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Wrocław University of Technology

# Environmental Quality Management

Andrzej Szczurek

# METHODS AND MEASURING TECHNIQUES OF AIR POLLUTANTS

Wrocław 2011

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# 1 INTRODUCTION

Air pollution is defined as the presence in the outdoor atmosphere (ambient air) of one or more contaminants in such quantities and for such duration that they are harmful or injurious to human health or welfare, animal or plant life, or property, or may unreasonably interfere with the enjoyment of life or property. The degradation of air quality is a major environmental problem that affects many urban and industrial sites and the surrounding regions worldwide. Air pollution can reach levels at which it significantly influences human health, diminishes crop yield, and destroys infrastructure and patrimony. It is becoming of major influence on the quality of life, posing a risk both to human health and to the environment. There is now overwhelming consensus that poor air quality negatively impacts on human beings and the environment. The World Health Organization has estimated that 2.4 million people die each year from the causes directly attributable to air pollution. Population exposure to increased levels of gases and particulates requires action from public authorities at national, regional and international levels. Thus, the need for concerted and effective action to improve air quality is increasing recognized. In order to develop appropriate air quality management plans, it is necessary to have reliable information about the state of pollution. A great number of methods and techniques are used to get qualitative and quantitative information about air pollutants. They can be based on bioindication, sensory (organoleptic) analysis, calculation methods (modeling) and instrumental analysis. Bioindicators are organisms or communities of organisms which react to environmental influences by changing their vital functions and/or chemical composition. Their presence or absence in a biotic community is particularly useful in indicating pollution loads over long periods. Lichens are the most widely recognized plant group in air pollution monitoring. Sensory analysis is a scientific discipline that applies principles of experimental design and statistical analysis to the use of human senses (sight, smell, taste, touch and hearing) for the purposes of evaluating first of all consumer products. In environmental protection, sensory evaluation is mainly used for classification and quantification of odorous gases. Calculation methods are applied in air quality/pollution modeling and for emission estimation. The results of modeling are used: for assessing emissions from individual chimneys, in issuing emission permits (usually for single sources), for environmental impact studies related to, for example, industrial plants and new roads, for investigating photochemical smog in cities, for studying haze overseas, for tracking emissions from cities over hundreds of kilometers, to predict meteorological and air pollution parameters on interregional, city, or local scales, for simulation periods from a day to a year or more. Calculation methods are often applied in practice, because even highly developed countries are limited in the number of observation sites that can be maintained due to the high cost of the sophisticated equipment required. Undoubtedly, the most reliable sources of information useful for air pollution estimation are based on instrumental methods and techniques of gas analysis. The measurements of atmospheric pollutants are an expensive and very often complicated but indispensable undertaking if the air quality of a region or city is to be evaluated. Different types of instruments can be used to measure atmospheric pollutants at various conditions. Interest in the control of air quality has led to the development of increasingly complex methods and techniques for precise analysis of potentially dangerous gases. These specialized instrumental techniques are capable of performing *trace analysis*. Nowadays, the analysis at the ppm and even ppb level is routine. In addition, large numbers of samples may be analyzed very quickly (on-line, in real time measurements). Many instrumental methods can be automated. Generally, less skill and training is usually required to perform instrumental analysis than classical analysis. The aim of this work is to present the most important instrumental methods, which can be used for the air pollutant measurement.

# 2 GENERAL CONSIDERATIONS

Air pollutants are gaseous, liquid, or solid substances which (when present in sufficient concentration, for a sufficient time, and under certain conditions) tend to interfere with human comfort, health or welfare, and cause environmental damage. Nowadays, the measurements of these substances play a very constructive role in the process of the environment protection. Of course, they do not improve the environmental conditions directly. However, they are one of the most important sources of information about air pollution. Air pollutant measurements are very often one of the main elements of environmental monitoring system which is designed to obtain a statistical description of the concentration of one or more pollutants. Air pollutants exist in different environments. They can be measured in:

- industry, agriculture, means of transport;
- workplace atmosphere;
- indoor air;
- outdoor air.

Air pollution measurement activities are typically separated into two classifications: source (emission) monitoring and ambient air (immission) monitoring. Emission is defined as a discharge or release of pollutants into the air from a source. A special type of emission is a fugitive emission. It is emission that is not captured by the system process. In general, immission is the impact of emissions on the environment. Among these are mainly air pollutants, odours, noise, vibration, light, radiation and heat. In the first case, it is an environmental concentration of a pollutant resulting from a combination of emissions and dispersals (often synonymous with e.g. exposure). Atmospheric contaminants can be directly measured as they are emitted by a source in mass/volume of emission (e.g. grams/m$^3$) or mass/process parameter (e.g. grams/kg of fuel consumed) or emission rate (the weight of a pollutant emitted per unit of time e.g. tons / year, grams/second). Air pollution can also be measured in the atmosphere as a concentration (e.g. micrograms/m$^3$). Emission and immission measurements in the field of air quality control are carried out by the competent authorities themselves as well as by specialized institutes designated in a certain procedure with their measurement tasks. Generally, the measurements serve to monitor compliance with air quality control provisions, and they determine concentrations of air pollutants at source (emission) and at the place of impact (immission), i.e. in ambient air.

Source monitoring concerns mainly:

- process gases;
- stack emission;
- exhaust gases.

Typical concentrations of gases in this measurement area are in the range 10 000 - 0.1 mg/m$^3$.

Standard procedures exist in many countries for air pollutant measurements in industry, agriculture and means of transport. However, many of these are complex and expensive to operate, and suitable only for large or highly polluting industry, where the costs can be justified. Emission sources are usually categorized as stationary or mobile. The approaches and requirements for the measurement of pollutants from these two categories of sources are basically different. Source monitoring involves the measurement of emissions directly from:

- a stationary source (a place or object from which pollutants are released and which stays in place. Stationary sources include power plants, gas stations, incinerators, and houses. They contain ducts, vents, stacks or chimneys);
- or a mobile emission source (motor vehicles and other moving objects that release pollution).

Mobile sources include cars, trucks, buses, planes, trains, motorcycles and gasoline-powered lawn mowers. They are divided into two groups: road vehicles, which include cars, trucks, and buses, and non-road vehicles, which include trains, planes, and lawn mowers).

Stationary source data is used to:

- determine the quality and concentrations of pollutants entering the environment from a specific source;
- obtain emission data (provide data for emission inventories);
- control the performance of regulations and emission standards (demonstrate legal compliance with regulations and confirm that the established permit limits are being met);
- determine how the emission is affected by process variations;
- evaluate control devices for the reduction of pollutant emissions (determining the effectiveness of control equipment);
- measure the efficiency of pollution control equipment (determining collector efficiency for the acceptance of purchased equipment and determining the need for maintenance of process or control equipment);
- allow process operators to control their processes within prescribed limits and to achieve optimum process efficiency (measuring product loss or optimizing process operating variables);

- obtain data for engineering design;
- determine the sources contributing to pollution at a receptor;
- assess the impacts of improvement strategies on the local environment;
- gather data of emissions from several sources for the input to air quality management models;
- provide data as an input to ozone and/or health risk prediction models.

Major stationary sources may have continuous emissions monitors (CEMs) installed to report real-time emissions based on pre-established reporting cycles.

The problems of source monitoring are distinct from those of ambient air monitoring. Ambient air monitoring involves the measurement of specific pollutants present in an immediate surrounding atmosphere. The measurements in this field concern urban, rural or wilderness atmosphere. The six most important pollutants to monitor regularly are what the WHO terms the “classical” pollutants:

- carbon monoxide (CO);
- sulfur dioxide ($SO_2$);
- nitrogen oxides ($NO_x$);
- ozone ($O_3$);
- lead;
- PM2.5/PM10 (particulate matter smaller than 2.5 and 10 microns in aerodynamic diameter, respectively).

Typical concentrations of these substances are between 10 – 0.00001 $mg/m^3$.

Standard methods exist in many countries for the inorganic pollutants:

- total and PM10 dust;
- metals;
- acid gases and ozone.

Methods for organic pollutants are less well-established. Most major urban areas often operate several ambient air monitoring instruments, each dedicated to measuring specific target pollutants.

Ambient air monitoring data is generally used to:

- determine whether air pollutant concentrations are hazardous in the atmosphere or if ambient air standards have been exceeded;
- provide air pollution data to the general public in a timely manner;
- establish the extent of air pollution problems;
- evaluate the effects of air pollution on public health (characterize the potential human health risk in an area);
- assess whether the established standards are being met;
- judge compliance with and/or progress made towards meeting ambient air quality standards;

- establish and operate pollution alert network;
- evaluate the effectiveness of air pollution control programs;
- activate emergency control procedures that prevent or alleviate air pollution episodes;
- observe pollution trends throughout the region, including non-urban areas;
- provide a data base for research evaluation of the effects (urban, land-use, and transportation planning);
- study the processes in the atmosphere, e.g. transport and deposition of pollutants, chemical, photochemical, biochemical conversion of pollutants;
- estimate exposure rate and accumulation of pollutants by living organisms;
- determine air quality trends in concentration changes and forecast air quality;
- develop and evaluate of abatement strategies;
- track the progress of plans for meeting air quality standards;
- develop and validate diffusion models;
- develop responsible and cost-effective pollution control strategies.

The national, regional or local ambient air monitoring networks are designed to determine one of the following basic monitoring objectives listed below:

- determining the highest concentration expected to occur in the area covered by the network;
- measuring typical concentrations in the areas of high population density;
- determining the impact of significant sources or source categories on air quality (monitoring the effect of an emission source);
- pinpointing the source of an undesirable pollutant;
- checking for hotspots in the city’s transportation network;
- determining background concentration levels;
- establishing a baseline prior to a proposed installation of a large source;
- determining the extent of regional pollutant transport among populated areas; and in support of secondary standards;
- measuring air pollution impacts on visibility, vegetation damage, or welfare-based impacts;
- obtaining permanent records for legal action or for modifying regulations, and correlating pollutant dispersion with meteorological, climatological, or topographic data, and with the changes in societal activities.

It is good practice to monitor air quality at a variety of locations, including urban “hot spots” (areas affected by vehicular and industrial emissions), residential areas representative of population exposure, and rural areas (as an indication of background concentrations). The data will show which pollutants are exceeding national and international air quality standards and guidelines, such as the WHO’s health-based air quality guidelines. These international standards and guidelines are for concentrations averaged over as long as a year, so continuous monitoring is important to make comparison possible.

There are many various requirements related to methods and instruments for air pollution measurement. The molecules of air pollutants differ greatly in their chemical and physical properties, in the nature of their environment, and in their concentration ranges. Air pollution has tremendous spatial and temporal variation. Because the concentration and quality of atmospheric contaminants fluctuate in both time and space, measurement techniques must be designed to accommodate these fluctuations and to provide a result which can be used for the intended purpose. Furthermore, the application may have specific requirements such as rapid response time, ultrasensitivity, multipollutant capability, or capability for remote measurements. The measurement techniques for emission and immission determination differ primarily in terms of the pollutant concentrations to be measured. Immission concentrations are a factor of $10^{-3} – 10^{-5}$ lower than emission concentrations. Therefore, immission measurement instruments must have a markedly lower detection limit than the instruments for the measurement of emissions. On the other hand, emission measurements often require complex treatment of samples and low interference from interfering components at high concentrations. They also require low susceptibility to aggressive gases. For these reasons, no single method and technique appears to offer a panacea for all measurement needs. It is of great importance that the measurements are reliable and accurate. Compliance with these requirements is ensured by a whole range of quality assurance measures, which have been gradually developed, tested and introduced to measurement practice over the last several decades. Emission measurement technology has achieved a high technical standard in order to meet the requirements. The same is true for immission measurement technology which has also advanced in response to increasingly ambitious monitoring objectives. It should be noted that emission and immision measurements involve determinations of particles as well as gases.

Because air pollution presents temporal variation, measurements are performed using batch (discrete) or continuous monitoring methods and techniques. The first case is based on time-integrated sampling. Contaminants are collected over a specified period of time (such as one, three or six days). Then a technician collects the sample and sends it to a certified laboratory for measurement and analysis. In continuous monitoring, air is measured constantly, in real time and the data is automatically transmitted to a central database. In this way, the periodic measurements are distinct from continuous monitoring techniques, which provide immediate measurements of the pollution.

The measurements of air pollution can be established on the basis of manual or automatic methods. The first group of methods is used mainly for periodic measurements. Manual methods offer some opportunities. They are applied for the following reasons:

- to provide chemical identification of unknown pollutants using analytical methods that require laboratory facilities;

- to provide greater selectivity or sensitivity than that available with automatic methods;
- to calibrate instruments for continuous measurements;
- to avoid the expense of installing and maintaining equipment for the continuous monitoring.

In manual methods, the sample has to be collected over discrete period of time and the analysis is performed by a separate procedure in a laboratory. In this approach**,** a measurement campaign is carried out at periodic intervals, for example, once every six months. These methods of measurement are described as time-consuming. They can take several hours, therefore the results of measurements are delayed in time. The manual procedures are relatively labour-intensive, and limited in the amount of information provided. Therefore, they have gradually been phased out where possible by the more sophisticated direct-reading instruments based on continuous methods of air pollution analysis. Apart from periodic maintenance, the operational requirements of the latter are minimal. However, they require considerably more effort in data processing and analysis, because of the much greater volumes of data produced.

Automatic methods are used in situations that require pollution assessments:

- on a continuous basis;
- when temporal variability is important.

This approach is applied e.g.:

- when it is important to know the frequency of the occurrence of large concentrations;
- to determine compliance with ambient air quality standards;
- in the studies of air pollutant dispersion and transport in an atmosphere;
- in the studies of atmospheric chemistry, where the chemical changes in the atmosphere are to be followed over some period in response to the changes in sunlight, temperature or other weather conditions;
- for monitoring of variations in emission levels;
- for process control purposes.

Automatic methods offer quick response (the results are obtained in real-time). For the automatic measurements of air pollutants, the most advanced techniques in the field of chemistry, physics and microelectronics must be used. This strategy of measurements is expensive. Additionally, automatic monitoring of air pollutants must be correlated with manual methods.

The quality of air pollution determination strongly depends on the applied methods and techniques. A wide range of instruments is available for the analysis of air pollutants, from the very simple to the highly sophisticated ones, and with a corresponding variation in costs. It should be noted that the necessary measurement techniques are very often significantly different in comparison with standard analytical instruments. To monitor an air pollutant it would be desirable to have a device which would be able to yield an instantaneous and specific response for it which might be integrated and recorded with time. With few exceptions, however, such devices are not available. Ideally, the desired instruments for air pollution monitoring system should have the following characteristics:

- be portable and suitable for collecting measurement in a variety of locations;
- be rugged;
- be real-time;
- require no laboratory analysis;
- automatically record on a data logger capable of interfacing with a personal computer;
- be accurate across the full range of expected concentrations (indoor and outdoor);
- be considerably less expensive compared to current technology;
- be free of interference from other air pollutants;
- show performance commensurate with the standardized and accepted monitoring methods currently in use;
- be easily deployed and operated by a non-technical person;
- have modest electrical power requirements (e.g. battery operated or low power demand).

The trend to improve instrumentation aims to achieve the following features:

- simplicity of concentration and operation;
- reliability and reproducibility of operation over long time intervals;
- adequate sensitivity to meet the requirements of specific applications;
- specific response to pollutant or pollutants of interest.

Additional criteria apply to continuous air monitoring operations:

- unattended operation;
- real-time data output;
- systems capable of monitoring two or more pollutants concurrently by the same measuring technique;
- ability to monitor an increasingly wide range of pollutants;
- capability for direct input to computers.

The measurement of air pollutants is a complex, multi-step process. All of the stages are important because:

- they cannot be easily separated;
- they are interdependent;
- the final result, valid data, depends upon successfully completing each of them.

In general, the measurement of air pollutants consists of the following stages:

- design, planning and preparation;

- selection of measuring points (sampling location);
- sample collection (sampling);
- sample analysis;
- calibration of instruments;
- acquisition and transmission of data;
- data analysis;
- reporting and visualization.

In the manual approach, the stages of the measurement process are treated as the independent operations. They are performed according to separate procedures. In continuous methods, the mentioned stages are the elements of one process. They are performed together by an automatic, measuring system.

# 3 DESIGN, PLANNING AND PREPARATION OF MEASUREMENTS

The stage of planning, design and preparation of measurements should consist of the parts described below.

1. A statement of the objectives of the measurement program determining the aim and requirements of the pollution study.

This step can be completed by addressing such questions as:

- what is the reason for air pollution measurements?
- what questions need to be answered by the measurement program?
- what pollutants or environmental indicators need to be measured in order to provide the information required?
- what are the intended uses of the measurement results?

2. Planning of the measurement.

The quality and applicability of the test can be assured by taking a few preliminary steps and formulating a test plan. A test plan is more than just specifying a test procedure. A complete test plan must include such items as: sampling and analytical methodology, quality assurance procedures for sampling and analysis, parameters to be recorded, time of the test and people present. Test plan content should include:

- identification and a brief description of the emission source to be tested or ambient air monitoring location;
- identification of the parameters of interest (what pollutants need to be measured, their concentration, physical and chemical properties);
- review of available methods and measuring techniques (instrumentation);
- identification of the range and extent of measurements;
- specification of spatial and temporal limits, scale of interferences;

- selection of the most required and appropriate methods and equipment for sampling, sample analysis, calibration, data acquisition, analysis, reporting and presentation (reference standard methods should be used, any proposed modifications must be justified);
- description of the sampling train(s) to be used, including schematic diagrams, if appropriate;
- estimation of conditions in sampling site;
- choice of the sample size, the sampling time, frequency of sampling, the number and length of sampling runs which will constitute a complete test;
- field quality assurance/quality control procedures (e.g. field blanks, sample storage and transport methods);
- laboratory quality assurance/quality control procedures (e.g. manner and frequency of blanks, spikes and standards);
- selection of personnel performing the tests (qualifications, names and titles of staff);
- type and availability of resources;
- development of protocol and final report form;
- estimation of staff, operation and data processing costs.

In selecting designated methods and instruments for a monitoring application, consideration should be given to such aspects as:

- the suitability of the measurement principle;
- the suitability for the weather and/or geographic conditions at the site;
- analyzer's sensitivity and available operating ranges suitable for the site;
- susceptibility to interferences that may be present at the monitoring site;
- requirements for support gases or other equipment;
- reliability;
- maintenance requirements;
- initial as well as operating costs;
- features such as internal or fully automatic zero and span checking or adjustment capability, etc.;
- compatibility with current and future network, i.e. software and connections (RS232, Ethernet);
- manual or automated methods.

The required performance specifications, terms of warranty, time limits for delivery and acceptance testing, and the activities in the event that the analyzer falls short of performance requirements should be documented. It should be noted that designation of a method indicates only that it meets certain minimum standards. Competitive differences still exist among designated analyzers. Some analyzers or methods may have performance, operational, economic or other advantages over others. A careful selection process based on the individual air monitoring application and circumstances is very important.

3. Health and safety precautions.

Appropriate risk management steps must be put in place. The risks may arise from any number of hazards associated with the tasks to be done and the physical conditions prevailing.

Some of the hazards involved include:

- working at height or on temporary platforms;
- exposure to toxic, corrosive or hot gases;
- electrical hazard;
- trip hazards from cables;
- noise or heat from plant equipment;
- objects falling from work platform or into the duct;
- flammability hazards.

4. Test of instruments.
5. Pretest of measurements.
6. Development of the measurement schedule and detailed design.

## Network Design

Network design and site selection is fundamental in providing a harmonized and comparable measuring system for air pollution monitoring. In general, there are no hard and fast rules for network design, since any decisions made will be determined ultimately by the overall monitoring objectives. In practice, the number and distribution of air quality monitoring stations required in any extended network depends on the area to be covered, the spatial variability of the pollutants being measured and the required data usage. Four broad categories of site monitoring should be covered:

- urban background;
- road side;
- background;
- industrial.

If identification or quantification of public health hazards associated with air pollution is an important factor, then the network design should consider the needs of, and information from, epidemiological studies. This may require site-or pollutant-specific approaches.

The number of monitoring stations in the network will depend on:

- ambient concentrations, in relation to limit and alert values;
- the population likely to be exposed to such concentrations (the number of stations needed for alert monitoring will depend on the geographical scale of the alert warning, e.g. zone, regional, country);

- the scale of environmental effects (though as only human-health limit values are proposed for the particles, this is not relevant here);
- the spatial variability of the pollutant.

**Planning a source emission test program**

Planning a source emission test program requires that the objectives be clearly defined to ensure that the data will meet the stated objectives. Designing an adequate sampling program requires good knowledge and understanding of the system to be sampled. The data user, sampling team and staff from the analyzing laboratory should be involved in the planning stage if the program is to be successful. The following information should be acquired prior to sampling and testing:

- detailed information on the process conditions;
- the process conditions under which the test is required;
- the location of the sampling plane;
- provision of access holes and safe working platform;
- selection of the number of sampling points;
- safe access to the area;
- suitable sampling equipment;
- the availability of sufficiently sensitive and specific methods of analysis;
- the distance from and capacity of the analytical laboratory.

# 4 CRITERIA OF SAMPLING SITE SELECTION

## 4.1 SAMPLING SITES FOR AMBIENT AIR QUALITY DETERMINATION

Air pollutant concentration differs depending on the location and time. Therefore, with any air monitoring program the selection of an appropriate sampling site is of paramount importance. Of particular interest for the selection of sampling sites is their representativeness. The measured value of each point must be representative of the peripheral air quality.

The criteria of sampling site location generally can be divided into two groups. The first one relates to the system intended for individual measurements. This class of criteria should provide a true representation of the receptor defined in the study objectives. The second group refers to the location of sites for monitoring networks. These criteria provide the area-wide data required to achieve the goal of monitoring system.

Actually, there is no comprehensive set of rules adopted as a standard procedure for the location of individual sampling points or sites for monitoring system. It is caused by the great diversity of factors that should be taken into account in choosing sampling sites for a specific purpose. The choice of the sites for ambient air sampling has to be based on information considering:

- purpose of measurements;
- meteorological and topographical factors;
- behavior of pollutants in the atmosphere;
- spatial distribution and variability of the measured pollutant;
- location of emission sources (natural and anthropogenic).

The locations for monitoring stations depend on the purpose of the monitoring. Most monitoring networks are designed with human health objectives in mind, and monitoring stations are therefore established in population centers. Many governments (local, regional or national) give specific guidelines on where to monitor within these areas – next to busy roads, in city center locations, or at a location of particular concern (e.g. a school, hospital). Background monitoring stations are also established, to act as a "control" when determining source apportionment.

Air pollutant concentration differs depending on the location and time. The measured value of each point must be representative of the peripheral air quality. Atmospheric considerations may include the spatial and temporal variability of the pollutants and their transport to the monitoring site. Meteorology must be considered in determining not only the geographical location of a monitoring site but also such factors as height, direction, and the extension of sampling probes. The following meteorological factors can greatly influence the dispersal of pollutants:

- wind speed;
- wind direction;
- wind variability.

Wind speed affects the travel time from the pollutant source to the receptor and the dilution of polluted air in the downwind direction. The concentrations of air pollutants are inversely proportional to the wind speed. Wind direction influences the general movements of pollutants in the atmosphere. The review of available data can indicate mean wind direction in the vicinity of the major sources of emissions. Wind variability refers to the random motions in both horizontal and vertical velocity components of the wind. These random motions can be considered atmospheric turbulence, which is either mechanical (caused by structures and changes in terrain) or thermal (caused by heating and cooling of land masses or bodies of water). If the scale of turbulent motion is larger than the size of the pollutant plume, the turbulence will move the entire plume and cause looping and fanning; if smaller, it will cause the plume to diffuse and spread out. If the meteorological phenomena impact with some regularity, data may need to be interpreted in light of these atmospheric conditions. Other meteorological conditions to consider are atmospheric stability and lapse rate (the decrease of an atmospheric variable with height). Meteorological conditions, particularly those that can affect light transmission, should also be considered in selecting the location for open path analyzers (e.g. the influence of relative humidity on the creation of fog, the percentage of heavy snow, and the possible formation of haze). The percent fog, percent snow fall, percent haze, and hourly visibility (from nearest airport) may impact data completeness. Meteorological data considerations should, therefore, include the following measurements: hourly precipitation amounts for climatological comparisons, hourly relative humidity, percent haze and airport visibility.

Pollutant concentration at each measurement point changes in accordance with the peripheral natural environment (i.e. hills, trees, ponds, marshes) and the existence of man-made structures such as buildings and roads, and the height of the measurement point. Both the transport and the diffusion of air pollutants are complicated by topographical features. Thus, measurement points should be representative of the area to minimize complications arising from the landscape and buildings, etc. Before final site selection, the topography of the area must be reviewed to ensure that the purpose of monitoring at that site will not be adversely affected. Land use and topographical characterization of specific areas can be determined from maps as well as from land use maps. Detailed information can be determined through visual observations, aerial photography and surveys. Such information can be important in determining the exact locations of pollutant sources in and around the prospective monitoring site areas. The final placement of the monitor at a selected site depends on physical obstructions and activities in the immediate area, accessibility/availability of utilities and other support facilities in correlation with the defined purpose of the specific monitor and its design. Because obstructions such as trees and fences can significantly alter the air flow, monitors should be placed away from obstructions. It is important for the air flow around the monitor to be representative of the general air flow in the area to prevent sampling bias. Meteorological and topographical factors may play an important role in defining the optimum location of sites.

Pollutants undergo changes in their compositions between their emission and their detection; therefore, the impact of that change on the measuring system should be considered. Atmospheric chemical reactions such as the production of $O_3$ in the presence of $NO_x$ and hydrocarbons (HCs) and the time delay between the emission of $NO_x$ and HCs and the detection peak of $O_3$ values may require either a sampling network for the precursors of $O_3$ and/or a different network for the actual $O_3$ measurement.

An emission source inventory, even in rough form, is often required to locate sampling sites. Air dispersion modeling studies can aid the practitioner in the monitoring site location process. Where flexibility exists and there is scope for putting the data into an air quality simulation model, preliminary work with the model using artificial data from possible sampling locations will often indicate an efficient choice.

The sampling site selection process involves also considerations of the following factors:

- economics;
- security;
- logistics.

### Economics

The amount of resources required for the entire sample collection activity, including operators, instrumentation, installation, safety equipment, maintenance, data retrieval/data transfer, data analysis, quality assurance and data interpretation.

### Security

Security against vandalism - experience has shown that in some cases, a particular site may not be appropriate for the establishment of an ambient monitoring station simply due to problems with the security of the equipment in a certain area. If the problems cannot be remedied via the use of standard security measures such as lighting, fences, etc., then attempts should be made to locate the site as near to the identified sector as possible while maintaining adequate security.

### Logistics

It is the process of dealing with the procurement, maintenance and transportation of material and personnel for a monitoring operation. This process requires full knowledge of all aspects of the data collection operation including: planning staffing, reconnaissance procurement of goods and services, training communications, scheduling inventory, safety.

Location criteria for sampling sites are highly dependent on the specific objective of the study. However, some general rules are used in measurement practice. Installment 1.5~2 m above the ground is preferable when one considers the effect of air pollution on the human body and the area in which people are most active. A height of 1.5 m would be preferred for the assessment of potential human exposure near heavy traffic situations, but for practical reasons (for example, prevention of vandalism) a height of around 2.5 m is generally considered to be acceptable. For city background situations a maximum height of 4 m is generally recommended, but the specific sitting must be considered and higher positions (up to 8 m) may be necessary in some circumstances. The air temperature should be measured at 1.2~1.5 m, and wind velocity should be measured 6~10 m above the ground for weather observations. The flow around the inlet sampling probe should be unrestricted, without any obstructions affecting the air flow in the vicinity of the sampler. (e.g. some meters away from buildings, balconies, trees, etc.). Sampling inlets cannot be exposed to contamination from localized sources e.g. a chimney on a roof top. The inlet probe should not be positioned in the very near vicinity of the sources in order to avoid drifting air pollution plumes (e.g. not near chimneys serving the stations own heating system). The samplers exhaust outlet should be positioned so that recirculation of exhaust air to the sample inlet is avoided. The effects of buildings and such-like that exist at this level should be minimized as much as possible in towns crowded with buildings because the data may not be representative of the degree of pollution in the local area when the survey site is set up at ground level, as opposed to a flat site. When high volume air samplers are used to measure particulate matter, dust fly up from the ground must be born in mind as well. Its installation must carefully be considered, especially when measurements are conducted on dry ground. For general area air quality monitoring, the sampling sites should not be directly downwind from major emission sources, such as motorways or industrial stacks. Sampling sites should not be located under the lee (in the aerodynamic shadow) of major obstructions such as e.g. tall buildings. They must be accessible and yet secure from tampering. The site should provide an adequate, reliable power supply to run the sampling equipment as necessary. For PM10 it is considered that four broad categories of monitoring site should be covered:

- urban background;
- road side;
- background;
- industrial.

Within each of these categories the monitoring stations should be located to monitor in freely mixed air where the concentrations of PM10 and public exposure are expected to be the highest. These sites should be positioned where the potential for human exposure, over the time scale of the limit values (i.e. daily and/or yearly), is greatest. Various configurations have been used in the design of monitoring network, e.g.:

- location of sites on concentric circular lines centered on the area of interest;
- location of sites on typical trajectories of surface winds;
- location of random heavy density of sites in the core of interest with random open spacing further out;
- location of sites on an equally spaced grid patterns.

The choice of sampling sites, especially in the case of monitoring network, is usually dictated by financial constraints and local conditions, e.g. electrical power, access, security. The site selection procedures should be fully documented at the classification stage and compass point photographs of the surrounding area should be provided together with a detailed map. This will allow the sites to be characterized in terms of local sources, topography etc. The sites should be reviewed at regular intervals with repeated documentation (including photographs) to ensure that selection criteria remain valid over time.

## 4.2 SAMPLING SITES FOR STACK EMISSION DETERMINATION

Parameters require for the emission measurement can be divided into three categories:

- gaseous pollutants;
- particulates (or dust);
- volume flow (or stack gas velocity).

In stack emission monitoring the importance of the location of equipment and sampling facilities is paramount. Stack emission measurements require defined and stable flow conditions at the sample location. This allows the velocity and concentration of the measured component in the stack emission to be determined. If suitable sampling facilities are not available, it will mean that sampling of pollutants cannot be done in compliance with the required sampling methods. This means that the uncertainty associated with the results is greatly increased. In these circumstances meaningful results from stack emissions monitoring cannot be achieved. Defined and stable flow conditions at the sample location are essential to determine the velocity and concentration of the measured component. It is essential that designers of new plants remember to take account of stack emission monitoring at the plant's design stage. Once a plant is built, it is extremely difficult, if not impossible, to retrofit appropriate sampling facilities. The sampling of particulates from stack emissions, together with the measurement of the volume flow rate demands the most rigorous selection of sampling location. Accurate sampling of particulates requires that waste gas flow is laminar and that the sample is taken iso-kinetically. The criteria used in site selection for stack emission determination must also include:

- safety of the location for the test personnel;
- relationship to the points of particular interest (e.g. at the pollution control device, for device efficiency testing);
- availability of a platform for men and equipment;
- access to the stack interior from a suitable port;
- provision of power supply for sampling equipment;
- satisfaction of flow disturbance criteria.

Many of the above criteria will have to be compromised as the ideal sampling location seldom exists. However, safety considerations cannot be compromised as stack sampling is a hazardous undertaking even under good conditions.

Various criteria have been specified for avoiding flow disturbances. Before installing any sampling ports, the best available sampling plane must be chosen. The sampling plane is defined as the plane normal to the centerline of the duct at the sampling position. The sample plane must be positioned in such a way that there are homogeneous flow conditions, which allow representative samples of the stack gas emission to be taken. The sampling plane should be positioned in a length of a straight duct where the distribution of particulates can be expected to be uniform. Generally, a sampling location in vertical flue sited eight (in some countries at least five) flue equivalent diameters downstream and two flue equivalent diameters upstream from a flow disturbance such as a bend, inlet or outlet, is considered good.

**Flue (stack) equivalent diameter = 4 (area of flue cross-section/perimeter of flue cross section) = actual diameter for circular flue.**

If the sampling plane is positioned in a stack which is discharging to the open air, the distance between the sampling plane and the stack top should be at least 5 duct diameters. Every effort should be made to locate the sampling ports away from the sources of turbulence such as fans, duct bends and duct junctions. Bends, branches, obstructions, fans and leaks can all cause undesirable variations in the velocity profiles, which may make the location unsuitable for sampling. Where suitable sample planes exist in both vertical and horizontal sections of ductwork, the former should be chosen. Since many emission sources will not provide a site meeting this criteria, a method has been developed to compensate for non-ideal sampling locations with increased sample points across the stack cross-section. Generally, multi-point sampling at selected points across the sampling plane is performed. The mass concentration of a stack emission is the concentration of the measured component averaged over the cross section of the stack, averaged over a defined time period. Concentration distributions may differ across a stack and over time. If concentration and/or velocity profiles, which are variable in space and time occur, the emissions are determined as integral for time and space over the stack area. This means that the average concentration and velocity at several measurement points across a stack may need to be determined. The number of points is dependent upon the cross-sectional area of the stack and the distance of the sampling plane from flow disturbance within the stack. The location of sampling points at the centroids of equal areas across the stack cross-section is recommended. Gases, unlike particulates, are not subject to momentum forces when moving in a gas stream. Multi-point sampling is generally not required for the sampling of gaseous emissions. A single port is usually sufficient for the collection of a gas sample. However, in some situations, notably after the junction of several different streams, stratification of the gas stream will persist for some distance downstream. Stack gases may be non-homogeneous due to differences in chemical composition, or differences in temperature and velocity, which may lead to stratification and swirling. A survey of a suitable constituent of the gas stream such as carbon dioxide or oxygen should be performed to determine the degree of stratification. In cases where stratification does not exist, single point sampling at one quarter the diameter across the stack should be representative of the gaseous emission. If the gases are not mixed well, it is necessary to sample the gases using a multiple point technique (a grid measurement) across the sampling plane to give an overall average of the particulate emission. If stratification exists, the gaseous emission determination will require multi-point sampling techniques, unless an alternative sampling plane can be found. When a grid measurement technique is required, it is necessary to be able to measure the velocity at several points across the sample plane.

The following facilities must be provided:

1. Access to sample ports:
    - access must be via secure stairway, permanent or gangway;
    - a working platform must be adjacent to the sampling ports and provide adequate space for handling the equipment. The sample location must be situated where it is possible to erect suitable working platforms. Ideally, the measurement site should be easily and safely accessible via stairs. Particulate-and velocity-based measurements require a sufficiently large working area around the stack along the measurement lines, so that the measurement points can be sampled with appropriate length probes;
    - open sides of platforms must be fitted with safety handrails;
    - shelter and protection from the elements may be required at exposed sites,

particularly for the stacks which require particulate sampling. Lifting apparatus may be required to raise sampling equipment to elevated locations.

2. Provision of utilities:
   - a power supply must be made available within the vicinity of all sampling points. The supply can be either 220V, or a transformer may be used to convert the required voltage. Provision of power must be consistent with safety maintenance.

# 5 SAMPLING

## 5.1 SAMPLING – GENERAL CHARACTERIZATION.

Sampling is defined as a collection of a mass pollutant for latter analysis. In the case of ambient air, sampling may be considered as the collection of air samples in unconfined location exposed to the atmosphere.

It is generally recognized that the concentration of pollutants in the air changes from time to time, because of meteorology, fluctuations in source emissions and atmospheric reactions (e.g. sunlight and ozone). Therefore, the determination of an average concentration is most often desirable for the low-level and long-term exposure risk assessment. Since the air is complex and heterogeneous, continuously evolving in time and space and being influenced by atmospheric and geographical conditions, sampling is crucial in air analysis. Moreover, due to the low levels of pollutants present in the atmosphere, enrichment is often required. Sampling cannot be affected by the atmospheric conditions such as extremes of temperature, adverse weather, vapours (e.g. water) that may condense in the sample device creating a complex, multiphase system and removing soluble pollutants from the sample gas stream.

Source sampling in air pollution work may be considered as the collection of airborne pollutants before emission to the atmosphere and dilution by the air. In general, the sample(s) analyzed must be representative of the gas stream being tested. Therefore, the objective of sampling is to ensure that the sampled gas stream is representative of either the total or a known portion of the source emissions. Proper sampling in the case of a stationary source requires a thorough knowledge of the process to be studied.  The nature of process conditions and their effect upon emission parameters should be determined by means of a discussion with a knowledgeable person in charge of the facility. Two requirements are specified for valid source testing. Firstly, the sample should accurately reflect the true magnitude of the pollutant emission at a specific point in a stack at a specific instant of time. This requirement is determined by the design of the sampling instrument. The second requirement is to obtain enough measurements varying in space and time such that their combined results will accurately represent the entire source emission. The last requirement needs considering the fluctuations of the source emission both in space, across the stack diameter, and in time.

Air pollutants can be sampled by different techniques dependent on the purpose of the sampling and the availability of analytical instrument. The criteria used in method selection should include two requirements. The sampling must provide samples:

- representative;
- free from undesirable interference.

In the selection of an appropriate method, some important factors should be considered.

1. The type and nature of the air pollutant to be measured. For gases, consideration should be given to the reactivity of the gas.
2. The integrity and stability of the sample. Chemical reaction, adsorption, condensation and impaction cannot take place in the sampling equipment.
3. The sampling procedure. It should be optimal for the analytical procedure.
4. Data requirements. Different levels of accuracy, sensitivity, selectivity (the avoidance of chemical interference) and concentrations range may be required.
5. Concentration variations. The variations in concentration with time may require, for example, an automatic device to take a series of samples over a long period of time or a simple and a safe device for a lay person to use during a pollution incident.
6. Physical constraints of the atmosphere in the sampling site. Sampling cannot be affected by conditions such as extremes of temperature, high pressure, vapours (e.g. water) that may condense in the sample device creating a complex, multiphase system and removing soluble pollutants from the sample gas stream.
7. The sampling period. This may need to be as short as only a few seconds, or as long as several weeks.
8. Weight and size of equipment, power and water requirements. These requirements can vary considerably in different methods.
9. Portability. The size and weight of the equipment can vary considerably as can its power and water requirements.
10. Easiness of use and convenience. For example, the use of impingers and bubblers is minimized for personal monitoring.
11. Safety considerations. Fire hazard and toxic materials affect not just the person who is directly involved in sampling, but also the environment and other personnel at the sample location.
12. Cost. Not only the capital cost of instruments but also their maintenance, staff training and calibration costs must be considered.

Sampling of some gases is difficult because they are hard to detect, but in general, reactive and condensable gases such as formaldehyde, HCl, $NH_3$ and HF, present the greatest measurement challenges. Such gases may react with other components within the stack gas stream. They may:

- adsorb onto surfaces;

- condense or be absorbed by liquid condensate within a cold extractive sampling system;
- polymerise before reaching the analyzer.

