

## 5. Ambient Air Quality Monitoring and Assessment

### 5.1 Assessment tools and functions

This chapter reviews some of the methodologies and systems used for the assessment of ambient air quality, with particular reference to the requirement for population exposure assessment and for determining compliance with standards or guidelines. The pollutants considered in detail are, SO<sub>2</sub>, NO<sub>2</sub>, CO, O<sub>3</sub>, SPM and lead. These have a variety of potentially acute and chronic population health impacts, discussed in Chapter 3. Accordingly, the evaluation of air quality against guidelines may need to consider a range of time scales for effects, ranging from 10 minutes (SO<sub>2</sub>) to one year (NO<sub>2</sub>, SO<sub>2</sub>, lead).

The three main air quality assessment tools are:

- ambient monitoring
- models
- emission inventories/measurement

The ultimate purpose of monitoring is not merely to collect data, but to provide the information necessary for scientists, policy makers and planners to make informed decisions on managing and improving the environment. Monitoring fulfils a central role in this process, providing the necessary sound scientific basis for policy and strategy development, objective setting, compliance measurement against targets and enforcement action (Figure 5.1).

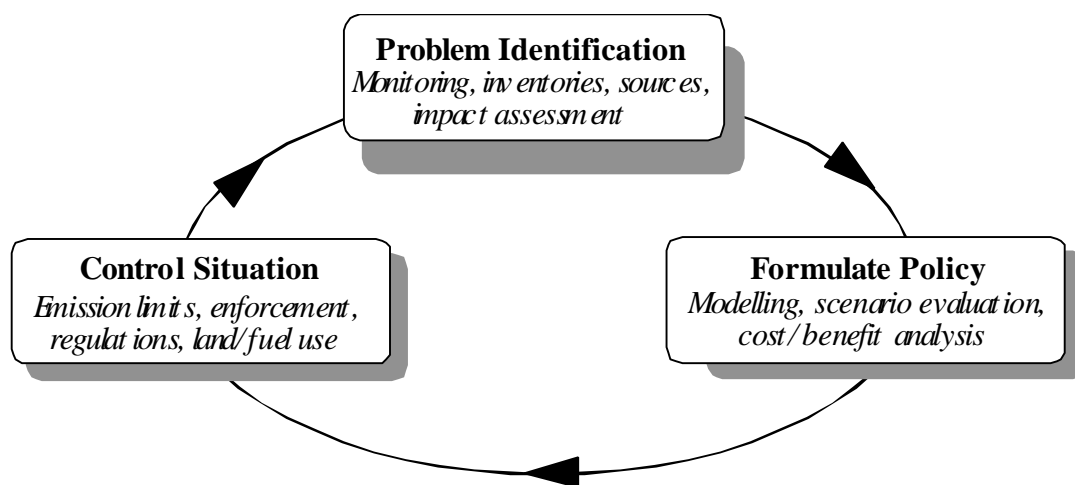


Figure 5.1. The Role of Monitoring in Air Quality Management

However, the limitations of monitoring should be recognized. In many circumstances, measurements alone may be insufficient -or impractical- for the purpose of fully defining population exposure in a city or country. No monitoring programme, however well funded and designed, can hope to comprehensively quantify patterns of air pollution in both space and time. At best, monitoring provides an incomplete - but useful - picture of current environmental quality. Monitoring therefore often needs to be used in conjunction with other objective assessment techniques, including modelling, emission measurement and inventories, interpolation and mapping. These are discussed in greater detail in Chapter 6.

Conversely, reliance on modelling alone is not recommended. Although models can provide a powerful tool for interpolation, prediction, and optimization of control strategies, they depend on the availability of reliable emission data. A complete inventory for a city or country may need to include emissions from

point, area and mobile sources; in some circumstances, assessment of pollutants transported into the area under study may also need to be considered. It is important, also, that the models utilized are appropriate to local conditions, sources and topography, as well as being selected for compatibility with available emission and meteorological datasets.

Inventories will, for the most part, be estimated using emission factors appropriate to the various source sectors (verified by measurement), and used in conjunction with surrogate statistics such as population density, fuel use, vehicle kilometres or industrial throughput. Emission measurements will usually only be available for large industrial point sources, or from representative vehicle types under standardized driving conditions.

All three assessment tools are interdependent in scope and application. Accordingly, monitoring, modelling and emission assessments should be regarded as complementary components in any integrated approach to exposure assessment or determining compliance against air quality criteria. Thus, for a reasonably complete picture of population exposure, ambient monitoring data will need to be supplemented by corresponding information from microenvironment and individual exposure surveys. This chapter focuses on ambient monitoring techniques and systems. Historically, these have provided most of the data used for exposure assessment. Recent publications have dealt in some detail with microenvironment and individual exposure monitoring (WHO 1999a). These issues are discussed in Chapter 4.

## **5.2 Monitoring objectives**

The first step in designing or implementing any monitoring system is to define its overall objectives. Setting diffuse, overly restrictive or ambitious monitoring objectives will result in cost-ineffective programmes with poor data utility. In such circumstances, it will not be possible to make optimal use of the available manpower and resources. Thus it is vital that clear, realistic and achievable monitoring objectives be set. This enables appropriate Data Quality Objectives (DQOs) to be defined (Box 5.2). In turn, this makes it possible for a targeted and cost-effective Quality Assurance Programme (QAP) to be developed. Overall requirements for such a programme are addressed in outline in section 5.3. A clear definition of overall monitoring objectives and DQOs is therefore essential to enable networks to be optimally designed, priority pollutants and measurement methods to be selected, and data management/reporting requirements to be identified (Figure 5. 2).

The relationships between the data collected and the information to be derived from it must be taken into account when a monitoring programme is planned. This emphasizes the need for users and potential users of the data to be involved in the planning of surveys, not only to ensure that they are appropriate to their needs, but also to justify the resource commitment. It should be recognized that monitoring networks are invariably designed for a variety of functions. These may include policy and strategy development, local or national planning, measurement against international standards, identification/quantification of risk and public awareness. Typical monitoring functions are summarized in Box 5.1. Every monitoring survey or network is therefore different, being influenced by a unique mix of local/national issues and objectives.

**Box 5.1 - Key Monitoring Objectives**

- Determining population exposure and health impact assessment.
- Informing the public about air quality and raising awareness.
- Identifying threats to natural ecosystems.
- Determining compliance with national or international standards.
- Providing objective inputs to Air Quality Management, traffic and land-use planning.
- Source apportionment and identification.
- Policy development and prioritisation of management actions.
- Development/validation of management tools (models, Geographical Information Systems etc.).
- Assessing point or area source impacts.
- Trend qualification, to identify future problems or progress against management/control targets.

**Box 5.2 - Data Quality Objectives**

*The essential requirements to be met by measurements, if overall monitoring objectives are to be achieved.*

- Measurement accuracy and precision.
- Traceability to metrology standards.
- Temporal completeness (data capture).
- Spatial representativeness and coverage.
- Consistency - from site to site and over time.
- International comparability/harmonization.

