

### 4.9.5 Diffusion tubes

**455.** Diffusion tube data in the UK Nitrogen Dioxide Diffusion Tube Network undergo similar QA/QC procedures with the same aims as those for the automatic data, but with differences appropriate to the method.

**456.** The monitoring sites are classified using the same system as for the automatic sites, although all diffusion tube sites are now either roadside or urban background. All monitoring locations selected by local authorities are checked from maps and photographs supplied. A manual for the survey (AEA Technology, 2003) has been prepared as can be found at: http://www.aeat.co.uk/netcen/airqual/reports/$NO_2$man/$NO_2$instr.pdf

**457.** Data are manually checked as they are received from the local authorities on a monthly basis. Any problems identified at this stage are discussed with the local authority concerned.

**458.** Two quality assurance schemes are operated to control analytical laboratories contributing data to the network. The Health and Safety Executive operate a laboratory proficiency test scheme as part of the Workplace Analytical Scheme for Proficiency (WASP) and, in addition, a field intercalibration of diffusion tubes from all laboratories takes place annually. The latest report has been published (AEA Technology, 2002).

**459.** At the end of each calendar year, the dataset is checked in its entirety and also fed back to the local authorities for final checking and any additional comments on their own data. When these checks have been completed, the data are formally ratified.

## 4.9.6 Provisional and ratified data

**460.** Data from the UK national air quality monitoring networks are marked as ‘provisional’ or ‘ratified’ depending on what stage they are at in the process of ratification. When data are first collected from the analyser on site, they are scaled with calibration data from the last calibration. In many cases, this will produce satisfactory data, with problems only arising if the instrument is unstable or drifting rapidly. The data are then automatically screened using computer algorithms to highlight suspect data, but no data are deleted at this stage. This process occurs in real time and all data that are not marked as suspect are sent to the National Air Quality Information Archive within about 1 hour of being collected. Data sent to the archive at this stage are marked as provisional.

**461.** All of the provisional data, together with all the identified suspect data, then undergo full ratification, as described in Section 4.9.4 in 3-month blocks. As part of the ratification process, the suspect data may be reinstated if deemed to be genuine. Following the ratification process, the fully ratified dataset are re-sent to the Air Quality Archive (in 3-monthly blocks, 3 months in arrears) and the provisional data are overwritten with the ratified data.

**462.** A similar procedure is adopted for the $NO_2$ diffusion tube data except that the provisional data are not collected automatically but on manually returned forms from the many network participants. The initial screening is undertaken manually and the provisional data are updated to the Archive every 3 months. These provisional data are then ratified annually to produce the final ratified dataset for the year, using the procedures outlined in Section 4.9.5. This ratified data set then overwrites and updates the Archive once per year, approximately 6 months after the year ends.

**463.** All data provided in this report have undergone quality assurance and quality control checking and are therefore regarded as ratified.

## 4.10 Future developments relating to European standardisation

**464.** As mentioned in Section 4.8.2, one of the elements of the European Air Quality legislation is a set of written standards that are currently being produced by the European Centre for Standardisation (CEN). These are designed to ensure that all Member States are making their measurements with the required level of accuracy, and Member States must follow these standards unless they can demonstrate that their own methods give equivalent results.

**465.** The draft standard for chemiluminescent NO and $NO_2$ measurements, prEN 14211 (CEN, 2003a), has been written by a CEN Working Group of technical experts from the Member States. As this AQEG report is being written, comments are being sought on the draft from the wider measurement community through national standardisation bodies, for example BSI in the UK. These comments are expected to lead to changes in at least the detail of the standard before it comes into force. It would therefore be premature to predict the ways in which National Network measurements will need to change to comply with European requirements in future. They will depend on the results of tests on analysers as they are assessed against the final set of performance characteristics, and on the detailed requirements for daily calibration checks and longer term Quality Assurance/Quality Control, for example. When published, this CEN standard will legally replace the existing British standard covering ambient NO and $NO_2$ measurements, ISO 7996:1985. The CEN standard will place more stringent requirements on the measurement process than the ISO standard.

**466.** A formally accredited route for certifying instruments against the performance characteristics is already in place within the Environment Agency's MCERTS scheme.

**467.** Regarding diffusive sampling, a series of CEN standards has recently been published (CEN, 2003b) as EN 13528 Ambient Air Quality – Diffusive samplers for the determination of concentrations of gases and vapours: Part 1 – General Requirements; Part 2 – Specific Requirements and Test Methods; and Part 3 – Guide to selection, use and maintenance. These standards have a different approach to that for chemiluminescent measurement in that they were not specifically written to support the EU legislation, and so are not obligatory, and they do not go into a similar level of detail as to how measurements should be made. The scope of these standards includes samplers for $NO_2$, NO, $SO_2$, $NH_3$, $O_3$, formaldehyde, and volatile organic compounds. Further CEN standards covering individual pollutants such as $NO_2$ in detail may be produced, but the position at present is not clear.