### Surface adsorption

Different compounds may adsorb onto the surface of various materials within the sampling system components and therefore be removed from the sample stream before reaching the analyzer. The extent of the adsorption depends on many factors, including: the physical properties of the compound of interest, the gas concentration of the analytes and interferences, the type of material comprising the adsorption surface, the amount of exposed surface area, the surface condition, the gas and surface temperatures, and the time needed for the adsorption process to reach equilibrium. The effects of many of these factors are interdependent and vary with age and previous use (or abuse) of the sampling system. The selection of appropriate sampling system materials is important in minimizing the adsorption of many compounds. In general, selection of inert materials minimizes adsorption but several other factors must be considered. For example, measurement of ppm levels of criteria pollutants such as $SO_2$ and $NO_x$ usually can be accomplished with sampling system components fabricated of high quality stainless steel, Teflon, or glass. In many applications, Teflon is viewed as a completely inert material. However, less adsorptive materials, such as polyether ether ketone (PEEK) may be required for the tubing used in measurement applications of ppb level of organic compounds. Similarly, the use of Teflon is not recommended for measurement of “organofluorine” compounds because they are chemically similar to the Teflon polymer and may result in a positive measurement bias. In general, increasing the surface temperature of a solid will reduce gas adsorption on the solid. The heat transferred from the surface increases the internal energy of the adsorbed molecule helping it to overcome the weak molecular attraction and escape from the surface. For highly adsorptive gases, sample lines may be operated near the physical temperature limits. However, for some compounds such as CO, permeation through the walls of Teflon tubing occurs to a greater extent at higher temperatures. The presence of “active sites”, e.g. irregularities in a material surface at the molecular level, provides locations for chemisorption or the formation of weak chemical bonds with gas molecules that significantly affect the adsorption of gases. In the measurement of low concentrations of organics, highly polished stainless steel vessels with thermally deposited nickel are used to minimize the effects of adsorption. The virgin surface is virtually free of active sites and good sample recovery efficiencies have been obtained for many compounds. When small amounts of moisture are present in the samples, less adsorption will occur. Speculation is that the water molecules preferentially occupy the reactive sites and thus minimize adsorption of other analytes. Similarly, improved recovery efficiencies have been observed in the presence of 2% moisture by volume. Surface corrosion, due to the deposition of acids or other factors, creates many active sites in metal surfaces and greatly changes the adsorptive effects of the surface for many compounds. The potential for degradation of a sampling system over time is great because stack gases often contain significant concentrations of sulfuric, nitric, hydrochloric, or other acids. A sampling system that initially performs very well may be rendered completely incapable of transporting HCl to the analyzer due to the corrosion caused by the accumulation of condensate within the system. In addition, deposits of particulate matter on filters or other surfaces within the sampling system may greatly increase adsorption. For these reasons, the age and history of using a sampling system affect its performance. Therefore, periodic checks of the sampling system are required. Variations in the gas concentration or changes in other parameters affect the adsorption equilibrium resulting in subsequent increased adsorption or desorption of the compound of interest. Adsorption affects the response time of an extractive sampling system; the greater the adsorption, the longer the time required for a measurement system to display a stable and fully equilibrated response to a step change in gas concentration. The effects of adsorption may sometimes be determined through response time tests using dry calibration gases. However, as discussed above, the adsorption also may be affected by the presence of moisture or other components in the stack gas samples. Small unswept volumes within the sampling system (e.g. calibration injection lines) can mimic the effects of adsorption by allowing analytes to diffuse during sampling, thus confounding attempts to quantify adsorption. Because sampling systems often are fabricated of many components and different materials, isolating adsorption problems can be quite difficult.

### Solubility and condensation

The stack gas streams at stationary sources contain compounds that will condense if the sample temperature is reduced. Depending on the type of the sampling system used, water vapor may condense as the sample temperature is lowered. Other compounds, such as sulfuric acid, may condense along with water vapor to form acid condensate, or sulfuric acid may condense even when the sample temperature is maintained above the moisture dew point.

Condensate formed by cooling stack gas samples can be a complex mixture of substances. This condensate may be detrimental to the sampling system materials and cause corrosion or other problems. Some compounds, such as HCl and $NH_3$, are highly soluble in water. The presence of condensate within the sampling system will scrub water soluble compounds such as HCl. Obviously, if HCl is the compound of interest, the presence of condensed moisture in the sampling system will invalidate measurements. In other cases, where measurements of insoluble compounds are made in a sample stream that contains HCl, the presence of condensed moisture in the sampling system may protect the analyzer from damage. Thus, a decision to use a condenser system to remove moisture depends on the solubility of the compound of interest and other materials present in the stack gas matrix. Industrial process emission streams will reflect a wide range of moisture contents, depending on the nature of the process and the type of control equipment that is installed. The moisture content that will be encountered in a particular application must be known:1) to size condensers or dryers used for moisture removal, 2) to select an appropriate dilution factor to maintain the sample above its dew point, or 3) simply to gauge the significance of the problem. The moisture content of combustion source exhaust streams typically ranges from 8 to 20 percent by volume depending on the fuel combusted. Hazardous waste incinerators with quench towers and spray dryers may have emission streams containing as much as 50 percent water. Portland cement kiln exhaust streams are likely to contain moisture ranging from 10 to 35 percent by volume depending on the type of process (i.e. dry process, precalciner or wet process kiln). On the other end of the spectrum, sulfuric acid plants will have no moisture at all in the stack gas. The moisture content may be estimated based on the knowledge of the process or it may be measured directly over the range of process/control equipment operating conditions. The absorption of a somewhat water soluble component will reach an equilibrium between the liquid and gas phases given sufficient time and a constant concentration of the component in the gas phase. (This is not the case where chemical reactions with other components occur in a solution.) However, most sampling systems form new condensate continuously, and the concentration in the gas sample may also change with time. Therefore, the application of equilibrium solubility constants may be inappropriate, or at best, an indication of a one-sided limit for estimating the extent of this phenomena. The design of condensers in extractive systems should minimize the contact of the condensate and the sample stream to minimize the absorption of slightly water soluble compounds. It is also important that the condensate is not allowed to accumulate; it should be continuously removed to minimize absorption of soluble compounds and the opportunities for reactions with other stack gas constituents. Solubility losses of many pollutants are poorly understood. VOC or organic hazardous air pollutant monitoring applications may contain mixtures of soluble, slightly soluble, and insoluble components. A few studies at hazardous waste incinerators and sewage sludge incinerators have indicated that heated sampling systems with total hydrocarbon (THC) analyzers measure higher concentrations of volatile organics than the systems that include refrigerant moisture removal systems. Thus, some regulatory applications specify the use of a heated system even though operational problems are reduced extensively with a “cold” system. Unfortunately, the identity of the specific compounds that are removed in a water condenser and the degree to which they are removed are largely unknown because THC systems provide no information about the individual organic species that are present.

### Chemical Reactions

Chemical reactions can occur between various stack gas components resulting in the formation of new chemical species. Because of the complex nature of some stationary source emissions, it is difficult to determine the extent of these chemical reactions. Polymerization, neutralization, and sublimation/condensation reactions are suggested frequently by scientists, engineers and technicians as causing sampling and analytical problems. Many undocumented myths exist about the various chemical reactions both within the stack and within the sampling system. Determining whether chemical reactions occur in the stack or in the sampling system when performing extractive testing is very difficult, because the analyzer only detects what the sampling system can deliver. Detection of chemical reactions that occur within the source are virtually impossible to determine because some species are short-lived, while others reach a state where the products of the chemical reaction are in equilibrium with the reactants.

Polymerization reactions are those that occur when a compound reacts with itself (or a similar compound) to form a large molecule. An example of this phenomenon is the reaction of formaldehyde with itself to form paraformaldehyde. This compound is a solid that may be formed in sampling systems with cold spots. Individual formaldehyde molecules react with each other at the surface of these cold spots to form a polymer layer. This deposition results in a negative measurement bias for formaldehyde. The results of polymerization reactions manifest themselves in a manner similar to surface adsorption.

Neutralization reactions are those reactions that have a net effect in reducing an acidic or basic component in the stack gas. In the pure sense, neutralization reactions usually occur in solutions where hydrogen ions ($H^+$) and hydroxide ions ($OH^-$) react to form water. In the gas phase, neutralization may occur by solubilization first and neutralization second, or by direct adsorption of components onto particulate matter. The apparent removal of HCl by CaO (lime) in baghouses following spray dryers on the particulate filter cake of a sampling system are examples of this type of reaction. Reaction of HF with silica in glass surfaces to form SiF, is another neutralization reaction.

Salts can form when two or more gaseous compounds react. An important example is the equilibrium reaction between gaseous hydrochloric acid (HCl) and ammonia ($NH_3$) to form solid ammonium chloride ($NH_4Cl$). Both HCl and $NH_3$ are volatile, non-condensable gases while ammonium chloride is a water soluble solid compound having an exceptionally low vapor pressure. This reaction is known to occur under atmospheric conditions and may cause either positive or negative measurement biases that are dependent upon the stack gas and sample delivery temperatures. Another example of a salt-forming reaction is the combination of $SO_2$, $NH_3$, and water to form ammonium bisulfate. This reaction can occur in the atmosphere downstream of a source, producing a detached plume and in some cases particulate fall-out. This reaction can also occur within the condenser of a continuous emission system creating low biases for either $SO_2$ or $NH_3$ measurements.

For these reasons, depending upon the components making up the tested gas stream, special sampling equipment may be needed and special operation and maintenance procedures may be required to achieve reliable results. In addition to the measurement technologies of the instrumentation, one must also consider the technology of sample handling and transport. Because sampling involves the collection of targeted matter, thus the sampling flow rate is required to achieve the transfer volume of the matter to be measured. When sampling is carried out, transfer volume of the targeted matter may be obtained by the dynamic or static method. In the first case gas movers e.g. suction pumps, are applied. Static flow rate is based on molecular diffusion or permeation (without using power). According to the presence or absence of a pump in a sampling train, the sampling methods can be classified as:

- active;
- passive.

The category of a sampling method is very important, because it determines the averaging time of sample collection. Among the usually used modes, there are:

- continuous mode (pollutant concentrations are determined with automated methods, and recorded or displayed continuously);
- integrated mode (pollutant concentrations are measured with manual or automated methods from integrated hourly or daily samples on a fixed schedule (i.e. manual PM2.5);
- static mode (pollutant is estimated or effects are determined from long-term e.g. weekly or monthly exposures).

The sampling process consists of three stages:

- collection of a sample;
- determination of the flow rate;
- handling and custody of a sample.

## 5.2 COLLECTION OF GAS POLLUTANTS

In practice, the collection of gases is based on:

- grab sampling;
- dynamic (active) sampling;
- passive sampling.

### *5.2.1 GRAB SAMPLING*

Sampling techniques for the collection of the whole sample without concentration of gases or vapors are called grab sampling. Generally, it involves the direct collection and isolation of the test air in an impermeable container without concentration of gases or vapors. The encapsulated sample is sent to the laboratory for the direct analysis. Clearly, this sampling technique is limited to those gaseous constituents for which sensitive analytical techniques are available, or which there is a high concentration of a given constituent in the test atmosphere.

Due to the fact that the sample is not concentrated, it is much more sensitive to contamination by leaks. For many low-boiling compounds such as methane, ethane, propane and $O_2$, $N_2$ or $CO_2$, this type of sampling is the preferred and/or sole method of collection. Many techniques may be used for grab sampling. They are based on different containers:

- syringes (syringe sampling);
- plastic bags (flexible container sampling);
- glass containers (rigid container sampling);
- metal canisters (rigid container sampling).

A gas syringe, also known as a glass collecting bottle, is a piece of laboratory glassware used to draw a volume of a gas. The syringe should have a hermetic seal around the top and sides, and move more freely than a normal syringe. Syringe sampling techniques are useful for rapid and convenient sampling of the atmospheres for gases with sensitive analytical techniques or high concentrations of gas. Such techniques offer a relatively simple sampling but applications are limited to specific small volumes of a sample.

A simple procedure for containing a sample of an atmosphere is to enclose it in a plastic bag container. However, before it could arrive at the laboratory it would have changed so much that many types of pollutants could no longer be given a valid analysis:

- reactive compounds, such as ozone, nitrogen dioxide and sulfur dioxide, would continue reactivity and changing;
- these reactive compounds would also undergo new reactions with the walls of the bag and the chemicals in it;
- vapors would adsorb onto the surface of the bag and be irretrievably lost;
- vapors in the plastic would desorb into the sampled air - adding pollution to it;
- light, diffusive molecules such as hydrogen, helium and methane that can sorb into and through the bag would be exchanged with the surrounding atmosphere; the sample might also be contaminated by the reverse process;
- dusts, fibres and aerosols would be attracted to the walls of the bag and become irretrievably lost;
- condensation from wet or humid atmospheres would remove the water soluble pollutants.

Various flexible containers have been evaluated and used for grab sampling of gaseous constituents. The bags may be constructed of:

- polyester film;
- aluminum foil lined polyester;
- polyvinyl chloride film;
- various fluorinated plastics.

The typical commercial materials used in plastic bags are:

- aluminized Schotch-pak;
- Mylar (DuPoint);
- Saran (Dow Chemistry);
- Tedlar (DuPoint).

These plastics are appropriate for inert gas collection and storage. Foil lined polyester bags are recommended in a standard procedure for low molecular weight atmospheric hydrocarbons. These bags are reported as unsuitable for the collection of highly polar gases like $SO_2$, $NO_2$ or $O_3$. Tedlar is a polyvinyl fluoride film, which is non-adsorptive and itself relatively free of contamination. Tedlar bags are especially resistant to wall losses for many reactive gases. These bags have been in use in a large toxics air monitoring network. Gas sample bags are a convenient and accurate means of gas and vapor samples in the air. This is particularly true in the areas where the concentration is above the detection limits of common analytical instruments. Many chemical hazards can be effectively collected by sample bags. But, while the collection method is simple, the selection of the bag, fittings, and tubing is critical. Whether a substance can be sampled and stored in a plastic bag should be determined in the laboratory prior to field use. In all cases, the containers must be evaluated for their reactivity with or adsorption of, gaseous constituents. Literature references may also be used to determine the proper usage of bag sampling. Entry into bags is by a fitting seated in and connected to the bag to form an integral part of the bag. Some bags have two fittings to facilitate sample taking by simply passing sample air through the bag. For all bag sampling techniques, some means of filling is required. A displacement method of sampling was developed, in which a deflated bag is contained in a rigid, airtight vessel (box). The sample is introduced and expelled to/from the bag by removing and refilling the gas in the vessel outside the bag. The sample is taken by applying suction from a vacuum blower to the air surrounding the box. The advantages of this method include that the air sample within the bag can easily be emitted and reintroduced, but the bag material must be selected with due consideration for the component to be measured. Gas bag sampling may be also accomplished without a pump. Bags can be reused after purging with clean air and checking for any residual gaseous components. Even “inert” plastics display outgassing properties. They must be flushed and completely evacuated before sampling by collapsed bag techniques or thoroughly flushed where manual sampling is done. In some cases, where adsorption is reproducible, preconditioning of the container with large concentrations of the gaseous constituent to be sampled may be used. The bags are particularly well suited for integrated air sampling. The bags must be carefully checked for leaks, particularly at valves and seals. They should not be filled to capacity in order to allow for temperature and pressure variations which may cause gas expansion and encourage leakage. Finally, the bags must be protected to transit against rupture or association with contaminated atmospheres and the samples should be analyzed as soon as possible after collection.

Many types of rigid containers may be used for sampling, e.g. glass bottles, metal canisters. Rigid containers may be applied either by pre-evacuation of the container and filling in the test atmosphere or flushing the test atmosphere through the container several times before sealing the container. Vacuuming the vessel before collection is suitable for situations where ‘instant’ sampling is required. In this method sampling can be done by simply opening the valve at the collection point. Evacuated containers are not recommended for reactive gas sampling because of possible reactions of the gas with the sealing wax plug. This can be overcome by filling the container with an absorber with specific chemical reactivity for the constituent sought.

Glass containers can be used both in an evacuated or pass-through displacement mode. In the displacement mode gas sample tubes are opened on both ends. A pump is attached to one end and a sampling probe is attached on the other end. The pump is activated and approximately 10 times the sampling tube volume is passed through the system. The stopcocks are immediately shut and the sample is then secured. Alternatively, the tubes may be evacuated using a vacuum pump, then the sample is collected by simply opening one of the stopcocks. Glass containers, by nature of their small volumes, provide basically instantaneous "grab" samples. They are also convenient for collecting samples directly in a chemical adsorbent in which they are later analyzed. In this case, rather than sample tubes, 1-3 l flasks are better suited, with only one stopcock used for both evacuation and later sample entry. In general, glass containers are excellent for inert gases such as oxygen, nitrogen, methane, carbon monoxide and carbon dioxide. Reactive gases, such as sulfur dioxide are not recommended for direct collection and storage. The sampling of the reactive compounds, should be based on the chemical absorbent technique, which fixes and stabilizes the reactive gas prior to analysis.

Rigid containers are usually used as metal canisters. Metal canisters are made of:

- stainless steel (e.g. Gresham);
- passivated stainless steel (SUMMA);
- PTFE-coated stainless steel (Swagelok-Whitey, Highlands, Ohio);
- aluminium.

Inert surface of canister may be coated for sampling media. A gas sample is collected by the difference in pressure between ambient and inside of canister. During sampling process, canister is evacuated for sub-atmospheric pressure or pressurized. Metal containers are widely used for the collection of the inert gases. They are not suitable for a majority of the reactive gases. Metal containers come in a variety of sizes from 1 to 34 $dm^3$. An advantage of using the large sizes is that a longer, more integrated, sampling time is possible when compared to the glass containers. The other advantage of a canister system is that it allows the relatively long storage of sampled air for repeating analysis. Extensive studies of SUMMA containers have shown excellent stability in the order of weeks, for hydrocarbons and various halocarbons even in the low and sub-parts per billion. The stainless canisters may be used for long term (up to 24h) sampling for ambient hydrocarbons and halocarbons. It is possible, since a treatment (polishing) process for the containers has been introduced, which reduces the surface adsorption of gases by reduction of the internal exposed metal surface area. The samples may be transferred from canister to a pre-concentration unit which concentrates and at the same time minimizes the sample volume to be injected into a Gas Chromatograph/Mass Spectrometer (GC/MS). Compared to the sorbent-based sampling method, the canister-based sampling method has many practical advantages, e.g.:

- the collection of a whole air sample;
- sufficient sample volume for multiple analysis;
- no source of power (passive sampling);
- simplicity of sampling procedure and applicability to a broad range of VOCs.

The advantages of grab sampling methods are numerous:

- they require relatively simple equipment;
- they offer a variety and flexibility to many air sampling applications;
- the containers are reusable (of course, the appropriate cleaning procedures must be applied);
- the volume of the air sampled does not have to be accurately determined.

This method of sampling has also disadvantages, e.g.:

- it is limited to gases for which sensitive analytical methods are available or which are present in high concentration in the air;
- due to the fact that the sample is not concentrated, it is much more sensitive to contamination by leaks;
- grab sampling is feasible only for pollutants and pollutant mixtures that are sufficiently unreactive or do not adsorb or condense on the walls of the container during the period between sampling and analysis;
- for that reason, the containers must be evaluated for their reactivity with or adsorption of the sampled gases.

### *5.2.2 DYNAMIC SAMPLING*

The sampling is "dynamic" or "active" when a sample is mechanically drawn through the sampler. The sampling techniques based on this method extract and concentrate gases, vapors and particles from gaseous samples. Active sampling methods collect pollutant samples either by physical or chemical means for subsequent analysis in a laboratory. A known volume of air is pumped through a collector such as a filter or chemical solution for a set period of time, which is then removed for the analysis. Samples can be taken daily (24 hour), thereby providing detailed information about pollutant levels. The dynamic sampling is performed by suitable sampler (sampling system). There are several basic concepts common to all integrated dynamic samplers:

- a known volume of sample air is introduced into a sample collection device over a known sampling interval;
- the collection device removes the pollutant(s) being collected by some chemical or physical principle;
- the quantity of pollutant collected is determined by appropriate chemical or physical laboratory procedures;
- the average concentration of the pollutant is calculated for sampling interval based on the quantity of pollutant measured and the air volume sampled.

In the process of dynamic sampling three issues are of vital importance:

- the intake and transfer of the representative sample;
- the accurate control of the flow rate;
- the collection of the pollutant in a manner allowing for an accurate qualitative and quantitative analysis.

Therefore, the system for dynamic sampling consists of four component subsystems:

- the intake and transfer subsystem;
- the collection subsystem;
- the flow measurement subsystem;
- the air mover.

It should be noted that malfunction of any one subsystem will hinder the successful performance of the whole sampler. Therefore, the performance of each component must be evaluated when synthesizing the overall sampling system.

The features of the intake are basically determined by the objective of the sampling program. The primary consideration in evaluating the intake for a given sampling system is the ability of the device to inhale faithfully the total quantity or a reproducible representative portion of the airborne constituent being studied from a given volume of a sampled gas. Upon satisfaction of the above constraint on the intake, the transfer system must then transport the constituent to the collection device without modifying the quantity or any properties of the constituent. The following phenomena should be eliminated in the intake and transfer subsystem:

- adhesion of aerosols and gases to tube walls;
- condensation of volatile components within the transfer lines;
- reaction of gaseous components with transfer system materials;
- adsorption and reaction with collected particulates or gases.

### Intake and transfer subsystem for gases

Although gaseous pollutants are not subject to the inertial and electrostatic effects which occur in the case of particles, special precautions are necessary to avoid the presentation of a modified or diminished sample to the analysis step. Several general considerations in intake and transfer of gaseous pollutants should be mentioned. Gases and vapors follow the normal laws of diffusion and mix freely with the surrounding atmosphere. They are not affected by inertial or electrostatic forces which may disturb particles. These characteristics make gaseous pollutants easier to sample than aerosols. Where heavy concentrations of a gas may present in a stagnant or slow moving air mass, a density differential between the gas and air may result in an uneven distribution of the gas within the air mass. This possibility is generally overcome by sampling from a turbulent or in a well-mixed air mass. Gaseous constituents of the atmosphere or flue gases are in a relatively high energy state and may be reactive with components of the sampling system or other gaseous constituents. In many cases, it may be necessary to pretreat the sampled air stream before the gas reaches the collection component of the sampling system. In such cases as, e.g. prefiltration of particulates or moisture removal, the pretreating units may remove significant quantities of the gaseous constituent to be sampled. Where pretreatment is used, the pretreatment units should be analyzed for their content of the relevant gaseous constituents. All possible precautions should be taken against inward or outward leakage. However, sealing lubricants may collect gaseous constituents and their use should be avoided or carefully evaluated. Self lubricating

PTFE joints and stopcocks are preferable and these can relatively air tight seals. Diffusion of gases through apparently impermeable materials such as rubber, neoprene and plasticized PVC is possible and should be evaluated where samples will be stored for periods longer than a few hours. Condensation of atmospheric moisture within sample lines can create reactive conditions for some combinations of gaseous constituents, or the moisture may simply collect gaseous constituents before they reach the collection component. Many gaseous constituents are photochemically reactive and may undergo reactive changes within the sampling system if they remain exposed to light energy. Light sealed containers for sampling systems would simply eliminate this problem. The sampling system must be designed to draw continually a fresh sample of the atmosphere being studied and should not allow the resampling of the air which has passed through the system. An extended exhaust line to a location remote from the sample intake will normally prevent resampling. To ensure the unaltered state of the sample:

- the sampling probe must be made of inert materials such as Teflon or glass;
- the length of the transport line should be short;
- particulate matter and moisture cannot accumulate inside of the sampling line.

Stagnant gases, such as calm ambient air, do not require isokinetic conditions for efficient sampling of all particle sizes because slow moving particles have little or no momentum.

### The collection subsystem for gases

The collection subsystem for gases may incorporate:

- adsorption (dry collection subsystems);
- absorption (wet collection subsystems);
- condensation.

Several factors need to be considered in selecting an adsorbent:

- a high relative surface area is important to maintain a large contact area for adsorption, while retaining the maximum space between adsorbent granules for maximum air flow rates;
- relative affinity for polar or non-polar compounds is important for selecting the adsorbent to sample a sample given gaseous constituents (activated carbon is non-polar and therefore, has affinity for organic compounds to the exclusion of polar gases, including water. Silica gel and alumina are polar and have increasing affinity for higher polarity gases.);
- the adsorbents must not be chemically reactive with the gases to be collected, unless chemisorption is used intentionally;
- the adsorbent should not be prone to fracturing, crushing or flaking which may result in carrying over fine particulates with the sampled air stream;
- the retention capacity of the adsorbent should be predictable and high in order to avoid non-quantitative recovery of gaseous constituents;

- the desorption properties of adsorbents must be amenable to quantitative recovery of the collected sample, preferably with regeneration of the adsorbent for subsequent use.

Materials which are commonly used as adsorbents include:

- activated carbon;
- silica gel;
- zeolite molecular sieves;
- synthetic polymeric materials (GC support phases, e.g. Tenax);
- graphitized carbons (e.g. Carbotraps);
- carbon molecular sieves.

### Activated charcoal

By far the commonest sorbent is porous charcoal where the microporosity has been enhanced by activation, typically using steam oxidation. Activated carbon is relatively unselective and as such is useful for screening atmospheric constituents. This material is the most widely used adsorbent for the concentration and storage of organic vapors from air streams. Nut shell charcoals are particularly useful for this purpose as they are hard and non-friable, and possess an original porosity very suitable for activation. Coconut shells are the most abundant and cheapest starting material, although olive pits are sometimes used in Mediterranean areas. A drawback of using plant materials is the existence of a residual inorganic ash content. The atoms of sodium, potassium, magnesium, calcium, etc., disrupt the regular charcoal structure and the local electrical configuration. The results are sites of enhanced catalytic activity and water uptake, and charcoal whose adsorption and desorption properties vary with the provenance of the starting material and conditions of activation. Water uptake is a problem with activated charcoals. When the relative humidity is greater than about 50%, sufficient water is adsorbed that when further water molecules are adsorbed by hydrogen bonding to their fellows islands of water coalesce to form a water layer, and the surface becomes hydrophilic. The capacity of charcoals for water in this region approaches 30% of their dry mass. This water can displace adsorbed organic molecules, react with them (e.g. 2-butanone forming 3-hydroxy-2-butanone), or form an immiscible phase on desorption into which polar molecules (e.g. acetone) can partition and essentially be lost to analysis. Charcoals based on petroleum or by-products of the petroleum industry (such as Witcarb or JXC charcoal, and Anasorb 747) contain far less inorganic material and can be fashioned into a charcoal with very reproducible properties. However, they rarely approach the huge microporous capacity of nut-shell charcoals, and are more expensive. Charcoals made from coal also exist, but there are few comparisons of their properties with those of other charcoals used for this purpose. Coconut shell charcoal is used in the majority of NIOSH and OSHA methods, and widely in official methods in European countries.

### Anasorb 747

This is a charcoal made from petroleum mixed with an organic solvent and formed into beads. Removal of the solvent leaves a regular porosity which is enhanced by activation. The material is produced as round, hard beads in a tight size range around 0.75 mm diameter, which leads to even packing in the bed. Although it has a lower capacity than coconut charcoal, it absorbs less water for a given volume of sampled air over almost all humidities, and desorption efficiencies for polar compounds are generally higher. In addition, compounds unstable on coconut charcoal (e.g. vinyl compounds, acrylates and ketones) are more stable on Anasorb 747 which is not identical to Carboxen 564 as is sometimes claimed.

### Silica gel

Silica gel is somewhat more selective than activated carbon. This material is a highly polar substance, and therefore will preferentially adsorb water more strongly than organic gases and vapors. Silica gel has been used for the determination of non-polar hydrocarbons in the air. However, water vapor is strongly adsorbed from humid air and can displace adsorbed organic molecules. Over the years silica gel has been replaced with other sorbents; it is now used only for certain highly polar organic compounds, such as methanol, aminoethanol, amines, alkanolamines, and gluteraldehyde, as well as for some inorganic species, and as a substrate for coating with derivatizing agents.

### Zeolite molecular sieves

Zeolite molecular sieves are used in a few methods, for example in sampling butadiene, or nitrous oxide.

### Tenax TA

GC phases may be very selective. Tenax TA, often referred to simply as Tenax, is a macroporous, semi-crystalline polymer manufactured from poly-2,6-diphenyl phenylene oxide (DPPO). It has a relatively low surface area (about 15 $m^2 g^{-1}$). The consequent low adsorption capacity of Tenax limits its application in the atmospheres of high concentrations, since, as previously noted, breakthrough is dependent on concentration. However, its ability to be conditioned to have a very low background (less than 1 ng per component), together with its high temperature stability that allows for the recovery of many semi-volatile molecules, makes it a very useful sorbent for collecting multiple organic compounds from the atmospheres of low concentrations, such as when monitoring ambient or relatively unpolluted indoor air. It is used for air sampling at a part per billion and lower levels of VOCs. Because of its high thermal stability, Tenax can also be combined with carbonaceous sorbents in sorbent tubes containing multiple-beds. Tenax has been directly combined with graphite (Tenax GR) in various proportions. However, it is debatable whether this offers any advantage over having separate beds. Tenax is attacked by oxidizing gases in the atmosphere, such as ozone, and nitrogen oxides, with the formation of artefact compounds such as acetophenone and benzaldehyde from ozone and 2,6-diphenyl-*p*-benzoquinone from nitrogen oxides. The same compounds may also be formed via radicals formed through the reaction of oxidants with adsorbed VOCs. Reactive compounds such as unsaturated terpenes, can also be degraded through reaction with ozone, although this problem is not unique to Tenax. Ozone scrubbers may be used to minimize this problem although none appeared perfectly suitable. Tenax is nonpolar, relatively hydrophobic, although the capacity for polar compounds, such as alcohols, appears to increase at high humidities suggesting some minor water uptake. Generally, water vapor should not affect sampling in any way. Tenax is granular and available in a wide-range of mesh sizes. The relatively inert nature, high thermal stability and rapid desorption kinetics make it a very suitable sorbent for the secondary cold-trap of thermal desorbers.

### Chromosorb 106

Chromosorb 106 has a greater capacity than Tenax, and can be used at much higher concentrations. Its thermal stability is lower than that of Tenax, and so it is not suitable for semi-volatile compounds or for mixing with other sorbents. In addition, it cannot be conditioned to as low a background, especially for aromatic species, and the background tends to increase with storage. It is not certain whether this represents sorbent breakdown to release monomer, or insufficient cleaning followed by migration of adsorbed molecules from depth. Nevertheless, it is not suitable for accurately sampling low ppb concentrations, although it remains one of the most popular and versatile sorbents for sampling for industrial hygiene applications. It is very hydrophobic and relatively unaffected by ozone. Porapak N has also been used in thermal desorption applications.

### Carboxens

The sorbents called Carboxens are manufactured from the partial to full carbonization of porous polymers. By careful process control, a range of properties can be produced. The most commonly encountered is Carboxen 564, which has a high porosity, and which is relatively hydrophobic. It provides enhanced storage stability for reactive compounds (e.g. vinyl acetate and 2-butanone), but is not sufficiently inert at high temperatures to be useful in thermal desorption techniques. Other Carboxens can be very hydrophobic, and have specific applications.

### Porous polymers

Tenax is rarely used with solvent desorption, as it has low capacity for volatile compounds, and is incompatible with many solvent systems. It is used in specialized methods, e.g., for certain explosive chemicals. Amberlite XAD-2 and Chromosorb 102 are similar mesoporous polymers with moderate surface areas that are often used for large, semi-volatile molecules such as polyaromatic hydrocarbons and pesticides. Amberlite XAD-2 is often used as a support for derivatizing agents. Porapak N and certain other members of the Amberlite series (e.g., XAD-7) have polar adsorption sites suitable for polar molecules. The most frequently encountered polymers used with solvent desorption are microporous polystyrenes. The degree of porosity can be controlled by the amount of cross-linking, and divinylbenzene is often incorporated for this purpose. The polymers absorb no significant water and exhibit inert surfaces to reactive molecules such as terpenes. They are compatible with common desorption solvents. Chromosorb 106, Amberlite XAD-4, Porapak Q and Hayesep D are all similar in this respect. Their surface areas lie in the region of 400–800 $m^2$ $g^{-1}$, and they all have considerable capacity for volatile molecules, although not for the most volatile ones (e.g. dichloromethane). Chromosorb 106 is most commonly used sometimes with a back-up of charcoal to collect the highly volatile components. However, it is significantly more expensive than charcoal, and sorbents are not reused after solvent desorption.

### Graphitized carbons

The type examples of these sorbents are the Carbotraps. Carbotrap C has a low surface area (around 10 $m^2$ $g^{-1}$), and is normally used in combination with other sorbents in multi-bed tubes. Carbotrap B, known also simply as Carbotrap, has a higher surface area (around 100 $m^2$ $g^{-1}$) and is sometimes used alone, but is more commonly also found in multi-bed tubes (see below). The graphitized carbons are made from carbon black and tend to be soft and friable, which can cause problems if tiny particles are allowed to enter the thermal desorber apparatus. While relatively hydrophobic, graphitized carbons do absorb some water. Certain compounds, such as terpenes and chlorinated hydrocarbons can be unstable when adsorbed on these sorbents. The disappearance of terpenes may be due to re-arrangements catalyzed by the carbon surface. Ozone does not produce artefacts from the sorbent itself. Very recently, a high surface area version has been developed, which promises to have useful applications.

### Carbon molecular sieves

Molecular sieves have an abundance of micropores in a size range of molecular dimensions. Molecules larger than the pores will pass straight through the bed, and hence the “sieve” effect. On the other hand, small molecules, which can fit snugly within the pores are held very tightly. Carbon molecular sieves are rarely used alone, except when targeting specific chemicals. They typically are used as the rear section in multi-bed tubes. Carbon molecular sieves have very high capacities for small, volatile molecules, such as methyl chloride, dichloromethane and vinyl chloride. Unfortunately, water also collects in these small pores, although this does not have a great effect on the capacity as these sorbents are much less hydrophilic than coconut charcoal, since they are manufactured from polymers such as polyvinylidene chloride. Water can be a problem in thermal desorption analyses, either because it can freeze in the cryotrap and block it, or because when rapidly heated the momentary overpressure can lead to split discrimination, or because it can alter the polarity of the carrier gas or column. The adsorbed molecules are held very tightly so that a solvent with a high heat of adsorption is required for effective displacement and recovery. Carbon disulfide is suitable, but methanol is not. Many kinds of carbon molecular sieve are available (e.g. Carbosieve S-III, Carboxen 1000, Carboxen 1003, Spherocarb, Anasorb CMS. Retention volume studies have indicated large differences between these sorbents. Until comparisons are carried out it is advisable not to treat these sorbents as equivalent, and to use only the material evaluated in the specific method.

### Sorbents for sampling inorganic gases and vapors

Most of the previous discussion concerned the collection of organic gases and vapors. Some inorganic gases and vapors are also important, particularly in occupational hygiene. A mixed copper/manganese oxide (Hydrar or Hopcalite) is used for collecting mercury vapor. High-purity silica gel is commonly used for collecting acid gases (e.g. HCl, $H_2SO_4$). Acid-coated sorbents (e.g. silica gel, charcoal, firebrick) are used for basic gases such as ammonia, phosphine and hydrazine. Alkali-treated charcoal is used for collecting sulfur dioxide. Triethanolamine coated on an inert sorbent is commonly used for nitrogen oxides and sulfur dioxide. In ambient monitoring methods real-time techniques are available for most of these applications. However, sorbent-based diffusive sampling methods are popular as a cheap method for obtaining widespread spatial coverage. Such methods exist for ozone, nitrogen oxides, sulfur dioxide, ammonia, and carbon monoxide, amongst others.

Sorbent beds used for sampling are usually placed in tubes, which consist of two sections. The first of them is used for the sorption of the sample. The second one known as the back-up or secondary section can be used to guard against breakthrough in field situations. Breakthrough is the appearance of sampled molecules in the outlet stream, either because of saturation within the bed, or displacement by another chemical. The notional point of breakthrough is an outlet stream concentration equal to 5% of the inlet concentration. Sampling is no longer efficient when this occurs, and, as breakthrough progresses, the sample will be less and less representative of the external environment. Over a wide range of flow-rates, breakthrough is independent of flow-rate, depending only on the total volume of the sample passed. The breakthrough is dependent on concentration, and also on temperature, and the presence of other species in the atmosphere. Practical tests of breakthrough with constant atmospheres at or above the target value are preferred. Where concentrations are high, this is possible using a standard gas chromatography (GC) system, or other detectors, connected to the outlet of the sampler. When concentrations are low, more elaborate detection methods are required. The breakthrough volume is adjusted by an additional safety factor (usually reduced by one-third) to account for the presence of other chemicals in the environment. One particularly common interfering chemical is water vapor. High humidity can dramatically affect breakthrough volumes on hydrophilic sorbents such as silica gel or charcoal (which is nominally hydrophobic but becomes hydrophilic at high humidity). For best results, breakthrough determinations should be carried out with humidified air. The alternative approach to determining breakthrough (extrapolated chromatographic retention volumes) suffers from being unrealistic as the effects of high concentrations and the presence of competing vapors (especially water vapor) are not taken into account.

Tubes containing beds of different sorbents have become popular in recent years. For example, these combinations include Tenax TA or GR and carbon molecular sieve, and low surface area graphitized carbon/medium surface area graphitized carbon/carbon molecular sieve. These tubes have the advantage of potentially being able to collect most volatile compounds of interest in a single sample and, with suitable gas chromatographic column and temperature program, obtain a result with a single analysis.

When the samples have been obtained by trapping on a solid sorbent, it is necessary to desorb them. In practice, two methods are used for the quantitative recovery of the collected sample. Therefore, the adsorption type of sampling can be subdivided into two classes:

- solvent recovery;
- thermal desorption.

These classes are distinguished by the way the pollutant is recovered. The pollutant is recovered by being dissolved by an organic solvent from the solid sorbent. This provides a solution of the pollutant, which is usually analyzed by injecting a small portion of it into a gas chromatograph. Carbon disulfide is a good solvent for non-polar compounds. Therefore, it is particularly suitable for hydrocarbon analysis. However, it can react with certain compounds (e.g. amines), and can interfere with the analysis of certain volatile chlorinated hydrocarbons.

Thermal desorption is connected with a wide range of tubes with different packings to suit different applications. The pollutants are recovered by heating the tube to vaporize them and discharge the whole sample into a gas chromatograph in one injection. The important differences from solvent recovery are:

- the whole sample, not a small part of it, can be injected and this improves the limit of detection;
- there is no solvent peak to obscure part of the chromatogram.

The principal disadvantage of sorbent sampling is that it is not a real-time technique. It is possible to sample ambient air over a long period by taking short-term samples (e.g. 5 min) out of every hour, and automated equipment is now available in which one tube is being analyzed while another is collecting sample to ensure complete temporal coverage. Another shortcomings are the limitations on the range of compounds that can be collected. More than one sorbent is required to cover all classes of compounds (for example three different sorbents would normally be required to sample amines, aldehydes and aromatic hydrocarbons). Sampling based on adsorption is commonly used in the following cases:

- where information is required concerning the spatial distribution of chemicals in the atmosphere;
- where personal samples are required;
- where complex mixtures of organic compounds are best resolved by laboratory analysis;
- where long-term measurements are required.

In general, canisters are more useful for highly volatile ($C_1$ and $C_2$ hydrocarbons) and reactive compounds (e.g. 1,3-butadiene), while sorbent tubes are more useful for less volatile and polar compounds, although there is a wide middle ground where both could be applicable. It is also possible for sorbent tubes to be used for semi-volatile compounds, even with thermal desorption.

Sorbents are also sometimes used as supports for chemicals which can react with specific analytes to form a more stable or more easily analyzed derivative. Sorbents may also be used as supports for the color reactions used in detector tube technologies. These methods are described as a trapping by reaction.

Absorption of gases from the atmosphere is a solubility phenomenon whereby gas molecules are preferentially dissolved in a liquid collecting phase. The degree of absorption of a given gaseous constituent in a particular solvent is limited by the equilibrium partial pressure of the vapor over its liquid solution. This limitation can be overcome where the gaseous constituent undergoes a relatively irreversible chemical reaction with the absorbent. The efficiency of absorption of gases into a liquid phase is also very dependent on contact surface area and absorbing devices are designed to achieve the maximum area contact between gas bubbles and the absorbent. This is normally achieved by transforming the air stream to small, finely dispersed bubbles with a relatively long travel time through the absorbent. Various absorption devices have been designed to provide efficient absorption. Sampling techniques employ:

- simple bubblers;
- bubblers with fritted glass diffusers;
- bead packed absorbers are widely used.

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 contaminant (Fig. 1). Most gases and vapors can be collected in this way, followed by an appropriate laboratory analysis of the resulting solutions.