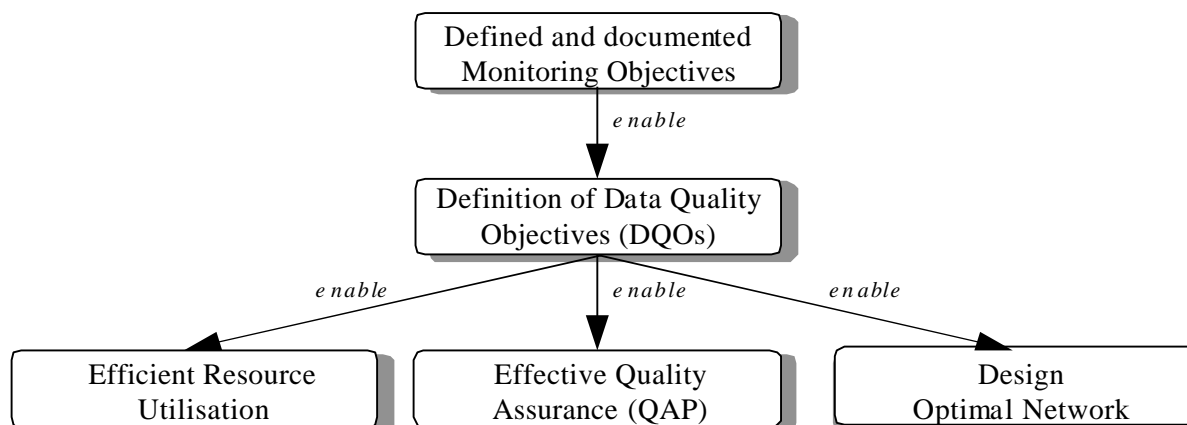


Figure 5.2 The Importance of Objective Setting

**5.3 Quality assurance and quality control (QA/QC)**

Quality assurance and control (QA/QC) is an essential part of any air monitoring system. It is a programme of activities that ensures that measurements meet defined and appropriate standards of quality, with a stated level of confidence. It should be emphasized that the function of QA/QC is not to achieve the highest possible data quality. This is an unrealistic objective, which cannot be achieved under practical resource constraints. Rather, it is a set of activities, which ensures that measurements comply

with the specific DQOs for the monitoring programme. In other words, QA/QC ensures that data are fit for the purpose. Major QA/QC objectives are summarized in Box 5.3, whilst the functional components of a QA/QC programme are identified in Box 5.4.

Quality assurance activities cover all pre-measurement phases of monitoring, including determining monitoring and data quality objectives, system design, site selection, equipment evaluation and operator training. Quality control functions affect directly measurement-related activities such as site operation, calibration, data management, field audits and training. The successful implementation of each component of a QA/QC scheme is necessary to ensure the success of the complete programme. QA/QC may be regarded as a chain of activities designed to deliver credible and accurate data, but a chain is only as strong as its weakest link!

***Box 5.3 - QA/QC for Air Monitoring: overall objectives***

- Measurements accurate, precise and credible.
- Data representative of ambient or exposure conditions.
- Results comparable and traceable.
- Measurements consistent over time.
- High data capture, evenly distributed.
- Optimal use of resources.

***Box 5.4 - QA/QC for Air Monitoring: the major components***

- |                          |   |
|--------------------------|---|
| <i>Quality Assurance</i> | <ul style="list-style-type: none"> <li>• Definition of monitoring and data quality objectives.</li> <li>• Network design, management and training systems.</li> <li>• Site selection and establishment.</li> <li>• Equipment evaluation and selection.</li> <li>• Routine site operations.</li> </ul> |
| <i>Quality Control</i>   | <ul style="list-style-type: none"> <li>• Establishment of calibration/traceability chain.</li> <li>• Network audits and inter-calibrations.</li> <li>• System maintenance and support.</li> <li>• Data review and management.</li> </ul>  |

Although the main principles of QA/QC system design apply to most network or instrumentation types, there are often characteristic differences in their emphasis and practical implementation. It is a common oversight to place too much emphasis on laboratory-based quality assurance activities, as these are often easier to control and monitor.

Although such QA/QC tasks are vital, particularly for sampler-based measurement programmes involving substantial laboratory analysis, considerable emphasis in any network quality system needs to be focused on the point of measurement. Mistakes or problems at the start of the measurement chain cannot be readily corrected afterwards. Sample system design and maintenance (see Section 5.4.3), regular site visits, audits and inter-calibrations therefore play an important role in network quality assurance.

Another unifying feature of network quality systems is the need for effective data screening and validation. In any measurement programme -however well designed or operated- equipment malfunction, human error, power failures, interference and a variety of other disturbances may result in the collection of spurious data. To maximize data integrity and utility, therefore, these must be identified and removed before a final, definitive dataset can be generated or used.

The design of an effective and targeted QA/QC programme is only the first step in the process of quality management. The programme needs to be fully documented, and compliance with its procedures and requirements actively monitored. Monitoring programmes often evolve over time as objectives, legislation, resources or air pollution problems change. Quality assurance programmes therefore also need to be regularly reviewed, to ensure that they remain properly targeted and fit for purpose.

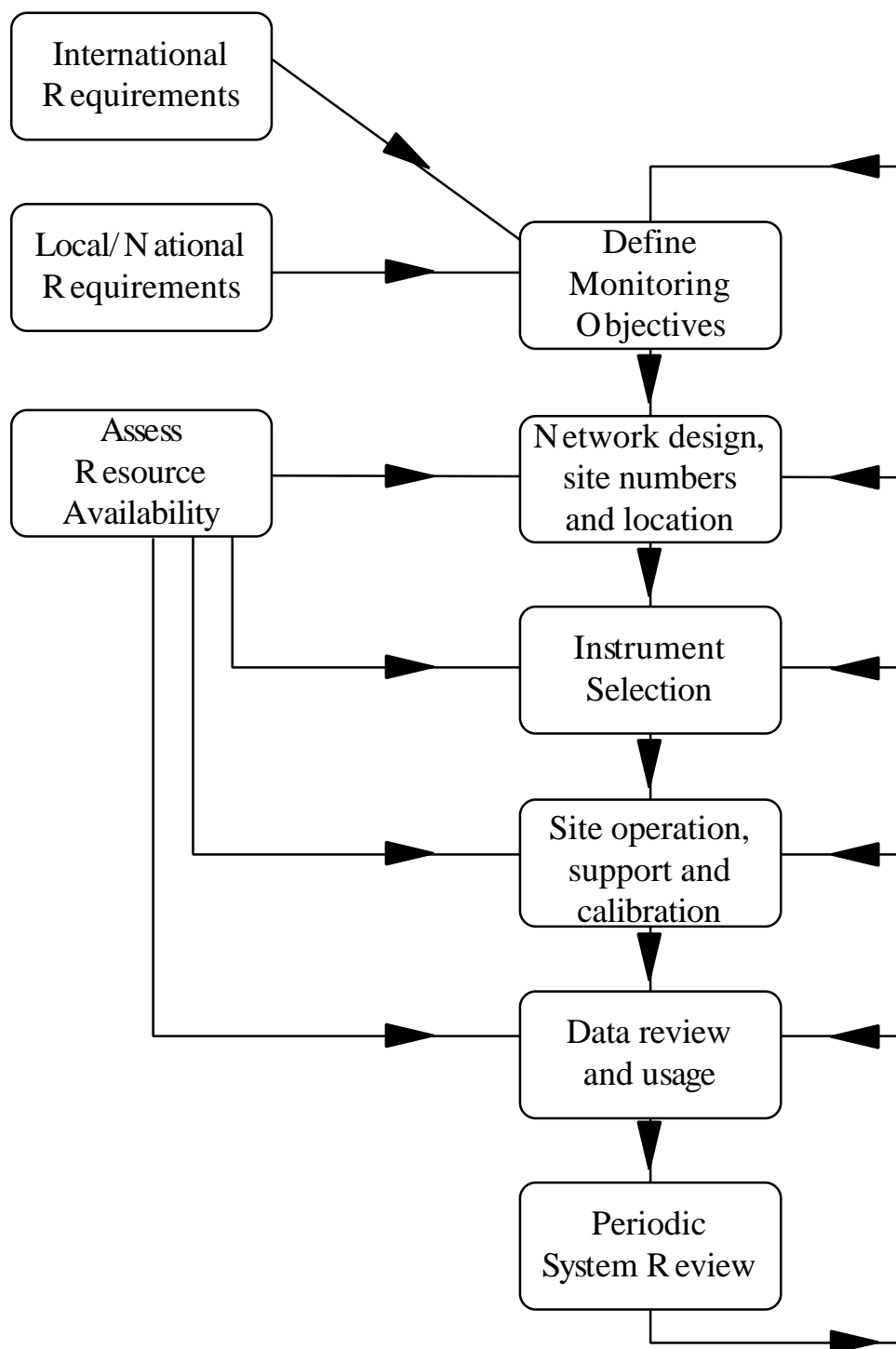
A step-by-step model for the development and implementation of QA/QC programmes for air monitoring is depicted in Figure 5.3. QA/QC systems are considered in greater detail elsewhere (UNEP/WHO 1994a; Bower 1997).

