AIR POLLUTION MONITORING

Air pollution from both stationary (e.g. factories) and mobile (e.g. cars) sources includes many substances, such as carbon monoxide or lead, which are harmful in themselves, primary pollutants, and other substances which react with other chemicals to form new harmful substances , secondary pollutants, (e.g. sulfur dioxide reacting with water and air to produce the sulfuric acid of acid rain)..

Primary pollutants

Primary pollutants monitored in New Zealand: particulates (smoke, dust and haze), sulfur dioxide, carbon monoxide, the oxides of nitrogen, benzene, hydrogen sulfide and fluorides.

Secondary pollutants

Secondary pollutants are monitored in New Zealand: ozone, photochemical smog and acid rain. None of these currently are found in high enough concentrations to be a significant concern.

Monitoring Pollutants

Air pollution monitoring is done by a number of organisations in New Zealand, including the Institute of Environmental Science and Research (ESR), the National Institute for Water and Atmosphere (NIWA), Regional Councils and industry. These pollutants are monitored through a variety of manual and instrumental methods with instrumental methods progressively replacing the manual ones.

Manual sampling

Manual methods include passive samplers (in which solid matter is collected from the air flow by a filter); paper tape samplers (where pollutants are collected, or react with a coating on a paper tape which is advanced at regular time intervals); and bubblers (which involve gases being bubbled through solutions in which particular pollutants undergo a reaction). The particular pollutants for which these methods can be used are outlined in **Table 2**.

Instrumental methods

Most of the instruments used are based on absorption or emission spectroscopic methods: non-dispersive infra-red (NDIR), chemiluminescence; flame photometry, and fluorescence. In the case of airborne particles instruments have been developed on the basis of light scattering, absorption of low-energy (beta) radiation, and the use of a continuously recording microbalance. As with manual methods, the instrumental techniques are best suited to specific pollutants, as shown in **Table 2**.

Levels of pollution

New Zealand, with the exception of a few specific areas, has quite low levels of pollution. Those pollutants which are of some concern are primarily carbon monoxide and oxides of nitrogen, both of which are associated with vehicle emissions. Fine particulate matter has also become a concern over the last few years. This is due to increasing levels of smoke from domestic fires.

INTRODUCTION

In New Zealand the control of air pollution is governed by the Resource Management Act 1991, which is administered by Regional Councils throughout the country. The Act provides for sustainable management of natural resources, including air. Discharges of contaminants to air are prohibited under the Act, unless the discharge is expressly allowed by a rule in a regional plan, a resource consant (issued by the Council) or regulations. The Act also requires Regional Councils to carry out air monitoring, as a means of checking how effectively it is managing air quality.

SOURCES OF AIR POLLUTION

Air pollutants are both hazardous substances and substances which undergo chemical reactions in the atmosphere to produce hazardous substances. These can be produced either locally by a particular industrial process ('stationary' pollutants), or by moving objects such as cars ('mobile' pollutants)

We are mainly concerned with the following primary and secondary pollutants.

Primary pollutants

Primary pollutants are those in which the substance emitted is itself hazardous. Some primary pollutants also produce other dangerous substances after undergoing chemical reactions in the atmosphere, and these are known as secondary pollutants. Primary pollutants include the following substances.

Particulates

This includes dust, smoke, aerosols and haze - any finely divided airborne solid material. Particulates are commonly generated by fires, motor vehicles, some industries (particularly road building, quarries and fossil fuel power stations) and various natural sources including volcanoes, plant and animal matter and dirt. Particulates are aesthetically displeasing, can irritate the eyes and cause repiratory problems. In recent years concerns have been raised about the possible health effects of 'fine' particulate matter (less than 10μm diameter). These have been shown to be associated with increases in hospitalisation and even deaths from respitorary illnesses and heart disease.

Sulphur dioxide, SO_2

Sulphur dioxide is often produced by the industrial processes which produce particulates, the primary sources of SO_2 being coal, fuel oil and diesel. Being a corrosive acidic gas, sulphur dioxide damages buildings and other materials, and can cause respiratory problems.

Carbon monoxide, CO

The commonest source of carbon monoxide is motor vehicle emisions, where it results from the combustion of petrol in the presence of insufficient oxygen. It is also a result of some fuel-consuming industries and domestic fires. Carbon monoxide is a colourless, odourless, highly toxic gas that displaces oxygen in human blood, causing oxygen deprivation.

The oxides of nitrogen, NO_x

NO_x refers to the mixture of nitric oxide (NO) and nitrogen dioxide (NO_2) formed by the oxidation of nitrogen during the combustion of air. The majority of NO_x is produced in motor vehicle emissions, although other sources can have significant local impact. NO_x is a contributor to several secondary pollutants, and NO_2 is a respiratory irritant that can also corrode metals at high concentrations.

Benzene

Over the last few years leaded petrols have been phased out of use. However this has resulted in higher levels of benzene and other aromatics in the substitute unleaded petrol. Benzene breaks down quickly in the environment and is not stored in the tissues of plants or animals. However, it is still hazardous to humans at high levels as it can cause several diseases of the blood including leukemia (cancer of the white blood cells). Benzene monitoring programmes were started in New Zealand in 1994 and are continuing because the levels in some locations were found to be reasonably high.

Hydrogen sulphide, H_2S

Hydrogen sulphide is mainly associated with geothermal activity at Rotorua, where it is responsible for the 'rotten eggs' smell, but it is also formed from the anaerobic decomposition of many organic wastes and is a by-product of paper manufacture and leather tanning (see article). It is highly poisonous (more toxic than hydrogen cyanide), and because it initially anaesthetises the sensory organs it can build up to high concentrations without warning and cause paralysis and then asphyxiation.