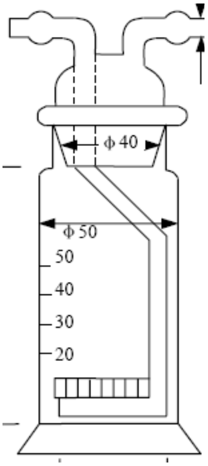


**FIGURE 1** A bubbler sampler.

Condensation of gaseous pollutants depends upon cooling the gas stream to temperatures below the boiling or freezing points of the gases to be collected. The efficiency of this sampling method relies on the difference between the sample concentration and the vapor pressure value at the temperature of the said component, the absorption rate, degree of dissolution to the collection material, shape of the trap, and gas flow rate, etc. The temperatures used in a condensation device are selected to ensure adequate condensation of the gas by lowering its vapor pressure to generally less than 1.33 mb. Various refrigerants are possible, for example:

- ice and water (0°C);
- ice and NaCl (-21 °C);
- dry ice and acetone (-78.5 °C);
- liquid air (-147 °C);
- liquid oxygen (-183 °C);
- liquid nitrogen (196 °C).

Because of the low temperatures involved, good insulation must be provided; therefore, the equipment involved in condensation devices is rather bulky. Dewar flasks are commonly used to contain the refrigerant and collecting trap. The primary problem encountered in condensation devices is the large volume of water vapor in the air which will freeze out. This is often overcome by providing sequential traps at progressively lower temperatures, with the first trap designed to collect primarily water vapor. Although condensation subsystems are not suitable for unattended operation, they have the advantage of providing preserved bulk atmospheric samples which are readily amenable to further analysis. There are three types of cryogenic samplers each suited to different situations and pollutants.

- Total cryogenic sampler. This is used for water-insoluble species; the whole of the atmosphere is liquefied, the bulk gases are distilled off and the remainder is evaporated within the sample container to give a concentrated atmosphere of the volatile, water-insoluble species.
- Condensate sampler. This is used for water-soluble species; it operates by condensing and freezing the contaminants together with sufficient atmospheric moisture to provide an aqueous solution of the water-soluble components.
- Cryogenic tube. This is used for the total volatiles and is similar in effect to a thermal desorption tube, except that the vapors are trapped by being frozen in a tube immersed in a cryogen.

The dynamic sampling has several advantages. This method may provide effective concentration of gaseous pollutants. There is considerable versatility considering the large number of configurations and methods of pollutant collection available. In many cases the sensitivity of the method may be increased by increasing sample flow or sampling time. This kind of flexibility is important for the methods developed for industrial occupational settings where concentrations of the pollutant being measured tend to be higher than in typical office buildings. Multiple units can often be combined in sequential sampler that produces a series of timed samples over a significant period of time. Sampling can be conducted at locations which may be inaccessible to continuous instruments. A dynamic sampling presents also disadvantages. The set-up and analytical times for many of these methods are significant. Some sampling methods require the handling of corrosive or toxic absorbing solutions which may pose hazards in occupied indoor spaces. These methods tend to require manual operation which increases costs and the risk of human error. Quality assurance procedures for sampling and analysis are often complex and time-consuming. Because of the time required for the analysis of samples the period between sampling and reception of the results can be significant. Handling and shipping of the collection medium may allow the sample to become contaminated. The use of field blanks can be used to compensate for this, but it increases the analytical costs.

### *5.2.3 PASSIVE SAMPLING*

A passive (diffusion) sampling operates by allowing gas or vapor molecules to diffuse through a defined volume of still air (or, less often, through a polymer membrane) until they reach a sorbent bed. Typically, the same sorbents are used in diffusive samplers as in pumped sorbent tubes, and again, the selection normally depends on the method of recovery (solvent or thermal desorption) and the method of analysis (GC, HPLC, etc.). The movement of gas is controlled by Fick's First Law, in which the rate of diffusion is a function of the concentration difference between the two ends of the diffusion path and the geometry of the path. The uptake rate of a diffusive sampler is related to the concentration at the sorbent surface. It is important for such technique to be properly validated before the results can be considered quantitative. In general, given a fixed geometry and a zero concentration at the sorbent bed due to adsorption or reaction, the mass collected is a function of the external concentration and the diffusion coefficient of the molecules. Because the diffusion coefficient varies in a known manner with temperature and pressure, the result has to be corrected for these parameters. Passive (diffusion) sampling is useful for determining gas concentrations where accumulated environmental exposure rather than short time resolution is required. The passive sampler has important advantages over conventional, active samplers - it is small and unobtrusive. The passive sampler is completely silent as it requires no pumps or electrical power. Passive samplers cost only a few dollars each. No professional instruction or monitoring is necessary; a single page of instructions is sufficient to show how a passive sampler should be used. The device is typically exposed in the field for one week. It is located in the field under a simple rain shelter. After exposure, samplers are returned to an analytical laboratory for analysis (they can be mailed back to the laboratory). Passive samplers have been developed for the assessment of some gases (e.g. $SO_2$, $NO_2$, formaldehyde, BTX, etc.).

## 5.3 AEROSOL SAMPLING

Aerosol is defined as a dispersion of solid or liquid particles in a gaseous media, where particle means a small discrete mass of solid or liquid matter. A classification of aerosols is often based on the thoracic fraction (it is defined as the mass fraction of inhaled particles which penetrate beyond the larynx). The Suspended Particle

Matter (SPM) is the notion of all particles surrounded by air in a given, undisturbed volume of air. SPM in the air is generally is a complex, multi-phase system of all airborne solid and low vapor pressure liquid particles having aerodynamic particle sizes from below 0.01-100 µm and larger. Historically, SPM measurement has concentrated on total suspended particulates (TSP), with no preference to size selection. Particulate matter is the material that represents particles with an aerodynamic diameter of 10 µm or less, or, more strictly, particles which pass through a size selective inlet with a 50% efficiency cut-off at 10 µm aerodynamic diameter. The class of fine particles includes particles with an aerodynamic diameter of 2.5 µm or less, or, more strictly, particles which pass through a size selective inlet with a 50% efficiency cut-off at 2.5 µm aerodynamic diameter. Ambient fine particulate matter consists basically of five species: sulfates, ammonium nitrate, organics, elemental carbon, and soil dust. Coarse mode is a size range of particles between 2.5 microns and 10 microns. The sum of the masses of coarse and fine particles (all particles smaller than 10 microns) is called PM10. Coarse particles are mostly composed of soils. Inhalable particulate matter is defined as particles with aerodynamic diameters smaller than about 10 micrometers, capable of being drawn into the human bronchial system (particles that are capable of being inhaled into the human lung). Larger particles tend to be filtered out in the upper respiratory tract. Aerosols may be characterized by:

- physical parameters (e.g. size distribution, shape, refractive index, concentration);
- chemical characteristics (e.g. qualitative and quantitative composition, acidity/alkalinity);
- temporal characteristics (chemical and physical characteristics changing with time);
- spatial characteristics (characteristics changing with location).

The collection of aerosols is based on:

- particles settling from the atmosphere (dustfall);
- dynamic (active) method of sampling.

### *5.3.1 DUSTFALL SAMPLING*

Dustfall (dust deposition) sampling has found application in the areas where nuisance dust (coarse particles) is a problem. It is used first of all to monitor deposition of particulate matter. In general, large particles that settle readily out of the atmosphere are collected by deposition. Particles larger than about 10 µm in diameter may be collected in this way, although this method is particularly effective for particles 100 µm 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. Particles settling from the atmosphere are collected via a funnel into a container. Deposit gauges to monitor the deposition of particulate matter are probably the earliest instruments used for air pollution measurement. For routine work they all fall into the same broad category of devices, namely a bowl or cylinder with horizontal, upward facing, collecting surface. The supporting wooden box provides stability and helps to keep the funnel level. The collectors are normally exposed for periods of up to a month. After a suitable exposure period, the collected sample is returned to the laboratory for analysis. The major drawback of dustfall sampling is that the presence of the deposit gauge introduces disturbance into the falling pattern of particles. Despite drawbacks, deposit gauges still have their uses, but in recent years greater attention is being paid to collecting dust samples with the aim of identifying and isolating nuisance sources, rather than for routine collection of data for statistical purposes.

### *5.3.2 DYNAMIC SAMPLING OF AEROSOLS*

Sampling system for a dynamic (active) sampling of aerosols must consist of:

- a sample inlet;
- a collection medium;
- a flow regulated pump.

#### Intake and transfer subsystem for aerosols

As a result of the discrete mass nature of the particles of an aerosol, the sampling of a representative sample of the aerosol requires special consideration. The most bothersome aspect of aerosol sampling is a result of the momentum of the particles. It is a product of its mass multiplied by its velocity. Components of an aerosol are iscrete mass particles, therefore they will be subject to inertial effects relative to the gas stream. Particles are much larger than gas molecules. For that reason, each time the flow direction of the gas stream changes, as at a bend in a pipe or in flow around an object, they tend to continue on their original line and are displaced somewhat from the original part of the gas stream. Figure 2 shows the pattern of the flow lines in the vicinity of a thin-walled sampling probe.

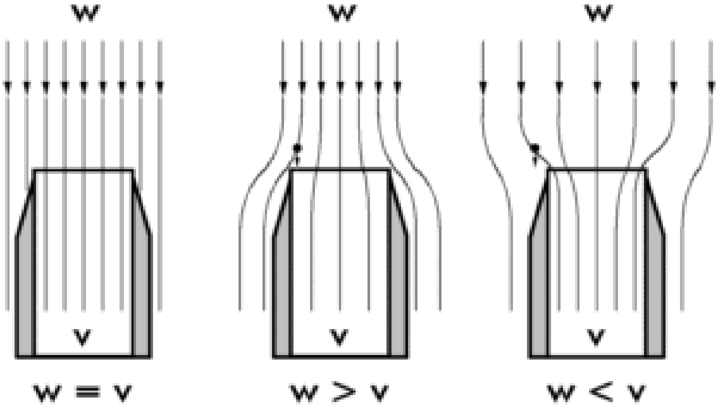


**FIGURE 2** Pattern of the flow lines in the vicinity of a thin-walled sampling probe.

In the case **w = v**, all particles flowing toward the intake opening are equally collected. This condition (w = v) is referred to as isokinetic (equal velocity) sampling. If the sampling velocity is less than the isokinetic rate (**w>v**), at first sight it would appear that the emission will be underestimated. However, because the sampling rate is too low, there is a divergence in flow around the sampling inlet. Small particles are able to follow the flow and a percentage of them will not be sampled. Larger particles, on the other hand, are not able to follow the flow because of their greater inertia and more of these particles will enter the sampler. Thus a sub-isokinetic sampling rate will lead to a bias in the sampled particle size distribution towards the larger particles. This could lead to an overestimation of the particulate concentration depending on the original size distribution. If the sampletaking velocity is too high (**w<v**), heavy particles fail to adhere to the flow lines and end up bypassing the probe. Additionally, sampling at a rate in excess of the isokinetic rate will lead to a bias in the sampled particle size distribution towards the smaller particles. This could lead to an underestimation of the emission concentration depending on the original size distribution. The error occurring in the case of *under*-isokinetic sampling (center) is many times larger than in the reverse case. To obtain a representative sample independent of particle size, it is necessary to remove the sample stream isokinetically. Isokinetic sampling refers to taking a sample under such conditions that there is no change in the momentum, so that the sample will be representative of the gases and aerosols in that portion of the sampled stream. Due to the wide range of particle sizes normally present in process emission streams, it is necessary to sample isokinetically to ensure that a representative sample of the particulate emission is obtained. Under isokinetic conditions, all particle sizes are collected efficiently. The attainment of isokinetic sampling conditions is fundamental to the collection of quantitatively representative aerosol samples, for which particle inertia is significant. The result of anisokinetic sampling will be inaccurate determination of total mass concentration of particles. In addition to this effect, an inaccurate particle size distribution will be obtained because of the relation of particle size to inertial effects. Small particle sizes, under 3μm diameter, do not require isokinetic sampling for efficient collection since their small mass minimizes inertial effects. This isokinetic method of sampling is accomplished by:

- using a thin-walled tube aligned with the stream flow;
- drawing sample into it at the same linear velocity as the stream flow at that point.

Sampling velocity and alignment are both important conditions of isokinetic sampling.

## The collection subsystem for aerosols

The collection subsystem for aerosols may incorporate:

- filtration;
- thermal or electrostatic precipitation;
- inertial and gravitational collection.

The capture of aerosol particles by filtration is the most common method of aerosol sampling. Filtration is a simple, versatile, and economical means for collecting samples of aerosol particles. The general requirements for aerosol sampling by filtration are:

- well-defined size fractions;
- filter media which are compatible with the intended analysis methods;
- sampled air volumes which are stable and provide sufficient deposit for the desired analyses without overloading the filter;
- sampling surfaces which do not react with the measured species;
- available, cost-effective, and practical sampling hardware and operating procedures.

Filtration for the collection of aerosols depends upon drawing the air sample through a network of small openings which may be formed from:

- the overlap of fibres as in fibreglass or cellulose filters;
- random pores with fixed media as in sintered glass filters;
- controlled sized pores in organic media as in membrane filters;
- random pathways through a granular medium.

The type of filter media chosen depends upon several factors:

- the collection efficiency required for a given particle size must be established;
- the pressure drop developed across the filter as the filter mat builds up must considered in assembling the overall sampling system;
- the background concentration of trace constituents within the filter media which might interfere with subsequent analysis must be determined;
- the chemical and physical resistance of the filter media to the particular air environment to be sampled must be considered;
- the hygroscopic properties of the filter media are important when the humidity of the air to be sampled cannot be controlled.

A wide spectrum of filters, with markedly different physical and chemical properties, is available commercially for aerosol measurement applications in a variety of filter materials, pore sizes, and collection characteristics, as well as a variety of shapes such as discs and sheets sized to fit commonly available filter holders. Probably the most common method of sampling particulate pollution is by collecting it on filter paper (cellulose filters) by drawing a sample through a filter which is held in a clamp. Selection of the filter paper depends on the characteristics of the matter to be measured and the method of analysis. Glass fibre filters offer less resistance to gas flow than cellulose filters. Thus, more particulate matter is collected on the surface of the filter than is the case with cellulose. The advantage of glass fibre filters is that they can withstand higher temperature (up to 800°C) than cellulose (250 to 300°C) and vaporization of the carbonaceous content of the sample may be an important means of improving analytical resolution. One serious disadvantage of glass fibre filters is that they are rather fragile and extreme care should be taken when using them for gravimetrics to ensure that the fibres do not break away in handling, particularly after being clamped into sampling apparatus. Cellulose and glass fibre filters of suitable porosity will be appropriate for routine determination of the total mass of particulate pollution. If subsequent chemical analysis is required, the background contamination from these filters should be checked before sampling if subsequent sensitive analytical work is to be carried out. For microscopic work, cellulose and glass fibre filters are unsuitable, because the particulate matter tends to become trapped amongst the fibres of the filters, and thus membrane and nucleopore filters are preferable. Membrane filter is defined as a thin filter, usually made of a synthetic polymer, with microscopic holes in it. Particles are collected only on the surface facing the air flow. Membrane filters are mostly prepared from one of several cellulose esters and the pore size of the filters can be controlled by the manufacturing process. These filters may be used to trap particles down to far less than 0.1 μm in diameter. Membrane filters can be made transparent for microscopic work. In addition, samples may be prepared for electronic microscopy. One of the main drawbacks of membrane filters is that they have a high resistance to air flow and tend to brittle if flexed. In practice, it is therefore advisable to support them by means of porous carbon plate or very fine stainless steel mesh. Nucleopore filters are polycarbonate sheet which has been irradiated by neutrons and etched to give pores of constant dimensions. The mechanism of filtration of suspended particles is a product of several processes including impaction, diffusion precipitation and electrostatic attraction. Hence, efficiency is a complex function of many variables, including pore size, particle size, face velocity and filter loading. In general, membrane and Nucleopore filters are more efficiency than cellulose and glass fibre, and of the former the membrane filter is generally better. Membrane and Nucleopore filters have very low ash content and low levels of background impurities and are thus ideal for more sophisticated analytical work. In most cases the filter medium is provided as a thin sheet which must be mounted in a filter housing to provide structural support. Several types of screen and mesh supports are commercially available. The support material must be consistent with the sampling task and should not react with any of the constituents which could conceivably be present in the air sample. After the sampling is completed, the particulate mass on the filter is determined gravimetrically or by chemical analysis.

Precipitation for the collection of aerosols depends upon exposing the air stream to either a thermal or electrostatic gradient. In the case of thermal precipitation, a sharp temperature gradient is created by a high temperature wire suspended across a cylindrical collection chamber. A thermal precipitator removes particles from an aerosol by passing it through a relatively narrow channel having a significant temperature gradient perpendicular to the direction of the flow. The basic instrument is limited to a relatively low flow rate (ranging from 7 $cm^3$/min to 1.0 l/min). The temperature gradient causes the particles to migrate towards the cooler collecting surface, apparently because molecules of gas migrate around suspended particles from the cooler region to the warmer region, causing the particles to move toward the cooler region by reaction. The movement of a particle in the direction of decreasing temperature, called its thermophoretic velocity, causes the particle to deposit on a collecting surface appropriate to the type of subsequent evaluation. The device is extremely efficient for particle sizes from 5 μm down to 0.01 μm and possibly smaller. It means that thermal precipitators collect virtually all particles from 5 μm down to 0.01 μm and probably smaller with high collection efficiency, provided that a sufficient thermal gradient is established in the sampling region. The very high efficiency of collection of sub-micron particles and the little effect of the degree of charge on the particle on the collection efficiency are important advantages of thermal precipitators. However, the low sampling rate of thermal precipitators (ranging from 7 $cm^3$/min to 1.0 l/min) is unsuitable for some applications. Another disadvantage is that many relatively volatile aerosols could not be collected in a thermal precipitator because of the possibility of evaporation in the vicinity of the heated surface. Finally, the standard thermal precipitator is bulky and has rather poor size selection characteristics for separating distinct aerosol size fractions. The thermal precipitator is recommended primarily for specialized research studies where efficient collection of particles for microscopic investigations is required, but not for general aerosol sampling usage. Electrostatic precipitation differs from other particle collection mechanisms in that electrical forces rather than inertial or thermal are used to separate the particles from the gas in which they are suspended. The collection of a particle by electrostatic precipitation involves two separate and distinct operations. First, the particle must acquire electric charges. Second, the charged particle must be accelerated toward an electrode of opposite polarity by the electric field. Particles can acquire electric charges by several mechanisms; however, for speed, efficiency, and controllability of the charging process, the high voltage corona discharge is used. In the case of electrostatic precipitation, a high voltage potential (12 kV d.c. or 20 kV, a.c.) is maintained across the plates of a capacitor with the air to be sampled flowing between the capacitor plates. The ionizing potential created by electrostatic field produces ions in the gas stream which, in turn, tend to collide with particles and charge them. The charged particles then migrate under the influence of the electrostatic field to collecting electrode. The collection efficiency of an electrostatic precipitator sampler is dependent on the operating parameters, e.g. current, voltage, and flow rate; the particle parameters, e.g. particle size, shape, dielectric properties, and mass loading; and the carrier gas parameters, e.g. humidity, ambient pressure, temperature and composition. Collection efficiency is increased by high charging currents, high voltage gradients, and low flow rates. For particles > 0.5 μm diameter, the charging, and hence the collection efficiency, is strongly dependent on the potential gradient in the charging field; whereas for smaller particles, the charging current, i.e. the number of air ion charge carriers, is more significant. Electrical force is exerted directly on the particles instead of on the whole gas volume; thus, relatively little power is required to precipitate the particles or to move the gas steam through the collector. Electrostatic precipitator samplers have two significant advantages over filter samplers:

- the sampling rate is not affected by mass loading;
- the sample is in a readily recoverable form.

This device has been found to be virtually 100% efficient for a wide range of particle sizes. This device collects at a high efficiency with relatively little physical disruption of the particles. Precautions must be observed to avoid excessive voltage, as direct arcing across the plates may occur and sampling efficiency will drop to nil. Additionally, re-entrainment of particles from the collection surface may occur as a result of high voltage sparking. This effect is strongly dependent on the air velocity. It is a disadvantage where large particles are more easily re-entrained than smaller ones. Also, the device is clearly unsuitable for the use in explosive atmospheres.

Inertial and gravitational collection depends upon the action of an external remote force on the aerosol particles to cause their movement toward a collecting surface. In contrast to the filters that generally collect particles of all sizes, these instruments distinguish between particle sizes. They are used for size-selective sampling or size-segregated aerosol collection of airborne particles depending on the aerodynamic diameter of the particle. Inertial and gravitational collectors include:

- impactors;
- cyclones;
- aerosol centrifuges;
- impingers;
- elutriators.

Impaction is a forcible contact of matter particles. A term often used synonymously with impingement. The term impactor encompasses a large class of aerosol collection instruments for which particle impaction in a non-rotating flow is the primary mechanism of particle capture. The air carrying particles passes through a nozzle and impaction occurs when streamlines bend as the air flow bypasses a solid object (i.e. a collection plate) perpendicular to the nozzle axis. Particles larger than the cut-size of the impactor will slip across the streamlines and impact upon the plate while smaller particles will follow the streamlines and penetrate the impactor stage to be either collected on a filter or passed into some other instrument for real-time mass or number concentration measurement. The dependence of the particle size collection efficiency on jet velocity has been used to advantage in the design of cascade impactors. These are devices which use a series of sequential jets and collection plates with increasing jet velocities and/or decreasing gaps between the jet and the collecting plate.

Each impactor stage consists of one or more jets followed by a collection plate and successive stages are designed to collect smaller particles. As the air stream progresses through the device, smaller particles will be collected more efficiently. Those particles which penetrate all the impaction stages are collected by a final absolute filter. As a result, the cascade impactor fractionates the air sample to obtain a particle size distribution. The size collected by any individual stage depends upon the jet diameter and the air stream velocity in the jet as well as the distance to the impaction surface. Therefore, the collection of smaller particles in subsequent stages is achieved by using a combination of smaller diameter jets, higher jet air velocities, or decreased distance to the impaction surface. Generally, inertial impactors can be used over a wide range of conditions. The major limitations to impactors when considering their use are particle bounce from the collection surface and re-entrainment because of the continuous blowing of the jet on the particle deposit. The large agglomerated particles will shatter upon impinging on the collecting plate and may resuspend giving an inaccurate size distribution. However, this is minimized by using a sticky surface on the impaction plate, e.g. numerous types of greases and oils. Furthermore, overloading of collected particle deposits on the impaction plates and inter-stage losses are other limitations. Because traditional impactors do not provide much size resolution for sub micrometer particles, micro-orifice and low-pressure impactors have been developed to obtain smaller cut-point diameters as small as 0.05 µm. Low-pressure impactors resemble ordinary impactors but operate at reduced pressures of 5 to 40 kPa (0.05 to 0.4 atm). Micro-orifice impactors operate closer to atmospheric pressure (0.8 to 0.9 atm) but employ very small orifices (40 to 200 µm in diameter) and the number of nozzles is large to obtain an adequate flow rate. Virtual impactors and inertial spectrometers are two special types of impactors. Impaction of particles on stagnant air rather than a solid plate is a characteristic feature of virtual impactors. A virtual sampler is one in which particle size separation is accomplished by impaction into an air stream of differing velocity rather than onto an impaction surface. Virtual impactor is very similar to a conventional inertial impactor, with the primary difference being that the impaction plate has been replaced by a collection probe below the impactor jet in order to avoid any errors due to particle bounce or re-entrainment. Dichotomous samplers are often classified as virtual impactor instruments. These devices are defined as any particle samplers that separately collect coarse (2.5-10 µm) and fine particles (<2.5 µm) from one atmosphere. Inertial spectrometer, on the other hand, provides particle size distribution information on one stage rather than several stages as in the cascade impactor dependent on particle aerodynamic diameter and air velocity. The inertial spectrometer provides aerodynamic separation for particles in the size range of 1-10 µm, where it uses filtration for particle collection and is not susceptible to particle bounce sampling errors.

Impingement is an act of bringing matter forcibly in contact. As used in air sampling, impingement refers to a process for the collection of particulate matter in which the gas being sampled is directed forcibly against a surface. Impingement for the collection of aerosols consists of forcing the air flow through a jet which increases the velocity of the air stream and thereby the momentum of associated particles, followed by the collision of the air stream with an abrupt obstruction. The particles will tend to collect on the obstruction by reason of their high momentum and the abrupt change in flow direction necessitated by the obstruction. Impingers utilize inertial properties of particles to effect collection and operate much like impactors, except that the sampled air stream jet is immersed in water at the bottom of a flask. Because the impinger uses particle inertia for collection and that, in turn, depends upon the mass and velocity of the particles, the size collection efficiency of impingers depends on the flow rate. The sampled air stream is accelerated in the impinger orifice to the velocities of 60 m/s or greater. The air stream exits underneath the liquid surface immediately above an impaction plate or at a specified distance above the bottom of the collection flask. Particles impinge on the plate or flask bottom, stop, and are subsequently retained by the liquid. Impingers are effective for the collection of particles in the 1 µm to 20 µm size range. The lower size collected depends on jet velocity and diameter. The upper size collected by impingers is limited because large particles cannot follow the air stream into the impinger. In the case of centrifugal collection, the air stream is made to follow a spiral pathway in a sampler, with the resulting centrifugal action on the particles causing them to move outward to a collecting surface. Cyclones use centrifugal forces for particle collection and utilize a vertical flow inside a cylindrical or conical chamber. Particles with sufficient inertia are unable to follow the air streamlines and impact onto the cyclone walls. The particles are either retained on the cyclone walls or migrate to the bottom of the cyclone cone, while finer particles remain entrained in the air during the upwards spiral. Aerosol sampling cyclones both in the workplace and in ambient air are small, typically 1 cm to 5 cm in diameter, operating at flows as small as a few liters per minute. In most cases, cyclones are used to provide a particle precut to another aerosol collector such as a filter or an impactor. Respirable particle sampling is one of the most common applications of cyclones, wherein the cyclone is operated upstream of a filter. The cyclone is used to remove the larger, non-respirable particles such that the material collected on the filter is representative of that which penetrates into the non-ciliated deep lung spaces of humans. Cyclones are also used in ambient air sampling to separate the coarse mode aerosols (particle diameters > 2 μm) from the fine mode aerosols (particle diameters < 2 μm). The collection efficiency is dependent upon the particle aerodynamic diameter and the cut-size of the cyclone is governed by the flow rate, the size of the inlet and outlet tubes, the gas viscosity, and the size of the cylinder. Cyclones have several advantages in air sampling including their large capacity for loading and insensitivity to orientation. Furthermore, they have relatively low cost of construction, easiness of operation, and are easily maintained. Unlike impactors, they are not subject to errors due to particle bounce and re-entrainment and do not require special collection surface coatings. However, the flow pattern inside cyclones is complex and not easily modeled; thus, it is not easy to predict cyclone performance without reference to empirical correlations. In the case of gravity collection, the gravitational attraction of the particle mass towards the earth causes particles to settle at a rate dependent on the fluid drag forces counteracting gravity. For smaller particles, the settling rate is small in relation to air movements with the effect that small particles remain suspended. Elutriators use gravitational settling in a laminar flow to separate particles by aerodynamic diameter. They provide segregation for particles greater than 3 μm. Two types of elutriators, vertical and horizontal, are available. The vertical elutriator consists of a vertical duct through which air flows slowly upward. Particles whose sedimentation velocity is greater than the duct velocity cannot follow the air flow and settle out. The ability of the device to distinguish particle sizes is reduced by the distribution of velocities in the duct; nonetheless, it is an effective method for removing large particles. One example of vertical elutriators is the cotton dust sampler designed for the sampling of particles below 15 μm using a flow rate of 7.4 l/min. In a horizontal elutriator, aerosol is passed slowly along a horizontal channel. Particles settle onto the bottom of the flow channel at locations dependent upon the particle size, particle density, gas velocity, and channel height. The larger aerodynamic particles settle near the entrance while the smaller particles are deposited near the exit. Two devices that incorporate this technique for particle classification are the horizontal elutriator used for respirable dust sampling, e.g. Hexhlet horizontal elutriator and the Timbrell aerosol spectrometer. Their main advantage is the predictable performance based on gravitational settling of the particles during passage between horizontal collecting plates. Disadvantages include the restriction to a fixed orientation (wind-dependent), possible re-entrainment of particle deposits and the difficulty of miniaturization. Aerosol centrifuges refer to a class of aerosol samplers that spin at high velocity in order to subject particles to large centrifugal force which is used to deposit the particles on the outer edge of an aerosol chamber. Although several centrifuges have been developed, spiral centrifuge is the one that has seen the greatest application. Generally, the particles are collected on a foil which lines the outer wall of the channel and is removed for particle analysis after collection where the deposition distance along the foil is directly related to the aerodynamic diameter of the particle. The resolution of the centrifuge depends on the ratio of the aerosol sampler flow rate to the total flow rate and the overall particle classification may be achieved within the range $0.01 < d^{ae} < 5$ µm at sampling flow rates up to about 1 l/min. Conventional aerosol centrifuges can be easily calibrated and provide exceptionally high particle size resolution but generally operate at relatively low sample flow rates (usually less than 1 l/min). At such low sample flow rates, the amount of particulate material collected at any given part of the instrument is too small to be assessed gravimetrically and also substantial biases to the particle aerodynamic size distribution may be expected at such a low sampling flow rate. For particles greater than a few micrometers, most centrifuges are subject to inlet losses. However, in contrast to impactors, particle bounce is not a problem because centrifugal force holds the particles tightly to the collection surface.

Both collection methods (gravity and centrifugal) are limited to larger particles than are collected by other collection subsystems, with their use aimed primarily at preliminary separation of larger particles before a secondary collector.

### Ambient aerosol collection

Isokinetic sampling of atmospheric aerosol is defined as a technique for collecting airborne particulate in which the sampling device has a collection efficiency of unity for all sizes of particles in sampled air, regardless of wind velocity and direction of the instrument. The air stream entering the collector has a velocity (speed and direction) equal to that of the air in gas stream just ahead of the sampling port of the collector. High volume methods are used in TSP, $PM_{10}$, $PM_{2.5}$, air toxics samplers. Low volume methods are used for the determination of $PM_{10}$, $PM_{2.5}$, $PM_{coarse}$. Sampling of particulate matter pollutants (PM) in the ambient air has traditionally been performed via gravimetric means over a 24-hour period using a manual, volumetric, filter-based air sampler (a “Hi-Vol”). It is based on the following formula:

$$\frac{Gross - Tare}{Air\ Volume}\left[\frac{mg}{m^3}\right]$$

With this device, a constant volumetric flow rate of ambient air is drawn through a pre-weighed glass fibre filter. PM is trapped on the filter as the air passes through. The total air volume over the 24-hour period is measured, and the mass of particles caught on the filter is later determined by weighing the filter with PM on it and subtracting the clean filter weight. The mass of PM is then divided by the air volume to determine the average mass concentration of PM in the air during that 24-hour period. The sample inlet defines the size range of the particles collected. In broad terms, the normal size ranges sampled are TSP, PM10 or other fractions of TSP. In practice, most TSP inlets in fact have a particle size cut-off limit, which may or may not be well defined. In the PM10 method, a particle size classification head is attached to a Hi-Vol sampler so that only particulates with an aerodynamic diameter smaller than 10 μm are collected on the filter. PM10 sample inlets are generally based on a limited number of commercial designs, whose characteristics have been well defined in wind tunnel and ambient field tests. TSP sample inlets generally operate with high ($100m^3$/hr), medium ($\approx 10$ $m^3$/hr) or low flow rates ($0.083m^3$/hr). Commercial PM10 sample inlets are available for high, medium and low volume samplers. Recently, specific PM2.5 sampling heads have become available for commercial low volume samplers. The PM2.5 inlets, and quality assurance procedures are much more demanding than those used for the old total suspended particulate test, but the fundamental principle (gravimetric methods to determine a time-averaged concentration) remains the same. At present, fine particulate material like PM5, PM1 or PM0.5 is generally determined by cascade impactors with high or low flow rates. To ensure correct operation, all sample inlets and sample lines, especially size selecting inlets, require regular maintenance (for example cleaning of sample lines and greasing of some inlets) in accord with the manufacturers instructions. Advantages of gravimetric ambient aerosol sampling techniques: recognized reference method, low capital cost. Disadvantages of gravimetric ambient aerosol sampling techniques: limited time resolution (typically 24-hr), long turnaround times, labor intensive, and gravimetric lab maintenance/cost.

### Emission source aerosol collection

In emission source aerosol sampling, it is crucial to collect a representative sample of airborne pollutants before emission to atmosphere and dilution by air. It is not simple task, because there is no simple method to cope with the variable and complex nature of source emissions. Selection of an appropriate sampling method should be based on such factors as:

- the chemical composition of the compounds emitted;
- he expected concentration range;
- the chemical and physical properties (boiling point, reactivity, solubility etc.);
- the characteristics of the discharge (temperature, moisture etc.).

Samples must be collected using a calibrated probe and a sampling train. Particulate samples are collected via a probe in the duct at each of the flow-measuring points and the sampling rate adjusted to provide isokinetic sampling. The probes used for collecting particulate samples, using isokinetic collection, require a larger size of sampling port than which is needed for the collection of gaseous samples. Suction to the probe is provided by a suitable gas mover e.g. vacuum pump. This device draws the particulate-laden gas through the selected nozzle and through the filter medium in suitable holders, usually of the "quick-release" type with fiberglass filter support pads. The sampling train usually includes a dry-gas meter to indicate the total volume of gas sampled from "before" and "after" readings. This can be used to check against the calculated flow derived from nozzle flow rate and time. An electronic flowmeter may also be used to give a gas flow rate (litres/minute) and when this is multiplied by the sampling time, the total amount of gas sampled can be calculated. The sampling line is also equipped with a temperature measuring device (thermometer, thermocouple or thermistor) and vacuum gauge. These devices are necessary for the checks on sampling temperature and pump pressure. After the required sampling is completed, the filters with their load are transported in their designated containers for gravimetric and other analyses. Even when precautions are taken there can be several reasons why the sample is not truly representative. The probe always has a finite wall thickness that disturbs the flow. The point sampled may not be representative of the whole gas stream. If the flow is turbulent at the point of sampling it is not possible to obtain a truly isokinetic sample. The sample will contain a smaller portion of the larger particles, or the sample may be lost by deposition or changed by agglomeration in the sample line before it reaches the collection filter. The documentation concerning sampling should include information about:

- time and date;
- sample location;
- sample collection rate;
- sample pressure;
- sample temperature;
- dew point;
- plant operating conditions;
- flow rates and variability;
- production rates and variability;
- pressures;
- temperatures.

## 5.4 DETERMINATION OF SAMPLE FLOW

Sample volume is an essential parameter in the determination of ambient air pollutant concentrations. In practice, when measuring air pollutant concentration, the air volume that is sampled together with the targeted components is also determined. Any attempt to measure accurately the concentration of a given constituent is fundamentally dependent upon the accurate knowledge of the original gas volume relationship with the sample being analyzed. The sample flow measuring devices generally fall into two classes:

- volume meters;
- rate meters.

Volume meters measure the total integrated volume which has passed through them for a given period of time. They have the advantage of providing a direct record of the volume of gas sampled. The common types of volume meters that are available are:

- the dry test gas meter;
- the wet test gas meter;
- the cycloid gas meter.

The dry test meters are most commonly used because of their relative sturdiness, low cost and weight, in comparison with the latter two meters. They measure volume flow by mechanical displacement of internal bellows by the air flow. The displacement is recorded on a mechanical counter via a series of levers. The properly maintained and calibrated unit is considered accurate to 1%.

Rate meters measure the instantaneous volume flow rate through the sampling system. This rate multiplied by the sampling time gives the total volume sampled. The volume flow rate is typically obtained by measuring the velocity of a fluid in a duct or pipe and multiplying it by the known cross-sectional area (at the point of measurement) of that duct or pipe. The advantage of rate meters is their relatively small size in comparison to the bulky dry test gas meter. The disadvantage of these devices is that frequent checks are required to ensure accurate calculation of the total volume sampled. The common types of rate meters that are available include:

- orifice meter;
- Venturi meters;
- flow nozzle meters;
- Pitot tubes;
- rotameters;
- hot wire anemometers;
- turbine anemometers;
- ultrasonic flow sensors.

Orifice plate meters, Venturi meters, flow nozzle meters and Pitot tubes are the differential pressure flow devices. All of these sensing elements are combined with a low differential pressure transmitter to produce a signal that is proportional to the square root of the fluid velocity. Sensor manufacturers offer a wide variety of application specific sensors used for airflow and pressure measurements. To understand orifice, nozzle and Venturi meters it is necessary to explore the Bernoulli equation. In flow metering devices based on the Bernoulli equation, the downstream pressure after an obstruction will be lower than the upstream pressure before the obstruction. The critical orifice is a simple metal hole inserted downstream of a sampling device and upstream of the sampling pump (Fig. 3).

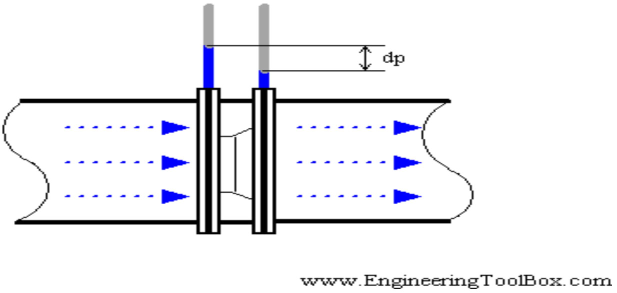


FIGURE 3 A critical orifice.

The Venturi meter device operates by gradually narrowing the diameter of the pipe, and measuring the resultant drop in pressure (Fig. 4). An expanding section of the meter then returns the flow to very near its original pressure. As with the orifice plate, the differential pressure measurement is converted into a corresponding flow rate. The Venturi meter provides the highest accuracy with the smallest pressure loss, but is more expensive and requires more installation space than either the orifice or flow nozzle meters. The Venturi tube applications are generally restricted to those requiring a low pressure drop and a high accuracy reading. They are widely used in large diameter pipes. These devices may be adapted to provide continuous flow recording.

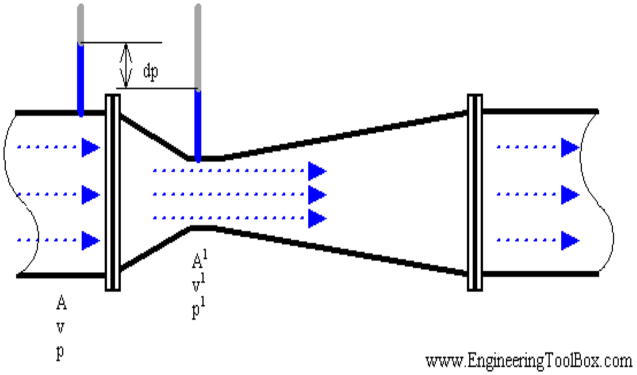
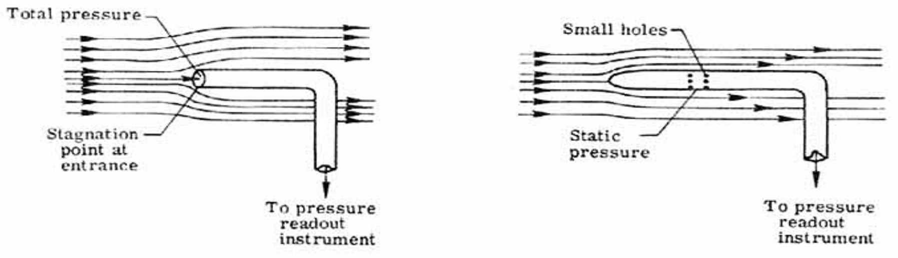


FIGURE 4 A Venturi meter device.

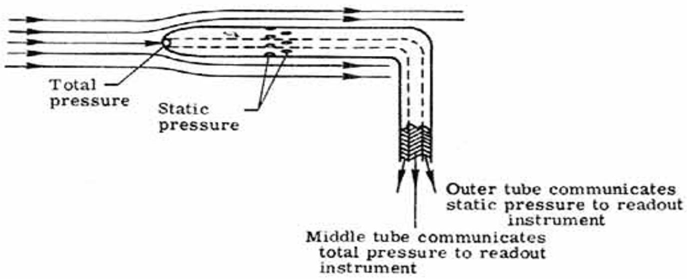
Flow nozzles may be thought of as a variation on the Venturi tube. The nozzle opening is an elliptical restriction in the flow but with no outlet area for pressure recovery. Pressure taps are located approximately 1/2 pipe diameter downstream and 1 pipe diameter upstream. The flow nozzle is a high velocity flow meter used where turbulence is high (Reynolds numbers above 50,000) such as in steam flow at high temperatures. The pressure drop of a flow nozzle falls between that of the Venturi tube and the orifice plate (30 to 95 percent).