## **5.4 Network design**

There are no universal rules for network design, since any decisions will be determined ultimately by the overall monitoring objectives and resource availability. Although monitoring systems can have just a single, specific objective, it is more common for them to have a broad range of targeted programme functions. No survey design can hope to completely address all the possible monitoring objectives listed in Box 5.1. However, the design of surveys to meet these individual requirements often has common features, and can use common data (to avoid duplication of effort) and overlapping data to verify the credibility of results and conclusions. The overall design goal is to ensure that the maximum information can be derived from the minimum effort. In some countries, networks may be operated by a variety of organisations, including different Government Departments. In such a circumstance, harmonization of the programmes and sharing of data is vital to avoid unnecessary effort and to maximize overall cost-effectiveness.

### **5.4.1 Resource constraints and issues**

A key issue, which needs to be addressed at a very early stage of the network design process, is that of resource availability (Box 5.5). In practice, this is usually the major determinant in network design, which will exert a particularly strong influence on the choice of site numbers, pollutants to be monitored and instrumentation selected.



**Figure 5.3. QA/QC for Air Monitoring: a Step-by-step Approach**

A wide range of commitments and costs is likely to be incurred in any air monitoring programme. Some of these are listed in Box 5.6. Before any firm capital or resource commitment, it is therefore essential to plan the survey, assess resource availability, select the most appropriate equipment and choose monitoring sites.

**Box 5.5 - Network Design: important resource constraints**

- \$ money (capital and ongoing).
- ☺ skilled manpower.
- 🕒 time.

When any equipment purchase must be made, consideration is needed of its long-term operational or financial sustainability. Local sustainability requires the continuing availability of agents (or an in-house capability) for repair and maintenance, together with the necessary skill-base for routine equipment operation and calibration. Financial sustainability requires an ongoing budget for equipment operation, typically amounting to about 10% per annum of the initial capital expenditure.

**Box 5.6 - Costs of Air Monitoring**

- Capital purchase of analysers, samplers, site and laboratory infrastructure.
- Equipment service, maintenance and repair.
- Staff and subcontractor costs - operational and management.
- QA/QC audits, intercalibrations, training, data management.
- Running costs - site rental, electricity, consumables, spare parts, calibration gases, telephone, lab analysis, transport etc.

An ongoing resource commitment to QA/QC is also required in any monitoring survey or network, to ensure that its measurement quality and availability are fully consistent with overall programme objectives. Typically, a budget of between 20-40% of the total annual operating costs may be appropriate for this purpose, depending on the complexity of the programme and the stringency of its DQOs.

**5.4.2 Site numbers and selection**

For the purposes of designing a network to assess population exposure and compliance with health guidelines, a number of basic issues need to be addressed (Box 5.7).

**Box 5.7 - Compliance Monitoring- basic issues**

- Where is the population?
- What pollutant concentrations are they exposed to?
- ... and for how long?
- In what areas and micro-environments is exposure important?

In practice, the number and distribution of air quality monitoring stations required in any network, or the number of samplers used in a survey, also depend on the area to be covered, the spatial variability of the pollutants being measured and the required data usage (Box 5.8).

***Box 5.8 - Network Design: Site Numbers***

*Will depend on:*

- required data use/objectives.
- area to be covered.
- spatial variability of pollutants.
- resource availability.
- instruments deployed.

There are a number of approaches to network design and site selection. Exposure assessment, in particular, will often need to target both source-oriented monitoring sites (often synonymous with worst-case or 'hot-spot' environments) and background locations optimized for quantifying general population exposure. Depending on the pollutants under assessment, data from a wide variety of location types may therefore be necessary to build up a reasonably complete picture of exposure patterns (Box 5.9).

Although the overall requirement of any network or survey is to maximize spatial coverage and representativeness, in practice this goal is only approached by grid-based monitoring strategies: these can be optimized to provide detailed information on spatial variability and exposure patterns for priority pollutants. However, this approach is highly resource-intensive and not, in consequence, widely used.

To reduce resource requirements, a grid approach can be utilized in conjunction with intermittent or mobile sampling, although use of this technique is not consistent with the need to maximize temporal representativeness as well as spatial coverage (see section 5.4.3).

A more flexible approach to network design, appropriate over city-wide or national scale, involves siting monitoring stations or sampling points at carefully selected representative locations, chosen on the basis of required data and known emission/dispersion patterns of the pollutants under study. This approach to network design requires considerably fewer sites than grid strategies and is, in consequence, cheaper to implement. However, sites must be carefully selected if measured data are to be useful. Moreover, modelling and other objective assessment techniques may need to be utilized to 'fill in the gaps' in any such monitoring strategy.

<i>Box 5.9 – Possible Monitoring Locations Relevant to Exposure Assessment</i>	
<b>Site Classification</b>	<b>Description</b>
• city/urban centre	An urban location representative of general population exposure in towns or city centres, e.g. pedestrian precincts and shopping areas
• urban background	An urban location distanced from sources and therefore broadly representative of city-wide background conditions
• suburban/residential	A location type situated in a residential area on the outskirts of a town or city
• kerbside/near road	A site sampling within 1-5 metres of a busy road
• industrial	An area where industrial sources make an important contribution to long-term or peak concentrations
• rural	An open countryside location distanced as far as possible from roads, populated and industrial areas.
• source/target-oriented	Any special source-orientated or micro-environment site. For example, garages, car parks or tunnels, or a site located at a targeted receptor point such as schools or hospitals
• indoor	Will include domestic and office environments (excluding occupational), together with in-car and commuting environments- see Chapter 6.