Fluorides

These have two main sources: the Comalco aluminium smelter and fertiliser works . Fluorides can have adverse effects on plants, and in some cases concentrate in the leaves so that animals eating the plants ingest significant quantities. Fluoride in animals converts the hydroxyapatite in bones and teeth into fluoroapatite:

$$Ca_5(PO_4)_3OH + F^- \leftrightarrows Ca_5(PO_4)_3F + OH^-$$

This is initially advantageous (indeed water is fluoridated to cause this to take place) but if it occurs to too great an extent it produces discoloured patches and eventually weakens the teeth.

Secondary Pollutants

These are pollutants formed by chemical reactions in the atmosphere, either with other chemicals or with light.

Ozone (O_3) and photochemical smog

Ozone is formed *via.* two main pathways. The first is by the reaction of NO_x with any of a wide range of volatile organic compounds in the presence of sunlight. Such volatile organic compounds are found in motor vehicle exhaust and industrial solvents. Further ozone is formed by the decomposition of NO_2 in sunlight and the reaction of the decomposition products with oxygen itself to give ozone:

$$NO_2 \rightarrow NO + O^{\cdot}$$

$$O^{\cdot} + O_2 \rightarrow O_3$$

Ozone is the major constituent of photochemical smog, which is a complex mixture also containing oxidised organics, including aldehydes (RCOOH) such as formaldehyde, peroxides (ROOR), acrolein and peroxyacylnitrates. This chemical "brew" causes damage to sensitive plants and crops, eye and lung irritation, accelerated degradation of materials such as rubber, and a marked deterioration in atmospheric visibility.

Acid rain
This is a mixture of nitric and sulphuric acids, which are formed by the interaction of NO_2 and SO_2 with moisture and oxygen in the air. Acid rain corrodes building materials and has harmful effects on plant and animal life, but to date has not been a significant problem in New Zealand.

POLLUTION MONITORING DEVICES

A wide range of methods is available for the measurement of air pollutants, from the very simple to the highly sophisticated, and with a corresponding variation in costs. Descriptions of the most common procedures are given below. The manual procedures described are relatively labour intensive, and limited in the amount of information provided. As a result these have gradually been phased out where possible in favour of the more sophisticated direct-reading instruments. Apart from periodic maintenance, the operational requirements of the latter are minimal. However, they do require considerably more effort in data processing and analysis, because of the much greater volumes of data produced.

Most of the techniques described have been used for air monitoring in New Zealand over the last thirty or so years. In the past most of this work was done by the Department of Health, which was responsible under the old Clean Air Act 1972. Now the work is done by Regional Councils, or by science providers such as the Institute of Environmental Science and Research (ESR) and the National Institute for Water and Atmosphere (NIWA). Some monitoring is also done by specific industries as part of their requirements of their resource consents.

Manual methods

Passive samplers
The simplest approach to sampling of gaseous air pollutants involves passive collection onto a chemically treated surface or material. The driving force for collection is diffusion through the air and/or movement due to wind. Once in contact with the collector, the pollutant is retained by chemical reaction.

Results generated by these methods are useful in a relative sense, but because of the variability of the factors affecting collection and retention of the pollutant it is difficult to establish any simple relationships to the airborne concentrations.

Paper tape samplers
The usefulness of the above systems can be extended if air is forcibly drawn through or over the treated surface by means of a pump. An example of this is the paper tape sampler shown in **Figure 1**. Numerous applications have been reported for gases such as H_2S, HCN, NH_3, NO_2, SO_2, Cl_2, $COCl_2$, amines and isocyanates.

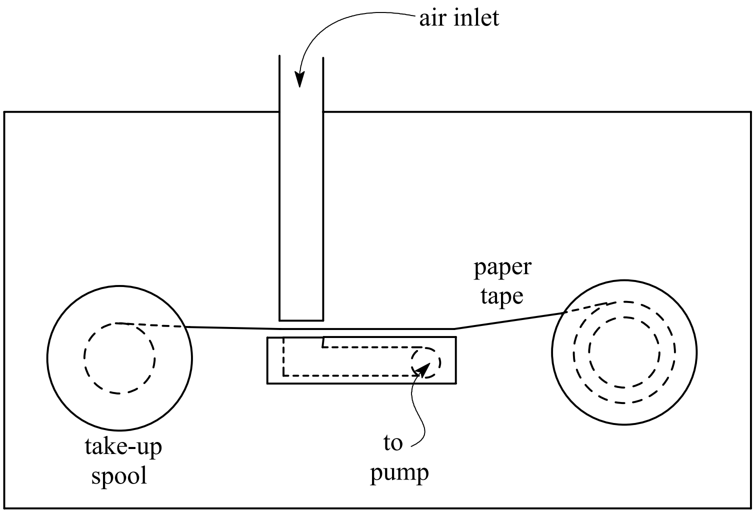

Figure 1 - Paper-Tape Sampler

In most commercial systems the tape is automatically advanced at selected time intervals to produce a series of discrete spots or samples. Some units also incorporate a direct measurement system for use when stain development takes place *in situ*. In others it is necessary to remove the tape for measurement or analysis of each spot.

A paper tape system has also been developed into a continuous monitoring system for particulate matter, using the attenuation of low energy radiation. This is described under the section on suspended particulate monitoring methods given below.

Bubbler Systems
One of the most universal approaches for the collection of gaseous pollutants is to bubble the air through a solution designed to absorb or react with the contaminants. Most gases and vapours can be collected in this way, followed by an appropriate laboratory analysis of the resulting solutions.

Instrumental Monitoring Methods

A wide range of instrumental methods have been reported for the monitoring of air pollutants. Many of the systems are based on photometric techniques, and the most common examples of these are described below.

Non-Dispersive Infra-Red (NDIR)
NDIR analysers have been developed to monitor SO_2, NO_x, CO, and other gases that absorb in the infra-red, including CO_2 and hydrocarbons. However it is probably true to say that this is the "preferred" technique only for CO monitoring of pollutants in ambient air. The technique is of relatively low sensitivity, and is more applicable to the concentrations found in source emissions than in ambient air.