The differential pressure flow devices in common use include Pitot tubes (Fig. 5).



(a) Pitot tube.

(b) Static tube.



(c) Pitot-static tube.

FIGURE 5 A Pitot tube.

The signal generated in this instrument can be related to the flow according to the following equation:

$$velocity = C\sqrt{\frac{2VP\,g_c}{\rho}}$$

where Velocity – velocity of fluid; P - pressure; ρ - density of fluid; $g_c$ - gravitational constant; C - unit conversion factor. As a permanently mounted sensor, the Pitot tube is limited to small ducts and applications with low accuracy requirements due to the need to sense the velocity at more than one point to achieve reliable measurements in larger ducts. The need to sense multiple points in the cross section of a duct gave rise to averaging type sensors with arrays of pressure sensing points. Once the velocity is obtained, the flow can be calculated by multiplying by the cross-sectional area of the duct. Velocity range is limited by the range and resolution of the pressure transmitter used. Maximum velocity is only limited by the durability of the sensor.

Vortex shedding flow meters operate on the principle (Von Karman) that when a fluid flows around an obstruction in the flow stream, vortices are shed from alternating sides of the obstruction in a repeating and continuous fashion. The frequency at which the shedding alternates is proportional to the velocity of the flowing fluid. Differential pressure type flow meter has advantages of simple structure, low cost, lots of experiences at the fields, many studies of the devices (proven performance), and standardization. On the other hand, it has disadvantages of relatively large error, permanent pressure loss (energy loss), and block with slurry or particles.

A rotameter is a device based on the principle of Stoke's law, for measuring the rate of the fluid flow. It consists of a tapered vertical tube typically made of glass or plastic, with a float inside that is pushed up by flow and pulled down by gravity. At a higher flow rate more area (between the float and the tube) is needed to accommodate the flow, so the float rises. The flow section is graduated in arbitrary units. By means of calibration, the flow value of the arbitrary scale is established and the flow is then indicated by noting the level of the float on the scale. Glass rotameters are preferred when sampling for reactive gases or vapors. The rotameter is popular because it has a linear scale, a relatively long measurement range, and low pressure drop. It is simple to install and maintain. A rotameter requires no external power or fuel, it uses only the inherent properties of the fluid, along with gravity, to measure flow rate. Due to its use of gravity, a rotameter must always be vertically oriented and right way up, with the fluid flowing upwards. Due to its reliance on the ability of the fluid or gas to displace the float, the graduations on a given rotameter will only be accurate for a given substance.

“Hot Wire” or thermal anemometers operate on the principle that the amount of heat removed from a heated temperature sensor by a flowing fluid can be related to the velocity of that fluid. They utilize the dependence of the convective cooling rate of a hot wire on the velocity of gas flow past the wire to determine flow velocity and thereby flow rate. Hot wire sensors are available as single-point instruments for test purposes, or in multi-point arrays for fixed installation. These devices are better at low airflow measurements than differential pressure types.

Mass flowmeter is a device that measures the mass flow rate of air passing a point, usually using the rate of cooling or heat transfer from a heated probe.

Mass flow controller (MFC) is a device used to measure and control the flow of gases. It is designed and calibrated to control a specific type of gas at a particular range of flow rates. The MFC can be given a setpoint from 0 to 100% of its full scale range but is typically operated in the 10 to 90% of full scale where the best accuracy is achieved. The device will then control the rate of flow to the given setpoint. Mass flow controllers require the supply gas to be within a specific pressure range.

Turbine and propeller type meters operate on the principle that the fluid flowing through the turbine or propeller will induce a rotational speed that can be related to the fluid velocity. These devices are commonly used where good accuracy is required for critical flow control or measurement for energy computations.

Ultrasonic flow sensors measure the velocity of sound waves propagating through a fluid between two points on the length of a pipe. The velocity of the sound wave is dependent upon the velocity of the fluid such that a sound wave traveling upstream from one point to the other is slower than the velocity of the same wave in the fluid at rest. It means that the downstream velocity of the sound wave between the points is greater than that of the same wave in a fluid at rest. This is due to the Doppler effect. The flow of the fluid can be measured as a function of the difference in time travel between the upstream wave and the downstream wave. Ultrasonic flow sensors are non-intrusive and are available at moderate cost. Many models are designed to clamp on to existing pipe. Ultrasonic Doppler flow meters have accuracies of 1 to 5% to the flow rate.

## 5.5 SAMPLE HANDLING AND CUSTODY

A critical activity within any measurement involving sampling is:

- the handling of sample media prior to sampling;
- handling/transporting sample media to the field;
- handling samples from the field at the time of collection;
- storage of samples (at field or other locations);
- transport of samples from the field site to the analytical laboratory for analysis.

Documentation ensuring that proper handling has occurred throughout these activities is part of the custody record, which provides a mechanism for tracking samples through sample collection, processing and their transport.

# 6 METHODS AND TECHNIQUES OF AIR POLLUTANT ANALYSIS

## 6.1 METHODS AND TECHNIQUES OF GASEOUS POLLUTANT ANALYSIS

A wide range of analytical methods and techniques have been reported for the analysis of each type of air pollutants (sulfur dioxide, nitrogen oxides, carbon monoxide, ozone, hydrocarbons, particulate matter). The choice is determined by the requirements of:

- sensitivity;
- selectivity (the avoidance of chemical interferences);
- concentration range.

### *6.1.1 ELECTROCHEMICAL METHODS OF ANALYSIS*

Electrochemical methods are a branch of analytical chemistry concerned with the relation between electricity and chemical change. The aggregate of the methods of qualitative and quantitative analysis based on electrochemical phenomena occurring within a medium or at the phase boundary and related to changes in the structure, chemical composition, or concentration of the compound being analyzed. In electrochemical methods of detection, either the current or the potential is measured during an electrochemical reaction. The gas or liquid containing the trace impurity to be analyzed is sent through an electrochemical cell containing a liquid or solid electrolyte and in which an electrochemical reaction specific to the impurity takes place. These methods are divided into five major groups:

- potentiometry;
- voltammetry;
- coulometry;
- conductometry;
- dielectrometry.

Potentiometry combines the methods based on the measurement of the electromotive force (EMF) reversible electrochemical circuits, when the potential of the working electrode is close to the equilibrium value. In general, the electromotive force is the maximum potential difference between two electrodes of a galvanic or voltaic cell. This quantity is related to the tendency for an element, a compound or an ion to acquire (i.e. gain) or release (lose) electrons. In this method, the potential of a cell is related to the concentration (activity) of a reactant which is a component of the cell fluid. This method includes redox titration, ionometry and potentiometric titration. Voltammetry is based on the study of the dependence of polarization current on the voltage applied to an electrochemical cell when the potential of the working electrode differs significantly from the equilibrium value. Voltammetry, with its variety of methods, constitutes the largest group of electrochemical methods of analysis and is commonly used for the determination of compounds in solutions and melts (for example, polarography and amperometry). Amperometry is a detection method in which the current is proportional to the concentration of the species generating the current. Coulometry combines the methods of analysis based on the measurement of the amount of material deposited on an electrode in the course of an electrochemical reaction in accordance with Faraday’s laws. Coulometry is the method in which the current is directly proportional to the flow rate of the substance involved in the electrochemical reaction, and the amount of charge which flows is proportional to the amount of substances taking part in the reaction. In this method, the potential of the working electrode differs from the equilibrium value. A distinction is made between coulometry at constant potential and coulometry at constant current. The latter includes both direct and indirect methods: electroanalysis, and coulometric titration. Conductometry encompasses methods in which the electrical conductivity of electrolytes (aqueous and nonaqueous solutions, colloid systems, melts, and solids) is measured. In the conductometry, the quantity of a substance present in a mixture is determined by the measurement of its effect on the electrical conductivity of the mixture. These methods are based on the change in the concentration of a compound or the chemical composition of a medium in the interelectrode space. It is not linked with the electrode potential, which is usually close to the equilibrium value. Conductometry includes both direct analytical methods (used, for example, in salinometers) and indirect analytical methods (for example, in gas analysis) using either direct or alternating current (low-or high-frequency current). It also includes chrono-conductometry and low-frequency and high-frequency titration. In practice, conductive analyzers of air pollutants sense the change in the electrical conductivity of a liquid reagent after reaction with the sample gas. Dielectrometry combines analytical methods based on the measurement of the dielectric constant of a substance resulting from the orientation of particles (molecules or ions) that have a dipole moment in an electric field. These methods are used to monitor the purity of dielectrics, for example, to detect small amounts of moisture. Dielectrometric titration is used to analyze solutions.

The gas dissolution conductometric method is used to determine the concentration of sulfur dioxide by allowing a hydrogen peroxide solution acidified by sulfuric acid to absorb sulfur dioxide in the sample gas (so that it becomes sulfuric acid) and then measuring the increase in conductivity due to this sulfuric acid. This method can be used to continuous measurement of $SO_2$ concentration in a sample of ambient air (Fig. 6). This method is applicable when the measurement is negligibly affected by those gases which are dissolved in the absorbent causing the conductivity change, e.g. chlorine, ammonia and carbon dioxide, or when the affection to the measurement by these gases can be removed. The response speed is slow.

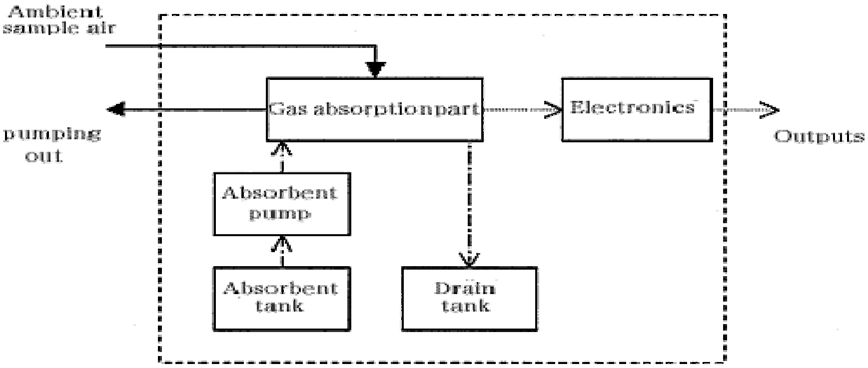


FIGURE 6 An example of conductimetric $SO_2$ analyzer.

Coulometry can be used for continuous measurement of $SO_2$, $H_2S$, $NO_2$ and the total oxidant concentration contained in the sample of ambient air. For example, this method allows to measure continuously the concentration of sulfur dioxide in ambient sample air detecting with the electrodes the change of bromine concentration decreased by the reaction of $SO_2$ in ambient sample air and bromine which is dissociated in the electrolyte of potassium bromide by electrolysis (Fig. 7). When the sample air is sent to an electrolyte containing a certain concentration of bromine at a given flow rate, the bromine is consumed in a reaction with hydrogen sulfide. The quantity of electricity required to replenish the consumed bromine by electrolysis is proportional to the concentration of hydrogen sulfide. The concentration of hydrogen sulfide in the sample air is also determined based on this quantity of electricity.

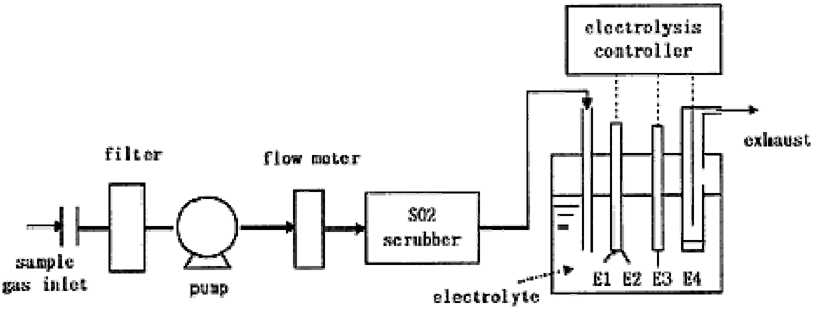


FIGURE 7 A coulometry analyzer for $H_2S$ measurement.

Potentiostatic electrolysis method can be also used for determination of nitrogen oxides. The NO and $NO_2$ which have been dispersed and then absorbed in electrolyte through a gas-permeable diaphragm are electrochemically oxidized on an electrode which is maintained at a constant potential. The electrolytic current generated during this oxidation is used to continuously measure the concentration of $NO_x$ in the sample gas. The analyzer using this method can be designed to be smaller and lighter, making itself suitable for portable use. Since the interference of $SO_2$ and $H_2S$ is large, another method is available, in which the measurement is performed after this interference is eliminated with an $SO_2$ scrubber. The electrode has a limited service life, requiring periodical replacements. In the case of the continuous measurement of the total oxidant concentration, absorbing solution (neutral potassium iodide solution) is used. When the sample ambient air and absorbing solution is made contact with constant flow rates, iodine proportional to the total oxidant concentration in the absorbing solution is liberated. This iodide shall be reduced electrolytically in the absorption solution and the total oxidant concentration in the sample ambient air shall be obtained from acquired coulomb.

The amperometric oxygen sensor is often referred to as a Clark Cell. This is basically an amperometric cell that is polarized around 800 mV. This cell, named after Dr. Clark, is built around the popular Ag/AgCl half-cell and a noble metal such as gold, platinum or palladium. Reduction of oxygen is achieved between 400 to 1200 mV, hence a need for a voltage of around 800 mV. This is provided externally by a battery source.

Anode: $2Ag + 2Cl^- \rightarrow 2AgCl + 2e^-$

Cathode (platinum, gold or palladium): $2e^- + \frac{1}{2} O_2 + H_2O \rightarrow 2 OH^-$

Total Reaction: $2e^- + \frac{1}{2} O_2 + H_2O + 2Ag + 2Cl^- \rightarrow 2 OH^- + 2AgCl + 2e^-$

From the above reaction, every time oxygen is reduced at the cathode, 4 electrons or current is generated directly proportional to the oxygen consumed (reduced) at the cathode. In this type of sensor, both the anode (typically silver) and cathode (typically gold) are immersed in an aqueous electrolyte of potassium chloride. The electrodes are separated from the sample by a semi-permeable membrane that provides the mechanism to diffuse oxygen into the sensor. The silver anode is typically held at a potential of 0.8V (polarizing voltage) with respect to the gold cathode. Molecular oxygen is consumed electrochemically with an accompanying flow of electrical current directly proportional to the oxygen concentration based on Faraday’s law. The current output generated from the sensor is measured and amplified electronically to provide a percent oxygen measurement. One of the advantages of this oxygen sensor is that while inoperative, there is no consumption of the electrode (anode). Storage times are almost indefinite. Similar to the galvanic oxygen sensor, they are not position sensitive. Because of the unique design of the amperometric oxygen sensor, it is the sensor of choice for dissolved oxygen measurements in liquids. For gas phase oxygen measurements, the amperometric oxygen sensor is suitable for percent level oxygen measurements only. The relatively high sensor replacement frequency is another potential drawback, as is the issue of maintaining the sensor membrane and electrolyte. Since the net result of the chemical reaction is AgCl, over time, a build up of AgCl will coat the anode. Once the whole anode is covered, reaction stops and the oxygen probe stops working. The probe can be reactivated by cleaning the anode to remove the AgCl deposit which can be a time-consuming procedure. The result of the above reaction produced more OH- ions which will move the pH value of the electrolyte. The electrolyte, which is around neutral pH value, will move into the alkaline range. This causes a zero shift, and over time, the electrolyte will need to be changed. The net reaction also consumes $Cl^-$ ions. Over time, the chloride ions will be consumed and the electrolyte will have to be replaced. The major disadvantage is the need for an external power source of approximately 800 mV to be applied to the electrode. As soon as the probe is disconnected, the power supply is cut off. On connecting the probe again, the user must wait for the probe to be polarized, that is, for the current loop to be stabilized. This warm-up time is approximately 10 minutes. Any measurement taken before this warm-up time period will normally be a higher value and will result in wrong readings. A variant to the amperometric oxygen sensor is what some manufacturers refer to as a non-depleting coulometric sensor where two similar electrodes are immersed in an electrolyte consisting of potassium hydroxide. Typically, an external EMF of 1.3 V DC is applied across both electrodes which act as the driving mechanism for reduction/oxidation reaction. The electrical current resulting from this reaction is directly proportional to the oxygen concentration in the sample gas. As is the case with other sensor types, the signal derived from the sensor is amplified and conditioned prior to displaying. Unlike the conventional amperometric oxygen sensor, this type of sensor can be used for both percent and trace oxygen measurements. However, unlike the zirconium oxide, one sensor cannot be used to measure both high percentage levels as well as trace concentrations of oxygen. One major advantage of this sensor type is its ability to measure parts per billion levels of oxygen. The sensors are position sensitive and the replacement costs are quite expensive, in some cases, paralleling that of an entire analyzer of another sensor type. They are not recommended for applications where oxygen concentrations exceed 25%.

The galvanic probe principle was introduced by Macreth in 1964 and has undergone a few changes. The ambient temperature electrochemical sensor, often referred to as a galvanic sensor, is typically a small, partially sealed, cylindrical device that contains two dissimilar electrodes immersed in an aqueous electrolyte, commonly potassium hydroxide. As oxygen molecules diffuse through a semi-permeable membrane installed on one side of the sensor, the oxygen molecules are reduced at the cathode to form a positively charge hydroxyl ion (Fig. 8). Hydroxyl ion migrates to the sensor anode where oxidation takes place. The resultant reduction/oxidation reaction generates an electrical current proportional to the oxygen concentration in the sample gas. The current generated is both measured and conditioned with external electronics and displayed on a digital panel meter either in percent or parts per million concentrations.

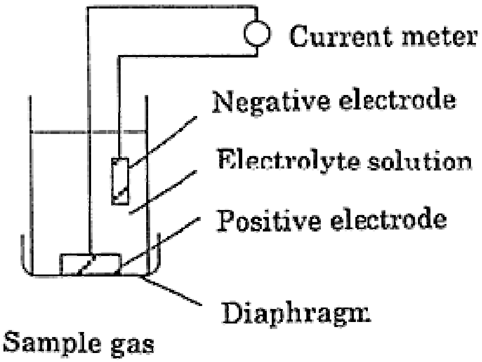


FIGURE 8 A galvanic cell for $O_2$ measurement.

The main advantage of a galvanic probe is that is does not need an external power supply to provide polarization as required by the Clark Cell. This is achieved by using two dissimilar metals. In the presence of an electrolyte, electromotive voltage is produced between the two metals. At approximately 800 mV, it is large enough to reduce the oxygen at the cathode. If lead and gold or lead and silver are used, the differential voltage is approximately 800 mV. At the cathode, the oxygen enters from the gas sample and is absorbed electrochemically. Electrons are used up in this process. At the anode, zinc or lead releases electrons and is oxidized to form lead oxide. The current flowing through the outer circuit in this process is proportional to the diffusing oxygen.

Anode (zinc or lead): $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode: $2e^- + \frac{1}{2} O_2 + H_2O \rightarrow 2OH^-$

Total reaction: $Zn + 2e^- + \frac{1}{2} O_2 + H_2O \rightarrow Zn^{2+} + 2e^- + 2OH^-$

$Zn + \frac{1}{2} O_2 + H_2O \rightarrow Zn(OH)_2 \rightarrow ZnO$ (white precipitate) $+ H_2O$ or $Zn + \frac{1}{2} O_2 \rightarrow ZnO$

Hence one molecule of oxygen produces 4 electrons, there is a direct relationship between the oxygen consumed at the cathode and the current produced by the cell. The net result of the chemical reaction is simply zinc or lead oxide which is reasonably stable and does not coat the anode. A porous barrier limits the diffusion from the gas phase so that a linear signal results corresponding to the concentration of oxygen. The surface of the anode material regenerates itself continuously. For example, the lead oxide dissolves in the electrolyte. Water is recreated and the electrolyte is not consumed. Theoretically, the electrolyte will go on forever without replenishment. However, the dissipation and absorption of moisture inevitably occur through the diaphragm because the electrolyte solution is used. It is also inevitable that the electrodes deteriorate, e.g. as the activity of the working electrode catalyst diminishes. Despite these drawbacks, in relation to the maintenance, the relevant analyzer can be designed to be compact. A galvanic probe is really a self-polarizing amperometric cell. The single biggest advantage is the fact that the cell is now always ready and there is no warm-up time. With the advance in mechanical designs, refinements in electrode materials, and enhanced electrolyte formulations, the galvanic oxygen sensors provide extended life over earlier versions, and are recognized for their accuracy in both the percent and traces oxygen ranges. Response times have also been improved. A major limitation of ambient temperature electrochemical sensors is their susceptibility to damage when used with the samples containing acid gas species such as hydrogen sulfide, hydrogen chloride, sulfur dioxide, etc. Unless the offending gas constituent is scrubbed prior to analysis, their presence will greatly shorten the life of the sensor. The galvanic sensor is also susceptible to over-pressurization. For applications where the sample pressure is high, a pressure regulator or control valve is normally recommended.

A zirconium oxide type electrochemical sensor is occasionally referred to as the “high temperature” electrochemical sensor and is based on the Nernst principle. These devices use a solid state electrolyte typically fabricated from zirconium oxide stabilized with yttrium oxide. The zirconium oxide probe is plated on opposing sides with platinum which serves as the sensor electrode. For a zirconium oxide sensor to operate properly, it must be heated to approximately 650°C. At this temperature, on a molecular basis, the zirconium lattice becomes porous, allowing the movement of oxygen ions from a higher concentration of oxygen to a lower one, based on the partial pressure of oxygen. To create this partial pressure differential, one electrode is usually exposed to the air (20.9% oxygen) while the other electrode is exposed to the sample gas. The movement of oxygen ions across the zirconium oxide produces a voltage between the two electrodes, the magnitude of which is based on the oxygen partial pressure differential created by the reference gas and sample gas. The measured potential difference is in proportion to the logarithm of partial pressure ratio of oxygen. Therefore, the oxygen in the sample gas can be found by sending a reference gas to one of the electrodes (Fig. 9a). The zero calibration cannot be performed for such a gas which contains no oxygen, e.g. when an $N_2$ gas cylinder is used. In such a case, an oxygen cylinder for about 10% of the range is used for this calibration. The zirconium oxide oxygen sensor exhibits excellent response time characteristics. Another virtue is that the same sensor can be used to measure 100% oxygen, as well as parts per billion concentrations. Due to the high temperatures of operation, the life of the sensor can be shortened by on/off operation. The coefficients of expansions associated with the materials of construction are such that the constant heating and cooling often causes “sensor fatigue”. A major limitation of zirconium oxide oxygen sensors is their unsuitability for trace oxygen measurements when reducing gases (hydrocarbons of any species, hydrogen, and carbon monoxide) are present in the sample gas. For the zirconia type oxygen analyzer, since its element reaches a high temperature, the oxygen decrease involved in the oxidation and combustion of combustible gases becomes negative interference. At operating temperatures of 650°C, the reducing gases will react with the oxygen, consuming it prior to the measurement, thus producing a lower oxygen reading than actual. The magnitude of the error is proportional to the concentration of reducing gas.

In the case of the limiting current type analyzer, electric potential is applied between the zirconia electrodes (Fig. 9b). The oxygen concentration limited by gas dispersion holes is in a proportional relation with the limiting current and this current value is detected. This analyzer is easy to handle because it requires no reference gas, its output is linear, and the reading is stable even at around 21%.

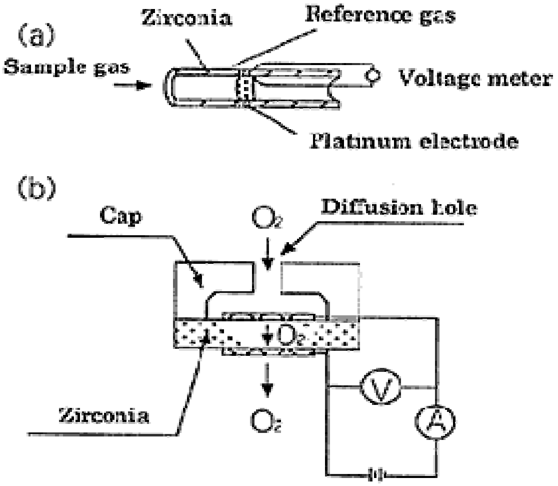


**FIGURE 9** Two types of zirconia electrochemical sensors.

Since the measurement cell itself is at a high temperature, some of the relevant analyzers allow it to be inserted directly into the exhaust combustion gas. Zirconium oxide oxygen sensors are the “de facto standard” for in-situ combustion control. They were developed by Robert Bosch GmbH during the late 1960s under supervision by Dr. Günter Bauman. The original sensing element is made with a thimble-shaped zirconia ceramic coated on both the exhaust and reference sides with a thin layer of platinum and comes in both heated and unheated forms. The planar-style sensor entered the market in 1998 (also pioneered by Robert Bosch GmbH) and significantly reduced the mass of the ceramic sensing element as well as incorporating the heater within the ceramic structure. This resulted in a sensor that both started operating sooner and responded faster. The most common application is to measure the exhaust gas concentration of oxygen for internal combustion engines in automobiles and other vehicles.

## *6.1.2 SPECTROCHEMICAL METHODS OF ANALYSIS*

In the spectrochemical methods of analysis, the analyte interacts with electromagnetic radiation. Most methods in this category are based on the measurement of the amount of light absorbed by a sample. The rest of the methods are generally based on the measurement of light emitted or scattered by a sample.

### 6.1.2.1 Colorimetric analysis

Colorimetric analysis is based on the colour produced by the reaction of the sample under analysis with a reagent and comparing it with the colours produced by a known standard. The possibility of using colour chemistry for monitoring gases, vapors or particulates in the air has been recognized for many years. The described methods of analysis involve paper tapes, detector tubes or bubblers as appropriate to the toxic agent. Many of these and other techniques have been developed and incorporated into commercial instruments.

One of the earliest methods of applying colour chemistry to gas detection was the use of a bubbler or impinger to trap the toxic gas or vapor from the atmosphere. The sample of the atmosphere to be analyzed is bubbled through a solution at affixed flow rate for a fixed period using a pump. The analysis of the pollutant may then be undertaken by adding reagents to generate a colour and measuring the intensity of the colour. Suitable methods of measuring colour intensity include using a comparator chart for a rough guide to the concentration of the toxic gas, a pocket comparator or, for a more accurate analysis, a spectrophotometer operating at a selected wavelength. A typical application of this technique is to determine sulfur dioxide, nitrogen dioxide, ozone, etc. The average daily sulfur dioxide concentrations can be measured by the colorimetric method using **the West-Gaeke method**. The sulfur dioxide is absorbed into a sodium tetrachloromercury solution (TCM) containing Chelaton III and converted to the sulphite ion. The compound formed reacts with fuchsin and formaldehyde in acid medium to yield a red-purple colour, which is measured spectrophotometrically at 586 nm. A colorimetric method using **thorin** is applied at selected stations with lower sulfur dioxide pollution levels. The air is drawn through a filter to capture solid particles and then through another filter impregnated with sodium hydroxide to determine sulfur dioxide. After extraction from the filter, the sulphate ions are precipitated with barium perchlorate. Excess barium ions are determined spectrophotometrically at 520 nm after reaction with thorin. The most common bubbler procedures for $NO_x$ use the Griess-Ilosvay method for the determination of nitrite ion. It is based on the following 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 $NO_2$. 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 for the determination of $NO_2$ in the air was reported by B.E. Saltzman, and this has since come to be known as **the Saltzman** or **Griess-Saltzman method.** Nitrogen dioxide in the air reacts with the

Saltzman reagent in an absorption solution (an aqueous solution of N-1 naphthyldiamine dihydrochloride, sulfanilic acid, and acetic acid) producing azo pigment. The concentration of nitrogen dioxide can be determined by measuring the absorbance of this pigment in a range near 545 nm. The method as described is specific for $NO_2$. However, NO may also be determined by prior oxidation. It is then oxidized by passing through an oxidation solution of sulfuric acid potassium permanganate, and its concentration is similarly determined. In order to increase the efficiency of catching nitrogen dioxide in the absorbing solution, this measuring method uses a bubbler to produce bubbles, thereby increasing the contact surface between the gas and the liquid. There are no major interferences in the Saltzman method, other than from excessively high concentrations of $SO_2$ or $O_3$. 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. In the **triethanolamine method**, $NO_2$ is absorbed into the solution of thiethanolamine with sulfanilic acid in acid medium of $H_3PO_4$ using NEDA. The intensity of the colour is measured spectrophotometrically at 540 nm. Most of the bubbler methods for ozone are based on the oxidizing 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:

$$O_3 + 3KI + H_2O \rightarrow KI3 + O_2 + 2KOH$$

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.

Paper-tape monitors use a colour process whereby reaction of the toxic gas or vapor takes place with colour-forming chemicals impregnated on a paper tape. There is thus a similarity between this technique and detector tubes in that colour reactions initially carried out in the solution are transferred to a solid medium in both cases. The major differences lie in the fact that detector tubes are used mainly for spot monitoring and personal monitoring as portable devices while paper-tape instruments are used mainly for continuous monitoring as fixed or transportable devices. Their principle of operation is based on a roll of treated paper tape which is mechanically fed through an instrument. When exposed to gas, the tape changes color and the color difference is detected through a photocell, and a result is displayed. Paper tape detectors are used for detection of hydrogen sulfide, chlorine, hydrazine, carbon monoxide, ozone, etc. One of the first applications for paper-tape monitoring on a large scale was the detection of toluene di-isocyanate which is used on large scale as a starting material for the manufacture of polyurethanes, particularly urethane foams.

### 6.1.2.2 Light absorption method

The light absorption methods are based upon the phenomenon that molecules will absorb light energy to rotate, vibrate, or change their electronic patterns in characteristic ways. This absorption occurs only for wavelengths of light that are in tune with the properties of the molecule. The relationship between absorption intensity of light and concentration of measurable component adheres to the Lambert-Beer Law and is expressed by equation

$$I = I_0 e^{-kcl}$$

where: I-intensity of transmitted infrared light, $I_0$-intensity of emitted infrared light, k- coefficient of absorption, c-concentration of measurable component, l-length of measurement cell. This law states that the transmittance T (ratio of transmitted and incident intensities) of radiation through an absorbing medium decreases exponentially by the product of the extinction coefficient k, the concentration c and the path length l. Furthermore, the extinction coefficient is dependent upon the wavelength of the radiation and the properties of the gas molecule. Light absorption techniques are categorized as being nondispersive or dispersive.

#### Nondispersive technique

In the nondispersive methods, the so-called nondispersive infrared (NDIR) and nondispersive ultraviolet (NDUV) techniques, the spectrum is not scanned. Here, a wavelength where light energy is absorbed is used as the basis for the instrument design. Such instruments are constructed quite simply.

Non-Dispersive Infrared (NDIR) techniques for the measurement of various gases rely on the energy absorption characteristics of a particular gas in the infrared region. The theory of operation of NDIR methods is similar and is based upon absorption of infrared energy in the 2 to 11 micron wavelength range. An NDIR photometer is basically an instrument that does not disperse the light emitted from an infra-red source. In other words, 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 an optical bandpass or gas filter, which is chosen to coincide with an absorption peak of the pollutant molecule.

The simplest photometer contains only one light path while, for greater stability, both sample and reference paths are provided to allow for variations in source intensity (Fig. 10). In these instruments, infrared energy passes through two identical tubes and falls on a detector. The first tube is the reference cell and is filled with a non-absorbing gas such as nitrogen. The second tube is the measurement cell and contains the gas sample to be analyzed. Energy in the region of interest is absorbed by the gas in the measurement cell, attenuating the energy passing through the cell and falling on the detector. This attenuated energy is compared to the unattenuated signal from the reference cell. The difference is proportional to the amount of absorbing gas in the measurement cell. A simple method to make the comparison easily with analog electronics is to use a "chopper wheel" assembly which prevents the energy from both cells from falling on the detector simultaneously. As the wheel spins, energy from the reference and measurement cells fall on the detector alternately, producing an AC signal with a magnitude proportional to the difference in energy.

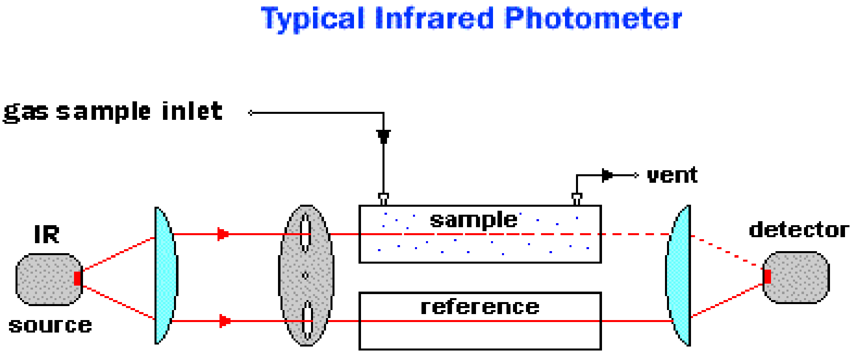


FIGURE 10 NDIR photometer with sample and reference paths.

The measurement cell can be equipped with different detectors. Generally, all detectors translate the difference in infrared energy into a sine wave that has a frequency determined by the chopping rate and a magnitude proportional to the energy difference. The solid state detector (a photoconducting or pyroelectric) is constructed of a material that changes its electrical conductance in response to IR light energy falling on it. Changes in the current flowing through the detection circuit are proportional to the difference in transmitted IR energy. The solid state detector has the advantage of being insensitive to external mechanical vibration. In addition, careful selection of detector material allows for simplified optical filter design.

The Luft type detectors are the oldest type found in common use. They operate typically in the 3 – 9 µm region of the electromagnetic spectrum although it is possible to work at wavelengths up to 15 µm. It is found in dual beam analyzers and uses a pair of chambers that are filled with the adsorbing gas interest. One chamber receives light through the inert gas-filled reference cell, the other receives light through the sample gas-filled cell. The chambers are separated by a capacitive diaphragm which distends in response to the difference in adsorption-induced gas expansion between the two detector chambers. This detector is extremely sensitive and selective, but is expensive to produce. Gases that may typically be detected by Luft cell instruments are carbon dioxide, carbon monoxide, nitrous oxide, sulfur hexafluoride, chlorofluorocarbons, sulfur dioxide and vapor solvents such as benzene, xylene, hexane and toluene. A typical application for the Luft analyzer would be detection of carbon monoxide either in the exhaust gas or in the ambient air.

The microflow (optopneumatic) detector is similar to the Luft detector, but employs a small orifice between the two detection chambers. In this detector, the radiation absorbed in the gas is changed into pressure fluctuation, followed by periodic flow of the gas between detector chambers. This flow is usually measured by means of hot-wire, hot-film anemometers or thermocouple arrangement in the orifice (Fig. 11). This detector is relatively immune to mechanical vibration, but is not as simple as the solid state type.

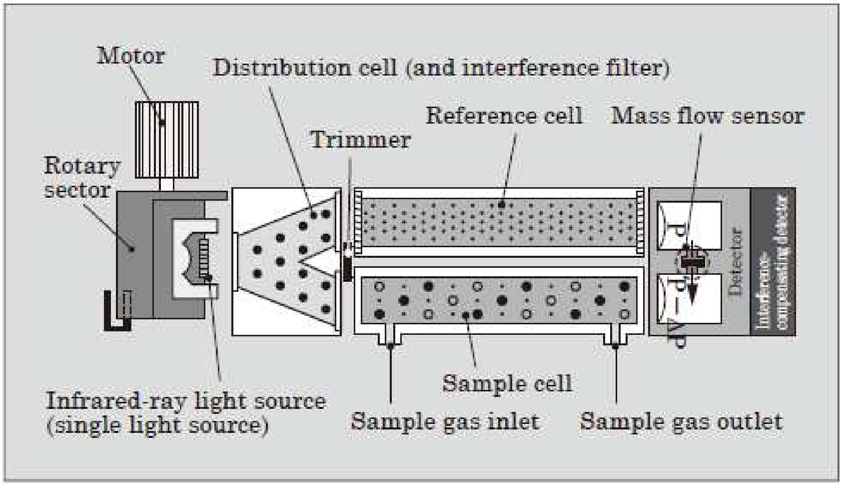


FIGURE 11 NDIR photometer with mass flow detector.

Optoacoustic detectors, utilizing the phenomenon of the excitation of sound waves in gases by a modulated light beam, are commonly used as the detectors of infrared radiation. The amount of the radiation absorbed by a gas is usually measured by means of a microphone. These detectors are known as Golay chambers and are used for the investigations of light absorption mechanism as well as for the trace analysis of gases and pollution monitoring.

Many species of gas have overlapping infrared absorption spectra which can cause cross-interference in the basic technique. Examples are water vapor, CO, $CO_2$, NO, $NO_2$, $NH_3$ and $SO_2$. Selectivity and interference rejection in NDIR analyzers is achieved either through the addition of optical band-pass filters, or gas-filled cells. Interference filters are placed in the path of broad band IR radiation. Two filters are used per component; one selects a measuring wavelength whilst the other selects reference wavelength. The filters are mounted on a rotating disc immediately in front of the infrared source. This arrangement gives rise to an IR beam alternating rapidly between the measuring wavelength and the reference wavelength for each component. This alternating beam passes through the gas being measured, eventually striking the IR detector. If any of the gases to be measured is present, then a significant amount of radiation will be absorbed at the measuring wavelength with very little or none being absorbed at the reference wavelength.

An important enhancement to this basic NDIR technique is Gas Filter Correlation (GFC). A rotating, gas-filled filter wheel contains two chambers. One chamber is filled with the species of interest while the other contains an optically inert gas (i.e. nitrogen). This filter wheel is interposed between the IR source and the single sample chamber. As the wheel rotates, the light passes through one side, then through the other as well as the sample chamber. IR energy in the region of interest is attenuated by one side of the wheel, but not the other. As a result, the difference in energy is inversely proportional to the amount of the species in the sample chamber. This has the advantage of providing more sensitivity at lower measured concentrations. Interferent species present in the gas sample attenuate both the sample and reference signals equally and will not be measured. A further enhancement of the GFC technique employs multiple filter wheels which align in combinations to permit the detection of multiple species within the same instrument (Fig. 12).

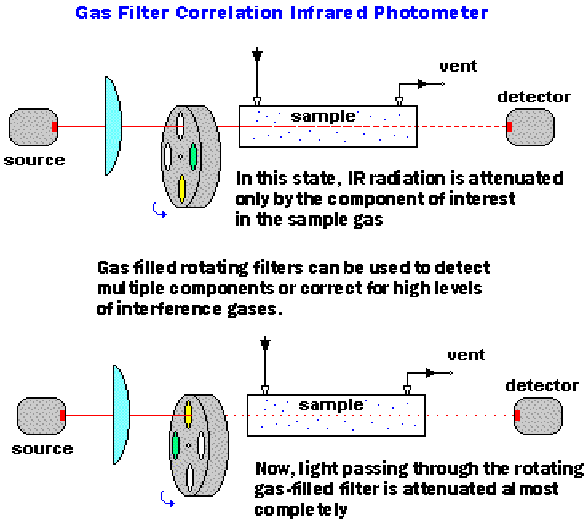


FIGURE 12 A gas filter correlation infrared photometer.

IR correlation absorption photometry can be used to measure e.g. CO. In this method, the light from the radiation source reaches the detector after passing through the gas correlation filter and the sample gas cell (Fig. 13). One is the light which has passed through the CO-filled cell of that filter and therefore contains no infrared rays of the wavelength band absorbed by CO. The other is the light which has passed through the other cell filled with $N_2$ or a similar inert gas. The concentration of CO is calculated from the difference between these two kinds of light.