Some general points to consider when selecting a site location are:

- **Overall monitoring objectives.** These usually determine the target areas for study, the priority pollutants and the number of sites required.
- **Sources and emissions.** Compilations of emission data can assist substantially in site selection. These will help to identify the most polluted areas, as well as other location types where population exposure may be significant. If a full emission inventory is not available, then surrogate statistics such as population density, traffic flows and fuel consumption may be of use in estimating likely pollution 'hot spots', where target receptor exposure may be maximized.
- **Meteorology and topography.** The prevailing weather conditions and local topography will strongly influence the dispersion of air pollutants or, in the case of secondary pollutants, affect their production in the atmosphere.
- **Model simulations.** The results of dispersion modelling, if available, can be used to predict pollutant dispersion and deposition patterns, thereby helping to identify areas where exposure may be maximized. To be of real use, reliable emissions and meteorological data are needed, together with an appropriate and validated model.
- **Existing air quality data.** If monitoring has already been carried out in the area of interest, the data from previous studies may prove useful in targeting problem areas. If no such studies have been carried out, special screening surveys may be designed to provide area-wide or local information on pollution problems. These often involve passive samplers and/or mobile monitoring laboratories.
- **Other information** such as demographic, health, population and land-use information are invaluable in targeting locations representative of both baseline and worst-case exposure. The use of Geographical Information Systems (GIS), in particular, allow both ambient measurements and other geo-co-ordinated

datasets to be used for exposure assessment, epidemiological studies and a range of air quality management activities.

The site-selection process must also take into account the spatial distribution and variability of criteria pollutants within urban environments. For example, concentrations of primary traffic pollutants such as CO are highest at roadside locations, whereas O<sub>3</sub> levels have higher spatial uniformity but will be lowest in near-road locations due to scavenging by vehicle NO<sub>x</sub> emissions. For this reason, it is usually not possible to optimize measurements for all pollutants at any one site location. In such circumstances, some degree of compromise will often be required. In general, the spatial variability of secondary pollutants, such as NO<sub>2</sub> and O<sub>3</sub>, tends to be more homogeneous than for primary pollutants such as CO and SO<sub>2</sub>. This greater variability of primary pollutants, in particular in proximity to sources, will have obvious implications for monitoring site density and numbers required in any survey.

Micro-scale siting considerations are also important in ensuring that meaningful and representative measurements are made. If baseline concentrations are to be assessed, then monitoring sites should be adequately separated from local pollutant sources (for example, roads or small boilers) or sinks (such as dense vegetation). Probe aerodynamics and site sheltering will also often be important. Free airflow around the sampling inlet will be necessary to ensure representative sampling; for this reason, sampling in a stagnant or sheltered micro-environment should be avoided.

A variety of practical considerations also apply when selecting monitoring sites. They must be accessible for site visits, but the potential for public interference or vandalism must also be recognized. Electricity for pollutant analysers and station infrastructure must be available, together with a telephone linkage for data telemetry, if utilized (Box 5.10).

***Box 5.10 - Network Design: Micro-Scale***

*Need to consider -*

- public safety.
- visual intrusiveness/aesthetics of site.
- security/vandalism.
- access to utilities and maintenance.
- planning permission.
- local sources/sinks.
- aerodynamic clearance/sheltering.

### **5.4.3 Sampling strategies and systems**

Monitoring involves assessing pollutant behaviour in both space and time. A good network design should therefore seek to optimize both spatial and temporal coverage, within available resource constraints (UNEP/WHO 1994a; Bower 1997). The previous section dealt with maximizing spatial coverage and obtaining representative measurements. Achieving good time-domain performances is not a problem for most commonly-used air monitoring methodologies (see Section 5.5). However, once priority pollutants are identified, the measurement technologies selected must be capable of a time resolution consistent with the pollutant averaging times specified in guidelines.

Continuously operating automatic analysers may be used to assess compliance with short- or long-term guidelines. Well-recognized semi-automatic methods such as acidimetric SO<sub>2</sub> samplers (see Section 5.7.1) will be perfectly adequate for measurement against daily standards or criteria. For automatic analysers or samplers to reliably measure ambient pollutant concentrations, it is essential that these

pollutants are transferred unchanged to the instrument reaction cell. The sampling manifold is a crucial and often overlooked component of any monitoring system, which strongly influences the overall accuracy and credibility of all the measurements made.

Integrating measurement methods such as passive samplers, although fundamentally limited in their time resolution, are useful for the assessment of long-term exposure, as well as being invaluable for a variety of area-screening, mapping and network design functions (UNEP/WHO 1994b). Problems can arise, however, when using manual sampling methods in an intermittent, mobile or random deployment strategy. Such an approach is usually adopted for operational or instrumentation reasons, or simply because it would not be possible to analyse the sample numbers or data produced by continuous operation. Intermittent sampling is still widely used world-wide. However, this sampling strategy may be of limited utility in assessing diurnal, seasonal or annual pollutant patterns or, indeed, for a reliable assessment of population exposure patterns.

When auditing monitoring sites world-wide, sampling system deficiencies are by far the most commonly encountered problem. Usually, these result from inappropriate designs or inadequate cleaning of the sampling system. Some design requirements, common to all gas sampling systems for analysers or samplers, are summarized in Box 5.11. Corresponding requirements for SPM are complex, and these are discussed in detail elsewhere (UNEP/WHO 1994c).

***Box 5.11 - Key Air Sampling System Requirements***

- Inertness to pollutants being sampled.
- Minimized air-residence time.
- Low airstream/sample line interaction.
- Excess flow above total analyser demand.
- Minimized pressure drop.
- Removal of interferences such as water vapour/pollutants.
- Avoidance of thermal "shock" (when hot, humid, ambient air is sampled into an air-conditioned enclosure).
- ease of cleaning and maintenance...
- ...which must be done regularly!

## **5.5 Instrument issues**

The capabilities of air monitoring methodologies, as well as their inevitable resource implications, exert a strong influence on network design. This section reviews some of these issues. Specific monitoring methods applicable to individual criteria pollutants are reviewed in Section 5.7.

Air monitoring methodologies can be divided into four main generic types, covering a wide range of costs and performance levels. These are passive samplers, active samplers, automatic analysers and remote sensors. The main advantages and characteristics of these monitoring technologies are summarized in Box 5.12.