An NDIR analyser is basically an instrument that does not disperse the light emitted from an infra-red source - i.e. the light is not split up into its component wavelengths by means of a prism or grating. Instead a broad band of light is produced by means of a bandpass filter, which is chosen to coincide with an absorption peak of the pollutant molecule. The IR band centres for some common gases are shown in **Table 1**.

Table 1 - NDIR band centres for some common atmospheric pollutants

Gas	Location of band centre / cm^{-1} [1]
carbon monoxide (CO)	2200
carbon dioxide (CO_2)	850 - 1250, 1900, 3700
water (H_2O)	1000 - 1400, 1800 - 2000, 3200
nitric oxide (NO)	1800 - 2000
nitrogen dioxide (NO_2)	500 - 1800
sulfur dioxide (SO_2)	700 - 1250

The layout of a typical NDIR analyser is shown in **Figure 2**. Infra-red radiation passes through a reference cell, usually containing clean dry air, and a separate cell containing the sample. The detector is referred to as a "microphone" type. It consists of two chambers separated by a thin metal diaphragm and filled with gas of the species being measured. As the molecules in the detector absorb the IR radiation their kinetic energy increases, causing the pressure in each chamber will increase. If, however, absorbing molecules are present in the sample cell, the amount of energy reaching that side of the detector will diminish. Thus a pressure differential develops between the two chambers, resulting in displacement of the diaphragm. This is sensed as a change in capacitance by the instrument electronics. As shown in the figure the instrument also includes a beam chopper. This serves to create an alternating signal in the detector, which makes it easier to detect and amplify.

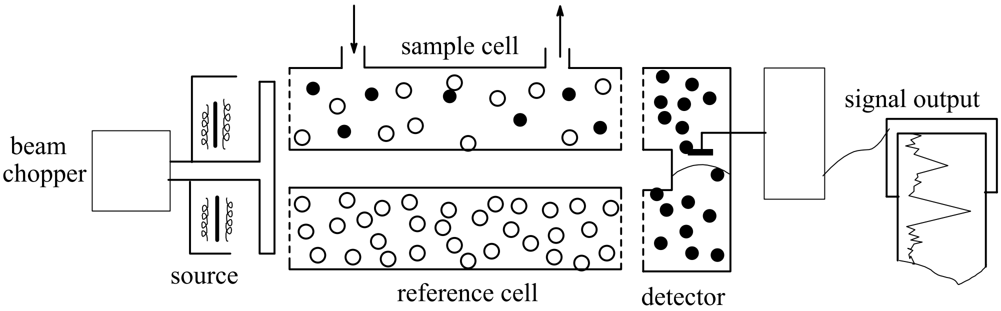

Figure 2 - An NDIR analyser

A common problem with this type of analyser is that other gases that absorb light in the same spectral region as the pollutant will cause a positive interference in the measurement. For CO analysers water vapour and CO_2 are potential interferents. Water can be readily removed from the sample by means of an inlet filter containing a desiccant, such as silica gel. In ambient air monitoring the effect of CO_2 is usually not significant.

Chemiluminescence

Chemiluminescence is the emission of light energy that results from some chemical reactions. The reaction between NO and O_3 is an example:

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[1] All IR readings are given using the units cm^{-1} (known as *wave numbers*). These are a measure of the energy of the radiation as $E = (c \div \lambda)$, meaning that $E \propto \lambda^{-1}$. The symbol ' λ ' (the Greek letter lambda) is the wavelength of the radiation being absorbed and has the units 'cm', thus the energy of this radiation has the units cm^{-1}.

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

These reactions produce a continuum of radiation in the range 500 to 3000 nm. The reaction between O_3 and ethylene is also chemiluminescent, with an emission in the region of 435 nm. Both of these phenomena have been used to produce continuous monitors for NO_x and O_3, respectively.

A typical layout of a chemiluminescence analyser for NO_x is shown in **Figure 3**. Ozone is generated by the UV irradiation of clean air and mixed in a reaction chamber with the sample air. Light from the reaction passes through an optical filter and is detected with a photomultiplier tube.

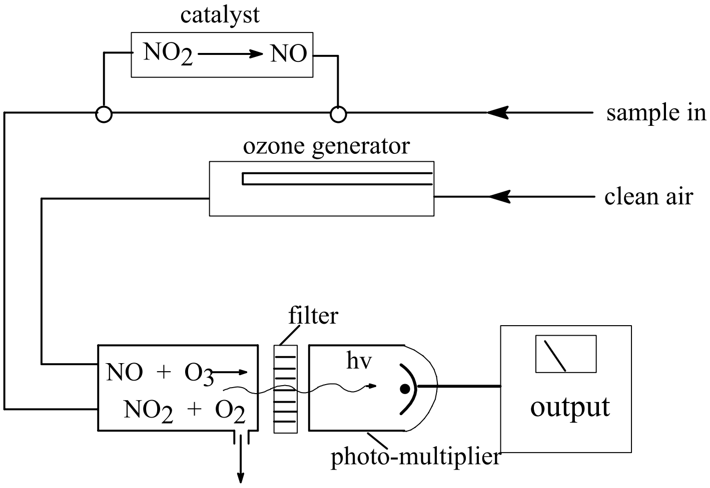


Figure 3 - Chemilunminenscence Detector for NO_x

Clearly, NO_2 in the sample will not be detected in this system. However, this can be reduced to NO by means of a heated catalyst, such as a stainless steel or molybdenum. If this is included in the system the instrument can respond to NO and NO_2, i.e. NO_x. In commercial analysers the converter is either incorporated as shown in **Figure 3**, with automatic valves to switch continuously between operation with and without the catalyst, or two separate channels with individual reaction chambers and detectors are used.

