CHAPTER 17

MEASUREMENT OF ATMOSPHERIC COMPOSITION

17.1 GENERAL

The main purpose of this chapter is to introduce instrument specialists to methods for the measurement of various components of atmospheric composition, with emphasis on the anthropogenic components which fall under the general heading of pollution. Such measurements are often accompanied by measurement of the basic meteorological variables, as introduced in the preceding chapters.

These measurements are taken with the main objectives of studying climate change, introducing measures for the reduction of negative impacts on the environment and for the direct protection of human health. Within WMO, the Global Atmosphere Watch (GAW) was established to coordinate atmospheric pollution measurements taken by WMO Member countries.

The GAW programme integrates many monitoring and research activities involving the measurement of the chemical and physical properties of the atmosphere. It serves as an early warning system to detect further changes in atmospheric greenhouse gases, the ozone layer, the long-range transport of air pollutants, the acidity and toxicity of rain, and the atmospheric burden of aerosols. The GAW was approved in June 1989 by the WMO Executive Council and is designed to strengthen and coordinate the WMO environmental data-gathering programme that began in the 1950s. The new GAW absorbed the Global Ozone Observing System (GO_3OS), the Background Air Pollution Monitoring Network (BAPMoN) and other smaller networks. The GAW provides framework design, standards, intercalibrations, and data collection systems for global monitoring and data evaluation.

The main variables to be determined are as follows:

(a) Greenhouse gases: including carbon dioxide, chlorofluorocarbons, methane and nitrous oxide;
(b) Ozone: including surface ozone, total column ozone, vertical profile and precursor gases;
(c) Radiation and the optical depth or transparency of the atmosphere: including turbidity, solar radiation, ultraviolet B, visibility, total atmospheric aerosol particle load and water vapour;
(d) Chemical composition of deposition: including dry and wet deposition of sulphur and nitrogen compounds and wet deposition of heavy metals (with precipitation);
(e) Reactive gas species: including sulphur dioxide and reduced sulphur species, nitrogen oxides and reduced nitrogen species, carbon monoxide and volatile organic compounds;
(f) Particle concentration and composition characteristics;
(g) Radionuclides: including krypton-85, radon, tritium and the isotopic composition of selected substances.

The instruments and methods used for the quantitative and qualitative determination of atmospheric constituents are complex and sometimes difficult to deal with. Therefore, besides correct operation, regular calibration of the equipment is essential for accurate and reliable measurements, and quality assurance is very important. Obtaining good results for most of the measurements described here is not feasible without the close involvement of specialist staff at a professional level.

17.2 MEASUREMENT OF SPECIFIC VARIABLES

The accurate operational measurement of atmospheric composition is still a difficult undertaking, mainly due to the very low concentrations of the chemical species of main interest, a frequent need for complicated measurement and analysis protocols, as well as problems related to the calibration of the required equipment. Proper exposure and siting of the sensors/equipment according to defined measurement protocols is of great importance. The following sections will briefly introduce the measurement of some variables. More detailed information can be found in WMO (1993).

17.2.1 Greenhouse gases

Increasing levels of greenhouse gases, particularly carbon dioxide (CO_2), are threatening to change the Earth's climate and weather and may lead to a gradual global warming in the twenty-first century. The magnitude of this warming, and the seriousness of its effects, will depend on future concentrations of greenhouse gases in the atmosphere. Monitoring greenhouse gas concentrations is therefore of critical importance to the future of the planet. Other greenhouse gases that are monitored from locations all over the globe include methane (CH_4), chlorofluorocarbons (CFCs) and nitrous oxide (N_2O). Tropospheric ozone is also considered to be a greenhouse gas.

WMO has been monitoring CO_2 levels since the 1960s when it established a worldwide network that has since become a part of GAW, the major WMO source of information on atmospheric chemistry. The WMO World Data Centre for Greenhouse Gases, located in Tokyo, Japan, was established in 1990 to archive data for the complete suite of greenhouse gases (WMO, 1995*a*).

Carbon dioxide

Carbon dioxide is one of the most common and important trace gases in the Earth-ocean-atmosphere system. It has both natural and industrial sources. Within the natural carbon cycle, CO_2 plays a key role in a number of biological processes. Because of the role that CO_2 plays as one of the more important greenhouse gases, scientists have attempted to understand its potential impact on climate and global change.

At present, background atmospheric CO_2 concentration measurements are mainly taken with non-dispersive infrared (NDIR) gas analysers. With special care, such as with the use of (carefully calibrated) reference gases, most types can achieve the required accuracy (±0.1 parts per million (ppm) in ambient concentrations of 360-390 ppm). Basically, an infrared source provides a beam of radiation that passes through a reference- and sample-measuring cell. The relative difference in intensity of radiation transmitted through the two cells and through an optical filter that passes the CO_2 absorption band at 4.25 μm is a measure of the CO_2 concentration difference between the gases contained in the two cells. During normal operation, a comparison gas of constant, but not necessarily precisely known, concentration is flushed through the reference cell. At regular intervals a suite of reference gases covering the normally measured range is passed through the sample cell, which calibrates the response of the analyser. All gases passed through the reference and sample cells are thoroughly dried, and the measurements are expressed as the CO_2 mole fraction in dry air.