<b>Box 5.12 - Air Monitoring Techniques</b>			
<b>Method</b>	<b>Advantages</b>	<b>Disadvantages</b>	<b>Capital Cost</b>
<i>Passive Samplers</i>	<ul style="list-style-type: none"> <li>• Very low cost.</li> <li>• Very simple.</li> <li>• No dependence on mains electricity.</li> <li>• Can be deployed in very large numbers</li> <li>• Useful for screening, mapping and baseline studies.</li> </ul>	<ul style="list-style-type: none"> <li>• Unproven for some pollutants.</li> <li>• In general only provide monthly and weekly averages.</li> <li>• Labour-intensive deployment/analysis.</li> <li>• Slow data throughput.</li> </ul>	US\$10-70 per sample.
<i>Active Samplers</i>	<ul style="list-style-type: none"> <li>• Low cost.</li> <li>• Easy to operate.</li> <li>• Reliable operation/performance.</li> <li>• Historical dataset.</li> </ul>	<ul style="list-style-type: none"> <li>• Provide daily averages.</li> <li>• Labour-intensive sample collection and analysis.</li> <li>• Laboratory analysis required.</li> </ul>	US\$1000-3000 per unit.
<i>Automatic Analysers</i>	<ul style="list-style-type: none"> <li>• Proven.</li> <li>• High performance.</li> <li>• Hourly data.</li> <li>• On-line information.</li> </ul>	<ul style="list-style-type: none"> <li>• Complex.</li> <li>• Expensive.</li> <li>• High skill requirement.</li> <li>• High recurrent costs.</li> </ul>	US\$10 000-15 000 per analyser.
<i>Remote sensors</i>	<ul style="list-style-type: none"> <li>• Provide path or range-resolved data.</li> <li>• Useful near sources.</li> <li>• Multi-component measurements.</li> </ul>	<ul style="list-style-type: none"> <li>• Very complex and expensive.</li> <li>• Difficult to support, operate, calibrate and validate.</li> <li>• Not readily comparable with point data.</li> <li>• Atmospheric visibility and interferences.</li> </ul>	US\$70 000 - 150 000 per sensor, or more.

### *Passive samplers*

These offer a simple and cost-effective method of screening air quality in an area. A sample integrated over a defined exposure time (typically a week to a month) is collected by molecular diffusion to a pollutant-specific absorbent material. The low unit costs permit sampling at a number of points in the area of interest. This is useful in highlighting “hot-spots” of high pollutant concentrations, such as major roads or emission sources, where more detailed studies may be needed. Careful survey design and attention to laboratory-based QA/QC of the sample analysis process is necessary to make best use of this technique.

### ***Active samplers***

Pollutants samples are collected either by physical or chemical means for subsequent analysis in a laboratory. Typically, a known volume of air is pumped through a collector such as a filter or chemical solution for a known period of time, which is then removed for analysis. There is a long history of active sampler measurements in many parts of the world, providing valuable baseline data for trend analyses and comparison. Sampling systems (for gases), sample conditioning, weighing systems (for SPM) and laboratory procedures are key factors influencing the quality of the final data.

### ***Automatic analysers***

These can provide high-resolution measurements (typically hourly averages or better) at a single point for most of the criteria pollutants (SO<sub>2</sub>, NO<sub>2</sub>, CO and SPM), as well as for other important species such as VOC. The sample is analysed on-line and in real-time, usually by electro-optic methods: UV or IR absorption, fluorescence or chemiluminescence are common detection principles. To ensure the data from automatic analysers are accurate and reliable, a high standard of maintenance, operational and quality assurance/control procedures is invariably required.

### ***Remote sensors***

These are recently developed instruments which use long-path spectroscopic techniques to make real-time concentration measurements of a range of pollutants. The data are obtained by integrating along a path between a light source and a detector. Long-path monitoring systems can have an important role to play in a number of monitoring situations, particularly in proximity to sources. A high standard of operational, calibration and data screening/management practice is essential if meaningful data are to be produced by such systems.

### ***General advice on instrument selection***

It is advisable to always choose the simplest technique that will do the job. Inappropriate, too complex or failure-prone equipment can result in poor network performance, limited data utility and - worst of all - a waste of money. Although monitoring objectives are the major factor to consider, resource constraints and the availability of skilled manpower must also be considered. There is a clear trade-off between equipment cost, complexity, reliability and performance. More advanced systems can provide increasingly refined data, but are usually more complex and difficult to handle.

Sampler methods are not necessarily less accurate than automatic analysers. For instance, data from co-located chemiluminescence NO<sub>x</sub> analysers and diffusion tubes can show excellent agreement, to within plus or minus 10%, providing both techniques are subject to high standards of quality assurance and operational practice (Smith et al. 1997). In practice, the combined use of samplers and automatic analysers in a 'hybrid' monitoring programme can offer a versatile and cost-effective approach to network design over a municipal or national scale. Such a network design will use passive or active samplers to provide good spatial coverage and area-resolution of measurements. Automatic analysers, deployed at carefully selected locations, can provide more detailed time-resolved data for assessing peak concentrations or comparison with short-term standards.

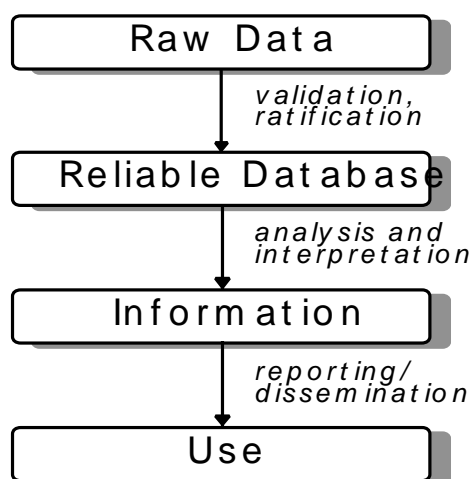
In some circumstances, additional use may be made of passive or active samplers. Reasonably robust statistical relationships can often be derived between peak, upper percentile and long-term average pollutant concentrations (Carless et al. 1994). Although these semi-empirical relationships may differ from pollutant to pollutant, as well as with generic site type, they may enable long-term datasets from sampler surveys to be used to assess broad compliance with short-term guidelines; or at least to identify

areas where exceedances are likely. This indirect assessment technique should, however, always be used with caution.

Deducing the levels of one pollutant from measurements of another may be possible when the local air pollution climate is dominated by emissions from one source sector, and where robust and well-established emission ratios exist for the species in question. For example, traffic-related benzene and lead levels may in some circumstances be estimated from corresponding CO concentrations. However, surrogate measurements of this kind must always be used with caution.

## 5.6 Turning data into information

As emphasised in the introduction to this chapter, the purpose of monitoring is not merely to collect data, but to produce useful information for planning, health professional, regulatory and public end-users (Figure 5.4). Raw data by themselves are of very limited utility. These first need to be screened (by validation) and collated to produce a reliable and credible dataset (UNEP/WHO 1994a; Bower 1997). In effective Air Quality Management Information Systems, the validated measurements will be archived together with corresponding emission datasets, model predictions and other input relevant to decision-making.



**Figure 5.4 Data throughput from a monitoring programme**

The next stage in data management is analysis and interpretation, designed to provide useful information in an appropriate format for end-users. A variety of proven analytical methodologies are available for air quality datasets. However, the appropriate level and method of data treatment will be determined by the ultimate end-use. A minimum level of data management could be the production of daily, monthly and annual summaries, involving simple statistical and graphical analyses that show both time and frequency distributions of the monitoring data. The use of Geographical Information Systems (GIS) should be considered, particularly when the intention is to combine pollution data with those from epidemiological and other geo-co-ordinated social, economic or demographic sources.