Flame Photometric Analysers

Gas chromatographers will be familiar with the flame photometric detector (FPD) which is used for the analysis of sulfur compounds. In this detector, samples eluting from a GC column are passed through a hydrogen-rich flame. If any sulfur-containing compounds are present the sulfur is reduced to a diatomic molecule, S_2, which is initially in an excited state. On decay to the ground state light is emitted over a wavelength range of 300 to 425 nm, centred at about 394 nm, i.e.

$$S_2^* \rightarrow S_2 + hv$$

The light emitted from the chamber is viewed by a photomultiplier filled with a narrow-bandpass filter.

A schematic of the FPD is shown in **Figure 4**. This has been incorporated into air monitoring instrumentation for the detection of sulfur.

The first way in which it has been used involves passing sample air directly into the detector as part of the air/fuel mixture. The system then becomes a continuous "total" sulfur monitor. Some degree of specificity can be achieved by the use of appropriate pre-filters (e.g. to remove H_2S in the presence of SO_2, and vice versa).

Commercial sulfur gas monitors are also available that are essentially custom-built gas chromatographs. Sample injection is by means of automatic gas sampling valves which are operated at regular intervals. The components of each discrete sample are then separated on an appropriate GC column, or columns, to give a continual series of individual chromatograms.

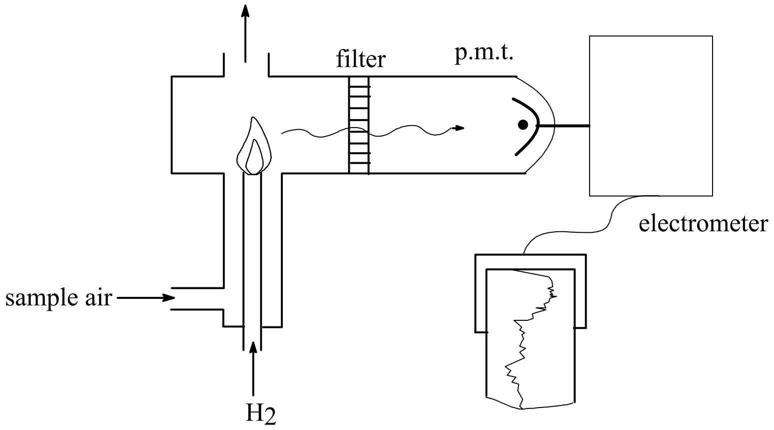


Figure 4 - Flame Photometric Detector

Thus the flame photometric detector can provide a sensitive and selective monitoring system for the sulfur-gases. Its major limitation is the dependence on hydrogen (which fuels the flame), as this introduces strict safety requirements in both the instrument and its installation.

Fluorescence Monitors

Another form of monitor using the principle of fluorescence has been developed, and this provides a satisfactory alternative to the FPD sulfur analysers. Fluorescence is a process whereby light energy of a given wavelength is absorbed and then reemitted at a different wavelength, i.e.

$$AB + h\nu \rightarrow AB^* \rightarrow AB + h\nu'$$

The change in wavelength occurs because the molecule that is excited remains in that state for some finite period of time (ca 10^{-8} - 10^{-4} s). This is sufficient for some of the energy to be dissipated in the form of vibration or rotation within the molecule. This results in the emission of light of a lower energy, and hence a longer wavelength.

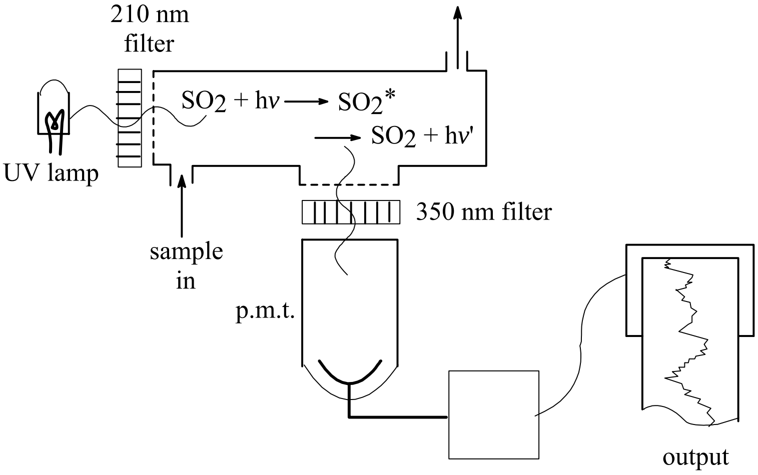


Figure 5 - Fluorescence Analyser for SO_2

This phenomenon has been utilised in the development of a monitor for SO_2. As shown in **Figure 5** a UV lamp provides a source of radiation, either continuous or pulsed, which is filtered to admit a narrow band of light into the cell, centred at about 210 nm. The fluorescent radiation is measured at right angles to the incident beam, using a photomultiplier.

Unlike the FPD analyser, the fluorescence system is specific for SO_2. Sample air must be dry and free of dust to avoid fouling of the cell. There is also the potential for interference from fluorescent organic compounds that may be present in the air, but these can also be removed with an appropriate pre-filter.

Suspended Particulate Monitoring Methods.
The term 'suspended particulate matter' refers to particules less than 20 microns (µm) in size, which can remain suspended in air for significant periods of time, ranging from a few minutes for the larger particles through to several days for very fine material (ca. < 0.1 µm). These particles can effect visual air quality and can have effects on human health. Traditionally this material was measured by sucking air through a filter and determining the weight of dust collected. The equipment used was known as a High-Volume Air Sampler, and collected all particles below 20 µm plus a proportion of larger particles as well. The results were referred to as total suspended particulate (TSP). In more recent times the equipment has been modified to collect only particules below 10 µm, which are trhe ones most likely to be inhaled and therefore have an effect on respiratory health. This measurement is known as inhalable particulate, or PM-10.