In order to obtain global intercomparability of background CO_2 measurements, a calibration system has been developed by the use of a three-level reference gas system. The system consists of primary, secondary and working reference gases and requires the exchange of reference gases between the different national programmes and a central calibration laboratory. The calibration laboratory is located at the National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Division (GMD) of the Earth System Research Laboratory (ESRL) in Boulder, Colorado, United States. The infrared analysis gives a constant trace of the ambient CO_2 concentration interspersed with calibration gas measurements at a set interval. At least once a week, a calibration test is made over a wider range of concentrations using the secondary standard.

An alternative method of CO_2 measurement which is generally applicable to many other trace gases requires the collection of air in specially designed glass or stainless steel flasks. These flasks are returned to a central laboratory where CO_2 is determined by NDIR analysers (Komhyr and others, 1989). This method has become a standard technique employed by a number of countries.

Chlorofluorocarbons

Chlorofluorocarbons (CFCs), which include CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2), are a family of compounds which do not naturally exist in the environment. Since their manufacture began in the 1930s, CFCs have been used as refrigerant gases, as solvents in industrial applications and dry cleaning, and as a propellant in aerosol cans. Because they are resistant to destruction in the troposphere and because their production has accelerated over time, CFCs were increasing in the lower atmosphere at a rate of about 4 per cent per year. With some restrictions on the use of CFCs in place, CFC-11 has been decreasing at about 1 per cent per year; however, CFC-12 is still increasing at about 1 per cent per year.

CFCs contribute to the greenhouse effect. They are a source of chlorine in the atmosphere and lead to the destruction of ozone, as observed particularly over Antarctica. They have a long residence time in the atmosphere.

The standard technique for analysing CFCs is to pass a whole air sample through a dryer, after which it is injected into a gas chromatograph. Electron capture detectors are used to detect the different gases. Calibration gas measurements are interspersed with air sample measurements to obtain absolute concentration. An alternative to on-site determination is collecting samples in clean, stainless steel flasks and returning them to a central laboratory for analysis (Prinn and others, 1983).

Nitrous oxide

Nitrous oxide (N_2O) is a gas that has both natural and anthropogenic sources and contributes to the enhanced greenhouse effect (about 6 per cent of the effect is attributable to N_2O). It has a very long atmospheric lifetime (125 years) and concentrations are increasing at the rate of 0.8 parts per billion (ppb) per year. Sources include the oceans, fossil fuel and biomass burning and agricultural soils. Nitrous oxide is inert in the troposphere and its major sink is its photochemical transformation in the stratosphere.

As with several trace gases, an electron capture gas chromatograph is used to measure N_2O. Concentrations are determined by interpreting the measurements with calibration gases of known N_2O concentration. Flask sampling of nitrous oxide is an alternative method of monitoring concentrations. Flasks would be returned to a central laboratory for analysis (Elkins and others, 1996).

Methane

Methane (CH_4) is the most abundant hydrocarbon in the atmosphere. Its tropospheric chemistry affects hydroxyl radical (OH) and carbon monoxide (CO) concentrations. In the stratosphere, the oxidation of CH_4 by OH is a major source of water vapour. Its reaction with chlorine atoms is a termination step in the chlorine-catalysed destruction of ozone. A strong infrared absorption band at 7.66 μm, where CO_2 and water (H_2O) absorb weakly, makes CH_4 an effective greenhouse gas. The reasons behind the reduction in the CH_4 growth rate from approximately 1 per cent per year in the atmosphere to approximately level concentrations are still largely unknown.

Most measurements of atmospheric methane are made by gas chromatography with flame ionization detection. The gas chromatograph systems are very reliable and technically less difficult to operate and maintain than other methods. Typically, CH_4 is separated from other components of an air sample with a molecular sieve column at a constant temperature. Flame ionization detection has a detection limit for CH_4 < 20 parts per billion by volume (ppbv) (1 ppbv = 1 in 10^9 molecules). Measurements are taken relative to a standard.

Standards composed of air with stable, well characterized CH_4 mixing ratios are critical to a measurement programme. As standards are depleted, it is necessary to propagate the measurement scale to new working standards.

Several sample introduction schemes are possible. A central processing facility for flask samples should have an automated manifold for alternate flask samples and standard introduction to the analytical system, but this can be done manually. For a field instrument, an automated stream selection valve is used to select between standards and samples.

An alternative measurement technique is to use a tunable diode laser to determine CH_4 mixing ratios by infrared absorption. This method is expensive to set up and maintain and requires a high degree of technical skill (Fried and others, 1993).

17.2.2 Ozone

Although ozone (O_3) comprises less than 0.5 ppm of the total atmosphere, its radiative and chemical properties make it a very significant constituent of the atmosphere. Methods for its measurement are described in Part 1, Chapter 16.

17.2.3 Radiation and the optical depth of the atmosphere

Measurements of the various solar radiation quantities and the optical depth of the atmosphere are required for many studies into the effects of atmospheric pollution. Measurement methods are described in Part 1, Chapter 7.