The information derived from measured data must be reported or otherwise disseminated in a timely manner to end-users. This can be in the form of complete datasets, processed summaries, peak or average statistics, exceedances of standards or targets, analytical results, graphs or maps. Formats for information transfer should be designed which are both appropriate to the capabilities of the network and to the requirements of the users. Communicating data or information may involve a number of transmission methods, including paper reports, CD-ROMs, electronic, broadcast and INTERNET media. Public information systems, often exploiting innovative broadcast and world wide web media, play an

increasingly important role in many countries in raising awareness, warning of pollution episodes and advising susceptible population subgroups.

## **5.7 Key pollutants and measurement methods**

This section summarizes the measurement techniques available for determining ambient concentrations of the main "classic" pollutants, SO<sub>2</sub>, NO<sub>2</sub>, CO, O<sub>3</sub>, SPM and lead. There is some overlap between these techniques and corresponding methodologies used for individual exposure and micro-environment surveys. At extreme ambient concentrations, moreover, some occupational exposure measurement systems, such as detector tubes, may be used in a semi-quantitative manner (Saltzman and Caplan 1995).

### **Sulphur dioxide**

As the main source of this pollutant is the combustion of fossil fuels containing sulphur, either in power stations or domestic/commercial space heating, the major local source types strongly influences monitoring and assessment strategies. Automatic analyzers need to be used if compliance against a short-term guideline is to be determined; a variety of active samplers are suitable for comparison with daily or annual guidelines. Passive samplers may be used to provide data for comparison with the long-term annual guideline.

#### ***Passive samplers***

There are currently no national or international standards governing the application of SO<sub>2</sub> diffusion tubes to ambient air monitoring, nor for their laboratory preparation and analysis. Protocols for sample preparation and analysis by spectrophotometry and ion exchange chromatography have, however, been published in scientific literature (Bennett et al. 1992; Downing et al. 1994; Hargreaves and Atkins 1988).

A variety of passive sampling techniques are available (UNEP/WHO 1994b). The most widely used include:

- The triethanolamine (TEA)/glycol/spectrophotometry method (Hangartner et al. 1989).
- The potassium hydroxide (KOH)/glycerol/spectrophotometry method (Hargreaves and Atkins 1988).
- The sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>)/glycerine/ion-exchange chromatography method (Ferm 1991).

Hybridization of these techniques is widespread. In the UK, for instance, KOH or NaOH is used as absorbent, but with the tube membrane proposed by Ferm (1991) and using ion-exchange chromatography as the analysis method. In practice, the ion-exchange chromatographic technique has been informally accepted as the standard method for SO<sub>2</sub> diffusion tube analysis. The typical sensitivity of this hybrid technique is  $\pm 8.5 \mu\text{g}/\text{m}^3$ : some under-reading against automatic analysers has been observed (about 30%), although agreement with active samplers is better (Downing et al. 1994).

#### ***Active samplers***

The equipment required for sampling gaseous sulphur compounds in ambient air is described in full in International Standard ISO 4219 (ISO 1979). This standard gives details of the equipment necessary to sample gaseous pollutants by absorption in a liquid bubbler. The standard also includes guidance for siting and installation of the apparatus. The principle of active-sampling methodologies is to draw ambient air through a collecting medium (typically a liquid bubbler), for a specified time, typically 24 hours. The volume of air is metered. The collecting medium is subsequently analysed and the concentration of pollutant in the sampled air determined. This proven method is well established, and

has been used in many monitoring networks worldwide for a number of years. In consequence, there is a long history of active sampler SO<sub>2</sub> measurements available for trend assessment.

There are several methods of SO<sub>2</sub> monitoring based on this principle, which can be carried out using the apparatus specified in ISO 4219. They differ with respect to the solutions used in the bubblers for SO<sub>2</sub> absorption and the method of analysis. The four most widely used methods are described below.

*Acidimetric (total acidity) method.* This method, given in ISO 4220 (ISO 1983), is used to determine a gaseous acid air pollution index. Although this method measures total acidity, and is not specific for SO<sub>2</sub>, it is adequate for general use. The simplicity of the method, and the fact that the reagents are relatively safe, makes it a popular choice for routine monitoring (AEA 1997). An accuracy of  $\pm 10\%$  has been estimated for SO<sub>2</sub> measurements using the total acidity method, taking account of all contributory factors. A precision of  $\pm 4 \mu\text{g}/\text{m}^3$  is achievable for this widely-used method (AEA 1997).

*Ion-exchange chromatography.* A variation on the above technique. The exposed peroxide solutions are analysed for sulphate ions by means of ion-exchange chromatography, rather than titration. This has the advantage of being sulphate-specific, but requires the use of an expensive ion-exchange chromatograph.

*Tetrachloromercurate (TCM) method.* This is also known as the Pararosaniline method ISO 6767 (ISO 1990). This is the reference method specified in the EC Directive on SO<sub>2</sub> and suspended particulate matter (EC 1980). However, the reagents used are very toxic, and for this reason the method is not widely used.

*Thorin method.* This method is given in ISO 4221 (ISO 1980). The reagents used include perchloric acid, barium perchlorate, dioxane and thorin. These are hazardous and must be handled and disposed of with care. Accordingly, this method is not commonly used world-wide.

### ***Automatic analysers***

The measurement of SO<sub>2</sub> in ambient air using automatic analysers is covered by ISO/DIS 10498 (ISO/DIS 1999). Well-established automatic monitoring techniques are available. The most widely used method for automatic SO<sub>2</sub> measurement is ultraviolet fluorescence (UVF). SO<sub>2</sub> molecules in the sample airstream are excited to higher, unstable energy states by UV radiation at 212 nm. These energy states decay, causing an emission of secondary fluorescent radiation with an intensity proportional to the concentration of SO<sub>2</sub> in the sample.

The accuracy of data from automatic SO<sub>2</sub> analysers depends on a range of factors encompassing the entire measurement chain. These include accuracy of calibration standards, analyser stability and sample losses in the measurement system. An accuracy of  $\pm 10\%$  has been estimated for SO<sub>2</sub> measurements in UK national automatic networks, taking account of all contributory factors. The precision of SO<sub>2</sub> measurements, determined from long-term variations in baseline response of in-service analysers, is estimated to be  $\pm 3 \mu\text{g}/\text{m}^3$  (AEA 1996).

### ***Remote sensors***

Remote optical sensor systems, such as the Differential Optical Absorption System (DOAS), use a long-path spectroscopic technique to make real-time measurements of the pollutant concentration by integrating readings along a path between a light source and a detector. Long-path monitoring systems can be used to measure SO<sub>2</sub>, but the methodology is less well established than that for automatic point monitors. The accuracy and precision of the data from these instruments are, therefore, much more difficult to determine. The method does not conform to ISO 7996 (ISO 1985b). Particularly careful

attention needs to be paid to instrument calibration and quality assurance to obtain meaningful data from remote sensing instruments.

## **Nitrogen dioxide**

Automatic analysers must be used for the direct determination of compliance against the hourly guideline, although much useful information can be inferred using passive samplers (see section 4.5). Either technique is applicable for comparing ambient levels against the annual guideline.