There are four methods currently being used in New Zealand for the measurement of PM-10. The most common is the High-Volume Air Sampler, fitted with a size selective inlet. Other systems in use are the β-attenuation tape sampler and the Tapered-Element Oscillating Microbalance (TEOM).

The High Volume Air Sampler operates by drawing air at a rate of about 1.5 m^3/ min through a 25 cm x 20 cm glass fibre filter, which is weighed before and after sampling under conditions of constant humidity. Samples are normally collected over 24 hours.

The β-attenuation unit operates by drawing air at a rate of 15 to 20 litres per minute through a continuous glass-fibre or teflon tape. A source of β-particles is used to sense the build-up of particles on the tape by changes in the amount of absorption. Measurements are normally averaged over one hour to obtain sufficient sensitivity, and the tape is advanced either at the end of each cycle or some other pre-set interval.

In the TEOM monitor air is drawn through a filter which is attached to a sensitive oscillating microbalance. Changes in the frequency of oscillation are directly related to the mass of material on the filter, and this is computed electronically once every few minutes. The sampling rate is 16.7 litres per minute and the unit operates continuously. The microfilters need to be changed every 1 to 4 weeks depending on particle loadings.

Monitoring Methods used for Specific Pollutants

A summary of methods used for monitoring all of the aerial pollutants of concern in New Zealand is given in **Table 2**. More detailed explanations of the methods used for some of the specific pollutants are given below.

Table 2 - Usage of monitoring methods for aerial pollutants

	particulates	**SO_2**	**CO**	**NO_x**	**Benzene**	**H_2S**	**fluorides**	**O_3**
Passive samplers	√	√		√	√	√	√	√
Paper tape	√					√		
Bubbler systems		√		√		√		√
NDIR			√					
Chemi-luminescence				√				√
FPD		√				√		
Fluoresence monitors		√				√		

SPECIAL MONITORING METHODS

More detailed explanations of some of the air monitoring methods are given below. These are mainly for the older non-instrumental methods which are no longer used routinely in this country. However the procedures are still of interest for the range of different chemistries involved. Also some of the methods may be suitable for use at secondary school level with appropriate modifications to suit the available equipment.

Particulate Matter

Solid particulate pollutants may be arbitrarily classified into the following categories which reflect both the physical characteristics of the materials and the procedures commonly employed in their measurement.

Dust Deposition

Large particules that settle readily out of the atmosphere are collected by deposition. Particles larger than about 10µm in diameter may be collected in this way, although it is those 100µm and above which are the most significant in terms of both visual impact and overall mass. Monitoring of dustfall is carried out by determining the amount of solid matter deposited over an exposed surface in a period of time. The device commonly used for dustfall monitoring is shown in **Figure 6**, although other types of collection equipment are available. This arrangement utilises readily available equipment, consisting of a 100 - 150 mm diameter glass funnel held inside a 4.5 litre bottle. The supporting wooden box provides stability and helps to keep the funnel level.

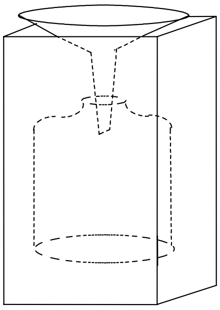


Figure 6 - Dustfall Collector

The collectors are normally exposed for periods of up to a month. At the end of this time the samples are filtered and analysed for any or all of the following: weight of insoluble material and ash content, quantity of liquid collected and pH, weight of dissolved solids, chemical analysis for trace metals, or anions such as sulfate, nitrate, and chloride. Results are reported in terms of weight of material collected over unit area and in unit time, i.e. mg m^{-2} day^{-1}. It should be noted that results produced by different systems will not necessarily be comparable. Results are best interpreted in a relative sense with one type of collector only.

Suspended Particulate Matter

This includes particles in the approximate range of 0.1 to 20µm, which may remain suspended in the atmosphere for periods of a few minutes through to a few days or even weeks. SPM was formerly monitored by the Department of Health using a glass fibre filter (**Figure 7**) through which air was pumped, which collected solid matter that could then be weighed and measured. The SPM concentration is calculated by dividing the weight of dust by the volume drawn through the filter.

The first of these is a $-attenuation monitor, in which the air is drawn through a glass fibre or paper filter, and the mass of dust collected measured by the attenuation of $-rays passed through it. The other is based on the scattering of light by the dust present in the air contained in a measurement chamber, giving results in kilometres of visibility.

Smoke

Smoke consists of fine particles, ca. 10µm and smaller. These have the greatest impact on atmospheric visibility, and are evaluated using optical techniques with or without prior collection (by e.g. filtration). Two main methods can be used.

The first procedure used for smoke monitoring is as described in a British Standard (B.S. 1747, part 2). Air is drawn through a filter paper held between two brass blocks, and the smoke stain produced is measured by light reflectance, but could also be assessed semi-quantitatively against a set of 'colour' standards. The equipment is normally incorporated into a sampling train for the measurement of both smoke and sulfur dioxide as shown in **Figure 8**. The normal sampling period is 24 hours. For convenience, sampling