17.2.4 Atmospheric deposition

Several components of the atmosphere are deposited at the Earth’s surface. The following sections will introduce principles for the measurement of wet and dry deposited components.

Wet deposition in rain and snow is a good integrator of the chemical and particulate content of the atmosphere; precipitation chemistry is the collection and analysis of precipitation. Dry deposition is the settling and impaction of aerosols and gases on a surface; this requires its own measuring systems. Measurements of wet and dry deposition have applications in studies of the effects of nutrients, acids and toxic materials, and their long-range transport.

17.2.4.1 Wet deposition

Precipitation chemistry measurements provide information on the exchange of trace materials between the atmosphere and the land/oceans, and hence are an important link in understanding the chemical cycles of such substances as sulphur, nitrogen and other trace materials.

When planning precipitation chemistry measurements, particular care must be taken so that any form of local contamination, such as dust or traces of oil or perspiration from human contact, is excluded to prevent compromising the usefulness of the measurements. This requires strict adherence to local siting requirements and site operation protocols (Bigelow, 1987).

Precipitation chemistry monitoring can generally be divided into two phases: collection of the sample and laboratory analysis. When a rain or snow event takes place at a site, a special open-close collector is activated to capture the sample, or, alternatively, the lid is removed from the manual collector. The amount of rain from the national precipitation gauge is also recorded. Optimal sampling periods are either weekly or daily, depending on available funding and personnel, as well as on the intended use of the data. From past monitoring experience, daily sampling, where the collector is checked at a given time each day, has been found to be the most scientifically useful because samples can be preserved quickly, thus preventing significant biological degradation of labile species. Daily data also are simpler to manipulate in source-receptor modelling exercises. Under the weekly protocol, all events are composited over a seven-day period, a practice that may compromise the measurement of some ions, but will clearly reduce programme costs. In some networks, acidity (pH) and conductivity are determined on-site as part of the quality control programme, and biocides (for example, chloroform or thymol) are added to the sample before shipping to the laboratory (Keene and Galloway, 1984; Gillett and Ayers, 1991).

The analysis phase begins when the sample is received by the laboratory or analysing facility. To optimize analysis and ensure high quality, central and/or national laboratories are recommended, with performance tested routinely through the quality assurance programmes of GAW. At these laboratories, the major ions are determined (sulphate (SO_4^{-2}), chloride (Cl^-), nitrate (NO_3^-), hydrogen (H^+(pH)), calcium (Ca^{+2}), magnesium (Mg^{+2}), sodium (Na^+), ammonia ($NH4^+$) and potassium (K^+)). Biogenic acids such as formic and acetic acids are an important source of free acidity in pristine areas and should be measured at background stations (Keene, Galloway and Holden, 1983). Conductivity is also usually measured as part of a comprehensive quality assurance programme. A wide variety of analysis techniques are used by the different laboratories, although ion chromatography and atomic absorption spectrophotometry tend to be the preferred automated analysis techniques (James, 1991).

17.2.4.2 Dry deposition

The term *dry deposition* commonly refers to any atmosphere-surface chemical exchange that occurs at times other than during precipitation events. However, this term can be misleading because some chemicals undergo a bidirectional exchange with the atmosphere. Air-surface exchange is a complex process whose rate is determined by a variety of factors, including atmospheric turbulence and stratification, the chemical and physical characteristics of the deposited compound, the presence and extent of a chemical gradient between the atmosphere and receptor surface, and the chemical, physical (height, surface area, etc.) and biological characteristics of the vegetation receptor surfaces.

Dry deposition is a slow but continuous flux of airborne contaminants to an underlying surface. It contrasts sharply with wet deposition, which is a rapid delivery of pollutants, highly concentrated in precipitation, during precipitation events. Moreover, dry deposition necessarily involves pollutants carried in the lowest layers of the atmosphere, in air that is in contact with the surface. The importance of dry deposition in most areas of the world has never been well documented. Dry deposition is generally far more a local problem than wet deposition. However, in highly industrialized areas, its regional importance is also thought to be great because of the large number of emission sources typically associated with power generation. In many areas, dry deposition is likely to be at least as important as wet deposition.

There are many methods available to estimate dry deposition at a point. Two common approaches are discussed below, namely eddy flux measurements and dry deposition inferential monitoring. Other methods, such as throughfall/stemflow techniques and snowpack accumulation, are not discussed.

Eddy correlation measurements are applicable for certain key pollutants (sulphur dioxide (SO_2), ozone (O_3), nitrogen oxides (NO_x), etc.). They provide direct measurement for comparison to inferential model-based estimates through the use of fast- and slow-response meteorological equipment and fast-response (> 1 Hz) chemical sensors. Reliable flux measurements can be taken using micrometeorological techniques, provided that the user works within a fairly narrowly defined theoretical framework that is somewhat dependent on the trace gas or particle species being measured. A good overview of micrometeorological theory and a short summary of chemical sensors and micrometeorological techniques used to measure turbulent fluxes may be found in Baldocchi, Hicks and Meyers (1988).