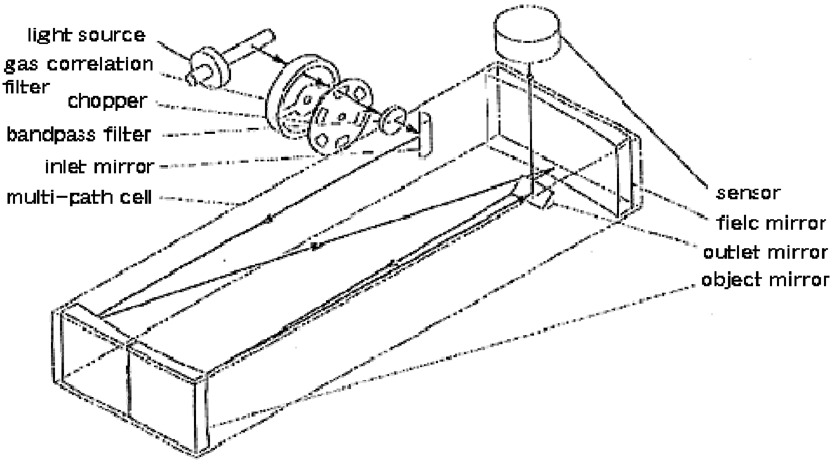


FIGURE 13 A gas correlation method.

Simple molecules with less than 5 or 6 atoms have infrared absorption spectra with fine structure. Gases fitting this description are ideal for photometers with optoacoustic or optopneumatic detectors and GFC types of analyzers, which correlate the spectra of the sample gas with the spectra of the pure component of interest. Interference filter correlation is capable of measuring gases with either fine structure in the spectra or broadband absorption. NDIR provides the following features:

- the effect of the flow rate is small;
- the response speed is high;
- high-sensitivity measurements are possible;
- the effects of interfering components are small;
- stable measurement data can be obtained by the addition of an automatic calibration unit;
- the maintenance and serviceability are easy.

This technique is of relatively low sensitivity, and is more applicable to the concentrations found in the source emissions than in ambient air. NDIR has been developed to monitor $SO_2$, $NO_x$, CO, and other gases that absorb in the infra-red, including $CO_2$ and hydrocarbons. Proximately 80 gases have been measured with NDIR photometers. However, it is probably true to say that this method is preferred for CO monitoring. Of the 80 gases, approximately 50% of the NDIR instruments sold are for measurement of carbon monoxide (CO).

A typical nondispersive method measures light absorption at two wavelengths, one where the molecule absorbs energy and one where it does not. This particular technique has been called differential absorption spectroscopy or differential optical absorption spectroscopy (DOAS) (Fig. 14). The ratio of the intensities, $I/I_0$, at the two wavelengths is known as the transmittance and is related exponentially to the concentration of the gas that absorbs light energy at the wavelength, $\lambda$. In the nondispersive, differential absorption technique I, is obtained from the detector when it responds at the wavelength $\lambda$. In many criteria pollutant monitors, the value of $I_0$, is obtained instead by using a reference gas or reference gas cell that does not absorb light energy at the measurement wavelength, i.e. $c = 0$, which gives $I = I_0$, when the light passes through the reference cell.

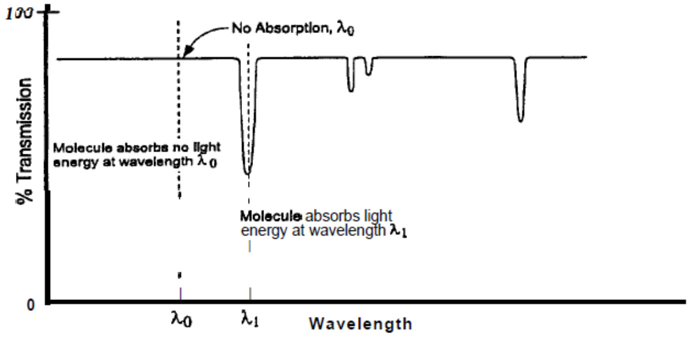


FIGURE 14 The example illustrating the differential absorption technique.

The differential absorption spectroscopic technique has been used for many years. Early instruments used filters to select the light wavelengths. Current methods applied to discriminate between wavelengths include:

1. Optical filters;
2. Diffraction gratings and photo-diode arrays;
3. Diffraction grating and moving slits;
4. Diode lasers.

These different techniques are illustrated in Figure 15.

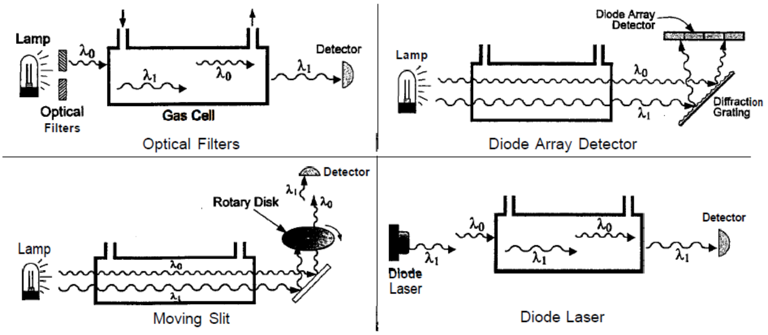


FIGURE 15 Differential optical absorption techniques.

DOAS method has been applied to measure criteria pollutants, ammonia, mercury vapor, and some organic compounds (benzene, xylene, and toluene). The commercialized application of the differential absorption technique employs diode lasers to measure HF and ammonia.

Ultraviolet (UV) absorptiometry is in general more sensitive than NDIR absorptiometry. Another advantage of this method is that water ($H_2O$) is transparent to UV. Ozone, $O_2$ and $NO_2$ are frequently measured with this technology. Other possibilities are $H_2S$, $CS_2$, $Cl_2$, $NH_3$, and other gases.

The ozone concentration in the sample of ambient air may be determined by measuring the variation of absorbing quantity of ultraviolet rays near 254 nm. The UV photometric method is not subject to interference from any of the common gaseous air pollutants. The sample ambient is drawn into the absorption cell through a scrubber which removes all ozone and light intensity ($I_0$) is determined. The valve is then switched to allow ambient air to fill the cell. During this measurement cycle, the light intensity (I) is determined. The Beer-Lambert Law gives the relationship between these measurements and the ozone concentration. UV photometric ambient ozone analyzer shall be composed of filter, ozone scrubber, three-way-valve, UV absorption cell, UV source lamp, detector, flowmeter, sample ambient air suction pump, as it is shown in Figure 16.

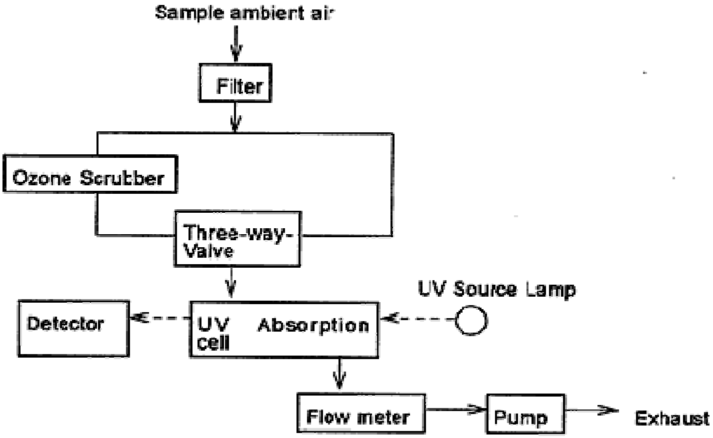


FIGURE 16 Example of UV photometer for ozone.

In the UV photometer for NO, $NO_2$ and $NO_x$ measurements, the concentration of NO or $NO_2$ is obtained by measuring the changes in the volume of ultraviolet rays in the range from 195 to 230 nm absorbed by NO or in the range from 350 to 450 nm absorbed by $NO_2$. To measure the concentrations of NO and $NO_2$ as the concentration of $NO_x$, two methods are available. One is to individually measure the concentrations of NO and $NO_2$ and then add the measured values. The other is to pass the sample gas through an oxidation type converter to convert NO into $NO_2$ and then measure the concentration of $NO_x$ as that of $NO_2$.

Ultraviolet absorptiometry is also used to determine the concentration of sulfur dioxide by photoelectrically measuring the changes in the absorbed quantity of ultraviolet rays in the wavelength range from 280 to 320 nm. For this purpose, the optical system adopts the multi-wavelength method using a spectroscope. Some models compensate for the interference effect of nitrogen dioxide, whose absorption spectrum overlaps that of sulfur dioxide, and other models perform non-dispersive measurements using a devised pretreatment. The basic features of this method are the same as those of infrared absorptiometry.

## Dispersive technique

By employing correlation or Luft cells filled with mixtures of gases, it is possible, in some cases, and with adequate resolution of peaks, to resolve two or three gases. However, where complex mixtures of gases require detection of where limits of the detection are low, more sophisticated methods are often required. A dispersive method, to provide wavelengths of the required frequency, may be applied using grating, prism or tunable source-filter. A scanning grating is the traditional method of providing the dispersive beam, often with a high degree of spectral resolution. In a typical system the grating is rotated in such a manner that wavelength range under investigation is scanned across a single detector. The reproducibility of the mechanical registration of the grating is directly related to the reproducibility of the wavelength selection. Therefore, fairly complex mechanical arrangements are required. Another approach is to use a fixed grating couple with a linear array detector. This overcomes the mechanical problems associated with scanning gratings and greatly decreases the time taken to record wavelength scan. However, the wavelength range covered is dictated by the resolution required and the size of the array. Thus a scanned grating is able to cover a large wavelength range, whereas a fixed grating coupled with linear array normally covers a restricted wavelength range.

Traditional variable filters or multifilter wheels are in some cases replaced by acousto-optic (optoacoustic) filters which allow tuning to any selected frequency in a matter of seconds, thus eliminating the need for gratings or several filters. Certain birefringent materials, which are termed acousto-optic materials, can be used as filters in spectrum analyzer. In such materials, a light beam propagating as a polarized extraordinary ray can, under certain conditions, be converted into an ordinary ray and, in addition, be spatially separated from original ray by diffraction from an acoustic wave propagating through the medium. This phenomenon has been used to fabricate an optical device capable of being tuned to particular optical wavelength by the application of a suitable acoustic frequency. In effect the element is capable of providing a tunable infrared source.

In the dispersive methods, the spectral absorption of a molecule is measured over a limited region of the electromagnetic spectrum. A spectral absorption pattern, or spectrum, characteristic of the molecule is obtained that can be used to both identify the molecule and determine the concentration of the molecule in the sample. Scanning spectrometers and Fourier transform infrared (FTIR) spectrometers generate such spectra. The FTIR spectroscopic method is a dispersive technique where an absorption spectrum over a limited spectral range is obtained for all infrared light absorbing compounds contained in the sample. Most commercially available FTIR analyzers operate in the mid-IR region (400 $cm^{-1}$ – 4,000 $cm^{-1}$). The technique allows for the measurement of more than one gas species at the same time and is sufficiently general that it can be used at a wide variety of sources. For these reasons, the technique has generated interest for a number of non-criteria pollutant monitoring applications. In contrast to using an optical filter or a laser to transmit light at a specific wavelength through the cell, the FTIR source transmits light over a broad range of wavelengths. The IR radiation is modulated with an interferometer before the light enters the sample, that is, the light energy at each wavelength is varied from zero to some maximum value by using a mirror that moves over a small distance, x (in FTIR systems, a laser is used to monitor the mirror position). This all results in generating an "interferogram" (an interference spectra %) that shows the net intensity of the absorbed radiation at the detector, versus the mirror position, x. The interferogram contains much information, but not in a particularly usable form. The system microprocessor applies a mathematical technique called the "Fourier transform" to recalculate the detector intensity as a function of wavelength instead of as a function of the mirror position x. This is what is desired, a complete absorption spectrum over the wavelength region of the spectrometer. Once the dispersed absorption spectrum information is obtained, the analyzer microprocessor must then extract both the qualitative and quantitative information desired. To do this, "library spectra" of the compounds being measured must be stored in the computer and referenced against the test data. The library spectra are obtained by analyzing samples of the compounds at known concentrations with the FTIR spectrometer. Various mathematical techniques are used in this process to obtain concentrations in parts per million. The FTIR technique involves the application of numerous technical and mathematical tricks, however, its operation can be summarized simply as follows:

IR light is emitted over a broad spectral range

↓

Mirror moving over distance x, modulates light

↓

Modulated IR light is absorbed by molecules in the sample cell to create "interferogram"

↓

Interferogram converted by Fourier transform to absorption spectrum

↓

Library spectrum matched to test data to give concentration in ppm for each compound being measured.

The method can be relatively straightforward if the compounds in the sample do not absorb light in the same wavelength regions, i.e. if their spectral "fingerprints" are not similar. If these fingerprints are similar, or overlap, the method becomes more difficult to apply. This is the case when the sample contains hydrocarbons or other organic compounds of similar structure. Also, because water and/or carbon dioxide are often present in the sample at percent levels, discriminating between the spectral absorption of organic compounds at ppm levels within the broad spectral absorption regions of these two gases becomes more difficult. The attraction of the FTIR technique is that it is a multi-component technique and reference spectra can be used for calibration. This does not mean that the FTIR technique does not have to be optimized for a given application. Each new use of the instrument requires the incorporation of library spectra of the compounds of interest over the range of concentrations expected at the source. Suitable reference spectra may have been generated by the analyzer manufacturer for similar applications. If appropriate reference spectra have not been generated, individual spectra of the target gases at known concentrations and specific temperatures and pressures must be obtained. The use of infrared methods in pollution measurement has been hampered by sensitivity limitations and by interferences from water vapor. Fourier transform spectrometer systems reduce these limitations by their high optical efficiency and their ability to manipulate spectra for removal of interfering bands.

### 6.1.2.3 Luminescence methods

Light generation by a process other than by heating is luminescence. Luminescence is based on the emission of light from a molecule that has been excited in some manner. Luminescence can be divided into categories by:

- duration (fluorescence or phosphorescence);
- the mechanism that creates the light.

By definition, fluorescent things stop emitting light very soon (about 10 ns) after the exciting energy is cut off. Phosphorescence continues for longer than fluorescence. Photoluminescence is the release of light after a molecule has been excited by ultraviolet, visible or infrared radiation. Fluorescence is a process whereby light energy of a given wavelength is absorbed and then re-emitted at a different wavelength, i.e.

$$AB + hv \rightarrow AB^* \rightarrow AB + hv'$$

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). It 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. The energy of this radiation is lower, and hence a longer wavelength is emitted. This phenomenon has been utilized in the development of air pollutant monitors.

Fluorescence analyzers are used for $SO_2$ ambient and source level measurements. Sulfur dioxide concentration may be measured by the ultraviolet fluorescence method, where the analyzed sample is exposed to UV-lamp irradiation with energetic excitation of $SO_2$ molecule. This method is based on the principle that $SO_2$ molecules absorb ultraviolet light $h\gamma$ and become excited at one wavelength

$$SO_2 + h\gamma \rightarrow SO_2\,^*$$

With the backward conversion of the molecule into the basic energetic level, energy as fluorescing radiation is released

$$SO_2{}^* \rightarrow SO_2 + h\gamma'$$

The intensity of fluorescence radiation $h\gamma'$ is proportional to the sulfur dioxide concentration and is detected by a photomultiplier. Fluorescence $SO_2$ analyzer consists of five main elements. They are shown in Figure 17.

1. The hydrocarbon scrubber. This element removes hydrocarbons contained in ambient air, which are excited with UV light and consequently emit fluorescence. The $SO_2$ molecules pass through the hydrocarbon scrubber unaffected.
2. Fluorescence chamber.
3. Light source. The exciting light source generates light energy $h\gamma$ by an electric discharge. A UV lamp provides a source of radiation, either continuous or pulsed.
4. Photoelectric detector. This element has to be located adjacent to the fluorescence chamber via an optical filter which selectively passes the fluorescence to an electrical signal of required level.
5. Electronics, etc.

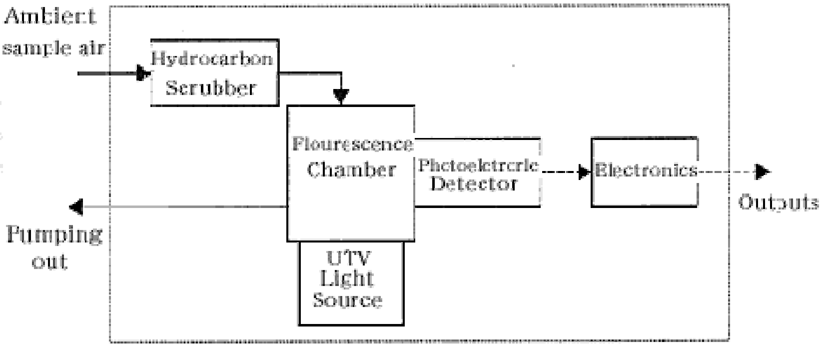


FIGURE 17 An example of fluorescence $SO_2$ analyzer.

This instrument measures $SO_2$ in air samples by irradiating the sample with ultraviolet (UV) light and measuring the resulting fluorescence with a photomultiplier tube (PMT). UV light is focused through a 214 nm bandpass filter into the reaction chamber where it excites the $SO_2$ molecules to give off their characteristic decay radiation. Between 190 and 230 nm, the $SO_2$ absorbs UV free of quenching by air and relatively free of interferences. A second filter with a bandpass of 250～390 nm allows only the decay radiation, or fluorescence, to fall on the PMT. The fluorescent radiation is measured at right angles to the incident beam. Signal processing converts the fluorescent energy falling on the photomultiplier into a voltage which is proportional to the $SO_2$ concentration in the sample. The fluorescence analyzer is specific for $SO_2$. Sample air must be dry and free of dust to avoid fouling 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 (the hydrocarbon scrubber).

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

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

These reactions produce a continuum of radiation in the range 500 to 3,000 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 NOx and $O_3$, respectively. The chemiluminescence reaction which occurs with NO and ozone is used to measure the concentration of NO. The NO in the sample gas and the $O_3$ produced from air using silent discharge or the radiation of ultraviolet rays are mixed with each other in the reaction cell. A part of the mixed gas becomes $NO_2$ ($NO_2^*$) in the excited state. With the conversion of the molecule into the basic energetic level, liberation of radiation as chemiluminescence occurs. In another words, when $NO_2^*$ returns to the normal state, it emits light. The intensity of this light is measured with a silicon photodiode or a photomultiplier to obtain the concentration of NO. To measure nitrogen dioxide, (a) the sample gas is passed through a converter filled with reducing catalyst and the concentration of nitrogen oxides (NO plus $NO_2$) is measured; and (b) this concentration is deducted by the value (for nitrogen monoxide) obtained without using the converter. The gas which has left the reactor still contains corrosive ozone. Therefore, this ozone is eliminated using adsorption or thermal decomposition before the gas is exhausted. This method features a high sensitivity, a broad dynamic range, a fast response, and measurements free from any interference other than $CO_2$. The effect of $CO_2$ varies depending on the structure of the reactor, the ratio of gas flow rates, and the internal pressure. If these factors are assumed to be constant, the effect is dependent on the concentration of $CO_2$ and the reading of NO is affected accordingly. This means that when the concentration of $CO_2$ remains stable, the interference of $CO_2$ is eliminated from the reading of NO by electrically compensating for that value. The converter which converts nitrogen dioxide into nitrogen monoxide has a limited service life, requiring periodical replacements and checks of its conversion efficiency. A scheme of chemiluminescence analyzer for the NO, $NO_2$ and $NO_x$ concentration measurement is shown in Figure 18.

The instrument is coupled with an internal molybdenum convertor and can be coupled with an external stainless steel convertor. The vacuum pump provides vacuum for the reaction chamber and filtered air for ozone generation. Ozone is generated by the UV irradiation of clean air and mixed in a reaction chamber with the sample air. To measure NO concentrations, the gas sample is blended with $O_3$ in a flow reactor. The resulting chemical reaction gives off chemiluminescence. The resulting chemiluminescence is monitored through an optical filter by a high-sensitivity photomultiplier positioned at one end of the reactor. The amount of light given off is directly proportional to the amount of NO in the sample. In the presence of excess $O_3$, chemiluminescence intensity is proportional to NO concentration. Greatest sensitivity is obtained at reduced pressure because of quenching effects at higher pressures. Nevertheless ambient NO concentrations can be measured also at atmospheric pressure. At reduced pressure with a cooled photomultiplier tube this method can detect 0.001 p.p.m. NO. Response is linear up to 10,000 p.p.m. with a linear dynamic range of $10^7$.

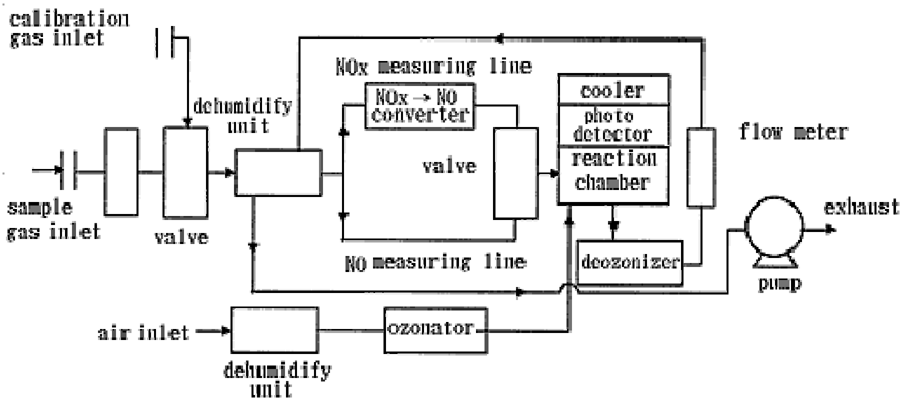


FIGURE 18 The scheme of chemiluminescence analyzer for the NO, $NO_2$ and $NO_x$ concentration measurement.

The reaction which generates light occurs only between NO and ozone. If $NO_x$ is to be measured, one of the optional $NO_2$ to NO converters must be installed. If $NO_2$ is to be measured, the optional NO/$NO_x$ valve must be installed, permitting NO and $NO_x$ to be separately measured, the difference being $NO_2$. The analyzer design makes possible the acquirement of information on nitrogen monoxide (NO), nitrogen dioxide ($NO_2$) and nitrogen oxides ($NO_x$) concentrations. When nitrogen monoxide in an air sample reacts with ozone, nitrogen dioxide is generated in its excited state. When the generated nitrogen dioxide returns to the ground state, it emits light (chemiluminescence). The concentration of nitrogen monoxide can be determined by measuring the intensity of this chemiluminescence. If the sample air is passed through a converter to convert nitrogen dioxide into nitrogen monoxide, the concentration of nitrogen oxides (nitrogen monoxide and nitrogen dioxide) can be obtained by measuring the intensity of the chemiluminescence. The concentration of nitrogen dioxide in the sample air can be obtained by calculating the difference between the two measured values. The emission spectrum obtained from the reaction between nitrogen monoxide and ozone is found within the wavelength zone between 600 and 3,000 nm. Its maximum wavelength is around 1,200 nm. In order to eliminate the effects of other chemiluminescence, an optical filter is used in the photoelectric sensor. The photoelectric sensor also uses a photomultiplier tube (PMT), but because of the characteristics of its photoelectric surface, the wavelength range available for detection is narrower (from 600 to 900 nm). Recently, therefore, some monitoring systems have begun to use photoelectric elements which are more sensitive to wide wavelengths (e.g. silicon photodiode). Because nitrogen monoxide and nitrogen oxides must be measured individually, different measuring methods are employed including the flow path switching method, the optical path switching method and the two-flow path/two-optical path method. Each of these methods has a problem with the stability of the passage selection valve or of the optical path switching chopper, and requires that the performance (such as responsiveness and time-course changes) be matched between two detectors. In principle, calibration is performed using nitrogen monoxide as the standard gas. Therefore, if the efficiency of converting nitrogen dioxide into nitrogen monoxide is below 100%, the measured concentration of nitrogen dioxide decreases by the same rate. There are two types of available converters: a thermal reaction converter that decomposes nitrogen dioxide at 600-800°C or a chemical reaction converter that uses graphite carbon, molybdenum, tungsten, metal-impregnated carbon or some other similar carbon to reduce nitrogen dioxide at 100-400°C. When the temperature rises to 400°C or more, ammonia is oxidized. This generates nitrogen monoxide, which causes an interference effect. For this reason, the chemical reaction converters, which use a carbonaceous substance at 300°C or less, are used predominantly. The chemical reaction converter itself is oxidized in the process of deoxidizing the nitrogen dioxide, so it must be replaced, in principle, every 12 months. However, this replacement frequency increases when the converter is used in the places where the concentration of nitrogen dioxide is high. The definite frequency should be determined by checking the conversion efficiency of the suitable converter. Care must be given to the fact that nitrogen oxides other than nitrogen compounds (e.g. PAN) are converted together with nitrogen dioxide into nitrogen monoxide and cause an interference effect. Moisture quenches the chemiluminescence resulting from the reaction between nitrogen monoxide and ozone, causing negative interference. The degree of this interference varies depending on the pressure and flow rate in the reaction chamber. If there is a great difference between the water content of the calibration gas and that of the measured air, the measurement is particularly affected. For this reason, the monitoring system is equipped with a semipermeable membrane filter, humidity controller, or the like that is used to maintain a constant water content of the sample air. The decrease in the reading of nitrogen monoxide is specified as 4.0% maximum when the temperature is 25°C and the relative humidity is 80%. Carbon dioxide, which causes quenching just as moisture does, may be ignored under normal conditions. However, note that carbon dioxide cannot be ignored if its concentration is high (more than several percent).

The analyzer for continuous measurement of the concentrations of ammonia ($NH_3$) in ambient air is based on an oxidative catalytic reaction and chemiluminescence method. Ammonia in ambient air sample is transformed into oxides of nitrogen with a catalyzer. Then the concentration of ammonia is determined by the increase in the concentration of the oxides of nitrogen by chemiluminescence method.

The concentration of ozone contained in the sample of ambient air may be determined by chemiluminescence method, by making reaction between ozone and ethylene. Ozone and ethylene react instantaneously to produce light in the visible region with a maximum at a wavelength of about 450 nm. The chemiluminescence radiation is measured by a photomultiplier tube.

### 6.1.2.4 Flame photometry

Flame photometry is based on the measurement of the light emitted by a substance in a flame. This is the method to continuously measure sulfur compounds in ambient sample air as the concentration of sulfur compounds by measuring the light intensity with a photomultiplier tube utilizing the light emission phenomenon which appears in the near ultraviolet region when these substances are thermally decomposed in a hydrogen flame. When a sample of air is burned in a hydrogen-rich flame, all volatile sulfur compounds are converted to diatomic sulfur, which is raised to an excited state as it rises in the flame. This excited species is sufficiently long-lived to reach a region above the flame, where it returns to the ground state condition. The transition from an excited state S to the ground state releases light energy. On decay to the ground state, light is emitted over a wavelength range of 300 to 425 nm, centered at about 394 nm, i.e.

$$S_2^* \rightarrow S_2 + h\gamma$$

The light emitted from the chamber is viewed by a photomultiplier filled with a narrow-bandpass filter. For analytical applications, the peak emission band at 394 nm can be resolved by the use of interference filters. Because two sulfur atoms are required to produce one excited molecule, the light intensity emitted is proportional to the sulfur concentration squared. The main advantages of this device are its specificity, for the absence of intermediate reaction, a real-time data output being almost instantaneous in its response to $SO_2$ concentration, and the wide range of measurable concentration. The FPD records, however, all sulfur compounds and though this term is practically synonymous with sulfur dioxide, interference from other sulfur pollutants can be accounted for. Some degree of specificity can be obtained by the use of appropriate pre-filters (e.g. to remove $H_2S$ in the presence of $SO_2$, and vice versa).

Flame photometric detection of hydrogen sulfide ($H_2S$) in the sample of air is performed by adding a pretreatment unit to the automated analyzer for sulfur dioxide. It is shown in Figure 19.

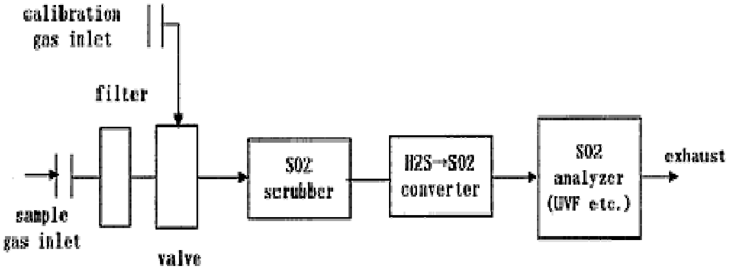


FIGURE 19 An example of flame photometric analyzer for $SO_2$ measurements.

In this device, the sample air is sent to the scrubber to eliminate sulfur dioxide. The remaining hydrogen sulfide is oxidized into sulfur dioxide with a catalytic converter, and then measured by the ultraviolet fluorescence method or a similar method. This method assumes that, after the sulfur dioxide has been removed, the total sulfuric compounds (total S) consist only of hydrogen sulfide. This means that the sulfuric compounds other than sulfur dioxide are measured more truly.

### *6.1.3 IONIZATION METHODS*

Ionization methods include:

- thermionic detection where ionization is induced thermally, either by flame or by an electrically heated filament;
- photo-ionization, which is caused by irradiation with UV light;
- mass spectrometry (ionization by high energy electrons);
- electron capture (a radioactive source is used to ionization).

#### 6.1.3.1 Thermionic detection

A Flame Ionization Detector (FID) measures organic compounds by utilizing a flame produced by the combustion of hydrogen and oxygen (air). The gaseous sample controlled at a constant flow rate is mixed with hydrogen for fuel use, and then the mixed gas is burned at the end of a thin nozzle. Ions (electrically charged particles) are produced during the combustion. They are attracted to a collector electrode with a polarizing voltage (Fig. 20). Two electrodes are installed across the flame. An appropriate electric field is applied to them. Ionic current will flow between the collector electrode and the opposite electrode. This ionic current is amplified with the amplifier and then sent to the meter, where the measured concentration of organic compounds is indicated. The resulting current of these ions is directly proportional to the organic carbon content in the sample. In principle, the FID method shows responses in proportion to the number of carbon atoms in hydrocarbons. Therefore, concentrations are shown as equivalent to those of methane in ppm by using units called "ppmC." FIDs have very large dynamic ranges, from 10 to 100,000 mg of organic carbon / cubic meter. This dynamic range can be further expanded by use of a dilutor kit which reduces very high VOC concentrations to within the dynamic range (or even linear range) of the analyzer. The dilutor kit can also be used to enrich oxygen deficient samples by adding ambient air that is rich in oxygen (20.9 % usually). Low oxygen can affect the characteristics of the hydrogen flame, causing readings to be artificially elevated and possibly extinguishing the flame. As a general rule of thumb, greater than 14 % oxygen is required to support the flame. If high concentrations of organic substances or inert gas samples with low oxygen concentrations are to be measured by an FID, it is advised that a dilutor kit be used to combat the problem.

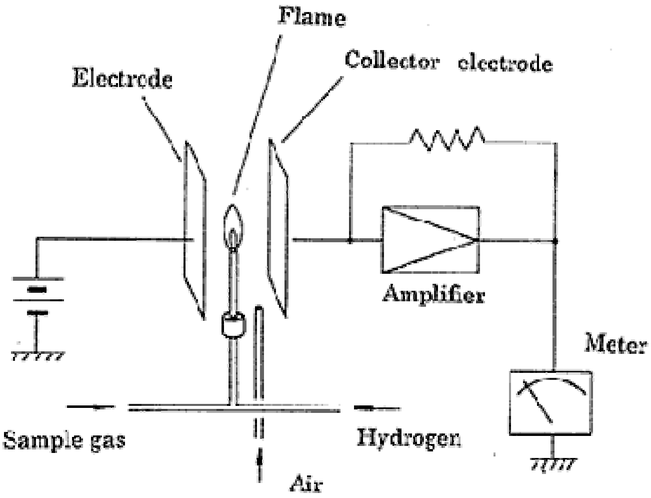


FIGURE 20 Typical Flame Ionization Detector.

The FID method has problems in relation to oxygen interference with responses to hydrocarbons (an error occurs if there is a difference in the oxygen concentrations of the calibration standard gas and the sample air) and the relative sensitivity (not completely proportional to the number of carbon atoms in the hydrocarbons). The degree to which these problems affect the results varies depending on the organic material type and combustion conditions. This means that the THC value varies depending on the composition of hydrocarbons and the monitoring system. The FID method should be used bearing these things in mind. Since the sensitivity of FID is dependent on the flow rates of the sample and hydrogen, care must be taken to control these flow rates. This analyzer provides excellent features including linearity across a broad range of concentrations, high sensitivity, and fast responses. However, if hydrocarbon coexists with oxygen, the response differs depending on the kind of hydrocarbon. In the case of a sample whose composition fluctuates greatly, the analyzer has a problem with quantitative analysis. In order to prevent the delay in response due to the adsorption and desorption of hydrocarbon at a high boiling point, the sample line might be heated. The hydrocarbon analyzer utilizes a heated system from the point of the sample interface throughout the entire analytical system to avoid cold spots where heavier hydrocarbons may be adsorbed and cause erroneous results. Flame ionization detection method presents the following benefits:

- wide dynamic and linear range;
- high sensitivity to most hydrocarbons;
- very stable and repeatable response;
- ability to measure methane;
- virtually unaffected by CO, $CO_2$ and water vapor;

The FID is convenient to use in source sampling situations since it does not respond appreciably to gases such as $O_2$, $N_2$, $H_2O$, CO, $SO_2$, and NO. However, organic compounds that contain nitrogen, oxygen, or halogen atoms may give a response reduced from that seen from hydrocarbons.

The determination of hydrocarbons is carried out by delivering semi-continuously air to a hydrogen flame ionization detector; its response is proportional to the total hydrocarbon content. As methane is a natural air component which is present in fairly high concentrations (about 1 p.p.m.), its concentration has to be determined and the value of total hydrocarbons may be corrected for the methane content. In order to measure the concentration of NMHC in the sample air, a method based on the combustion characteristics of NMHC and methane (which is difficult to burn) can be applied. It uses two lines, the THC measurement line (which directly sends the sample air to the FID) and the methane measurement line (which selectively oxidizes NMHC with a catalyst and sends it to the FID while leaving difficult-to-burn methane). The analyzer is schematically presented in Figure 21. The difference between the two measured values is calculated to obtain the concentration of NMHC. Basically, the line switching and data processing procedures are the same as in the chemiluminescence method used in the automated analyzer for nitrogen oxides.

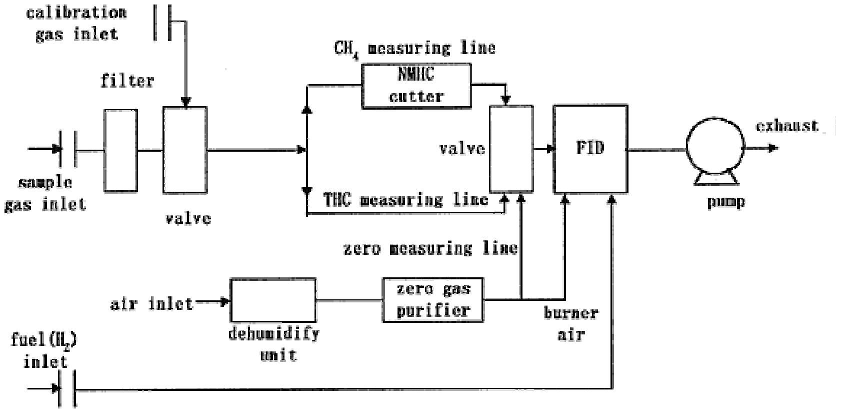


FIGURE 21 A scheme of analyzer for non-methane hydrocarbons (NMHC).

### 6.1.3.2 Photo-ionization method

In a photoionization detector (PID) organic molecules are ionized by ultraviolet light. A typical PID incorporates a UV lamp suitable for ionizing the analytes of interest and a pair of electrodes to measure a current proportional to the concentration (Fig. 22). Compounds R passing through the chamber are excited by photons of UV energy from the lamp and ionized according to the following equation:

$$R + h\gamma \rightarrow R^{+} + e^{-}$$

where $R^{+}$ is the ionized organic compound and hv represents the energy of the light having frequency $\gamma$ (h = Planck's constant). These ions are attracted to a collecting electrode, producing a current proportional to the concentration of the compound. Whether or not a compound can be detected by a PID depends upon the lamp energy and the energy required to remove an electron from the compound (its *ionization potential).* If the lamp energy is greater than the compound's ionization potential, the PID will detect it. The standard lamp is 10.6 eV, however other lamps are also available (9.6 and 11.8 eV). The 11.8 eV lamp permits detection of many compounds not ionized by the standard lamp, while the lower energy lamps allow more selectivity by not responding to undesired compounds with a higher ionization potential. The major components of the flue gas such as $O_2$, CO, $N_2$, $CO_2$ and $H_2O$ are not ionized. Because of its smaller dynamic range (0-2,000 ppm), the PID would not be the detector of choice for measuring high concentrations of vapors (unless a dilutor kit is used). A PID is also more susceptible to interference from water vapor than an FID. However, a PID does not require hydrogen or oxygen, so it would be the detector of choice when fuel is limited or unavailable, or when ambient oxygen concentrations are low. The PID is also more sensitive to aromatic and chlorinated compounds, and can measure some inorganic compounds that the FID does not detect at all (ammonia, carbon disulfide, carbon tetrachloride, chloroform, ethylamine, formaldehyde, and hydrogen sulfide, to name a few).

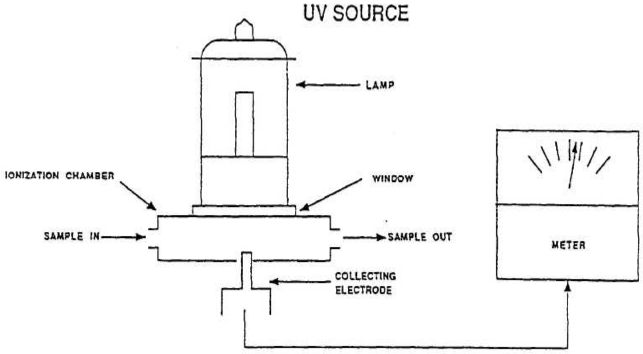


FIGURE 22 The scheme of typical photoionization detector.

There are the following benefits of photoionization detection:

- high sensitivity to aromatics, unsaturated hydrocarbons and chlorinated hydrocarbons;
- ability to measure some inorganic gases;
- very simple operation;
- no support gases required;
- non-destructive detector allows the sample to be recovered.

Depending upon the instrument, compounds detected by PIDs include: aliphatic and aromatic hydrocarbons, halogenated organics, alcohols, ketones, aldehydes, ethylene oxide, vinyl chloride, and inorganic compounds such as arsine, phosphine, and hydrogen sulfide. In general, compounds that have ionizable electrons can be detected.