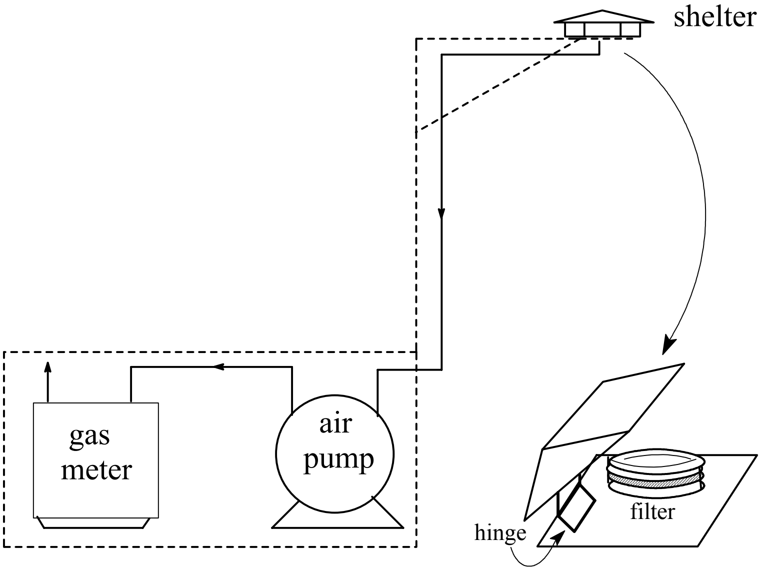


Figure 7 - Equipment for SPM monitoring

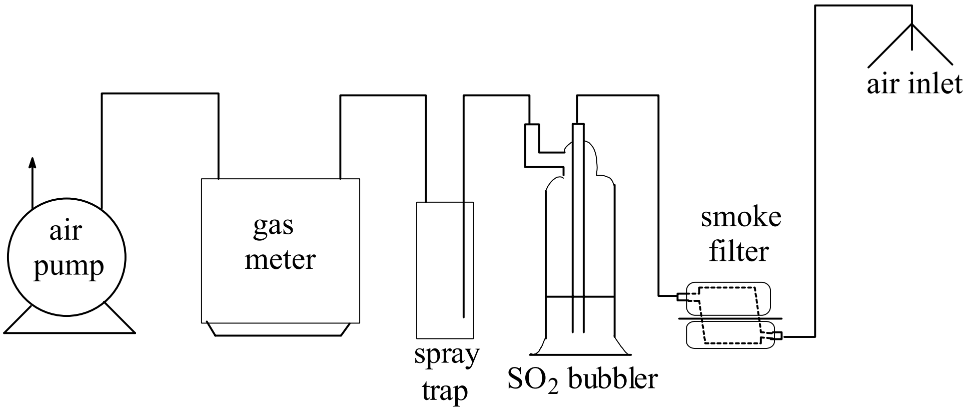


Figure 8 - Sampling Unit for Smoke and SO_2

units containing multiple sampling trains are sometimes used to allow continuous monitoring over extended periods. An alternative method that has been used in Christchurch is measuring the amount of matter collected on a paper tape that is advanced every two hours, which gives a picture of changes in pollution level throughout the day.

The measurement of smoke is based on the light reflectance of the pollutant, and the measurements are sometimes referred to as a "soiling index". The results are converted from reflectance to 'smoke units' on the basis of a calibration curve included in the British Standard, giving and indicator of the relative "dirtiness" of the smoke.

The following pollutants are all gaseous, and there are some general issues relevant to all such pollutants, in particular the need for sensitivity and selectivity. The concentrations of most pollutants in air are of the order of tens of micrograms per cubic metre, and thus unless large volumes of air are sampled the quantities of material available for analysis are quite low. Since many of the pollutants occur together in the air it is also important that the procedures used for any one component are not subject to interference from others.

Sulphur dioxide

A typical bubbler system is illustrated in **Figure 8** in the combined sampling unit for smoke and SO_2. In this case the absorber solution is dilute hydrogen peroxide adjusted to a pH of 4.5. This retains the SO_2 by converting it to sulfuric acid, i.e.

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$

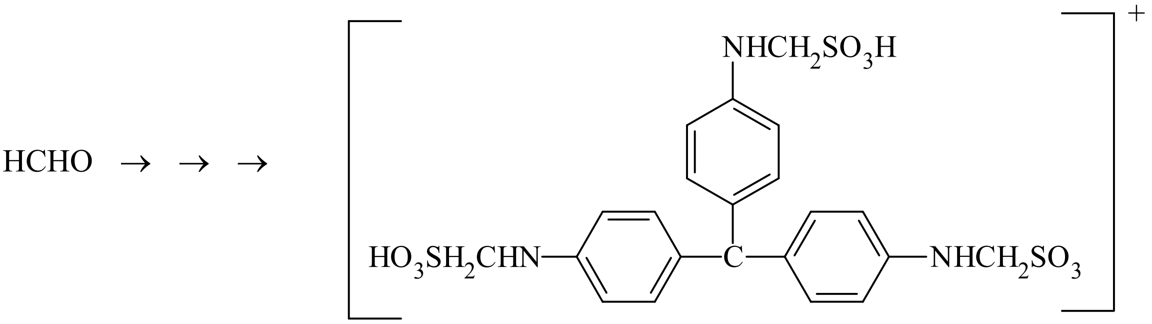
The quantity of pollutant collected can be determined by titration, with the endpoint at the original pH, using dilute base (e.g. 0.004 N sodium borate). Alternatively one can calculate the result directly from the pH change.

Obviously this method will not be specific for SO_2. Interferences can occur due to other gases, such as NO_2 or NH_3. The use of a pH of 4.5 is specifically designed to counter one potential interferent, CO_2, which under these conditions is not absorbed. If the absorber solution is analysed for sulfate ion rather than acidity the method can be made quite specific, but at the expense of increased analytical requirements of time and/or cost.