Dry deposition inferential monitoring stations make use of current generation data loggers and mean measurements of meteorological variables, and rely on filterpacks for time-integrated concentration sampling. While meteorological data are typically averaged over periods of 30 min, filterpacks are replaced weekly. Filterpacks in several configurations are now in routine use. A typical configuration will have a teflon prefilter in front to remove particles from the air stream, followed by a nylon filter to remove nitric acid and a third filter of cellulose impregnated, for example, with potassium carbonate (K_2CO_3) to capture sulphur. Usually K_2CO_3 is used to clean the filters (before use) and a potassium hydroxide solution is subsequently used for the impregnation. Optional methods include bubblers, denuders and passive monitors, although these techniques, unlike filterpacks, have not seen routine use in network measurement programmes. Required meteorological data include wind speed, direction standard deviation, incoming shortwave solar radiation, air temperature and humidity, surface wetness and precipitation amount. A thorough discussion of dry deposition inferential measurement techniques may be found in Hicks and others (1991).

17.2.5 **Reactive gases**

Reactive gases monitored with GAW include CO, SO_2 and NO_x. Although these gases do not contribute directly to the greenhouse effect, they can influence the chemistry of the important greenhouse gases through their interaction with the OH in the atmosphere. Furthermore, as pollutant gases, they are important in influencing the environment at the Earth's surface. For example, both SO_2 and NO_x react photochemically and are the major precursors of acid rain. Nitrogen oxides also play critical roles in determining tropospheric O_3 concentrations of photochemical smog at ground level and in the eutrophication of coastal estuaries.

17.2.5.1 Carbon monoxide

In the non-urban troposphere, CO is often the primary sink for OH. It is therefore an intimate component of the series of photochemical reactions that ultimately oxidize reduced carbon, nitrogen and sulphur trace gases. Although CO itself does not contribute directly to the greenhouse effect, because of its influence on OH, CO concentrations (with a lifetime of several months) have climatological importance as these indirectly affect the concentrations of many greenhouse gases.

Several analytical techniques are available with which to measure CO at atmospheric levels. Measurements can be taken by gas chromatography with either a flame ionization detector or a mercuric oxide reduction detector (Peterson and Rosson, 1993). Non-dispensive infrared radiation techniques also work, with modifications. The chromatography uses two columns in series, with silica gel first for the removal of impurities, followed by the separation of CO, hydrogen (H_2) and CH_4 on a molecular sieve. Using a flame iomization dectetor, CO is catalytically converted to CH_4 before entering the detector. In this case, the same gas chromatograph can be used to measure both CH_4 and CO (as well as other hydrocarbons). A measurement precision of 5–10 per cent is easily obtained. When using the mercury oxide (HgO) reduction detector, CO reacts with hot HgO releasing mercury (Hg) vapour, which is detected by ultraviolet absorption. Molecular hydrogen is also detected with this method. Precision is of the order of 1–2 per cent. HgO detectors often exhibit non-linear response over the range of atmospheric CO levels; however, this problem is minimized through the use of multiple calibration standards. The gas chromatograph methods require calibration of the samples to quantify their CO mixing ratios (Novelli and others, 1994).

Tunable diode laser spectroscopy also measures ambient levels of CO by infrared absorption. The drawbacks of this method are that the startup costs are much higher than for gas chromatography, a high degree of technical skill is required to maintain the instruments, and they are not well suited for remote operation (Sachse and others, 1987).

Reference standards consisting of dried air with carefully determined CO mixing ratios are essential to programmes which use gas chromatograpyh, gas fluid chromatography, NDIR, or tunable diode laser spectroscopy to measure CO. In the past, it has been difficult to obtain CO standards representing atmospheric levels. WMO has designated ESRL in Boulder, Colorado, United States, as the central calibration facility for CO. The ESRL is working in coordination with the Fraunhofer Institute (Garmisch-Partenkirchen, Germany), the Swiss Federal Laboratories for Materials Testing and Research (EMPA) (Dübendorf, Switzerland), and the Nitrous Oxide and Halocompounds Group (NOAA/ESRL, United States) to provide the research community with high-quality CO standards. However, caution must still be used when comparing previously obtained data sets from various laboratories to evaluate either geographical or temporal CO changes. This is primarily due to the use of different standard scales which may vary by as much as 30 per cent (Weeks and others, 1989). Also, low concentrations of CO in high pressure reference gas cylinders are likely to slowly change over time.

There is a very significant problem of contamination associated with the measurement of CO in flask samples. Flask samples of air are generally analysed by using one of the gas chromatography methods. Carbon monoxide may increase or decrease significantly in a few days to weeks in many types of containers. Methods and materials should be rigorously tested for contamination before beginning field measurements.

17.2.5.2 Sulphur dioxide

The sources of sulphur dioxide (SO_2) in the atmosphere include the sea, volcanic activity, anthropogenic emissions and biomass decay processes. Sulphur dioxide has a typical residence time of hours to days. The concentrations of SO_2 in remote areas can be lower than 0.05 ppbv, while in urban areas, concentrations may rise to greater than 10 ppbv. Power plant plumes and volcanic emissions may emit concentrations as high as 1000 ppbv. Sulphur dioxide is a greenhouse gas because it is an infrared absorber. However, because of its low concentration relative to other greenhouse gases, it is a less significant greenhouse gas.