### *Passive samplers*

Monitoring ambient NO<sub>2</sub> concentrations using passive diffusion tube samplers is now well established. This method provides an integrated, average concentration for the pollutant over the exposure period (typically 2-4 weeks) and is particularly well suited to baseline and screening studies for assessing the spatial distribution of NO<sub>2</sub> concentrations in an urban environment. The most widely used techniques are variants on the Palmes-type sampler, originally developed for the assessment of occupational exposure. This uses a tube sampler, employing TEA as absorbent. Sample analysis, after thermal desorption, is by spectrophotometry or ion-exchange chromatography (Palmes et al. 1976). Very large scale mapping surveys are possible using diffusion tubes, but careful attention both to the harmonization of analytical procedures and to the outputs from different analytical laboratories is essential for the success of large-scale passive sampler surveys.

Although extensively used throughout the UK and Europe there are, at present, no national or international standards governing the application of diffusion tubes for ambient air quality monitoring, nor for the laboratory preparation and analysis of diffusion tubes. Protocols for sampler preparation and analysis by spectrophotometry have, however, been published in the scientific literature (Palmes et al. 1976; Atkins et al. 1986); these have been informally accepted as standard procedures for NO<sub>2</sub> diffusion tube preparation and analysis.

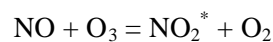
Recent comparisons of NO<sub>2</sub> diffusion tube measurements with co-located chemiluminescent NO<sub>x</sub> analysers show good agreement (Smith et al. 1997; Gerboles and Amantini 1993). Over the range of concentrations generally encountered in urban areas (20-80 µg/m<sup>3</sup>), it was found that on average NO<sub>2</sub> diffusion tubes, exposed for one month, tended to overestimate ambient NO<sub>2</sub> by approximately 10% compared with a chemiluminescent NO<sub>x</sub> analyser. Precision estimates of the diffusion tube technique have been quoted as 5-8% in similar studies.

### *Active samplers*

A variety of active sampler technologies are available (UNEP/WHO 1994b). The best known of these is the Griess-Saltzman method, covered by ISO 6768 (ISO 1985a). Although this method is sensitive and requires a relatively simple, inexpensive sampling apparatus, there are a number of disadvantages. It is a relatively skilled and labour-intensive technique, uses corrosive chemicals and is not readily applicable to sampling periods longer than 1-2 hours. There also remain doubts about calibration methods, collection efficiency and possible side-reactions. In consequence, this method cannot be recommended for general baseline monitoring applications.

### *Automatic analysers*

The reference method for automatic measurement of nitrogen oxide concentrations, as defined for compliance with EC Directive 85/203/EEC (EC 1985), is the automatic chemiluminescence method described in ISO standard 7996 (ISO 1985b). This method is widely used world wide. The method is based on the chemiluminescence energy emitted when NO in the sample airstream reacts with O<sub>3</sub> in an evacuated chamber to form an excited energy state of NO<sub>2</sub>. The chemiluminescent reaction is:



Emitted light from the excited NO<sub>2</sub><sup>\*</sup> is converted to an output voltage by a photomultiplier tube and amplifier.

Automatic NO<sub>2</sub> analysers based on liquid-phase chemiluminescence, produced by reacting NO<sub>2</sub> with a chemical solution, are also available. These highly sensitive but relatively fragile instruments are mostly employed for research applications and are not generally regarded as being suitable for routine baseline monitoring purposes.

The accuracy of data from automatic NO<sub>2</sub> analysers depends on a range of factors encompassing the entire measurement chain. These include the accuracy of calibration standards, analyser stability and sample losses in the measurement system. Final accuracy can therefore vary from network to network. An accuracy of ± 8% has been estimated for NO<sub>2</sub> measurements in well-run automatic networks, taking account of all contributory factors (AEA 1996). The precision of NO<sub>2</sub> measurements is estimated to be ±6.5 µg/m<sup>3</sup>, determined from long-term variations in the baseline responses of in-service analysers.

### *Remote sensors*

Long-path monitoring systems are available for the measurement of NO<sub>2</sub>, but the methodology is less well established than that for automatic point monitors. The accuracy and precision of the data from these instruments are, therefore, much more difficult to determine. The method does not conform to ISO 7996 (ISO 1995b) and, as noted previously, careful attention needs to be given to instrument calibration and quality assurance to obtain meaningful data.

## **Carbon monoxide**

CO in urban areas results almost entirely (typically ~90%) from road traffic emissions. Since CO is a primary pollutant, its ambient concentrations closely follow emissions. In urban areas, concentrations are therefore highest at the kerbside and decrease rapidly with increasing distance from the road. Mostly automatic analysers are being used for the direct assessment of ambient levels against guidelines.

### *Passive samplers*

A passive sampler has been developed for CO, utilizing a zeolite absorber and a narrow filamental diffusion passage to optimize uptake, and involving GC/FID analysis after thermal desorption (Lee et al. 1992). This technique may be useful for screening, mapping and 'hot-spot' identification. Its use does not, however, appear to be widespread at the present time.

### *Active samplers*

Grab samples may be collected for subsequent laboratory analysis. However, this technique is not known to be widely used.

### ***Automatic analysers***

The measurement of CO in ambient air is covered by international standards ISO/FDIS 4224 (ISO/FDIS 1999a) and ISO 8186. (ISO 1989)

Baseline ambient CO monitoring is normally carried out using IR analysers. A number of electrochemical CO analysers are available, but these are generally of low sensitivity and not suitable for routine ambient monitoring. However, they may have application in areas of high concentrations. A version of this sensor is incorporated in a commercially available roadside pollution monitoring system.

CO analysis is based on the absorption of IR radiation at wavelengths of 4.5-4.9 micrometres. Since other gases and particles can also absorb IR, the analyser must distinguish between absorption by CO and absorption by interferences. In the most common analyser type, this is done using a gas filter correlation wheel containing a cell of pure nitrogen and a cell of nitrogen plus CO. The cell containing CO removes the CO-sensitive wavelengths before the IR signal enters the absorption chamber, whilst all wavelengths are transmitted by the other cell. The difference in the intensity of the two absorption signals, divided by the intensity of the IR source, provides a measure of the ambient CO concentration.

The accuracy of data from automatic CO analysers depends on a range of factors encompassing the entire measurement chain. These include accuracy of calibration standards, analyser stability and sample losses in the measurement system. An accuracy of  $\pm 8\%$  and a precision of  $\pm 0.5 \text{ mg/m}^3$  may be achieved using this technique in well-managed and quality-assured programmes.

### **Ozone**

O<sub>3</sub> is not emitted directly from man-made sources in any significant quantities, but is formed in the atmosphere by sunlight-driven chemical reactions involving NO<sub>x</sub> and VOC (see Section 2.1.2). These reactions are not immediate, but may take from hours to days to complete. O<sub>3</sub> is chemically scavenged by primary NO<sub>x</sub> emissions from traffic, and is also removed from the atmosphere by deposition to the ground.

Both spatial and temporal distributions of O<sub>3</sub> differ markedly from those of other pollutants. In particular, significant impacts may occur in areas up to hundreds of kilometres downwind of the original precursor emissions, as a result of long-range as a result of long-range transport. Ambient concentrations and population exposure may often be maximized in suburban and rural areas. This has important implications for monitoring system design.