#### 6.1.3.3 Mass spectrometry

In the technique of mass spectrometry, molecules are ionized by high energy electrons, or by other means (such as chemical or photoionization process), and the resultant molecular ions and ion fragments are separated according to their mass to charge ratio (m/e). Mass spectrometry (MS) is an analytical technique in which atoms or molecules from a sample are ionized, separated according to their mass to charge ratio, and then recorded. In mass spectrometry, molecules are bombarded with high energy electrons. When an electron with a sufficient amount of energy collides with a sample molecule, it dislodges an electron from the sample molecule and creates a molecular ion called a cation ion radical. The cation radical is positively charged and has an odd number of electrons but has basically the same mass as the uncharged parent compound because the mass of an electron is negligible. The positively charged ions are then directed into an analyzer tube surrounded by a magnet. Under these circumstances, substances break up in a reproducible manner and give rise to a unique pattern of fragments of different masses, which are related to the molecular structure of each substance. The observed pattern and the abundance of the fragments of each mass can be measured by separating the fragments according to the mass. This is achieved by accelerating the fragments electrically and separating them in a magnetic field or in a mass filter, after which the abundance of fragments of each mass is measured in turn by a photo-multiplier. Given that different fragments will be formed, and they will have different sizes, particular types of cationic species will have characteristic mass-to-charge ratios (m/z). A mass spectrometer scans all the m/z values and gives a distribution of positive ions, called a mass spectrum. The mass spectrum is unique to the original molecule, as is an infrared or UV spectrum. The most intense peak in the mass spectrum is called the base peak and is assigned a relative intensity of 100. Mass spectrometers have broad analytical applicabilities because the ionisation process is fairly uniform for all compounds. One instrument can measure many compounds providing a cost effective means of monitoring. They are inherently fast, sensitive, and capable of a wide dynamic range (parts per billion to 100%). The mass spectrometer is quantitative and linear since its output is directly proportional to the concentration of the species in the sample. It is a reliable, stable and low maintenance instrument because it is electronically based rather than chemically based, as are many single sensors. Finally, the mass spectrometer has maximum flexibility because its broad capabilities can be selectively used under programmable microprocessor control. Mass spectrometers are distinguished by the type of mass separator used. Magnetic deflectors, time of flight separators, quadrupole mass analyzers, and ion-traps have all been used. For environmental applications, the quadrupole mass analyzer is used most commonly. The linear quadrupole mass analyzer operates by oscillating the ions in a radio-frequency field superimposed on the charged cylindrical rods.

Most of the ions will oscillate with increasing amplitude and strike the rods, but one set of rod voltage and radio-frequencies will exist where the ions of a specific m/e ratio will be able to pass through to the detector. The radio-frequency or rod voltage is therefore scanned to obtain the mass spectrum. The mass analyzers used in mass spectrometer systems are operated under high vacuum (1 x $l0^{-5}$ or 1 x $10^{-6}$ mm Hg) to minimize scattering by collision with other ions and gas molecules. This requires some type of vacuum pump and a system design that can maintain a proper vacuum. The cleanliness of the system is important also, and adsorbed materials on the walls of the analyzer can lead to the introduction of interfering ions. These requirements can lead to problems in source monitoring applications and must be overcome to achieve consistent results.

#### 6.1.3.4 Electron capture detector

Electron capture is a technique which is allied to ionization methods. The electron capture detector (ECD) is selective for certain groups of organic compounds such as those containing halogen atoms or nitro groups. The device consists of a cell, in which two electrodes are located, one of which contains a radioactive source. The electron capture detector works by using a radioisotope treated electrode that emits high energy electrons as it decays (β emission). The β electrons react with the carrier gas to produce secondary, free electrons which move to a positively charged anode to generate a current through the system. When an electromagnetic species is introduced into the detector, it captures electrons and reduces the standing current. The extent of this decrease is dependent upon the number of electron-capturing species present and their electro-negativity. The ECD is more sensitive for specific groups of compounds than is the FID, but the response can again vary from compound to compound. Issues associated with the transport, storage, and disposal of the radioactive material have also been of some concern.

### *6.1.4 THERMAL METHODS*

Methods based on a combustion heat are used only for the measurement of combustible gases.

A sample is passed over a catalytic sensor which is heated to above the ignition temperature of the measured gas. A coil of wire in this device is coated with glass or ceramic material which is, in turn, coated with a catalyst. A filament within the sensor is connected in an electrical bridge circuit. The coil is electrically heated to a temperature that will allow it to burn (catalyze) the monitored hydrocarbons. When burned, all hydrocarbons liberate heat proportional to the concentration of the hydrocarbons present. This heat increases the temperature of the wire coil, increasing its resistance. The increase in resistance is measured electrically and is the source of the signal. The heat of combustion increases the temperature of the wire coil, increasing its resistance and unbalances the bridge by an amount proportional to the concentration of the analyte in the sample.

The advantages of catalytic sensors:

- these devices are small, can be made mechanically rugged;
- the signal is generated directly by actually burning the gas, which is the

property of the gas being measured;

- they are specific (only measures combustible gases);
- they are inexpensive;
- long life (usually 2 to 4 years);
- they are simple to calibrate and maintain.

The disadvantages of catalytic sensors:

- the thermal technique is non-selective and is affected by normal atmospheric components such as water and $CO_2$;
- span loss is undetectable except during calibration;
- they can be poisoned by trace amounts of silicone, halocarbons and metallo-organic substances, unless special methods of prevention are used;
- they have small signal-to-noise ratio;
- signal can go back to zero in hydrocarbons concentrations above their stoichiometric mixtures;
- some sensors can be permanently damaged when exposed to high or continuous concentrations of gases being measured.

### *6.1.5 GAS CHROMATOGRAPHY*

Gas chromatography is typically used to isolate the individual components of a mixture of organic and inorganic compounds from each other for subsequent identification and quantitative analysis. This method is based on the selective distribution of compounds between a stationary phase and a mobile phase (carrier gas). In this process, the moving gas phase passes over a stationary material that is chosen to either absorb or adsorb the organic molecules contained in the gas. The stationary material or phase can be either a liquid or a solid and is contained in a long, thin tube referred to as a “column.” Columns are made of fused silica, glass, or stainless steel and vary in diameter depending upon the type of column packing (the stationary phase) used. In an ideal column operated under ideal conditions, each molecular species will exit the column at a different time. The equilibration between the individual compounds and the column stationary phase is a function of:

- the compound’s affinity for the stationary phase relative to the mobile phase;
- the temperature of the column;
- the flow rate of the mobile phase carrier gas.

Individual molecules are separated in the column by undergoing a series of equilibrations between the stationary and mobile phases. Selecting the appropriate column and optimizing the column temperature and carrier gas flow rate should enable separation of the gas sample into its individual components. A chromatographic system is also composed of a device for injecting the sample into the column, a carrier gas to sweep the sample gas through the column, a column oven, and a detector. The carrier gas, such as helium or nitrogen, sweeps the sample from the injection area into the heart of the system, the column. The separation performed in a chromatographic column is sensed by a detector and recorded. The detector at the end of the column ultimately produces an electrical signal that is proportional to the quantity of molecules present. Any detector designed for use in a gas chromatograph system must have a high sensitivity for low concentrations of organic molecules, and a rapid response time. Many detectors are available that meet these requirements; the most common in source monitoring applications are the flame ionization detector (FID) and the photoionization detector (PID). In more sophisticated applications, optical spectroscopic or mass spectroscopic techniques are employed. Separated peaks are identified and quantified by comparison of their peak areas to a calibration with known gas standards. However, for an unknown sample mixture, one will not know what standards to include in the calibration unless some prior knowledge of the flue gas composition is available. In that case, one must use techniques such as infrared, ultraviolet, or mass spectrometry to first identify the compounds and then select the column and appropriate standards.

### *6.1.6 GAS CHROMATOGRAPHY/MASS SPECTROMETRY*

Gas chromatography/mass spectrometry (GC/MS) is the combination of two analytical methods – gas chromatography and mass spectrometry. When these two methods are coupled together into the same analytical instrument, gas chromatography/mass spectrometry or GC-MS analysis are obtained. Gas chromatography (GC) effectively separates the different constituents of the sample for subsequent analysis and identification by mass spectrometry (MS). As a sample constituent elutes from the GC column, it enters the ionization chamber of the mass spectrometer where the molecules are ionized, typically by electron impact. It results in the loss of an electron from the molecule, a positive ion is formed. Some of the molecular ions are further fragmented into daughter ions and neutral fragments. The positive ions are then repelled out of the ionization chamber by a small positive charge within the chamber. Negative ions are also formed by the electron impact, but they are not analyzed. The positive ions are separated according to their mass by a mass analyzer. The mass analyzer most commonly used in GC/MS is the quadrapole filter, in which the ions pass by four hyperbolic magnetic poles created by a radio frequency field. The magnetic poles separate the ions by their mass/charge ratio, successively focusing ions with increasing mass onto a detector for counting. The analyzer scans step-wise through a set range of mass values to evaluate the relative abundance of ions at each mass value. The quadrapole filter can perform a complete mass scan within the duration of a single GC elution band. The first result from the compiled data is a total-ion chromatogram (TIC), which is a plot of the total mass eluting from the GC and detected by MS as a function of time. Each peak or band in the chromatogram represents a discrete chemical compound, or a mixture of compounds with identical retention times. The retention times in the chromatogram provide the first indication of the sample constituents. More specific identification of the compound(s) for each band can then be made from the mass spectrum corresponding to the band. Compounds are identified from the mass spectrum by their unique ion fragmentation patterns. This compound identification analysis is performed by a computerized comparison of the mass spectra for the sample with spectra library for known compounds. The analysis results can be quantified using the data from the chromatogram. The area under each peak in the chromatogram is proportional to the concentration of the compounds represented by that peak. The concentration for each compound in the sample is calculated from a standard curve of known concentrations established for that compound. The analysis sensitivity can be as low as a few nanograms. The samples for GC/MS can be gases, liquids, or solids. However, only those constituents that are gaseous and stable at the analysis temperature can be analyzed. Gases and liquids can be injected directly into the sample injector. Volatile compounds from solid materials are collected using a headspace sampler. The sample from a headspace attachment can be collected and injected at one time (static headspace), or the sample can be collected and analyzed continuously over a set time period (dynamic headspace). GC/MS is a versatile technique for the identification of complex volatile materials. The GC/MS combination provides both qualitative and quantitative information since it looks at each different type of molecule separately as it comes off of the column (Fig. 23). The GC/MS output gives a three-dimensional plot over time, giving information both on the type of compounds in the sample and the amount present.

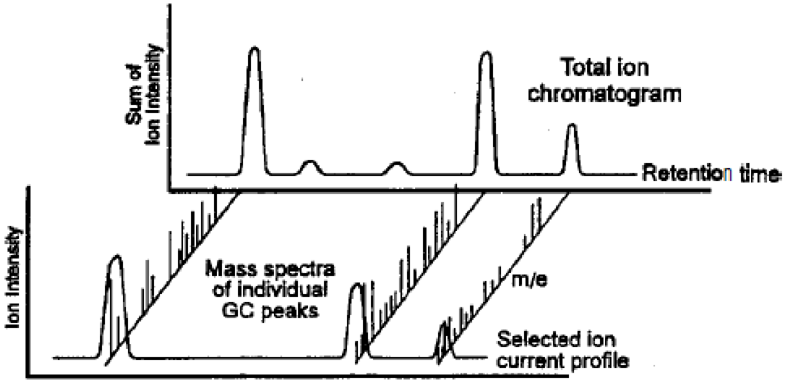


FIGURE 23 Total ion current chromatogram.

Mass spectrometers and GC mass spectrometers have been applied to monitor criteria pollutants on a continuous basis and are being used increasingly in the process analysis. Their use in environmental monitoring has focused primarily on the ambient monitoring of hazardous waste sites or leak monitoring in the chemical and petroleum industries.

### 6.1.7 PARAMAGNETIC ANALYZER

Paramagnetic analyzers are commonly used to measure oxygen, and are normally used in continuous emission monitoring systems (CEMS) to measure oxygen as the diluent gas. There are several types of this instrument. The most widespread are two types of paramagnetic analyzers of $O_2$:

- the magnetic force;

- magnetic wind type.

The magnetic force type oxygen analyzer is largely classified into the dumbbell type and the magnetic pressure type. Oxygen has a relatively high magnetic susceptibility as compared to other gases such as nitrogen, helium, argon, etc. and displays a paramagnetic behavior. A dumbbell type or, more properly, magneto dynamic, which uses a small dumbbell-shaped optical component to physically determine the oxygen concentration. This oxygen analyzer consists of a cylindrical-shaped container inside of which a small glass dumbbell is placed (Fig. 24).

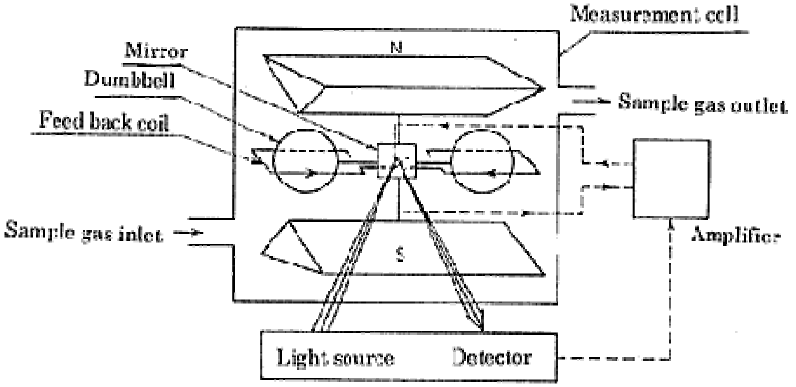


FIGURE 24 Dumbbell type of paramagnetic analyzer.

The dumbbell is filled with an inert gas such as nitrogen and suspended on a taut platinum wire within a non-uniform magnetic field. The dumbbell is designed to move freely as it is suspended from the wire. When the sample gas is introduced into the magnetic field, oxygen in the gas tends to approach the strongest part of the magnetic field while trying to push the dumbbell aside. This produces such force as pushes the dumbbell out of the magnetic field, causing the suspending wire to be twisted. This twist is detected as the movement of light from the reflective mirror secured at the center of the suspending wire. A precision optical system consisting of a light source, photodiode, and amplifier circuit is used to measure the degree of rotation of the dumbbell. In some paramagnetic oxygen sensor designs, an opposing current is applied to restore the dumbbell to its normal position. The current required to maintain the dumbbell in it normal state is directly proportional to the partial pressure of oxygen and is represented electronically in percent oxygen. In another words, the concentration of oxygen is measured from the intensity of this current. This method assures high linearity, minimizes the effects of coexisting gases, and provides high response. However, it is susceptible to mechanical shocks. These have also the limitation of having moving parts and optical components exposed to the sample gas, which may be corrosive.

The magnetic force oxygen analyzers can also be based on magnetic pressure sensors. In these instruments, the sample gas is introduced into a magnetic field which is uneven due to magnetic poles, oxygen (paramagnetic material) in the sample gas is attracted toward the strongest part of the magnetic field, in which the magnetic poles have come closer to each other (Fig. 25). A small amount of reference gas like pure nitrogen or air is externally supplied through a small hole made on one of the magnetic poles. The increase the pressure resulting from the attraction of oxygen is then detected with a capacitor microphone type detector or a mass flow sensor. In order to ensure the stable detection of signals, the two magnetic poles are alternately excited to amplify alternating current. In this method, the effects of coexisting gases are relatively small and the zero point is stable. For this measurement, a reference gas is required.

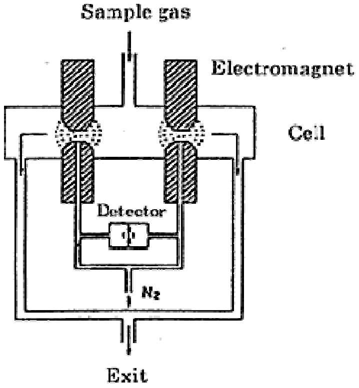


FIGURE 25 Magnetic pressure type of paramagnetic analyzer.

In the paramagnetic analyzers, the magnetic wind or thermomagnetic type detector can also be used, where there are no moving parts and the construction is of highly corrosion resistant materials, which results in an extremely robust instrument with a long service life. The detector has two chambers, each of which has a heating wire element located at the center (Fig 26).

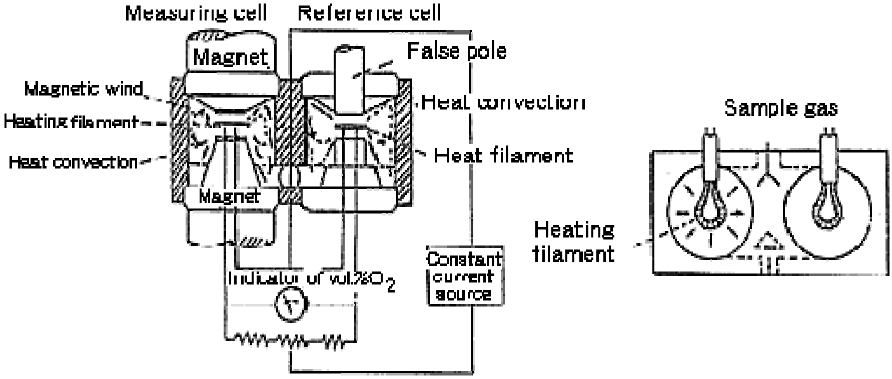


FIGURE 26 Magnetic wind or thermomagnetic type of paramagnetic analyzer.

A magnetic field is provided only on the measurement chamber. Once the gas under measurement is sent to the measurement chamber, oxygen is attracted by the magnetic field and then heated with the heating wire element. Thus, the magnetization factor decreases and a continuous flow of gas (magnetic flow) occurs. The magnetic flow cools the heating wire element as its intensity varies in proportion to the concentration of oxygen. Therefore, the resistance changes during this process are picked up as unbalanced voltage at the bridge to measure the concentration of oxygen. The magnetic wind type analyzer uses no movable part, making it highly resistant against vibrations and other similar effects. Such a relatively simple structure provides this analyzer with high durability. Carbon dioxide causes positive interference as the thermal conductivity varies greatly. If the concentration of $CO_2$ is stable enough, the interference of $CO_2$ is compensated for by applying electric compensation to the reading of $CO_2$ or by taking any other effective means.

## 6.2 METHODS AND TECHNIQUES OF PARTICULATE MATTER ANALYSIS

The term “particulate matter” is used to define any solid or liquid matter dispersed in the atmosphere. Particulate matter originates from a variety of sources and for its complex composition several parameters should be taken into account to evaluate the impact upon human health and materials. They may be summarized as follows:

- total mass loading expressed as a mass of particulate in a given volume of air;
- relative mass resulting from particles in a given size range to evaluate the relative contribution to respirable aerosols;
- chemical composition to evaluate the concentration of definite harmful chemicals such as $H_2SO_4$, silica, Hg, Be, asbestos, poly-cyclic hydrocarbons, etc.;
- optical parameters which should be investigated to evaluate effects such as visibility reduction.

Several measurement techniques based on different physical phenomena, (optical, radiation, electrical, and electromechanical vibration) are used in particulate monitoring systems.

### *6.2.1 PARTICLE SIZE MEASUREMENTS*

Particle size measurements for particulates extracted by filtration, electrostatic or thermal precipitation, or impaction may be performed using:

- microscopy;
- sieve analysis;
- gas or liquid sedimentation;
- centrifugal classification;
- electrical or optical counters.

For aerosol particulate size determination, however, questions arise such as whether the collected particles agglomerate after capture, or whether they are redispersed to the same degree in the measuring media as they originally were. These problems can be avoided mainly by performing aerodynamic particle size measurements on the original aerosol by using such devices as cascade impactors.

### *6.2.2 MASS MEASUREMENTS*

Measurement of the mass of material collected can be undertaken by direct weighing either off-line or on-line. Alternately, surrogate methods of mass determination, such as absorption can be used. In the black smoke method, measurement is made by determination of the reflectance of the filter stain by a calibrated reflectometer. Nephelometers are primarily only useful for measuring very fine particles (PM<2.5).

In general, particulate monitoring instruments use one of the following particle concentration measurement techniques:

- gravimetric;
- radiometric (beta-ray absorption method);
- oscillating microbalance (TEOM);
- optical;
- piezoelectric balance.

#### 6.2.2.1 Gravimetric or filter-based method

The concentration of suspended particulate matter is traditionally determined by a gravimetric method. The equipment used in this method is known as a High-Volume Air Sampler. The most common is the High-Volume Air Sampler fitted with a size selective inlet. Gravimetric or filter-based instruments collect particulates by drawing the air through suitable filter media. The sample is taken through continuous filtration of ambient air at a rate of about 1.5 $m^3$/ min on selected filtering material (e.g. membrane with a mean pore size of 0.85 μm, Teflone with a mean pore size of 1 μm or glass fibre with a capturing capacity more than 99.5%). Samples are normally collected over 24 hours. The filter head is turned with the open side down, at a distance of 1.5 - 3.0 m above the surface. The sampling frequencies correspond to the character of the sampling site location. The filters are later weighed at special laboratory facilities to determine the mass concentration of particulate collected. The amount of sample captured on the filter (in μg) is determined gravimetrically as a difference between the weight of the filter prior to and after the exposure.

Weighing of filter paper

The collection filter paper should be weighed before and after use with a direct reading balance with a sensitivity of 0.1mg or greater after leaving it in a balance room with fixed temperature and humidity for 24 hours. Great care must be taken when the filter paper is used as it is easily damaged. Each sample must be weighed at least twice. It should be confirmed that such readings are nearly identical. If they differ substantially, the weighing procedure must be repeated until stable values are obtained.

## Storing collection filter papers

It is best to analyze the filter paper immediately after sampling, but handling a number of samples is more effective in reality, so they should be stored in accordance with the type of filter paper material and analysis objective. The storage method for filter paper that has been used for collection differs depending on the analysis objectives. Heavy metal components can be stored at room temperature after being placed in a plastic bag or suchlike to avoid contamination from within the room. Anionic or organic components are very volatile and easily deteriorate at room temperature, so they need to be kept refrigerated or frozen. Also, there are some substances whose concentration certainly decreases under light at room temperature such as benzo[α]pyrene. Thus, it is better to store samples that are used to analyze a number of components in a dark and frozen state.

## Balance

The following points must be considered when the balance is used.

1. It is preferable to place the balance in an exclusive room such as a balance room. If there is no balance room, it should be placed somewhere that is used by few people and where the room temperature is stable.
2. The balance should not be placed anywhere that is at all unstable or shakable.
3. It should not be placed near a heat source such as a heater or in direct sunlight, but rather should be as far from any heat as possible.
4. If there is a balance room, the room humidity should ideally be 60% and temperature 20°C.
5. When using a balance, maintain an upright posture and do not place your elbows on the balance table. Do not get too close to the balance because the more minute the balance reading is affected by human body temperature.
6. Turn the operation handle very gently to make operating status of the balance.
7. When weighing a hygroscopic sample, it is best to weigh it after the operation of the balance is settled.
8. When weighing a sample with electrostatic chargeability, such as a membrane filter, use aluminum foil or suchlike to prevent electrostatic charging before weighing.

Gravimetric techniques have been used for years to quantify mass concentration levels of airborne particulate matter. The gravimetric method suffers definite limitations due to several factors which should be carefully controlled (sampling rate, linear flow rate and filter); it is, however, the only direct way for mass measurement and is the most suitable for this purpose.

Filter-based sampling is labor intensive. Filters must be conditioned, weighed before sampling, installed and removed from the instrument, and reconditioned and weighed again at a special facility. Results may not be available for days or weeks. Also, airflow rates and elapsed sampling time must be carefully monitored and recorded to ensure accurate results. Filter-based techniques integrate samples over a long period of time, usually 24-hours, to obtain the required minimum mass for analysis. Gravimetric monitoring is best for the projects where high-accuracy is needed and the time delay in receiving the data is not a problem. State monitoring networks designed to detect violations of air quality standards rely largely on gravimetric monitors.

#### 6.2.2.2 Radiometric method (beta-ray absorption method)

For SPM concentration measurement (suspended particulate matter fraction up to 10 μm particle size) the radiometric method may be used. It stands on beta-ray absorption in a sample captured on filtering material. In the beta gauge, the passage of electrons through a material is attenuated by the presence of the real mass concentration between the radioactive source and the detector. A known volume of air is drawn by a constant flow rate pump and filtered over the fibre tape which moves intermittently between a radiation counting gate and an air sampling gate (Fig. 27). The β-attenuation unit operates by drawing the air at a rate of 15 to 20 litres per minute through a continuous glass-fibre or Teflon tape. The mass of the filtered matter is determined through absorption of low-energy beta-radiation by rationing the impulse rates given by irradiation of the dusted and undusted filter. The difference between the beta-ray absorption of the exposed and non-exposed filtering material, which is proportional to the mass of the captured suspended particle matter, gives the information on its concentration. The radiation absorbed is proportional to the mass of filtered matter and is independent of its density, chemical composition and physical or optical properties. Thus the beta-ray irradiation on the particulate matter collection on the filtration paper gives only information about its quantity. The relationship between intensity of beta-ray transmitted and dust quantity is expressed by the following equation:

$$I = I_0 exp\left(\frac{-\mu_m}{X_m}\right)$$

where: I - beta-ray intensity transmitted through filter and particulate, $I_0$ - beta-ray intensity transmitted only through filter, $\mu_m$ - mass absorption coefficient ($cm^2/g$), $X_m$ - mass of particulate matter ($g/cm^2$). From this equation, the mass of SPM is calculated as

$$X_m = \frac{1}{\mu} ln\left(\frac{I_0}{I}\right)$$

Measurements are normally averaged over one hour to obtain sufficient sensitivity, and the tape is advanced either at the end of each cycle or at some other pre-set interval.

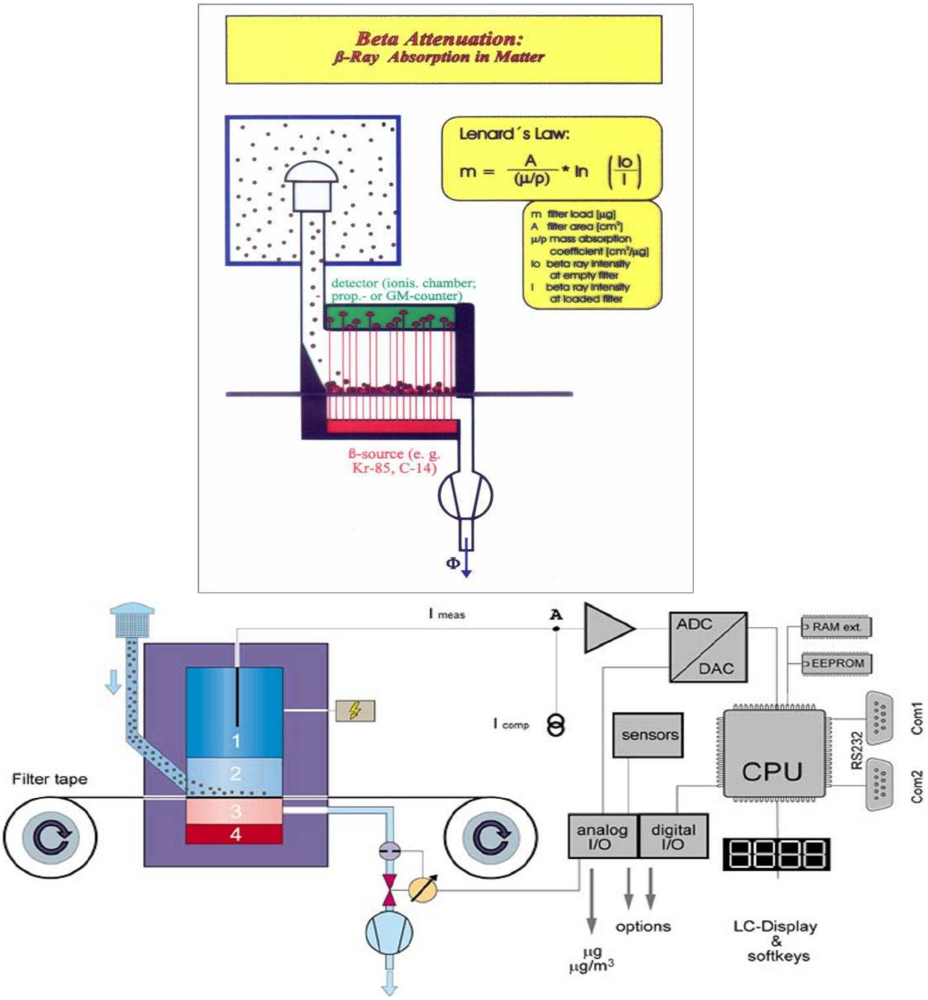


FIGURE 27 Typical beta gauge paper tape monitor.

### 6.2.2.3 Tapered element oscillating microbalance

The automated stations for ambient air quality monitoring very often use for the suspended particulate matter continuous measurements the tapered element oscillating microbalance (TEOM). The TEOM operates on the theory of the vibrating reed. A vibrating reed that is anchored at one end vibrates with a single frequency, with no harmonics. Thus, as mass is added to one end of the vibrating element, the resonant frequency changes, and this change is directly proportional to the accumulated mass. In this monitor, the air sample passes through a replaceable filter where the dust particles are captured and runs through a hollow tapered element to a vacuum pump with an electronic flow control (Fig. 28). The filter 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.

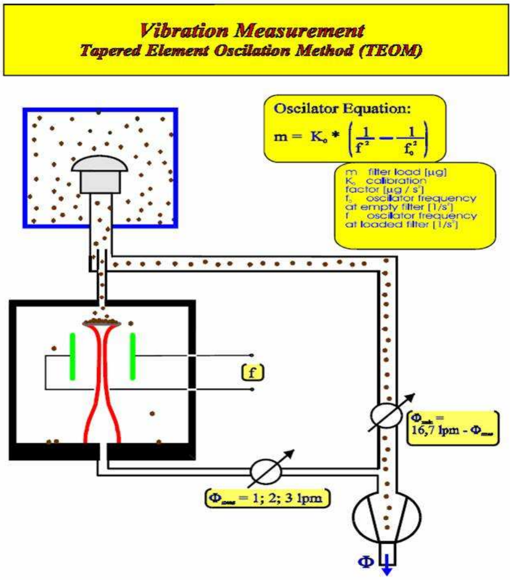


FIGURE 28 Tapered element oscillating microbalance.

### 6.2.2.4 Electromechanical method

Electromechanical devices have been developed on the principle that the frequency of a vibrating oscillator will change if the mass of the vibrating element changes. A piezoelectric crystal, a cantilevered beam, or oscillating metal band may be used to provide the mechanical vibration. When particulate matter comes into contact with the vibrating element, it adheres to it and changes its total mass, and consequently, its vibration frequency. This mass-dependent vibration frequency is then measured as the correlation parameter.

#### Piezoelectric balance method

An indicated value as a mass concentration is obtained from the decrease of the frequency of a quartz due to the adhesion of particle. The crystal oscillates with very high stability at its resonant mechanical frequency. A collector, such as an impactor or an electrostatic precipitator, deposits the suspended particles onto the electrode surface of the vibrating crystal. The resonant frequency shifts downward linearly with the added mass of the particles. Frequency is monitored with a standard digital counter. The time rate of change of the frequency is proportional to the mass concentration of ambient suspended particles. The advantage of piezoelectric balance method is high sensitivity.

#### 6.2.2.5 Triboelectric method

The triboelectric method is based on the measurements of the intensity of electric current resulting from the triboelectric effect, which consists in generating electrical charges during collisions or rubbing of solids against one another. These devices detect charge imparted to an intrusive steel probe by three mechanisms, charge transfer, frictional electrification and charge induction. When two dissimilar materials make contact, a net transfer of electrons from one material to the other can occur. This is not an effect based on the accumulation or transfer of static charges, but an effect based upon the intrinsic electronic properties of the materials themselves. The amount of charge transferred depends on the particle's work function, resistivity, dielectric constant, and the physical conditions of contact (particle deformation, duration of contact, area of contact, etc.).

#### 6.2.2.6 Optical methods

Optical instruments measure light-scattering (nephelometers) or light-absorbing (aethalometers) characteristics of the gas. This measurement can then be converted to obtain an estimate of the concentration of airborne particulates. Optical instruments offer several advantages over gravimetric methods, including real-time readings, portability, low power consumption, and relatively low cost. These devices have the disadvantage of being generally less accurate than gravimetric instruments at estimating particulate mass concentration. Optical instruments are best for the projects where real-time or near-real time data is needed, where a high degree of accuracy is not a requirement, and if instrument portability and ruggedness is desirable. Proper conversion of the light scattering measurement collected by nephelometers to estimate particle concentration requires development of customized conversion equations. The light scattering value measured depends on particle size distribution and optical properties of the specific aerosol mix in the area of interest.

### *6.2.3 THE ANALYSIS OF DUST DEPOSITION*

The samples of dust deposition are filtered and analyzed 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 the weight of material collected over unit area and in unit time. It should be noted that the results produced by different sampling systems will not necessarily be comparable. The results are best interpreted in a relative sense with one type of collector only.

### 6.2.4 THE ANALYSIS OF METALS

In addition to mercury (Hg), the following metals are regarded as hazardous air pollutants (air toxics): antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), lead (Pb), manganese (Mn), nickel (Nil, and selenium (Se). Considerable interest exists in the development of instrumental methods for metals. As in the initial development of gas monitors, multi-metal methods are essentially laboratory techniques adapted for field use. The analysis of metals in the ambient air samples can be based on:

- an atomic absorption spectrometry (AAS) (using e.g. membrane filters Synpor for sampling followed by mineralization using hot nitric acid); - polarographic method;
- inductively coupled plasma (ICP);
- inductively coupled plasma-atomic emission spectrometry (ICP-AES) with high-volume sampling on glass-fibre filters;
- a non destructive method of X-ray fluorescence (XRF) using a Teflon filter.

The techniques of x-ray fluorescence spectroscopy and atomic emission spectroscopy have seen the most application. X-ray fluorescence spectrometry is being applied in a manner similar to that of the beta gauge used to continuous monitoring of particulate matter. To analyze for metals, particulate bound and gaseous metals are collected on an activated carbon impregnated filter. The collected material is then exposed to x-rays, which excite the atoms to higher electronic levels. As the excited atoms de-excite, they fluoresce, emitting light at wavelengths specific for each metal. The amount of emitted light is measured and the flue gas metal concentration is calculated. X-ray fluorescence spectroscopy is a well-established technology; however, the commercial continuous monitoring systems applying the technique have not been fully developed. Current systems involve collecting and analyzing the filter samples in a batch mode, not a continuous mode.

In atomic emission spectroscopic systems, atoms can be excited in many ways and when excited sufficiently, will emit light energy. The atomic emission spectroscopic techniques differ by the manner in which the metal atoms are excited - either through the use of a laser, a radio-frequency plasma, or a microwave generated plasma. In an inductively coupled plasma spectrometry (ICP), a radio frequency generated plasma is used to heat the flue gas sample to temperatures greater than 10,000ºC . The light emitted by the metal atoms excited at this extreme temperature is measured using a diffraction grating and photodetectors as shown in the figure.

# 7 CALIBRATION

Calibration is defined as the comparison of a measurement standard, instrument, or item with a standard or instrument of higher accuracy to detect and quantify inaccuracies and to report or eliminate those inaccuracies by adjustment. It is the process of submitting the samples of a known value to an instrument, in order to establish the relationship of value to instrumental output. Calibration of an analyzer or an instrument establishes the quantitative relationship between an actual value of a standard, be it a pollutant concentration, a temperature, or a mass value, and the analyzer's response (chart recorder reading, output volts, digital output, etc.). This relationship is used to convert subsequent analyzer response values to corresponding concentration, temperature, or mass value.

## 7.1 VERIFICATION VERSUS CALIBRATION

In verification, the correlative information will usually be compared to the limits to determine whether the test instrument is "good" or "bad". In calibration, the information will be used as the basis for adjusting the instrument under test to improve the correlation and thus improve test instrument accuracy. In both cases, the role of the standard is to provide accurate values of the quantity being measured. Since the term calibration is associated with an adjustment in either the instrument or software, these adjustments should be minimized as much as possible. Quality control procedures that include verification checks and multi-point calibration verifications are considered “checks without correction” and are used to ensure that the instruments are within the calibration tolerances. Usually these tolerances have been developed so that as long as the instrument is within these tolerances, adjustments do not need to be made. However, verifications should be implemented at reasonable frequencies to avoid invalidating significant amounts of data. Usually, when the term “calibration” is used, it is assumed that multi-point verification is initially performed and the operator has concluded that calibration (adjustment) is necessary. Calibrations should be carried out at the field monitoring site by allowing the analyzer to sample test atmospheres containing known pollutant concentrations. The analyzer to be calibrated should be in operation for at least several hours (preferably overnight) prior to the calibration so that it is fully warmed up and its operation has stabilized. During the calibration, the analyzer should be operating in its normal sampling mode, and it should sample the test atmosphere through all filters, scrubbers, conditioners, and other components used during normal ambient sampling and through as much of the ambient air inlet system as is practicable. All operational adjustments to the analyzer should be completed prior to the calibration. Some analyzers can be operated on more than one range. Analyzers that will be used on more than one range or that have auto-ranging capability should be calibrated separately on each applicable range.

## 7.2 MULTI-POINT VERIFICATIONS/CALIBRATIONS

Multi-point calibrations consist of a zero and 4 upscale points, the highest being a concentration between 80 percent and 90 percent of the full scale range of the analyzer under calibration. They are used to establish or verify the linearity of analyzers upon initial installation, after major repairs and at specified frequencies. Most modern analyzers have a linear or very nearly linear response with concentration. If a non-linear analyzer is being calibrated, additional calibration points should be included to adequately define the calibration relationship, which should be a smooth curve. Calibration points should be plotted or evaluated statistically as they are obtained so that any deviant points can be investigated or repeated immediately. Most analyzers have zero and span adjustment controls, which should be adjusted based on the zero and highest test concentrations, respectively, to provide the desired scale range within the analyzer's specifications. For analyzers in routine operation, unadjusted analyzer zero and span response readings should be obtained prior to making any zero or span adjustments. Zero and span controls often interact with each other, so the adjustments may have to be repeated several times to obtain the desired final adjustments. After the zero and span adjustments have been completed and the analyzer has been allowed to stabilize on the new zero and span settings, all calibration test concentrations should be introduced into the analyzer for the final calibration. The analyzer readings are plotted against the respective test concentrations, and the best linear (or nonlinear if appropriate) curve to fit the points is determined. Ideally, least squares regression analysis (with an appropriate transformation of the data for non-linear analyzers) should be used to determine the slope and intercept for the best fit calibration line of the form

$$y = m \cdot x + a$$

where y represents the analyzer response, x represents the pollutant concentration, m is the slope, and a is the x axis intercept of the best fit calibration line. When this calibration relationship is subsequently used to compute concentration measurements (x) from analyzer response readings (y), the formula is transposed to the form

$$x = \frac{(y - a)}{m}$$

For the gaseous pollutants, the verification/calibration is considered acceptable if all calibration points fall within 2% of the full scale, best fit straight line. For manual samplers, devices (flow rate, temperature, pressure) are checked at different settings.

## 7.3 FREQUENCY OF CALIBRATION AND ANALYZER ADJUSTMENT

An analyzer should be calibrated (or recalibrated):

- upon initial installation;
- following physical relocation;
- after any repairs or service that might affect its calibration;
- following an interruption in operation of more than a few days;
- upon any indication of analyzer malfunction or change in calibration;
- at some routine interval.

When calibration relationships are applied to analyzer responses to determine actual concentrations, it is suggested that the analyzer be recalibrated periodically to maintain close agreement. The frequency of this routine periodic recalibration is a matter of judgment and is a trade-off among several considerations, including:

- the inherent stability of the analyzer under the prevailing conditions of temperature, pressure, line voltage, etc. at the monitoring site;
- the cost and inconvenience of carrying out the calibrations;
- the quality of the ambient measurements needed;
- the number of ambient measurements lost during the calibrations;
- the risk of collecting invalid data because of malfunction or response problem with the analyzer that would not be discovered until a calibration is carried out.

## 7.4 ADJUSTMENTS TO ANALYZERS

Ideally, all ambient measurements obtained from an analyzer should be calculated on the basis of the most current multipoint calibration or on the basis of both the previous and subsequent calibrations. Some acceptable level of drift (i.e. deviation from an original or nominal response curve) can be allowed before physical adjustments (a calibration) must be made because the calibration curve used to calculate the ambient measurements is kept in close agreement with the actual analyzer response. Precise adjustment of the zero and span controls may not be possible because of:

- limited resolution of the controls,
- interaction between the zero and span controls,
- possible delayed reaction to adjustment or a substantial stabilization period after adjustments are made.

## 7.5 CALIBRATION STANDARDS

The typical calibration or verification process consists of determining the correlation of an instrument under test with a standard. **A primary reference standard** can be defined as a homogenous material with specific properties, such as identity, unity, and potency that has been measured and certified by a qualified and recognized organization. It is important that primary reference standards are maintained, stored, and handled in a manner that maintains their integrity. Primary reference standards are usually quite expensive and are often used to calibrate, develop, or assay working or **secondary standards** (standards calibrated relative to a primary standard. They are used as a practical alternative to the primary which, of necessity, is not available to everyone). Calibration standards can be in a form of:

- reagents of high grade;
- gaseous standards of known concentrations that are certified;
- instruments and or standards of high sensitivity and repeatability.