Sulphur dioxide is a climatically active trace species. This is because in the atmosphere it reacts photochemically (homogeneous conversion) and on airborne particles (heterogeneous conversion) to produce sulphates. Atmospheric sulphate particles are active cloud condensation nuclei. An increase in the number of cloud condensation nuclei on a global scale may increase cloud albedo (Charlson and others, 1987). An enhancement in atmospheric sulphate particles in the stratosphere may increase short-wave reflection to space (Charlson and others, 1991). Sulphur dioxide also plays a significant role in producing acid deposition. It forms sulphate particles. These particles return to the Earth's surface via dry or wet deposition processes. Both processes transfer excess acidity to their deposition sites. This acidity may damage sensitive ecosystems.

Concentrations of SO_2 can be measured continuously by using either a pulsed-fluorescence analyser or a flame-photometric device. The response time of the pulsed-fluorescence sensor is slower, but its ease of calibration, dependability, accuracy and SO_2 specificity make it preferable (Luke, 1997; Kok and others, 1990). More sensitive gas-chromatographic techniques are available. They require significant technical expertise and regular attention. Concentrations of SO_2 can also be measured by using filter media. This method yields a potentially more accurate result. It is an integrative technique and requires frequent attention, and filter analysis costs are high.

Since SO_2 has a short atmospheric lifetime, understanding the sulphur cycle requires knowledge of the source and sink terms. This is best accomplished with sampling frequencies of less than 1 h. Therefore, the best technique for the long-term monitoring of SO_2 may be a combination of the pulsed-fluorescence analyser and filter sampling. Filter samples would be exposed at intervals, but often enough to act as a quality control for the continuous analyser.

Sulphur dioxide should be considered a reactive gas. It may stick to intake lines or oxidize within water drops condensed in the lines. Thus, intake lines should be made of inert material, for example, stainless steel, as short as possible, and thermostatically heated when condensation is likely to occur. Measurement on PFA Teflon is acceptable after appropriate tests have been conducted to ensure no loss from inappropriate filter additives.

A summary of techniques is presented in the special issue of the *Journal of Geophysical Research* discussing the Gas-Phase Sulfur Intercomparison Experiment (GASIE), beginning with an overview of the experiment by Stecher and others (1997).

17.2.5.3 Nitrogen oxides

Nitrogen oxides (NO_x) comprise a large family of trace gases that are ubiquitous in the Earth's troposphere. Their origin is from both anthropogenic (combustion) and natural (biomass burning, lightning, soil microbial activity) processes; transport from the stratosphere is also thought to be a source. NO_x play a crucial role in determining the ozone concentration in the air and are an important contributor to the acid precipitation problem, especially in North America. Although the need for knowledge of the abundance of these compounds is unquestioned even at the parts per trillion by volume (pptv) level (1 pptv = 1 in 10^{12} molecules), very little observational data outside urbanized areas are presently available owing to the scarcity of sensitive equipment, difficulty in accurately measuring NO_x and a high degree of skill or training needed to measure NO_x reliably at such low concentrations. The more important nitrogen oxide compounds are nitric oxide (NO), nitrogen oxide (NO_2) (the sum of these two compounds is often indicated as NO_x), nitric acid (HNO_3), aerosol nitrate and peroxy-acetyl-nitrate (PAN). Nitric oxide and NO_2 are the initial compounds produced, while the others are the product of chemical conversions in the atmosphere from the former. Nitrous oxide (N_2O) is a special case; its chemistry is very different from all other nitrogen oxides in that it is essentially inert in the troposphere. It is discussed in section 17.2.1 as one of the greenhouse gases.

When measuring these gases, it should be noted that conversions between the different compounds are generally rapid, and the most unambiguous data for NO_x are often expressed as the sum of all compounds (excluding N_2O), often denoted as total reactive nitrogen (NO_y). Obvious precautions related to human interference with the measurements have to be taken into account. Since the levels are so low, even at less remote locations, great care has to be taken to minimize potential contamination from any form of motorized transport, which is a principal source of No_x (and also CO and SO_2) (United States Environmental Protection Agency, 1996).

Nitric oxide and nitrogen oxide

Reliable measurements of nitric oxide (NO) and nitrogen oxide (NO_2) at background levels are possible by using instruments based on chemiluminescence of NO (with O_3) or NO_2 (indirectly using chemiluminescence following conversion to NO). NO_2 may also be measured directly with a luminol solution. However, commercial instruments are not sensitive enough. Low-level measurements require research-grade or modified detectors.