### ***Passive samplers***

A variety of techniques are available (UNEP/WHO 1994b). These include:

- 1,2-di-(4-pyridyl) ethylene absorbent- spectrophotometry (Monn and Hangartner 1990).
- KI –spectrophotometry (Grosjean and Hisham 1992).
- NaNO<sub>2</sub>/Na<sub>2</sub>CO<sub>3</sub>/glycerine -ion chromatography (Koutrakis et al. 1990).
- Indigo carmine-reflectance (Alexander et al. 1991).

These methods are not as widely used or validated as corresponding samplers for NO<sub>2</sub> and no clear consensus as to a standard technique has yet emerged.

### ***Active samplers***

The most widely used active sampler technique was the Neutral Buffered Potassium Iodide (NKBI) method. Although relatively simple and inexpensive, there are practical problems with deterioration of

the iodine complex and interference (most notably from NO<sub>2</sub> and SO<sub>2</sub>). These issues have reduced its use to the extent that the technique may now be regarded as obsolete.

### ***Automatic analysers***

ISO 10313 (ISO 1993a) is not of real relevance, as the chemiluminescence detection technique it describes is no longer widely used. The most commonly used technology is now that of UV absorption; this is specified as the reference method for the purposes of EC Directive 92/72/EEC (EC 1992). An ISO standard is being developed for the UV method.

UV absorption is a robust, well-developed technique. Ambient O<sub>3</sub> concentrations are calculated from the absorption of UV light at 254 nm wavelength. The sample passes through a detection cell of known length (l). An O<sub>3</sub>-removing scrubber is used to provide a zero reference light intensity, I<sub>0</sub>. The analyser alternately measures the absorption of air in the cell with no O<sub>3</sub> present and the absorption in the experimental sample cell, I<sub>s</sub>. The ambient O<sub>3</sub> concentration, c, may be simply calculated using the Beer-Lambert equation:

$$I_s = I_0 e^{-alc}$$

where a is the relevant absorption coefficient at 254 nm.

Given appropriate attention to system design, calibration and equipment support a typical measurement accuracy of ±11% and a precision of ±4 µg/m<sup>3</sup> should be readily achievable in well-run automatic networks.

### ***Remote sensors***

Open-path optical remote sensing techniques such as DOAS are available for O<sub>3</sub>, although the associated practical issues noted in previous sections are applicable.

## **Suspended particulate matter**

SPM is a generic term embracing all airborne particulate matter. This therefore encompasses a wide range of size fractions, morphologies and chemical compositions, as discussed in Chapter 2. Although coarse particle size ranges may cause significant local nuisance or soiling, it is the finer fractions, such as PM<sub>2.5</sub>, that are capable of deep lung/airway penetration. Concern about the potential health impacts of fine particulate matter has increased rapidly over recent years.

SPM monitoring is fundamentally different from the measurement of gaseous pollutants, and the methods are generally less precise. A wide variety of different sampling and detection methodologies is available, including the Tapered Element Oscillating Microbalance (TEOM), β-ray analysis, gravimetric sampling (low or high-volume) and a number of indirect optical, particle counting and light-scattering methods. The sampling system strongly affects the measurement process and appropriate aerodynamically designed inlets are essential for proper sample-fractionated determinations (UNEP/WHO 1994c).

### ***Active samplers***

Gravimetric samplers collect particulate matter onto a filter using high-volume (about 100 m<sup>3</sup>/hour) or low-volume (about 1 m<sup>3</sup>/hour) pumped sample flows. The weight of particulate matter deposited on the filter is used to calculate a 24-hour average mass concentration. No ISO or CEN standards have yet been promulgated for ambient measurement of PM<sub>10</sub> particulate matter using gravimetric samplers, although these are under development at the present time. An ISO standard for evaluating PM<sub>10</sub> inlet heads is, however, available (EN 1999). A United States Environmental Protection Agency procedure for PM<sub>10</sub>

using the high-volume sampler is given in Federal Register 40 CFR Part 50 (CFR 1993). However, compliance with this procedure does not ensure consistency with the anticipated CEN standards.

The various SPM monitoring techniques may not necessarily produce comparable measurements. Different sampling systems, operating temperature, filter media and filter history may also potentially affect measurement equivalence. The accuracy and precision of any measured mass concentration is, therefore, liable to a wide margin of error. A target accuracy of  $<10 \mu\text{g}/\text{m}^3$  and a precision of  $<5 \mu\text{g}/\text{m}^3$  (for daily average concentrations  $<100 \mu\text{g}/\text{m}^3$ ) are given for  $\text{PM}_{10}$  measurements by EN 12341 (EN 1999).

Medium- or low-volume gravimetric samplers are more portable and less noisy than high-volume samplers, making them more suitable for use in urban areas. However, the mass of particles collected is far less than with high-volume samplers, giving a greater potential for errors due to filter weighing. According to a recent large-scale instrument comparison, a number of commercially available high- and medium-volume samplers are equivalent to a reference Wide Ranging Aerosol Collector (WRAC) (EN 1999).

Correct filter handling, documentation and analysis is fundamental for obtaining valid data. The filters must be conditioned in a temperature- and humidity-controlled environment, typically  $20^\circ\text{C}$  and 50% relative humidity, for at least 24 hours before and after exposure. The filters must be accurately weighed using a suitable balance, that has been calibrated using an accredited method.

### ***Automatic analysers***

Instruments are commercially available using the following techniques:

- Tapered Element Oscillating Microbalance (TEOM).
- Beta-ray absorption analysers (ISO/FDIS 1999b).
- Light scattering systems.

Of the automatic instrument types available, the TEOM and  $\beta$ -ray systems have been operated widely for many years and are well tested in the field. The light scattering type of instrument has been developed more recently, and is therefore less well proven in service. Operating experience and co-located measurement campaigns indicate that measurements from the different instruments are not always equivalent or comparable.

For traceable and robust measurements, samplers must be fitted with a tested  $\text{PM}_{10}$  inlet head and an accurate flow control system. The  $\text{PM}_{10}$  sampling inlet should be tested to ISO Standard 7708 (ISO 1995) to ensure accurate size fractionation at the point of sampling. A target accuracy figure of  $<10 \mu\text{g}/\text{m}^3$  and precision of  $<5 \mu\text{g}/\text{m}^3$  (for daily average concentrations  $<100 \mu\text{g}/\text{m}^3$ ) are given in EN 12341 (EN 1999). Tests on in-service TEOM analysers deployed in UK networks demonstrate these figures to be realistic and achievable.

### **Lead**

The main sources of lead in air are the combustion of petrol containing lead-based additives and industrial emissions.

### ***Active samplers***

These are based on pumped sampling of large quantities of ambient air, capturing fine ambient particulate matter on a filter for subsequent analysis. Analysis of filters for lead is covered by ISO 9855 (E), which specifies atomic absorption spectroscopy as the standard analytical method (ISO 1993b). There is no

standard sampling method, although the EC Directive does specify some relevant sampling and filter criteria (EC 1982).

A variety of sampling methods are used, including high-, medium-, and low-volume samplers. There is no standard or reference sampling method. The UK method is broadly typical: this utilises an “M Type” sampler designed specifically for this purpose. Its flow rate is controlled to 5.4-7.1 m<sup>3</sup>/day, and Millipore Aerosol Field Monitor filters are exposed and changed weekly.

Passive sampling methods are not applicable.