Instruments which are used to calibrate other instruments are commonly referred to as “transfer standards”. Transfer standards are typically compared or “calibrated” against “primary standards” which are maintained and operated under controlled conditions such as a laboratory. Calibration gas is defined as:

- a gas mixture of specific component(s) at certified value(s) in an unreactive balance gas;
- used to quantify the same components in a similar gas sample.

The calibration gas standard establishes a known analyzer response to a certified chemical component concentration which enables the conversion of sample responses to a concentration with a determinable accuracy.

Analysts can use many methods to prepare standard mixtures of gaseous samples; some are simple and others are very complex. They can be roughly classified as:

- static methods;
- dynamic or blended methods.

### Static methods

Static samples are prepared by taking a known weight or volume of volatile organic gas or liquid and placing it in a container of known volume. These samples are prepared easily, everybody can understand how the procedure works, and minimal equipment is required beyond a volumetric device or a balance and a known-volume container. These devices are portable and can be taken to the field or to the factory floor. Essentially, the static method is goof proof. The accuracy is independent of user competence, and this method can be used by very inexperienced personnel. Static methods are not without pitfalls, however. The sources of error are not well defined. As the concentration of an individual component decreases, the stability of the standard mixture often decreases. For example, polar or reactive components can interact or adsorb on container walls. High molecular weight or high boiling point compounds can condense and also be lost within the container. The preparation of reactive mixtures is impossible because of prolonged contact and chemical reaction. Only dry mixtures are possible because humidity should be avoided. Static mixtures can be prepared at single concentrations only. For multi-point calibrations, analysts must use multiple containers, each of which has its own individual concentration; otherwise the base mixture requires an accurate dilution, which adds a level of complexity to the standard preparation. When working with a trace concentration static mixture, the traceability of the variables measured during the preparation of the mixture does not imply traceability of the delivered concentration. This type of traceable preparation technique generally is not recognized because of possible interactions or changes that may occur within the cylinder during storage. Thus, for the preparation of static standards, traceability of the delivered concentration requires comparison to a standard reference material or other traceable reference standard. The distinction between traceability of concentration and traceability of preparation is poorly understood in the analytical community, and vendors often gloss over this distinction when responding to inquiries about traceability.

### Dynamic methods

A wide variety of dynamic methods is available for the preparation of standards. Classification of dynamic blended methods:

- direct gas blending of mechanically controlled flows of pure analytes and matrix gases*;
- electrochemical evolution of analyte flow;
- exponential dilution of fixed analyte volume;
- permeation tube control of analyte flow*;
- diffusion tube control of analyte flow*;
- injection techniques;
- vaporization techniques.

* Best candidates for traceability.

Each of the methods has varying degrees of traceability.

Dynamic mechanical dilution is associated with two operational strategies: dilution of pure compounds and dilution of mixtures. In these strategies a steady stream of analyte vapor is directed into a flowing stream of inert gas. Usually, electronic thermal mass flowmeters are used to measure the gas flows. These flowmeters can be calibrated to within 1% of reading accuracy levels and can hold their calibrations for long periods of time. Mechanical dilution calibrant preparation avoids the storage stability problems associated with static mixtures. The error sources are reasonably well defined. Analysts can prepare both reactive and humid standard VOC mixtures. The preparation of multi-point calibration standards requires only a dilution gas or analyte stream flow rate change. One key advantage of direct blending is that it can be used throughout a very wide dynamic range and can generate higher concentrations than some other methods. Commercial products are available to prepare these dynamically created calibrants, and the technology is well developed. After startup, equilibration is rapid and calibration standards can be used right away. Achieving the required accuracy requires sophisticated flow measurement of input gas streams with direct mechanical dilution. First, the flowmeters must be calibrated with the actual gases to be metered. Second, the calibration must be performed against dilution gas and analyte vapor primary standards. It is difficult to determine traceability because of the limited range of available flow standards and calibration gases. Because flowmeters are calibrated with a surrogate gas for which a primary standard exists, users must apply a correction factor to the primary calibration to obtain calibration for the actual gas used. Because of these uncertainties, most mass flowmeter measurements are closer to ±5 % or more of full-scale accuracy rather than the theoretical ±1%. Generating accurate trace concentrations requires multiple stages of on-line dilution, which presents some practical mechanical problems. It is very difficult to prepare mixtures of liquid analytes because of the problem of creating a steady flow of analyte vapor from a liquid source. Furthermore, the production of calibration mixtures that contain large numbers of analytes is impractical unless the approach is dilution of a multicomponent static mixture. The direct mechanical blending technique is not goof proof — user technique can affect mixture accuracy.

The diffusion tube method makes uses of the phenomenon that a source of vapor at constant temperature and pressure contained at one end of a tube will flow by diffusion down the tube. If the vapor pressure at the exit end of the tube is much lower than at the feed end, a steady and predictable flow results. A reservoir at one end of a precision-bore capillary tube holds a small sample of liquid or solid analyte. At constant temperature, the vapor pressure of the analyte forms the constant pressure vapor source. A flowing stream of matrix gas passing over the other end of the capillary mixes with the diffusive vapor flow from the analyte to form the calibration gas mixture. Usually, the entire device is immersed in the matrix gas flow. The flow emitted by the diffusion tube depends on temperature and pressure.

Typically a 0.2 °C change in one or the other parameter causes an approximately 1% change in the flow from the diffusion tube. To achieve traceability, users must precisely control several experimental parameters with traceable measurements; namely temperature, weight loss from the diffusion tube, dilution gas flow rate, and total pressure. It goes without saying that analyte purity is of utmost importance. With diffusion tubes, it is also important to ensure that equilibration has occurred. Abnormal diffusion rates can result, however, if the internal surface of the capillary tube is contaminated with analyte liquid or solid. Once stabilized, diffusion equilibration should be concurrent with temperature equilibration. The advantages of diffusion tubes are their low cost and the easiness of use for creating low concentration, one-shot mixtures for screening or survey applications. Equilibration is rapid. This approach is good for low-vapor-pressure semivolatile liquids as well as heat-sensitive compounds. Diffusion tubes exhibit higher emission rates than permeation tubes. They are unsuitable for gases or pressurized mixtures. By using a recording balance or occasionally weighing the diffusion tube, analysts can monitor the emission rate during use, thereby increasing mixing accuracy during delivery. The interfacing requires careful attention to achieve constant pressures and temperatures, and error sources are not well defined. The diffusion tube method requires a high level of operator skill to achieve successful results.

In the permeation tube method, an analyte is held within a container on one side of a permeable membrane, which usually is polytetrafluoroethylene or fluorinated ethylene–propylene copolymer although other materials could be used. This method is similar to the diffusion tube method in that both techniques require analyte flow from a self-contained reservoir controlled by molecular dynamics. With permeation tubes, the flow is controlled by the permeability of a membrane to the analyte rather than diffusion across an open channel in a capillary tube, as is the case for diffusion tubes. A small quantity of gas, liquid, or solid is sealed inside a short length of plastic tubing. The tubing wall serves as a permeable membrane separating the pure analyte from the matrix gas flow. Any analyte permeating through the tubing wall creates a small, very stable flow of analyte vapor. Mixtures are created by immersing the tube in a flow of matrix gas. The permeability of a membrane to a compound is defined as the product of the diffusivity of the compound through the membrane and the solubility of the compound in the membrane. The flow of emitted analyte usually is determined gravimetrically by the same method used for diffusion tubes. The requirements for maintaining traceability are similar to those for diffusion tubes. The temperature of the permeation tube, the flow rate of the matrix or dilution gas, and the measurement of the emission rate must be traceable. One major difference compared with diffusion tubes is that the total pressure is not a factor of concern, but analyte purity is central to mixture accuracy. The key advantage of permeation tubes is the range of compounds for which the method can be used, including condensed gases, permanent gases, liquids, subliming solids, and many semivolatile organic compounds. The two major constraints for the analytes used in permeation tubes are that they must be available and stable in pure form and that they must have long-term stability at a temperature that will create at least 1 mm of mercury vapor pressure. High vapor pressure analytes can be handled in special permeation tubes designed to use compound vapor as the source of analyte. Permeation tubes avoid some of the storage stability problems of static mixtures. The two major constraints for the analytes used in permeation tubes are that they must be available and stable in pure form and that they must have long-term stability at a temperature that will create at least 1 mm of mercury vapor pressure. High vapor pressure analytes can be handled in special permeation tubes designed to use compound vapor as the source of analyte. Permeation tubes avoid some of the storage stability problems of static mixtures. The emission rate can be monitored by periodic weighings throughout the life of the tube ensuring mixture accuracy at delivery. The error sources in permeation tube systems are reasonably well defined. Because constant analyte delivery depends upon equilibration, the primary limitation of the permeation tube method is the speed of equilibration. Prestabilized permeation tubes typically require 2–24 h to equilibrate following a cold start-up. Achieving accuracy requires sophisticated flow and temperature measurement. The permeation tube concept is not widely understood, and its successful use requires operator education. Permeation tube systems produce a continuous flow of calibration mixture rather than a one-shot preparation. Therefore, permeation tubes generally require a continuous flow of matrix gas, even when they are not being used for calibration. When not in use, the flow should be vented. This type of system requires a modification of the typical analytical calibration standard strategy in which analysts make just enough standard to perform a calibration.

In the exponential dilution method, a known amount of analyte or analyte mixture is injected into a flask of known volume and stirred well. A controlled flow of dilution gas travels through the flask continuously, mixes with the analyte, and sweeps it from the flask. The resulting concentration of analyte in the output flow begins with the ratio of the volume of analyte to the volume of the flask and continuously declines in an exponential manner. The exponential dilution method is inexpensive and easy to understand. Each injection produces a full range of concentrations. The concentration at any given time is predictable using dilution theory. The technique can be used with a wide range of analytes, except for those with low volatility. For low analyte concentrations, the output of the flask can be diluted further with additional matrix gas. Error sources are not well defined for exponential dilution. Some of the problems apparent in the exponential dilution method for preparation of calibration standards include surface sample losses, mechanical wear of the mixing device, and difficulty of accurately measuring the initial sample concentration caused by uneven mixing effects.

Another means of generating gaseous standards is termed the "hanging drop" approach. In this procedure, a drop of the standard solution is introduced into a gas stream via a syringe. The syringe assembly is placed into a heated compartment so that the drop is continuously volatilized by carrier gas. The use of the hanging drop technique involves many parameters that introduce errors that could invalidate test results. Factors such as preparing the standard solution and determining the exact volatilization rate affect the resultant concentration of analyte in the calibration gas, and thus the accuracy of the calibration. This procedure should be used only when certified gaseous standards and permeation/diffusion standards are not available commercially.

Static mixtures are unquestionably the most user-friendly form for preparing gas standards. Their preparation procedures are straightforward, and the controlling variables (primarily mass measurements) can be traced easily. Two problems must be addressed with the preparation of every mixture: the stability of the mixture and the container's potential to contribute error to the mixture. Both of these considerations introduce undefined errors that destroy the value of traceability of the preparation process. The knowledge of the quantities of analyte and matrix placed into the container no longer implies the knowledge of concentration actually delivered. Thus, static mixtures are traceable only by comparison to other traceable concentration standards. Considering the aggressive nature of many analyte compounds, dynamic blending methods offer the path of least resistance to traceability. The strength of the dynamic approach is the avoidance of undefined error sources. If a known concentration is created through a traceable measurement, the fundamental variables are controlled, and the concentration is used immediately, then the unknown error sources of instability and container effects are avoided. The mixture is still traceable. The dynamic blending approach has an additional side benefit. All methods, including direct use of a standard reference material, are subject to systematic delivery errors resulting from the interaction of an analyte with the materials used to transport the mixture from its source to the analytical system. Because traceable standards are precious, analysts tend to use them sparingly. When the delivery system is not totally inert to the mixture, this sparing use can result in significant undefined errors. With a continuous flow of mixture, allowing additional equilibration time in the transport system has little cost and tends to minimize the effect of those undefined errors.

# 8 DATA ACQUISITION AND HANDLING SYSTEM

Monitoring programs of air pollution control are based on data and its correct interpretation. That data must be:

- available to users;
- reliable;
- of known quality;
- easily accessible to a variety of users;

- aggregated in a manner consistent with its prime use.

The data generated by gas analyzers or manual samplers must be captured, organized, and verified in order to be useful. Most of the data collected from monitoring programs is collected through automated systems at various facilities. These systems must be effectively managed by using a set of guidelines and principles adherence to which will ensure data integrity. The process of collecting the raw data from the monitor/sampler, storing it for an appropriate interval, aggregating or reducing the data, and transferring this data to final storage in a local data base (monitoring organizations database) is known as data acquisition.

Term data acquisition system is used for the system that collects, stores, summarizes, reports, prints, calculates or transfers data. A data acquisition and handling system (DAHS) is a combination of hardware and software that is used to record data and generate reports for submission to the regulatory agency.

## 8.1 TRANSFER DATA

The principal meaning in the data acquisition system has transfer data. This operation is defined as a preparing and moving data to external data bases. The transfer is usually an analog or digital format to a digital medium. Most continuous monitors have the ability to output data in at least two ways*:* analog output and an RS232 digital port. Some instrumentation may now be including USB, Ethernet and firewire capability. The instrument has a voltage potential that generally is a DC voltage. This voltage varies directly with the concentration collected. The data transfer may occur via modem to a central computer storage area or may be printed out as hard copy. In some instances, the data may be transferred from one storage medium (i.e. hard drive to a diskette, tape, or CD) to another storage medium. The analyzers have the capability to transfer digital signals, yet many monitoring organizations currently perform data acquisition of automated monitors by recording an analog output from each gas analyzer using an electronic data logger. Technically speaking, a data logger is any device that can be used to store data. However, most instrument manufacturers consider a data logger a standalone device that can read various types of electrical signals and store the data in internal memory for later download to a computer. Many of these devices can record inputs on a number of separate locations, reporting them as separate "channels". The advantage of data loggers is that they can operate independently of a computer, unlike many other types of data acquisition devices. Data loggers are available in various shapes and sizes. The range includes simple economical single-channel fixed function loggers to more powerful programmable devices capable of handling hundreds of inputs. Data transfer is usually accomplished in three ways. 1. Hard copy printout. Most DAS have the ability to create a hard copy report. Usually, this report is in tabular format showing 1 minute, 5 minute or hourly averages. Monitoring organizations are encouraged to keep hard copy printouts. 2. Downloading data from internal storage medium to external storage medium. External storage refers to storing and transferring the data on diskettes or CD. Many new generation DAS are computer platforms. The newer generation computers generally have the ability to download data to CD or zip drive. If remote access via telephone is not an option, then data can be hand transferred to a central office for downloading and data review. 3. Digital transfer via the telephone lines, internet, satellite or other advanced means of communication. All new generation DAS allow access to the computer via the telephone and modem. These systems allow fast and effective ways to download data to a central location.

In general, the transfer of in data acquisition and handling system is shown in Figure 29.

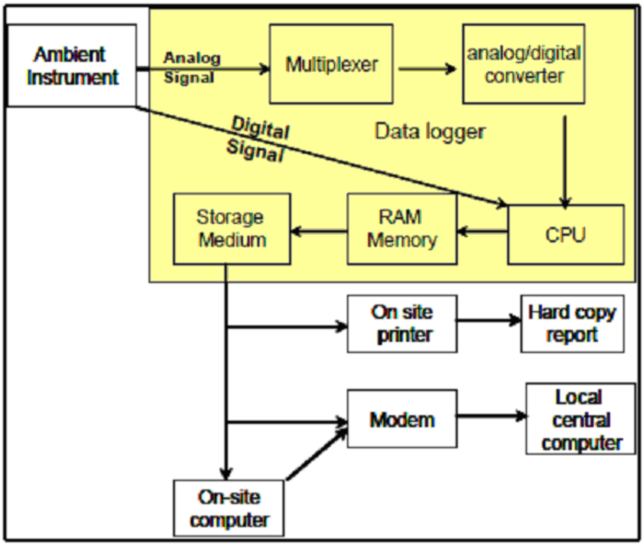


FIGURE 29 Data acquisition and handling system.

The flow of data from the field environmental data operations to the storage in the database requires several distinct and separate steps:

- initial selection of hardware and software for the acquisition, storage, retrieval and transmittal of data;
- organization and control of the data flow from the field sites and the analytical laboratory;
- input and validation of the data;
- manipulation, analysis and archival of the data;
- submittal of the data into the database.

## 8.2 REVIEW, VERIFICATION AND VALIDATION OF DATA.

Both manual and computer-oriented systems require review, verification and validation of data. Data review, verification and validation are techniques used to accept, reject or qualify data in an objective and consistent manner. In general, these assessment activities are performed by persons implementing the environmental data operations as well as by personnel “independent” of the operation, such as the organization’s QA personnel, and at some specified frequency. The following issues should be considered:

- sampling design;
- sample collection procedures;
- sample handling;
- analytical procedures;
- quality control;
- calibration;
- data reduction and processing.

### 8.2.1 DATA REVIEW

Data review is an ongoing process that is performed by the station operators and the data processing team. At a minimum, a cursory review is performed daily, preferably in the morning to provide a status of the data and instrument performance at monitoring sites. Detailed analysis can be extremely difficult for the data processing team when reviewing the raw data without the notations, notes and calibration information that the station operators provide for the group. As an individual scans tabulations, there is no way to determine that all values are valid. The purpose of manual inspection is to spot unusually high (or low) values (outliers) that might indicate a gross error in the data collection system. In order to recognize that the reported concentration of a given pollutant is extreme, the individual must have basic knowledge of the major pollutants and of air quality conditions prevalent at the reporting station. Data values considered questionable should be flagged for verification. Manual review of data tabulations also allows detection of uncorrected drift in the zero baseline of a continuous sensor. Zero drift may be indicated when the daily minimum concentration tends to increase or decrease from the norm over a period of several days. In an automated data processing system, the procedures for data validation can easily be incorporated into the basic software. The computer can be programmed to scan data values for extreme values, outliers or ranges. These checks can be further refined to account for time of day, time of week, and other cyclic conditions. Questionable data values are then flagged on the data tabulation to indicate a possible error. Other types of data review can consist of preliminary evaluations of a set of data, calculating some basic statistical quantiles and examining the data using graphical representations. When reviewing data:

- reported results should be compared with those expected and unusual results queried;
- results should be compared with historical data;
- problems should be identified e.g. unusual plant operating conditions;
- appropriate action must be taken to address the problems identified.

## 8.3 VERIFICATION

Verification can be defined as confirmation, through the provision of objective evidence that *specified requirements* have been fulfilled. The verification requirements for each data operation are included in the documents of organizations involved in monitoring program. They should include not only the verification of sampling and analysis processes but also operations like data entry, calculations and data reporting. The data verification process involves the inspection, analysis, and acceptance of the field data or samples. These inspections can take the form of technical systems audits (internal or external) or frequent inspections by field operators and lab technicians.

### *8.3.1 DATA VALIDATION*

Data validation is a routine process designed to ensure that the reported values meet the quality goals of the environmental data operations. Data validation is further defined as examination and provision of objective evidence that the particular requirements for a specific *intended use* are fulfilled. A progressive, systematic approach to data validation must be used to ensure and assess data quality. The purpose of data validation is to detect and then verify any data values that may not represent the actual air quality conditions at the sampling station. Effective data validation procedures are usually handled completely independently from the procedures of initial data collection. Because the computer can perform computations and make comparisons extremely rapidly, it can also make some determination concerning the validity of data values that are not necessarily high or low. Data validation procedures should be recommended as standard operating procedures.

### *8.3.2 REPORTING*

Analytical report must contain sufficient information for the end user to make a critical evaluation of its contents. The report format should comply with the specified requirements. In particular, the following information should be reported (where relevant) with the analytical result for each parameter determined. This information is either provided by the person taking the sample or by the laboratory conducting the analysis or monitoring:

- date and time of sampling;
- identification of the samples taken (including sample description, sample number and unique laboratory number);
- details of any sample preservation;
- reference to the analytical method used;
- estimation of the measurement uncertainty for the results;
- date of determination;
- results in the appropriate units;
- notations of any deviation from the standard method;
- any factor that may have affected reliability of the results.

## 8.4 DATA TRANSFER – PUBLIC REPORTING

The area of public reporting for air monitoring data may provide the largest number of data users. This area has been growing rapidly in the last few years as a result of the increased availability of air quality reporting, especially for ozone and PM2.5. Currently, hourly averages are the reporting interval for continuous particulate and gaseous data. For public reporting of the air monitoring data, web site will remain the primary medium for its distribution. Additionally, conventional paper records can be published. Monitoring results are usually compiled annually. The results should be submitted in the form of a summary report.

# 9 SYSTEMS FOR AIR POLLUTION DETERMINATION

Different instrumental approaches are used for air pollutant measurements. They depend on the applied mode of operation. In practice, it is possible to identify the following modes of operation:

- off-line/site;
- at-line/site;
- on-line/site;
- in-line/site (in-situ);
- non-invasive;
- remote.

### Off-line/site mode

In off-line/site mode of operation, the sample to be analyzed has to be physically removed from the sampling site and transported to a centralized laboratory, where the sample is analyzed using traditional, perhaps even sophisticated, automated instrumentation. The benefits of this approach include:

- the economy;
- the efficiency of time-sharing use of expensive instruments;
- the availability of expert staff for consultation, methods development and maintenance.

The disadvantages include:

- the time delay between submitting samples and reporting results, which questions the validity of the analysis;
- additional administrative costs;
- the competition among users for the resources (it raises conflict when there is demand for the use of the instrumentation from various plants at the same time).

### At-line/site mode

This term means that a dedicated instrument is located in close proximity to the required place, where it is to be used by the operators. The concept of at-line/site mode of operation arose out of the problems encountered with time and instrument demand for the off-line/site mode. In order for this approach to be successful and benefits of time, the instruments have to be "de-skilled" and a maintenance/troubleshooting regime investigated. Typical at-line instrumentation has easy to use operator interface. The advantages of this system include:

- faster sample processing comparing with off-line/site mode;
- stricter control of the analysis by the personnel (and therefore closer to real-time analysis);
- employment of a simpler instrument with less cost and maintenance and greater easiness of use.

The instrumentation needs to be more robust, and it often monitors generic parameters.

### On-line/site mode

The term on-line or on-site means that there is a physical connection between the measuring (monitoring) instruments and the detection point. The on-line/site philosophy is the element of monitoring system that is distinct from analytical chemistry as a rule. The on-line title is used when some form of automatic sample extraction and conditioning is used prior to analysis. Therefore, a reliable interface is required. An analyzer is situated in a tested environment. On-line instruments are used for continuous measurements (sample flows continuously through a detector). It is possible to subdivide this system into two categories:

- intermittent methods that require injection of a portion of the sample stream into the instrument;
- continuous methods that permit the sample to flow continuously through the instrument.

These devices provide near real-time results. Improvements in ruggedness and instrument reliability have led to a growth in this area of measurements. The sample is delivered automatically to an analyzer. This system provides continuous and near real-time results. The major disadvantage of this system is the need to construct a separate analytical line that properly samples the main stream and presents it to the instrument at a suitable temperature and pressure.

### In-line/site mode

The in-line/site mode is the next logical progression from the on-line mode and differs by the fact that no sample extraction and conditioning is necessary (the measurement is made in required place without extracting a sample). It is at this point that some confusion in terminology exists, as the preferred option is to situate the analyzer on a by-pass loop as this enables maintenance repair of the instrument without interrupting processing. This is a form of sample extraction but it does not condition. In this mode chemical analysis is done *in situ*, directly in the measuring point, using a probe that is chemically sensitive to the species of interest, without being corroded by the bulk material. The advances in materials of construction have allowed analyses to be carried out in harsh chemical environments. In this mode, the probe is connected to the main element of the analytical system with either electronic connectors, for electrochemical applications, or optical connectors for spectroscopic applications. The probes based on fibre optics are preferred in this field of application. The benefits of the fibre-optic arrangement are realized during retrofits to existing plants where space is of a premium, and traditional analyzers cannot be positioned into the existing space. A further benefit is making the cabling safe to be used in zoned environments, whereas the positioning of the analyzer in the plant would require a purged, temperature-controlled box. The analyzer in this case is situated in the control room or „safe" area where human access to results is easy.

### Non-invasive mode

Non-invasive mode of operation is based on the principle that the sample does not come into contact with the analytical instrument. Optical techniques such as NIR and Raman spectrometries can be employed non-invasively. Non-invasive systems are useful for process monitoring and control as the probe is not in direct contact with the sample and therefore it is not fouled and does not cause contamination.

### Remote mode

Air quality monitoring is generally conducted in the form of point measurements. It means that the concentration of air pollutants is measured at a selected site in space. This method of monitoring offers some unique advantages yet it also has drawbacks. The point measurements of air pollution are inadequate for identification and quantification of poorly mixed gases over large areas. Such conditions are characteristic for:

- smoke plumes from stacks and hazardous waste landfills;
- fugitive emissions from industrial plants or leakages emissions from chemical storage tanks;
- exhaust emissions from traffic (especially during rush hours).

This method cannot be used also for the measurements of trace species in distant points of atmosphere. The analysis of gaseous pollutants over areas that are not easily accessible is particularly suited to remote sensing techniques. Generally, remote sensing is the acquisition of information about an object or phenomenon by a device located at a considerable distance from the object or phenomenon. More precisely, it can be defined as: "The acquisition and measurement of data/information on some property(ies) of a phenomenon, object, or material by a recording device not in physical, intimate contact with the feature(s) under surveillance".

The remote sensing techniques employ measuring instruments physically removed from the atmosphere under study. Therefore, the sample is not taken into the analyzer in these techniques. It is a great advantage since the cost of the samplers is high. Data transmission difficulties are avoided.

The mode of instrument operation determines different types of measuring systems for air pollutant measurements. These systems can exist in the following forms:

- fixed (stationary);
- mobile;
- transportable;
- portable;
- combined.

# 10 CONTINUOUS EMISSION MONITORING SYSTEM

It is useful to study the causes and sources of the various air pollutants, as well as their physical and chemical characteristics, before air pollution control is discussed. There are many different air pollutants, all with differing physical and chemical characteristics, as well as a vast number and variety of air pollution sources. Therefore, a good understanding of the pollutants and their sources is necessary before a particular control technology can be selected for the best application to any particular situation. The source of information in this field is the measurement of emission. This term means the science of characterizing and measuring air pollutant emissions. The measurement of both ***type*** and ***quantity*** of these contaminants is an important part of obtaining the data needed to implement a meaningful control program. Emissions measurement is often treated as the process of monitoring particulate and gaseous emissions from a specific source.

The flue gases emitted from thermal power generation, boiler equipments, industrial furnaces used for steel production, cement production, etc. are one of the major causes of air pollution. For the measurement of the regulated substances in flue gas, in addition to the official method of manual analysis (the specified analytic method used in international organizations, and national or official testing institutions and research laboratories that conform to national standards), the installation of an environmental measurement systems containing a built-in continuous automatic analyzers is mandated in order to measure the total amount of emitted matter. The environmental measurement system used for flue gas is known as a continuous emission monitoring system (CEMS) and is equipped with an analyzer that has been approved by each country and is provided with functions for measuring the concentration, temperature, pressure and flow rate of regulated substances, and also with functions for forms control, for sending data to regulatory authorities, etc. A continuous emission monitoring system (CEMS) is the total equipment necessary for the determination of a gas or particulate matter concentration or emission rate using instrumental analyzer measurements and a correlation function, graph, or computer program to produce results in units applicable to the emission license requirement. Some license holders are required to continuously monitor their process emissions. In other words, continuous emission monitoring system means the set of equipments and programs required to analyze one or several specific compounds in the gaseous effluent emissions of a discharge unit, quantify the amount of specific compounds emitted per unit time, and process the information for reporting these emissions in the manner prescribed by appropriate regulations. These systems consist of equipments used to sample and condition, analyze, and provide permanent record of emissions or process parameters. There are many applications for continuous emission monitors, covering a variety of industries. The specification of the CEMS will depend not only on the type of process, but also the pollutant gases that are required to be measured. Pollutants that are routinely measured during stack emissions monitoring: CO, $CO_2$, $O_2$, $SO_2$, $NO_x$, HCl, TOC, particulate matter, dioxins, furans, PCBs and PAHs. Emissions measurement is the process of monitoring particulate and gaseous emissions from a specific source.

Monitoring pollutant emissions from stationary sources involves two principle functions: 1) extracting or locating a representative sample and 2) analyzing that sample. Monitoring methods in use today are illustrated in Figure 30.

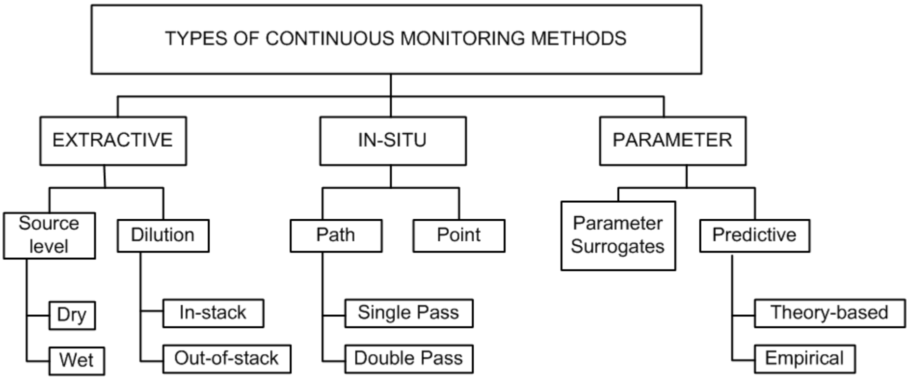


FIGURE 30 Continuous monitoring methods.

Continuous emissions monitors have been built using most types of sensor technology. There are systems using electrochemical, infrared, ultra-violet, chemiluminescent and other measurements for the toxic gases, whilst oxygen measurements are mainly carried out with electrochemical, zirconium or paramagnetic sensors (Table 1).

All these methods have their own advantages and drawbacks, be it technological or financial. In earlier days, the only common and affordable technology was electrochemical measurement, which led to a very hard life for the sensors. The electrochemical sensors are not designed for permanent use. They require short pauses with fresh air to regain a zero point and regenerate generally. Failure to adhere to this will lead to a very rapid demise of the sensor and a poor quality of measurement whilst the sensor is operating. There are a number of solutions to this problem, the simplest being to switch the sensors to fresh air for a certain proportion of the time. This may, however, cause difficulties with national regulations that insist on an unbroken measurement of the gas concentrations. It may also be a problem when the output signals from the CEMS are used as part of the control system for the burner system, as is becoming more common. The next variation was to have two or more banks of sensors. They are rotated from fresh air to measurement and then back again. The next advantage is that calibration of the sensors can be carried out when they are not in use, preventing any interruption to operation. This system is still quite common and has proved itself time and time again in practice. The major disadvantage is cost. The extra sensors cost money, as does the technology to switch gas inlets and signals between the banks.

TABLE 1 Examples of continuous emissions monitoring techniques for gaseous species.

| Method and technique | Type of system | Gases Measured | Comments |
|---|---|---|---|
| Chemiluminescence | Extractive | NO, $NO_2$, $NO_x$ | $NO_2$ is calculated ($NO_x$ – NO). |
| UV Fluorescence | Extractive | $SO_2$, ($H_2S$, Total Reduced Sulfur) | Gases in brackets can also be measured but not simultaneously. |
| Gas Filter Correlation (GFC) | Extractive | CO, $CO_2$, $NO_x$, $SO_2$, $N_2O$ | Multiple gases can be monitored, generally no more than 5. |
| Fourier Transform Infrared (FTIR) | Extractive, Cross duct | CO, $CO_2$, $SO_2$, $NO_x$, HCl, HF, etc. | Multiple gases can be monitored, typically 5. |
| Differential optical absorption spectroscopy (DOAS) | Cross-duct | CO, $CO_2$, $SO_2$, HCl, HF, NO, $NO_2$, $NH_3$, VOCs, $H_2O$ | Multiple gases can be monitored, typically 5. $NO_2$ measured directly. Additional gases can be added at relatively low cost. |
| Flame Ionisation Detector (FID) | Extractive | Total Hydrocarbons | Requires hydrogen carrier gas. |
| Tuneable Laser Diode (TLD) | Cross-duct | HCl, HF, $NH_3$, $CH_4$, CO, $CO_2$, $H_2O$ | Cost-effective for single component applications. |
| Zirconia oxide cell | In-situ | $O_2$ | Widely used, max. temp. of gases approximately 500°C |
| Paramagnetic | Extractive | $O_2$ | None |
| Photoacoustic spectroscopy (PAS) | Extractive | CO, $CO_2$, $SO_2$, HCl, HF, NO, $NO_2$, $NH_3$, VOCs, $H_2O$ | Can measure virtually any gas that absorbs IR. |
| Pb | 0 – 5200 | 8 ppm | 0.0021 |

|  |  |  |  |
|---|---|---|---|
|  | ppm |  |  |

Nevertheless, these systems are very popular, despite the additional equipment increasing the maintenance needs of the system. Infrared systems were common in continuous emissions monitors long before they were considered for portable equipment. The higher cost for this technology was not such a disadvantage in the CEMS branch, and the advantage of fewer maintenance needs was more important. Infrared sensors are inherently more stable, although they also require occasional zeroing for good repeatability. The calibration of infrared sensors is also necessary, although they will remain more stable than their electrochemical counterparts.

The main CEMS performance characteristics against which a CEMS will be assessed by a combination of laboratory and field testing are:

- lack-of-fit (linearity);
- cross-sensitivity to likely components of the stack gas other than the determinant;
- influence of sample pressure and sample temperature;
- response time;
- detection limit (repeatability at zero);
- repeatability at span;
- influence of ambient conditions on zero and span readings;
- performance and accuracy under field conditions;
- reproducibility under field conditions;
- availability and maintenance interval under field conditions;
- time-dependent zero and span drift under field conditions;
- susceptibility to physical disturbances;
- design features.

Traditionally, analyzers were designed to monitor a single gas species. If multiple gas analysis was required, then a series of analyzers was used. Now, with the requirement to monitor and report several pollutant gas emissions, the modern CEM system is capable of simultaneously monitoring and displaying concentrations of five or six species. The type of analyzer selected will depend on the species and concentrations to be monitored, as shown in Table 2.

Calibration frequency may be relaxed to weekly following demonstration of satisfactory instrument stability. Instrument linearity checks are required on a six-monthly basis or after significant maintenance. Standard gases must be certified and should be replaced or re-calibrated within two years of the initial certificate calibration date. The following three calibration gases should be used for each pollutant to be measured:

- high-range gas (the concentration should be between 80 and 100 percent of the analyzer range);
- mid-range gas (the concentration should be between 40 and 60 percent of

the analyzer range);

- zero gas (purified air or, if appropriate, nitrogen with a contaminant concentration less than 0.25% of the analyzer range for the appropriate pollutant gas may be used).

TABLE 2 Types of analyzers for different gas species.

| Species | Photometer | | Spectrophotometer | | Chemiluminescence |
|---|---|---|---|---|---|
| | IR | UV | IR | UV | |
| CO | X | | X | | |
| NO | X | X | X | X | X |
| $SO_2$ | X | X | X | X | |
| $NO_2$ | X | X | X | X | X |
| $CO_2$ | X | | X | | |
| $H_2O$ | X | | X | X | |

The data acquisition/controller subsystem is integral to the proper operation of the total system. The control system controls automatic functions of the system, such as calibration, probe purging, and alarming. The data acquisition system receives the analyzer data, converts it into appropriate units, records it, and provides reports for both internal and external use. CEMS data acquisition systems are frequently networked to engineering, corporate, and even agency offices, where the data are used for a variety of operational and management purposes. Data acquisition system (DAS) records and reports the data produced by the analyzer in CEMS. It is critical that the DAS should be flexible enough to provide data in a manner useful to the Quality Assurance (QA) testing. Also, the DAS must be able to report in units of the applicable limit(s) for the source. A data logger or other electronic data acquisition system may be used to provide a permanent record of gas analyzer data.

The choice of the CEM system will depend on many factors, including the monitoring and reporting requirements of the local environmental authority. The optimum design of an automated monitoring system depends on the purpose of the monitoring, the pollutants to be monitored, and the properties of flue gases. These factors determine the structure of CEM systems. They are mainly composed of several subsystems:

- the sampling interface;
- the gas analyzers;
- the data acquisition/controller system.

The sampling interface is a subsystem that either transports or separates the flue gas from the analyzer. CEM systems are usually characterized in terms of the design of this interface. An automated stack emission measurement system can be “extractive” or “in-situ” type. In the case of extractive systems, the interface consists of the system that extracts and conditions the gas prior to entering the analyzer. In in-situ systems, the interface is simpler, composed of flanges designed to align or support the monitor and blower systems used to minimize interference from particulate matter. Analyzers enabling both extractive and in-situ measurements based on different techniques exist for traditional gaseous emissions.

## 10.1 EXTRACTIVE SYSTEMS

Extractive systems involve continuous withdrawal of a sample from the gas stream and transport it to an analysis unit outside the stack. The standard extractive system consists of a sample probe, filter, sample line (umbilical), gas conditioning system, calibration gas system, and a series of gas analyzers which reflect the parameters being monitored. Typical monitored emissions include: sulfur dioxide, nitrogen oxides, carbon monoxide, carbon dioxide, hydrogen chloride, particulate matter, mercury, volatile organic compounds and oxygen. These systems can also measure air flow, flue gas opacity and moisture. One of the problems associated with extractive systems is that they are indeed "systems". Before being introduced into the analyzer(s), the sample is usually “conditioned” to remove any condensates and to reduce the temperature in order to protect the analytical equipment. Additionally, in order to measure gas concentrations, the gas sample must be free of particulate matter. The biggest challenge is to ensure that the gas that was introduced into the sampling system from the stack at the point of measurement arrives at the inlet of the analyzer in exactly the same state as it was in the stack. Many gases that are measured commonly ($SO_2$, $NO_2$, HCl, etc.) are, to varying degrees, water soluble and situations can arise in parts of a sampling system for analytes to ‘drop out’ due to dissolution in condensation (e.g. if ‘cold spots’ develop). Considerable care must, therefore, be taken to ensure that the sampling system is designed in such a way as to eliminate as far as possible any sample loss or degradation. This requires the use e.g. of valves, pumps, chillers, sample tubing, and other components necessary for gas transport and conditioning - components which require periodic maintenance. Failure to perform this maintenance and problems associated with poor system designs lead to frequent probe plugging, corrosion, and leaks.

The advantage of extractive system is time-sharing. This term means sequential sampling from multiple stacks by one analyzer, is one major advantage of extractive systems. The number of stacks that can be measured by one analyzer depends on the allowed cycle time, i.e. how often one specific stack has to be measured. Generally, the time-sharing principle is applied to combine one analyzer set with three to six stacks, depending on the monitoring requirements, the monitoring system itself, and the stability of the emission characteristics.

Different principles for sample extraction are in use due to the varying gas conditioning needs of different flue gases. The sample can then be analyzed as wet or dry gas. For wet gas measurement condensation is avoided, either by maintaining the temperature of the sample above its dew point throughout the whole sampling system and within the analyzer, or by diluting the sample with clean dry air. Therefore, the systems based on “wet” sample can be sub-divided into two basic types:

- heated;
- non-heated (dilution systems).

### 10.1.1 HEATED EXTRACTIVE SYSTEM

The heated extractive system consists of:

- in-stack sampling probe;
- coarse in-stack filter;
- sample transport tubing,
- sample pump;
- fine filter;
- analyzer(s);
- calibration system;
- data recorder.