The O_3 chemiluminescence technique is a continuous measurement method based upon the detection of photons released through the reaction of O_3 with NO. Ambient air is drawn into a reaction vessel at a controlled flow rate using a mechanical vacuum pump and mass flow controller. Ozone is generated within the instrument as a reagent by passing a flow of pure, dry oxygen through a high-voltage electrode and is directed into the reaction vessel where it reacts with NO in the ambient air flow to form NO_2. A fraction of the NO_2 is formed in an electronically excited state, a portion of which emits a photon as it relaxes back to the ground state. A red-sensitive photomultiplier tube is used to detect the emission spectrum. As mentioned above, NO_2 must first be converted to NO prior to detection. Typically, heated molybdenum or gold surfaces are used to convert the total reactive nitrogen species NO_y to NO. Photolytic conversion is a more selective method to measure NO_2, but may suffer from small interferences from nitrous acid (HONO), nitrate (NO_3) and PAN.

Instruments suitable for gradient measurements (a dry deposition measurement technique) are available commercially. Custom-built instruments have been deployed in a variety of eddy correlation studies of NO emissions from soils (Luke and Valigura, 1997).

Nitrogen oxide may be measured directly through its chemiluminescent reaction with luminol. The solution flows at a controlled rate down a fabric wick in front of a photomultiplier tube and blue photons are emitted by the chemiluminescence. Commercial versions of this instrument are available, and the technique does give rapid and sensitive measurements. However, the method suffers from non-linearity at NO_2 concentrations below 2 to 3 ppbv and exhibits a slight O_3 and a significant PAN interference (Luke and Valigura, 1997). Instruments must be adjusted frequently to account for calibration drift and shift in zero point with temperature.

Peroxy-acetyl-nitrate

Peroxy-acetyl-nitrate (PAN) is ubiquitous in the troposphere and is typically abundant in polluted urban air due to the reactivity of many anthropogenic hydrocarbons. PAN may undergo long-range transport at low temperatures and may be present at high latitudes. Studies of PAN are relatively few; however, PAN may be important because of phytotoxicity and abundance in urban areas. A thorough review of the sources, sinks and atmospheric chemistry of PAN may be found in Roberts (1990).

PAN is typically measured by using automated gas chromatographs, equipped with either electron capture detection or by thermal decomposition followed by detection of NO_2 via luminol chemiluminescence. The use of a luminol detector has a disadvantage due to its sensitivity to NO_2. The major problem with PAN measurements is the unreliability of calibration.

Nitric acid and aerosol nitrate

The primary anthropogenic nitrogen species emitted to the atmosphere is NO which is quickly transformed to NO_2 and then by several steps to mainly nitric acid (HNO_3), which is efficiently deposited to the surface of the Earth via both wet and dry deposition mechanisms. See section 17.2.4.1 for more information regarding the wet deposition pathway.

Nitric acid and aerosol nitrates are amenable to monitoring with filters. A standard procedure would require a train of filters in series, with the first filter, a Teflon filter to capture aerosol particles, including aerosol nitrate, followed by a nylon, or base-impregnated filter to capture acid gases including HNO_3. These filters are routinely exposed for periods of many hours, by sampling air at a flow rate of several litres per minute. The filters are then transported to a laboratory, extracted, and analysed for nitrate ions by ion chromatography. In order to derive the amount of air sampled, the pumping flow rate must be continually monitored. The most severe problem associated with the use of the filterpack method is the potential for artefact formation from the collection and volatilization of ammonium nitrate aerosols. These problems can be largely avoided by keeping sampling time short (Anlauf and others, 1985; Luke and Valigura, 1997).

Good alternative methods exist for measuring HNO_3. Denuders have been employed, but their use is not as widespread as that of the filterpack method because of the labour intensiveness of the procedure (Luke and Valigura, 1997). Mist chamber methods are also available and were developed as an alternative to the filterpack method. Klemm and others (1994) tested this methodology in the Canadian Taiga during a recent field programme.

Total reactive nitrogen

Collectively, the suite of nitrogen oxides is known as total reactive nitrogen (NO_y) as follows:

$$NO_y = NO + NO_2 + NO_3 + HONO + HNO_3 + HO_2NO_2 + 2[N_2O_5] + PAN + RONO_x + NO_3^- + \ldots$$

where NO_x represents the sum of NO and NO_2. Each of these compounds behaves differently in the atmosphere and deposits at a different rate. Many of these compounds are present in minute quantity and are difficult to convert quantitatively for measurement as NO. NO_y is measured by converting each of these compounds to NO and measuring them as compounds, as described earlier. This conversion is obtained by passing the air through a gold converter tube kept at approximately 300°C, together with a small amount of either pure CO or hydrogen gas (Luke and Valigura, 1997). Heated molybdenum screens, wire or tubing (temperature ~ 300–350°C) may also be used, without the necessity of adding CO or hydrogen.