The West-Gaeke method

This involves converting the SO_2 to the sulphite ion using a solution of potassium tetrachloromercurate, and then colorimetrically determining the concentration using a solution of pararosaniline and formaldehyde as follows:

$$(NH_2C_6H_4)_3C^+ + HCHO \rightarrow (NH_2C_6H_4)_2C^+C_6H_4NHCH_2OH \xrightarrow{HSO_3^-} (NH_2C_6H_4)_2C^+C_6H_4NHCH_2SO_3HOH^-$$



There are a number of potential interferences in this reaction, but most of these are eliminated by the addition of appropriate reagents. The nitrite ion formed from NO_2 is destroyed by reaction with sulfamic acid.

$$HOSO_2NH_2 + NO_2^- + H^+ \rightarrow N_2 + H_2SO_4 + H_2O$$

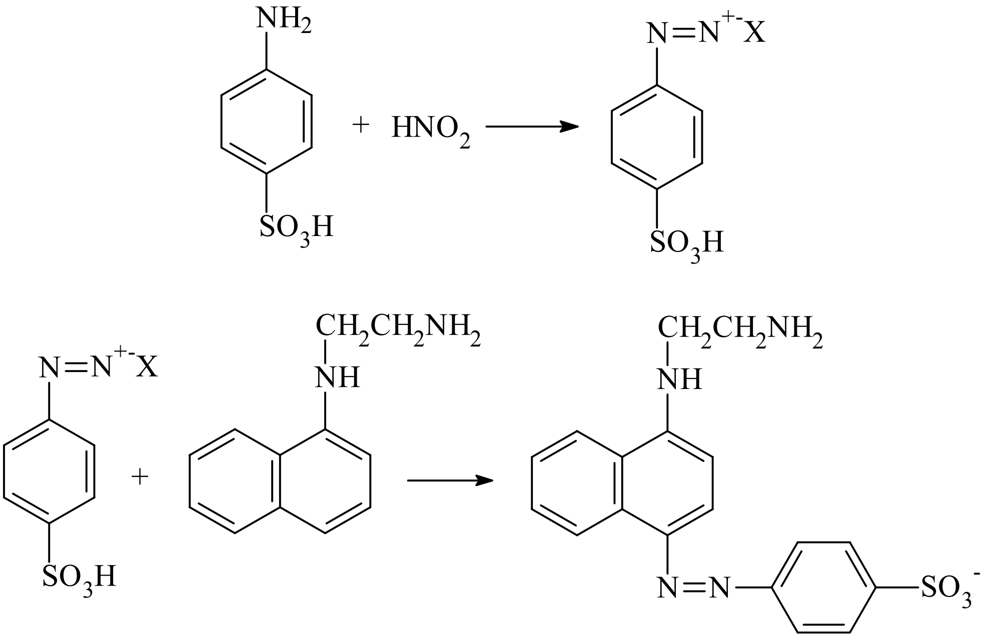
The use of EDTA in the absorber solution and phosphoric acid in the pararosaniline reagent solution serve to complex any metals present. Ozone is also a potential interferent, but a time delay of 20 minutes or more before analysis ensures that this breaks down in the absorber solution.

This is a more specific than that using hydrogen peroxide, but it is rarely used today because of concerns about the use of mercury required.

Oxides of nitrogen

The most common bubbler procedures for NO_x are based on the Griess-Ilosvay method for the determination of nitrite ion. This involves diazotisation of an aromatic amine in acid solution, followed by coupling of the diazo compound with an aromatic amine to form an intensely-coloured azo dye. One of the first applications of this method to the determination of NO_2 in air was reported by B.E. Saltzman, and this has since come to be known as the Saltzman or Griess-Saltzman method.

The absorber used in the Saltzman method is a mixture of sulfanilic acid and N-(l-naphthyl)- ethylenediamine in acetic acid solution. After fifteen minutes a pink solution, which can be measured at 550 nm, is formed in accordance with the following reactions:



The method as described is specific for NO_2. However, NO may also be determined by prior oxidation with acidified permanganate solution. A sampling train for the determination of both pollutants is shown in **Figure 9**. NO_2 is collected in the first bubbler. The second bubbler contains the permanganate solution, while the third (empty) bubbler serves as a spray trap. The fourth bubbler retains the oxidised NO.

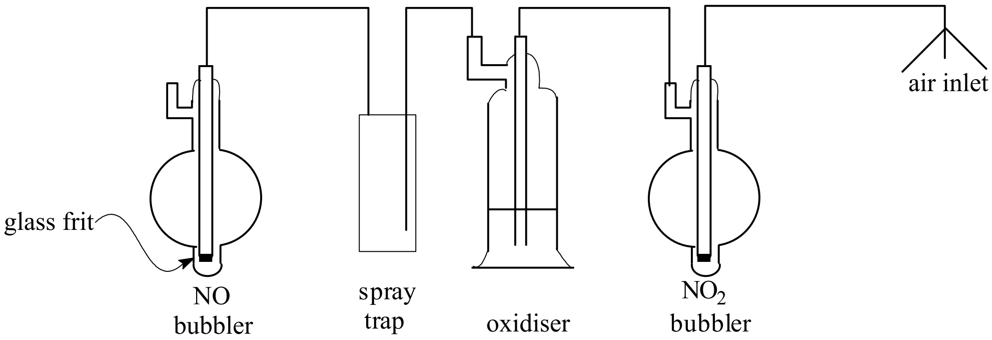


Figure 9 - Sampling Unit for NO_2 and NO

It will be seen in **Figure 9** that the bubblers used for NO_2 absorption are different from those shown previously. The flask is especially designed to allow sampling at relatively high flow rates (up to 0.4 L/min) with only a small volume of absorber liquid (10 mL). The glass frit is required to improve the collection efficiency of the system, by increasing the gas to liquid contact area.

There are no major interferences in the Saltzman method, other than from excessively high concentrations of SO_2 or O_3. The major difficulty with the method arises out of the conversion of NO_2 to nitrite ion prior to analysis. This is expected to occur according to the reaction:

$$2NO_2 + H_2O \rightarrow NO_2^- + NO_3^- + 2H^+$$

and an equivalence of 0.5 moles of nitrite ion is expected for each mole of NO_2. In practice one finds an equivalence of between 0.5 and 1.0, typically about 0.7, this is referred to as the Saltzman factor. There is no general agreement in the literature as to the "correct" value of the Saltzman factor, or whether in fact a constant value should be expected. To some extent the problem has become essentially a "non-issue", with the advent of instrumental methods for the direct determination of NO_x in air.