17.2.6 Chemical properties of particulate matter

The chemical properties of atmospheric particles can affect the environment in many ways. Toxic aerosols such as heavy metals (for example, lead (Pb), cadmium (Cd) or arsenic (As)) or particles from semi-volatile organic contaminants (for example, from polychlorinated biphenyl compounds) have been linked to a broad range of adverse effects on humans and animals, including effects to the reproductive, nervous, immune and endocrine systems, and changes in enzyme functioning (United States Environmental Protection Agency, 1997). Hygroscopic aerosols, for example, sea salt, sulphate and nitrate particles are active cloud condensation nuclei which govern the concentration and size distribution of cloud droplets, and thus affect cloud lifetime, amount and albedo and overall climate (Parungo and others, 1992). Hydrophobic aerosols, for example, soil dust and decayed bio-debris, can serve as ice nuclei and thus control precipitation amount. In order to improve our understanding of the trends and extent of aerosol effects on global change, it is important to measure the spatial and temporal variabilities of aerosol chemical properties.

The most simple and direct sampling technique is to collect particles on filters. Samples can be collected on one stage for bulk analysis or on several cascade stages for size discrimination. The samples are sent to a centralized laboratory for chemical analyses. Soluble portions of aerosol particles can be extracted with water and determined with an ion chromatograph for cation and anion concentrations. The insoluble particles are typically analysed with instrumental neutron activation analysis, proton induced X-ray emission, or inductivity coupled plasma mass spectrogrametry for elemental composition. Semi-volatile components are typically analysed by gas chromatography by using either an electron capture detector or coupled with a mass spectrometer (Parungo and others, 1992; Baker, 1997).

For all samples collected, the sampling and analytical procedures should be standardized to the degree possible at all sites. However, it is difficult to specify sampling regimes for such a broad array of materials which have tremendous spatial and temporal variation, particularly between urban and background regions. For many urban and rural regions, 12 h samples taken several times per week provide an adequate understanding of the concentration regime, while background areas may require longer exposures. If filter concentrations are to be coupled with source-receptor models, sampling frequencies may need to be tuned to the requirements imposed by meteorological conditions (Harris and Kahl, 1990).

17.2.7 **Radioactive gases**

Radioactive gases are trace gases in the atmosphere system which are both natural and from industrial sources. Regarding the latter, radioactive gases are especially produced by nuclear electric power generation, by other industrial processes and by former nuclear weapons tests. The concentration of the different components varies and in high enough concentrations can have negative impacts on humans.

The behaviour of radioactive contaminants in the atmosphere is governed by their chemical and physical nature. The dynamics of transport, diffusion, deposition and condensation for these materials will be nearly the same as for their non-radioactive counterparts. One possible exception to this generality is the fact that radioactive particles produce ionization in the surrounding air and leave charges on particles; this factor could change processes that are dependent upon charge effects. The radioactive properties of individual radioisotopes or particular mixture of radioisotopes are of importance in determining the quantity and nature of the radioactive materials reaching the receptor, as well as the resulting radiation dose (Slade, 1968).

17.2.7.1 **Radon**

Radon is an inert gas resulting from the alpha decay of radium, with a half-life of 3.82 days. Because radon fluxes from soils are typically 100 times those from the ocean, radon is useful as a tracer for air masses that have recently passed over land. Studies at the Mauna Loa observatory in Hawaii have identified diurnal episodes of radon transported from local sources, and long-term transport of air from distant continents. In conjunction with other measurements, radon data provide a useful constraint in evaluating air transport models and in identifying baseline atmospheric conditions. Because of its short residence time in the atmosphere and wide range of surface emanation rates, the interpretation of radon measurements is highly site-specific (Liu, McAfee and Cicerone, 1984; Hansen and others, 1990).

Radon-222 decays through a series of five progeny into lead 210, which is relatively stable at a half-life of 22 years. Two of these progeny undergo alpha decay. The daughter products are chemically reactive and quickly form complex hydrated ions that readily attach to particles and surfaces.

In a typical radon-monitoring instrument, air is drawn through a filter which removes all the ambient daughters but allows the inert radon gas to pass. Radon then enters a large chamber that allows a delay during which its progeny are produced. These are collected on a second filter, and their alpha activity is measured by a scintillation detector. The response of an instrument is dependent on a number of factors, such as the flow rate, chamber geometry, progeny capture efficiency, sampling interval, and counter efficiency. The usual sampling frequency is one to two samples per hour (Thomas and LeClare, 1970).

17.2.7.2 **Krypton-85**

Krypton-85 (^{85}Kr) is a radioactive noble gas that decays with a half-life of 10.76 years, emitting mainly β particles with a mean energy of 251 KeV. The main sources of ^{85}Kr are nuclear-fuel reprocessing plants and various nuclear reactors. The nuclear weapons tests carried out between 1945 and 1963 contributed about 5 per cent of the total ^{85}Kr in the atmosphere, whereas its natural sources can be neglected. Radioactive decay is practically the only mechanism of ^{85}Kr removal from the atmosphere. The present background concentrations of ^{85}Kr in the atmosphere are about 1 Bq/m^3 and are doubled every 20 years. At this level, ^{85}Kr is not dangerous for human beings, but the air ionization caused by ^{85}Kr decay will affect atmospheric electric properties. If ^{85}Kr levels continue to increase, changes in such atmospheric processes and properties as atmospheric electric conductivity, ion current, the Earth's magnetic field, formation of cloud condensation nuclei and aerosols, and the frequency of lightning may result and, thus, disturb the Earth's heat balance and precipitation patterns. These ^{85}Kr-induced consequences call for ^{85}Kr monitoring (WMO, 1995*b*).

To measure ^{85}Kr, air samples are collected using a charcoal trap that has been immersed in a container of liquid nitrogen. Samples are prepared chromatographically and reduced to cryogenic temperatures, forced through a concentrator and then desorbed by the flux of a helium gas carrier.

After leaving the chromatograph, the mixture is fed into the liquid air-cooled trap. Radiometric analysis is then performed using a scintillation detector (Novichkov, 1997).

The required precision for ^{85}Kr depends on the application of the information. For the purpose of climate change research, only the order of magnitude of the atmospheric concentration would be of interest. In this case, a precision as low as about 10 per cent would be acceptable. If however, ^{85}Kr is to be used as a tracer for the purpose of understanding transport and mixing processes, a precision of the order of 1 per cent would be required. The measurement of ^{85}Kr provides a good tool to validate or perhaps even calibrate global-scale transport and mixing characteristics of models (Novichkov, 1997).

17.3 QUALITY ASSURANCE

The primary objective of the GAW quality assurance system is to ensure that the data deposited in the World Data Centres are consistent, meet the GAW data quality objectives and are supported by comprehensive metadata. The quality assurance system is designed around Quality Assurance/Science Activity Centres (QA/SACs), which are, among other things, expected to critically review data submitted by individual stations. This will be achieved through adherence to GAW standard operating procedures. According to a decision of the Executive Council Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry in 1999 (WMO, 1999), QA/SACs should have global responsibility for specific atmospheric parameters. The GAW quality assurance procedures should not only address the quality of the measurement, but also the entire quality assurance process, beginning at the station with the training of station personnel and ending with the World Data Centres containing data of the required quality.

The recommended GAW quality assurance principles to ensure comparability and consistency of measurements involve the following (WMO, 2001):

(a) Adoption and use of internationally accepted methods and vocabulary to deal with uncertainty in measurements as outlined by the International Organization for Standardization (ISO, 1993; 1995);
(b) Use of harmonized measurement techniques based on standard operating procedures at all stations. A standard operating procedure is a written document that has been officially approved by the relevant Scientific Advisory Group and details the method for performing a certain operation, analysis or action by thoroughly prescribing the techniques and steps involved;
(c) Regular performance and system audits. In the context of GAW, a performance audit is understood as being a voluntary check for the conformity of a measurement where the audit criteria are the data quality objectives for that parameter. In the absence of formal data quality objectives, an audit will at least involve ensuring the traceability of measurements to the reference standard. A system audit is more generally defined as a check of the overall conformity of a station with the principles of the GAW quality assurance system. The reference for station conformity will evolve as the GAW quality assurance system evolves.

According to WMO (2001), the overall goals of the quality assurance system are the following:

(a) To establish data quality objectives and standard operating procedures for all parameters as recommended by the Scientific Advisory Groups;
(b) To identify and establish QA/SACs, World Calibration Centres and reference standards where needed;
(c) To harmonize the GAW quality assurance procedures;
(d) To increase the frequency of instrument calibrations and intercomparisons;
(e) To build alliances between and among global and regional stations (scientific and technical cooperation, twinning), as well as twinning between individuals (scientists and station personnel).

According to (WMO (2001), the current implementation includes the following:

Task 1: To establish a prioritized list of parameters urgently needing data quality objectives;
Task 2: To identify and establish QA/SACs for N_2O and CFCs;
Task 3: To identify and, where feasible, establish World Calibration Centres and reference standards for the remaining parameters;
Task 4: To develop standard operating procedures for the remaining parameters;
Task 5: To develop guidelines for GAW station system audits;
Task 6: To identify and establish Regional Calibration Centres, where necessary, which provide calibration and instrument intercomparison for GAW stations in the region.

The quality assurance-related tasks for the various GAW components are also covered by Global and Regional Calibration Centres. These centres perform the vital function of helping to ensure that the data submitted to the GAW World Data Centres are of sufficient quality. Their activities include the following:

(a) The careful calibration of instruments through station visits;

(b) Instrument intercomparisons and calibration campaigns;

(c) Laboratory measurement intercomparisons of circulated standard gases or reference samples;

(d) Systematic and frequent calibration checks of the world standards.

Although these direct calibration activities are required to maintain the required comparability of measurements during station visits, GAW Calibration Centres also provide on-site training and expert advice to help station personnel maintain the required data quality. Workshops are also held during intercomparisons and calibration campaigns. Further help is provided to less experienced personnel at new stations by personnel from well-established and technically advanced stations. In addition, GAW Training Centres sponsor frequent training sessions for station personnel, particularly those located in developing countries. These capacity-building activities are increasingly important as many GAW stations in developing countries have become operational. As reported in WMO (2001), the GAW quality assurance system is still incomplete. Currently, very few guidelines have been produced for quality assurance and standard operating procedures for the GAW programme, and no GAW reports are available concerning system audits. Further details on the current GAW implementation strategy are provided on the WMO website (http://www.wmo.int, "Global Atmosphere Watch" under "Topics").

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