Two variations to the Saltzman method should be mentioned before concluding this section, as these have been used quite extensively in the past in this country. One difficulty with the Saltzman method is that the colour formed in the absorber is likely to fade after a few hours, and thus the method is mainly suitable for short-term measurements. Most interest has been in 24-hour sampling, and for this a modification of the method in which the NO_2 is absorbed in aqueous triethanolamine solution has been used. Colour development is carried out as before, but with the addition of the Saltzman reagents at the end of the sampling period.

In a further modification, it is possible to move to a liquid-free sampling system by the use of triethanolamine (TEA) absorbed on to granulated pumice or firebrick. This has advantages in the development of semi-automated multi-day sampling units, as well as removing the need for fragile and expensive glassware. Here the air is drawn over an absorber of TEA on pumice, removing the NO_2, and then over CrO_3 (also on pumice) to oxidise the NO to NO_2. This NO_2 is then collected on an second TEA absorber. After sampling the pollutants are washed from the solid substrate with water and the solution is analysed for nitrite ion as before.

O_3 and Total Oxidants

Most of the bubbler methods for ozone are based on the oxidising properties of the gas, and hence the methods are indicative of total "oxidants" in the air sample.

The most commonly used procedure involves the reaction with neutral-buffered potassium iodide solution (NBKI). The reaction with ozone is approximated by:

$$O_3 + 3KI + H_2O \rightarrow KI_3 + O_2 + 2KOH$$

The liberated iodine is measured at 352 nm.

The most significant interferences in the method are from SO_2 and NO_2, both of which will also liberate iodine. The former can be removed by a prefilter treated with CrO_3. Interference due to the latter can be allowed for if NO_x is also measured at the same time.

The only major limitation with the method is that sampling must be restricted to periods of 30 minutes or less, because of the deterioration of the iodine complex with time.

LEVELS OF AIR POLLUTION IN NEW ZEALAND

During the last thirty years air pollution monitoring has been carried out in many areas of New Zealand. Until recently however, much of the activity was concentrated in Auckland and Christchurch; the former because of its size, motor vehicle population, and the extent of industrial development, and the latter because of a readily apparent pollution problem during the winter months. It is not intended to detail the results of this monitoring here. This information is readily available from the various sources listed under Further Information. For the purposes of this article a few general comments will suffice. Guidelines for air quality in New Zealand provided by the Ministry for the Environment, issued in 1994, are given in **Table 3**.

Generally New Zealand is considered to be a country with only low levels of air pollution, and in most areas and for most times of the year that is so. There are two main exceptions to this situation: Auckland and Christchurch.

Carbon monoxide (from car exhaust) is a pollutant of concern, especially in areas of trafic congestion, such as Queen Street in Auckland. Periodic pollution exceeding the air quality guideline levels shown in **Table 3** have been recorded in most of the main cities.

Elevated levels of oxides of nitrogen have also been recorded in Auckland and Christchurch although the levels are only moderately high by world standards.

High levels of motor vehicle derived pollutants are also often related to problems of photochemical smog, as these provide the necessary precursors for oxidant formation. In the past "elevated" levels of oxidants have been recorded in Auckland on 5-10 days of each year, during the summer months. However even the highest levels recorded are below the l-hour average of 150 $\mu g\ m^{-3}$ recommended by the Ministry for the Environment. This phenomenon is therefore not considered to be a problem in the Auckland region.

In Christchurch the major air pollution problem is related to the occurrence during the winter months of meteorological conditions conducive to poor atmospheric dispersion. This coincides with the time of greatest demand for home heating, and the result is a marked increase in the levels of visible smoke. The Ministry for the Evironment guideline of 120 $\mu g\ m^{-3}$ is regularly exceeded during the winter months.

Unlike many other cities overseas, the high levels of smoke in Christchurch are not generally accompanied by correspondingly high levels of SO_2. Rarely, if ever, are the levels above the MoE guideline for this pollutant (125 $\mu g\ m^{-3}$, 24-hour average).

Levels of NO in Christchurch can also be high during the winter months, reflecting a significant contribution to the problem from motor vehicles, as well as from domestic heating.

Table 3 - Air Quality Guidelines for New Zealand

Pollutant	Allowable Concentration	Time Period
inhalable particulate (PM_{10})	40 $\mu g\ m^{-3}$ 120 $\mu g\ m^{-3}$	annual mean 24 hr average
sulfur dioxide	50 $\mu g\ m^{-3}$ 125 $\mu g\ m^{-3}$ 350 $\mu g\ m^{-3}$ 500 $\mu g\ m^{-3}$	annual mean 24 hr average 1 hr average 10 min average
carbon monoxide	10 $mg\ m^{-3}$ 30 $mg\ m^{-3}$	8 hr average 1 hr average
nitrogen dioxide	100 $\mu g\ m^{-3}$ 300 $\mu g\ m^{-3}$	annual mean 1 hr average
ozone	100 $\mu g\ m^{-3}$ 150 $\mu g\ m^{-3}$	8 hr average 1 hr average
hydrogen sulfide	7.0 $\mu g\ m^{-3}$	1 hr average
fluoride	0.5 $\mu g\ m^{-3}$ 0.84 $\mu g\ m^{-3}$ 1.7 $\mu g\ m^{-3}$ 2.9 $\mu g\ m^{-3}$ 3.7 $\mu g\ m^{-3}$	3 month average 1 month average 7 day average 24 hr average 12 hr average

FURTHER INFORMATION

The results of air pollution monitoring can be obtained from Regional Councils and the Ministry for thr Environment. A summary of air pollution monitoring in New Zealand 1960-1994 is also available from ESR. A general review of some of the early air pollution monitoring in Auckland was given by Graham and Thom in Chemistry in New Zealand, 1980, p.18- 20.

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