A probe of some sort is installed in the stack to provide an appropriate sampling point. This element shall have an inside diameter of 6 mm or larger and shall be constructed of quartz, borosilicate glass, stainless steel, aluminum oxide or porcelain. Probes are generally equipped with probe nozzle. Quartz, borosilicate glass, stainless steel, porcelain or aluminum oxide may be used for this element. An internal or external probe heated filter will be needed to remove the largest particles that would otherwise block the transport line. This filter must be kept at a consistent high temperature to prevent condensation forming. The place must be chosen to allow regular inspection and changing of the filter elements. A differential pressure sensor can simplify the inspection of the filter elements. Additionally, a blowback system may be used to keep the probe from clogging. A heated sample line transports sample of flue gas to the gas analyzer(s). This element also contains thermocouples for monitoring temperature, calibration gas lines, and lines that are used to keep the probe free of dirt. A sample line is constructed of Teflon or other material which does not absorb or otherwise alter the sample gas. The sample gas is continually aspirated by means of a sample pump or ejector.

"Hot/wet systems" are extractive CEM systems that maintain the sample temperature above its dew point throughout the sampling system and within the analyzer to prevent condensate forming, which would scrub soluble gases such as $SO_2$ and $NO_2$ from the sample. It is achieved by ensuring that all the sample wet parts are maintained well above the temperature at which condensation would occur. In many applications, this would be approximately 200°C, however, in several applications, for example the monitoring of ammonia, the temperature would have to be maintained at approximately 325°C to ensure that ammonium chloride does not form. Obviously, all the components coming into contact with the sample have to be suitable to operate at the elevated temperature, including solenoid valves, filters, pump heads and the analyzer sample cell. These systems may be used for the measurement of water soluble compounds and are commonly used for monitoring non-criteria pollutants such as HCl, $NH_3$, and VOCs. Other compounds can also be measured provided that a suitable heated analyzer is available. Hot/ wet systems have been used for many years to monitor criteria pollutant emissions such as $SO_2$, $NO_2$, and CO. These systems must not only maintain the sample temperature above the dew point to avoid condensation, they must also minimize adsorption and avoid the potential for chemical reactions to occur. It can be shown on the example of HCl monitoring. This compound is: 1) very water soluble, 2) adsorbs onto common sampling system materials, and 3) participates in chemical reactions with other stack gas constituents at certain sources. Extractive HCl sampling systems have been used that minimize adsorption effects by operating Teflon sampling lines at the maximum operating temperature for Teflon. High sampling flow rates are maintained (20 liters per minute and short sampling lines are used in these systems to minimize the residence time and to minimize the surface area for adsorption. Heated head pumps fabricated of 316 stainless steel or other special alloys and with Teflon diaphragms are used to avoid condensation or adsorption. All cold spots within the sampling system such as connections between heated line segments or connections to pumps or manifolds must be eliminated. Nothing less than meticulous attention to ensuring that the entire sample path is heated will prove adequate. The performance of "system calibrations" where calibration gases are introduced at the outlet of the sampling probe are very important for these types of systems to identify and/or account for the effects of adsorption. System calibrations are sometimes avoided in practice because of the high consumption rate of calibration gases (and corresponding cost) due to the high sampling rates and the longer time is required to achieve an equilibrated instrument response. HCl also serves as an example of a chemically reactive component. HCl may participate in chemical reactions with lime or similar materials collected within the sampling system. Special provisions are required to minimize the collection of the particulate matter where a stack gas stream contains solids or liquids that are chemically reactive with the component of interest. Since the reaction of HCl with particulate material is most likely to occur on filters, the equipment must be designed to accommodate system calibrations where calibration gases are introduced upstream of the filters. This may help to detect whether reactions with the particulate matter are occurring. HCl may participate in reactions with ammonia to form ammonium chloride salts. This reaction is sensitive to the sample temperature. Where the sample temperature within the system is substantially below the stack gas temperature, the reaction may consume HCl and thus introduce a negative (low) bias in the HCl measurement results. Conversely, where the measurement system is maintained at a higher temperature than the stack temperature, particulate ammonium chloride may volatilize to form HCI and $NH_3$, thereby creating a positive bias in HCl monitoring results. The potential for such biases to occur at particular sources, and the effects of temperature changes between the stack and the analyzer, must be examined for hot/wet measurement systems.

Source sampling typically deals with gaseous pollutant concentrations in the ranges of tenths of a volume percent down to tens to hundreds of ppm. The gas sample in this system is not diluted, so higher range analytical instruments are used (i.e. 0-5,000 ppm). A wide range of single component and multi-gas analyzers are available for the use with extractive sampling systems. Nondispersive infrared analyzers are acceptable for carbon dioxide and carbon monoxide concentration determination. A paramagnetic analyzer or an electrochemical (fuel cell) analyzer is acceptable for oxygen measurement. An analyzer using chemiluminescence is acceptable for oxides of nitrogen measurements. The $NO_2$ to NO converter must have at least 90% efficiency in converting nitrogen dioxide ($NO_2$) in the sample gas to nitric oxide (NO). An $NO_2$ to NO converter is not necessary if data are presented to demonstrate that the $NO_2$ portion of the exhaust gas is less than 5 percent of the total $NO_x$ concentration. A low temperature (maximum 350°C) converter must be used when $NH_3$ is present. A high temperature (650°C) stainless steel converter may be used when no $NH_3$ is present. If data are not available to demonstrate that the concentration of $NO_2$ in the sample gas is less than 5% of the total $NO_x$ concentration, a test of the efficiency of the $NO_2$ converter must be conducted prior to each source test. An analyzer using infrared, ultraviolet absorption or fluorescence is acceptable for sulfur dioxide concentration determination. An analyzer using a flame ionization detector (FID) or a nondispersive infrared analyzer (NDIR) is acceptable for total hydrocarbon determination. Propane or methane is usually used as a span gas. The hydrocarbon species should be characterized prior to the source test to determine that the detector will respond predictably to the organic compounds present. Compound-specific calibration curves must be determined for use of either the FID or the NDIR analyzer to measure specific organic compounds. The most common methods of continuously monitoring organic compounds are either chromatographic or spectrometric. The chromatographic system samples a portion of the stack effluent and delivers it either to a chromatographic system or directly to a flame ionisation detector (FID). If no chromatographic separation of compounds occurs, the low molecular weight hydrocarbons such as methane, propane etc. as well as other volatile organic compounds are measured by the detector as a single total response. The continuous analyzer is normally calibrated against a methane or propane calibration gas and the results are expressed as parts per million carbon equivalents, although it is possible to calibrate the continuous monitor directly against a compressed gas standard e.g. hexane. For FIDs, the effect of the oxygen concentration of the monitored stack gas must be assessed. This effect can be reduced by using zero and span gas with the same oxygen concentration as the stack gas. Spectrometric systems typically use differential optical absorption spectroscopy or Fourier Transform Infrared Spectroscopy techniques to monitor individual organic compounds within the discharge. The analyzers shall be housed in a temperature-controlled, vibration-free environment. A requirement for instrumental analyzers is that the following performance characteristics are assessed before use:

- response time;
- zero and span drift;
- detection limit;
- effect of interfering substances;
- sensitivity to temperature change;
- effect pressure on instrument stability;
- noise level;

- repeatability;
- linearity.

A drawback to the wet gas measurement method is that moisture determination is needed to be able to convert the results to a dry basis. A heated hose requires about 100 Watts of power per metre of length, so long hoses are to be avoided if possible.

### 10.1.2 DILUTION SYSTEMS

To avoid the need to remove the water vapor and to ensure condensation does not occur in the sample line or analyzer components, a technique of diluting the sample at the take-off was developed. Protection against condensation is achieved by diluting the sample to a level at which even the lowest ambient temperature would not cause any condensation to form. The sample is transported from the take-off point to the system housing, where additional sample preparation components and the analyzers are mounted. The major drawback of this system is that, in addition to maintaining the dilution system, the analyzer has to be significantly more sensitive to monitor the diluted gas. Dilution systems quantitatively dilute stack gas samples with clean dry air to reduce the relative moisture content so that the sample is maintained above the dew point with little or no heating. Because moisture condensation is eliminated as a potential problem, heated sample lines and manifolds can be replaced with simpler, less expensive components. Sample gas condensers or permeation dryers are eliminated also. Usually an aspirator or ejector is used to move both sample and dilution gas thus, eliminating the need for a sample pump. On the other hand, cleanup systems to remove moisture, $CO_2$, oil, hydrocarbons, or other components from the dilution gas may be necessary. In-stack dilution probes use critical orifices to control sample flow rate and aspirators to both draw stack gas through the critical orifice and supply dilution air (Fig. 31).

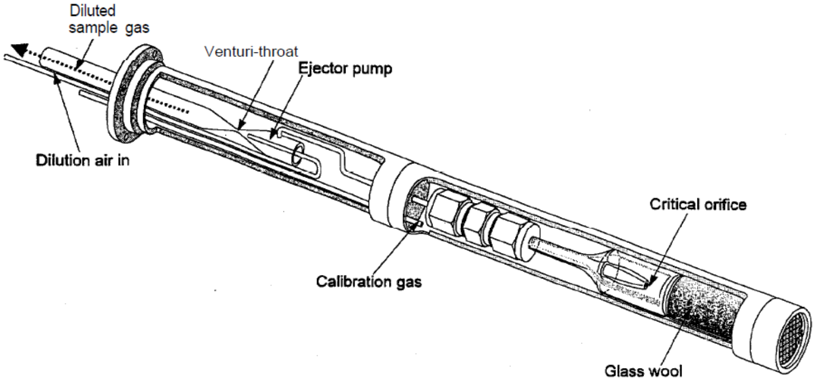


FIGURE 31 In-stack dilution probe.

The critical orifice in the dilution probe ensures that the sample extraction rate is independent of the aspirator vacuum, thus providing a constant sample flow rate and consistent dilution of the sample gas. Calibration gases are introduced upstream of the critical orifice and are diluted in exactly the same manner as stack gas samples. In-stack dilution probes are available from many manufacturers. Dilution ratios ranging from 20/l to 1,000/l are used in practice. Analyzers that were developed originally to monitor $SO_2$ and $NO_x$ concentrations in ambient air are used for emission monitoring. Variations in the sample dilution ratio, and resulting biases in monitoring results, may occur where in stack dilution probes are subject to varying stack temperature, pressure, or molecular weight. Newer designs of dilution systems have located the critical orifice and aspirator outside of the stack in a temperature controlled region to minimize the effects of stack gas temperature variations on the dilution ratio.

A dilution sampling system is not appropriate where an analyzer with the requisite sensitivity is not available to reliably measure the diluted samples. Usually, the minimum dilution ratio is determined based on the maximum expected moisture content of the stack gas and the minimum temperature in the sampling system or analyzer. Applying this dilution factor to the expected stack gas concentration provides an estimate of the required measurement range. An analyzer with sufficient sensitivity, resolution, and signal-to-noise capability must be available for this operating range. The analyzer must be designed for the specific measurement range; incorporating measurement cells with sufficient optical path length and appropriate filters, detectors, and other devices necessary for the measurement level. Simply increasing the electronic gain of an analyzer does not always change the measurement range.

Problems with adsorption may be encountered with dilution systems even though condensation of moisture is avoided. The use of heated sample lines can improve the system response times and can provide additional protection against condensation in applications where extremely cold ambient temperatures are encountered. However, one of the major advantages of using a dilution system is lost if heated sample lines are required. The accumulation of organic material within the aspirator of an in-stack dilution probe has been observed during monitor evaluation tests at a power plant. This was attributed to localized condensation occurring because of cooling by the dilution air. Pre-heating of the dilution air eliminated this problem. In addition, condensation of acids may occur in dilution sampling systems even though condensation of moisture is avoided. Accumulation of sulfuric acid has been observed in unheated dilution sampling lines at coal-fired electric utility boilers. One of the major advantages of dilution sampling systems is that they minimize the volume of sample gas extracted from the stack and thereby minimize the contamination of the system by particulate matter. The frequency of replacing filters and other maintenance activities is reduced for dilution systems because less particulate matter is introduced to the system. Nevertheless, the relative amounts of particulate matter and the gases extracted is the same for dilution and conventional extractive systems. Therefore, the potential for chemical reactions or adsorption between gases of interest and the particulate matter is not reduced. In dilution sampling, special costly analyzers are needed because of the low concentrations of the measured components.

### 10.1.3 NON-HEATED EXTRACTIVE SYSTEMS

These systems are very similar, especially in the part related to the analysis and data acquisition, to the heated systems. They are based on dry gas measurement. Therefore, the sample has to be dried before being analyzed. The simplest means of doing this is with an unheated sample line and drying on the ground. However, condensation will occur in the sample line, which can be allowed only in cases where the flue gas is not aggressive and when measuring scarcely condensable compounds, such as NO, CO or $O_2$. Condensation can be avoided by drying the sample at the stack using individual coolers. Probe coolers are relatively costly, and the stack area itself is often not the ideal place for coolers with their electronics and various moving parts. A heated sample line, followed by gas drying, can be used to avoid both condensation and the need for probe coolers at each stack. In this type of system, a sample is continually drawn from the stack and transported via a heated line to system housing which, in addition to the analyzers, contains all the necessary sample preparation components (Fig. 32).

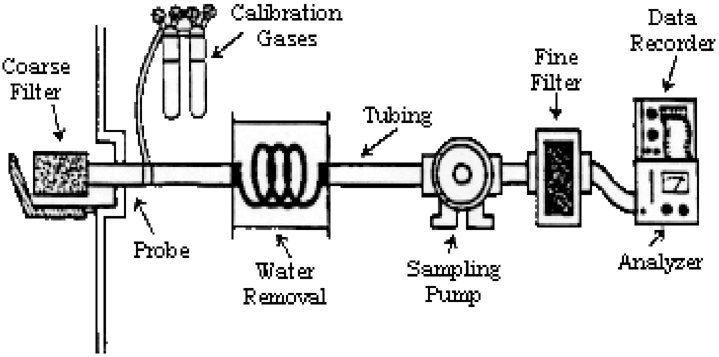


FIGURE 32 Non-heated Extractive System.

Part of the sample preparation is to remove the water vapor by rapidly chilling before analyzing the sample. The gas conditioner removes moisture from the gas sample and cools the gas to a consistent temperature before sending it to the analyzer. This is generally a condensing unit capable of dropping all water out of the sample without scrubbing out any pollutants. The sample conditioner shall be capable of reducing the sample gas temperature to 15°C or to 11°C lower than the ambient temperature, whichever is lower. In other words, as the gas enters the conditioning unit, it is rapidly cooled to around 3ºC to remove acid and water condensate. All parts of the conditioner exposed to the sample shall be glass, stainless steel or Teflon. The sample gas shall not be bubbled or dispersed through the condensate such that minimum contact shall be maintained between any condensate and the sample gas. A temperature gauge shall be used to determine the temperature of the condenser outlet. Other forms of conditioning unit are based on permeation dryers. If needed, a glass filter is used at the inlet or the outlet of the conditioner to prevent the accumulation of particulate material. After this preprocessing, the gas is then passed to the analytical analyzer, which may utilize either non dispersive infrared (NDIR), ultraviolet (UV) or chemiluminescence or any combination of these depending on the components being measured. Obviously, the system requires a significant amount of maintenance to ensure that all the sample preparation components are operating correctly. The major drawback with this type of CEM system is that a significant percentage of any soluble gas, such $NO_2$, $SO_2$ and, to a lesser extent, NO, is removed along with the water vapor. This is the most commonly used sampling principle in Europe, since it can be used to measure most of the traditional emission components, and because most of the components that are prone to vibration and extreme temperatures can be suitably located. From the cooling unit to the CEMS, a length of standard tubing can be used, thus saving energy and installation costs.

## 10.2 CLOSE-COUPLED SYSTEMS

Close-Coupled Systems can be described as a “close coupled” analyzer and probe, where the analyzer is directly connected to the probe installed in-situ at the point of measurement. This reduces any problems that may occur with extractive monitoring, especially heated extraction.

Close-coupled systems minimize extractive sampling components by effectively placing the measurement sensor in close proximity to the sampling point. Many of the problems observed in other extractive sampling systems are eliminated. Close-coupled systems have been developed for the measurement of criteria pollutants. They also have applications in monitoring non-criteria air pollutants particularly reactive and condensable gases. Several fundamentally different configurations have been developed. For example, a system for “total hydrocarbon” monitoring has been developed. In this case, the heated FID is located in a thermally controlled enclosure just outside the stack wall. The sample is conveyed only a very short distance, thus the surface area for adsorption/desorption reactions and the time allowed for reactions to occur before the sample reaches the detector are greatly minimized. This design allows for rapid responses of the measurement system and minimizes sampling system maintenance. Close-coupled systems have been also developed that use “reactive gas analyzers” for the measurement of $NH_3$, $SO_2$, and $H_2SO_4$. These measurement systems incorporate a means of contacting the sample gas stream with an absorbing solution at the outlet of the sampling probe. The absorbing solution may simply absorb the compound of interest or it may facilitate chemical reactions which convert this component to a more stable form. The chemical solution is continuously renewed and after exposure to the gas sample it is conveyed some distance to an analyzer which provides for the determination of concentration. This approach provides for the immediate reaction of the component of interest, and possibly the selective chemical removal of interfering species, to make the measurement. Many of the precautions evident in other systems that are necessary to avoid condensation, minimize adsorption; or avoid chemical reactions are not needed in this approach. Another close-coupled system configuration has been introduced which uses a solid state tunable diode laser analytical method. This technique is capable of measuring many components in the infrared spectrum and can be used for monitoring $NH_3$, HF, $H_2S$ and other toxic gases. In these systems, the laser source and photodetectors necessary for the measurement are contained in a control module at a remote convenient location as are the analyzers in extractive monitoring systems. A fiber optic cable is used to connect the control module to a sample probe. The probe provides for the continuous flow of stack gas through an optical cell mounted in a thermally controlled chamber immediately outside the stack as shown in Figure 33.

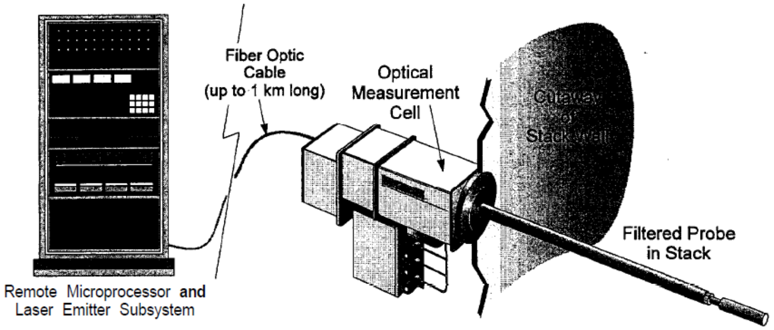


FIGURE 33 Close-coupled laser monitoring system.

Because this measurement system can employ fiber optic cables as long as 1 km, the advantages of a close-couple optical measurement cell and the convenience of a remote analyzer are provided. In addition, a number of sample probes can be connected to the same control module thereby offering additional cost savings for the applications where measurements are required at several locations.

## 10.3 In-Situ Measurement Systems

In-situ CEMS differ from extractive CEMS in that they use instruments to continuously monitor the flue gas directly and do not use an extracted, conditioned sample. In-situ systems for the measurement of gases determine the concentration of the gas of interest within the stack by either placing a detector within the stack or by projecting a light beam through a portion of the stack gas stream and analyzing various spectral phenomena. Point in-situ systems measure the concentration at a specific point or over a relatively short path length through the stack gas. Path or cross-stack in-situ CEMS, like the point in-situ CEMS, continuously measure the concentrations directly from the stack gas. However, instead of measuring the concentrations at a single point, they use a light beam projected across the entire path of the stream of gas to analyze the concentrations. Both in-situ techniques have the advantage of timeliness over the two extractive methods; there is no time-delay. They also avoid many of the sampling problems faced by the extractive methods such as the absorption of sample components, moisture from condensation, and chemical reactions between the sample components. Application of the in-situ sampling method is restricted to dry gases. But the scrubbers frequently used these days to meet tight emission limits cool down the gases and saturate them with moisture. So the gases are full of tiny water droplets, which falsify the dust measurement. To correct this, the extractive method must be used. The sampling system is equipped with heaters that eliminate the water droplets by evaporation before measurement takes place.

Regardless of the configuration, all in-situ systems must be designed to determine the concentration at stack conditions, which typically involves varying temperature; pressure, and moisture content. Other factors, such as particulate loading or the concentration of interfering gases, also vary and may affect the measurement process or accuracy of results. An advantage of in-situ systems is that many of the sampling problems associated with extractive systems are eliminated. Assuming that the stack gas temperature is above the dew point, condensation is not an issue. Adsorption of gases is irrelevant. Reactions between gases and particulate matter can be ignored for all in-situ systems except for those that use a thimble or filter to protect an in-stack detector. In-situ analyzers are particularly appropriate, and in some cases, the only option for the measurement of reactive and condensable gases because the influences of the extractive sampling system are eliminated. On the other hand, in-situ analyzers may need to compensate for variations in gas density due to temperature or pressure variations, variations in spectral absorption due to temperature shifts, as well as variations in particulate matter loading and the presence of other interfering species. The method used to compensate for these types of factors is inherent to the analytical technique. Consider for example, an optical infrared dispersive device. Variations in the effluent temperature change the gas density and thus the number of molecules present in the adsorption path at a particular concentration. Sensing of the effluent temperature is necessary to distinguish between changes in infrared adsorption due to concentration variations or due to temperature variations. Also, the actual spectral adsorption of infrared radiation varies as a function of temperature for different compounds. Thus, effluent spectra and reference spectra obtained at the same temperature must be “matched” in order to analyze the data accurately. Temperature compensation for spectral adsorption can be performed by obtaining a series of spectral libraries at different temperatures on a controlled calibration facility. This approach has been used for infrared gas filter correlation devices and UV differential adsorption instruments. A major challenge for in-situ analyzers is the ability to verify proper calibration while the instrument is installed. Because the effluent is present, determining if the zero concentration value is correct is difficult. Various schemes have been used to attempt to overcome this problem. Calibration at saturation (very high concentration) rather than at zero, incremental calibrations superimposing gas filters and the effluent gas, and using concentric slotted pipes or other mechanical means to temporarily provide a zero calibration have all been used with varying degrees of success. An in-situ monitor with a slotted probe for effluent measurements and gas audit cell to facilitate quality assurance checks using external calibration gases has been developed. The probe design ensures that calibration gases are at the same temperature as the effluent gases for reasons previously discussed. Another single-pass cross-stack in situ, analyzer uses a zero pipe to provide a reference optical path, free of adsorption, and a flow-through gas cell to facilitate the introduction of calibration gases. This instrument is an ultraviolet differential absorption instrument that can measure many gases including $SO_2$, NO, $H_2O$, $NH_3$, volatile organic compounds, and Hg (vapor). In-situ devices typically isolate optical components from the effluent stream by using optical windows and an air-purge system that provides a flow of filtered ambient air across the optical surfaces and then into the stack. The analytical technique must be insensitive to any dust accumulation on the optical surfaces; otherwise, the decrease in light transmittance might be interpreted as an increase in pollutant concentration. The sample interface system must be adequate to ensure that dust accumulation is held to acceptable levels between maintenance intervals. Otherwise, the intensity of the optical beam may be diminished to the point where deterioration in signal to noise levels reduces the accuracy of the measurement results. Optical windows must be fabricated of materials that transmit the measurement wavelengths and are resistant to chemical reactions and mechanical deterioration.

### 10.3.1 CROSS-DUCT AND REFLECTIVE CROSS-DUCT ANALYZERS

Cross-duct and reflective cross-duct analyzers were a significant step forward in continuous emission monitors, negating the need for expensive, bulky and high-maintenance sample systems. These systems do not involve pneumatics (e.g. pumps and sample lines) and generally work on optical gas absorption techniques. Basically, an energy source (IR or UV) is projected across the stack from one side to the other. This technique involves a transmitter and receiver system (or a transceiver).

Cross-stack systems which project a light beam across the stack may be either single pass or double-pass systems depending on whether the light source and detector are on the same or opposite ends of the light path. A double pass system is illustrated in Figure 34.

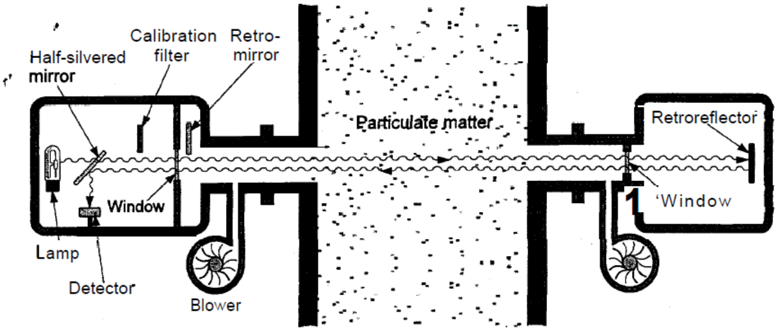


FIGURE 34 Double-pass transmissometer.

The cross-stack and reflective cross-stack systems rely on the stack as the sample cell, sending pulses of infrared or UV light through the stack to either a receiver or a reflector, which is then returned to the stack-mounted receiver unit (Fig. 35).

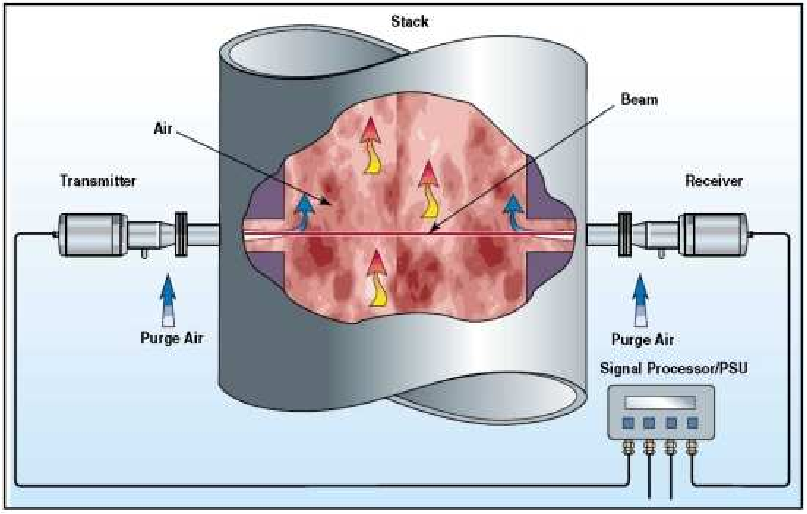


FIGURE 35 Cross duct analyzer.[www.procal.com]

Measurement is based on gas absorption laws such as the Beer-Lambert law. Specified target gases absorb some of the projected energy at specific wavelengths resulting in an altered energy state of the gas molecule. The analyzer measures the gases passing through the stack due to specific energy-absorbing spectral characteristics of the various gases. Various analytical techniques including FTIR and spectroscopy DOAS are employed in cross-duct monitoring systems. Most cross-duct systems have the ability to measure multiple gases over a range of wavelengths (mainly IR), although some manufacturers are combining UV and IR absorption systems to further extend the range of gases. Cross-duct continuous emissions monitoring systems have many advantages over the other techniques. A benefit is that the analyzed samples are true and unmodified. As there is no sample system used with these techniques, and the analyzers do not come into contact with the target gases, far less maintenance and operator involvement is required. These systems have also the disadvantages e.g. the inability to directly zero and calibrate the instruments. Calibration of cross-duct systems can be more complicated and, unlike extraction systems, it is impossible to calibrate the "whole system". There are also restrictions on the size of stacks which could be reliably monitored with this type of system. However, the benefits of cross-duct monitoring often outweigh such difficulties, especially if an automatic calibration system can be supplied to demonstrate accurate and reliable calibration checking.

### *10.3.2 IN-SITU OPEN PATH ANALYZER*

In this configuration (Fig. 36), the reflector is mounted on the probe and a slot in the probe allows the gas to pass between the in-stack window and the reflector. In an attempt to zero and calibrate the instrument, a second reflector is swung in front of the in-situ stack window and the system is zeroed. In addition, test gas can be passed into the enclosed portion of the probe, enabling the instrument to verify calibration.

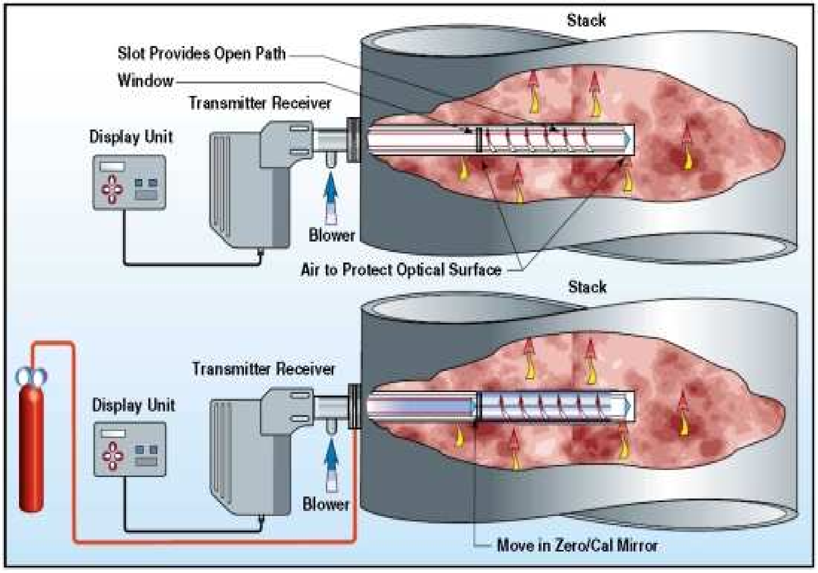


FIGURE 36 In-situ open path analyzer.

The major problem with this configuration is that the full system is not challenged - a second reflector is used and the effects on the first reflector are not taken into account.

### 10.3.3 *ENVELOPED FOLDED BEAM ANALYZERS*

In this configuration, the transmitter and receiver are mounted in one enclosure and the pulses of infrared or UV light passed out through a tube containing two lenses, one on the exit of the optical housing. The second (the process lens) is mounted in the stack. The pulses of infrared or UV radiation then pass through a second portion of the probe, which is fitted with sintered panels, allowing the flue gas to freely pass into the cell. The pulses of infrared or UV light strike a retroflector and are returned through the same path to the transmitter receiver (Fig. 37).

Clearly, extractive instruments can be challenged by diverting zero and then test gas into the sample cell, enabling the instrument to be recalibrated and any errors reported. This is also possible in the enveloped folded beam, as shown in Figure 42. Normally, the flue gas passes through the sintered panels, filling the in-situ gas cell, where the absorption of infrared or ultraviolet light takes place. Periodically, either automatically or on demand, a solenoid valve can be activated, allowing instrument air to be discharged into the in-situ cell, forcing out the flue gas, enabling the instrument to check zero and adjust if necessary. In the same way, certified test gas, traceable to a national standard, can be introduced into the sample cell, enabling the instrument to check, and, if necessary, adjust calibration.

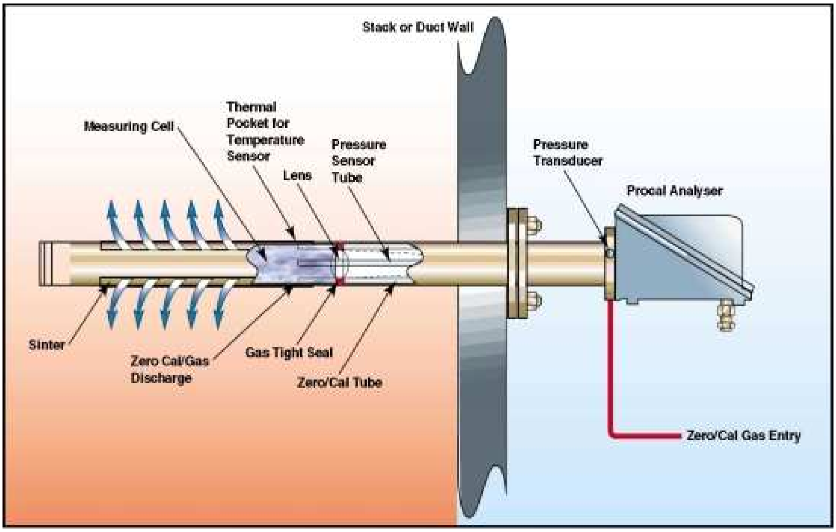


FIGURE 37 Enveloped folded beam analyzers.[ www.procal.com]

It is recommended that the auto-zero is carried out on a daily basis, however, experience has shown that calibration and verification need only be carried out every three months or so. The enveloped folded beam technique resolves many of the problems associated with extractive and cross-stack systems.

### *10.3.4 PRESSURE AND TEMPERATURE COMPENSATION*

To ensure that the instrument is within ±2% accuracy, it is necessary to carry out automatic correction for changes in sample temperature and pressure. This is achieved by continually monitoring the temperature and pressure within the sample cell and compensating for any changes. The pressure compensation deals with changes in barometric and flue gas pressure. In addition, if the certified test gas applied to the probe causes a pressure increase, pressure compensation would remove the effect.

### *10.3.5 TYPICAL INSTALLATION*

In a typical installation, the in-situ CEM system is flange mounted, with the in-situ sample cell protruding into the stack. The analyzer is connected via a serial link to the analyzer control unit, which displays, logs and retransmits the concentrations of the monitored flue gas components. In addition, the auto zero/calibration unit, fitted with three solenoid valves and controlled by the microprocessor in the analyzer, allows the periodic zero and calibration to be carried out. Several analyzers can be connected to a single control unit (Fig. 38).

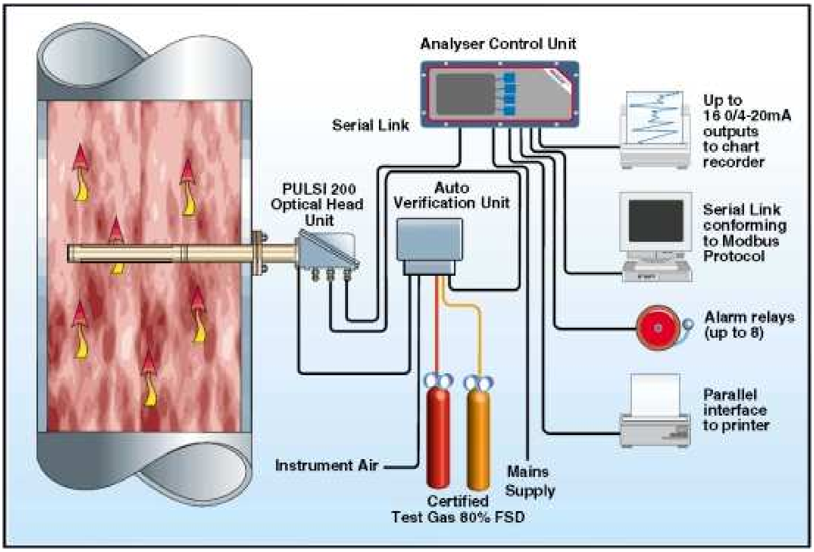


FIGURE 38 Typical installation.[ www.procal.com]

### 10.3.6 INTEGRATED STACK MONITORING SYSTEM

It is often necessary to report the pollutant measurements normalized to a level of $O_2$ or $CO_2$. This can be achieved by connecting an oxygen analyzer directly into the stack-mounted infrared/UV analyzer. The data from the oxygen analyzer is then transmitted to the analyzer control unit and used to calculate and display a normalized concentration of pollutant gas (Fig. 39).

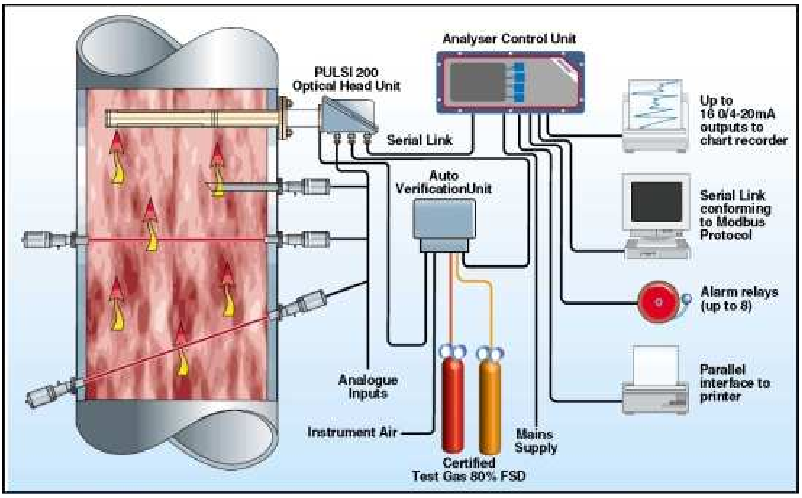


FIGURE 39 Integrated stack-monitoring system.[ www.procal.com]

## 10.4 CEM PARTICULATE SYSTEMS

Numerous technical issues are involved in choosing a continuous particulate monitoring system. First, the flue gas stream must be well characterized to determine the presence or absence of water droplets, particulate concentration levels, and the degree of particulate stratification. The following measurement methods and techniques are used in continuous particulate monitor systems:

- optical (light attenuation, light scattering);
- nuclear (beta ray attenuation);
- electrical (contact charge transfer).

Of these methods, the light attenuation technique using transmissometers has been the most extensively studied. Extinction-mass correlation methods are used routinely in many countries. The light scattering and beta gauge techniques are being applied increasingly due to the good correlations that can be obtained. Instruments for measuring particulate emissions to the atmosphere are some of the most common to be fitted to industrial processes. There are a number of instrument groups used for quantifying particulate emissions which include:

- optical transmission devices (transmissometers);
- dynamic transmission devices;
- light scatter devices;
- beta (β) gauge devices;
- tribo-electric probes;
- the tapered element oscillating microbalance (TEOM).

### *10.4.1 TRANSMISSOMETERS*

The transmissometer is an optical instrument based on light attenuation. The light attenuation or transmittance through the flue gas is determined by passing a light beam across the stack interior. The intensity of the light returning I, is compared with a previously determined reference signal $I_0$, to give the transmittance, $T = I/I_0$. A transmissometer may be constructed in two ways, using either a single pass system or a double pass system. In a single-pass system, the light crosses the stack directly to a detector. In a double-pass system, the light crosses the stack twice. The transceiver assembly on the left houses both the light source and light detector. By reflecting the projected light from a mirror located outside of the transceiver window, systems can be designed easily to check all of the electronic circuitry, including the lamp and photodetector, as part of the operating procedure. Most transmissometer systems include some type of air purging system or blower to keep the optical windows clean. The way in which a transmissometer is used can affect its design. If the transmissometer data are to be correlated with particulate mass, red or infrared light may be more appropriate than using visible light as in opacity monitors. The smaller particles (<5 μm in diameter) contribute greatly to the opacity but not to the particulate mass loading of the flue gas. Red light is not as sensitive to the small particles as it is to the larger particles, and thus gives a better correlation to particulate mass. Since the light transmittance, T, is reduced exponentially by an increase in mass concentration, a semilog plot of light transmittance versus concentration should yield a straight line, or linear correlation. Another method of developing the correlation is to first convert the transmittance data to optical density, where optical density, D, is defined as:

$$D = log\left(\frac{1}{T}\right)$$

Another expression that is used frequently for such correlations is "extinction," a parameter that normalizes the path length:

$$b = 2.303\frac{D}{l}$$

where: b-extinction, D-optical density, l-light path length.

A graphical plot of either optical density or extinction against the manually determined particulate concentration should give a straight line correlation. The measurement sensitivity of this technique is approximately 10 mg/m3 for a one meter optical path. Extinction-mass correlations have been developed successfully for many types of emission sources. However, as implied above, correlations may be sensitive to the changes in the particle-size distribution in the flue gas. Optical transmission instruments are capable of measuring smoke density in terms of transmission, opacity, Ringelmann units or optical density (extinction co-efficient). To derive an output in mg/m$^3$ requires the generation of a "transfer function" which is applied to the extinction coefficient. The transfer function is attained by performing a number of isokinetic extractive samples. The extinction coefficient is used because the relationship between mass concentration and CEM output is linear.

### *10.4.2 DYNAMIC TRANSMISSION DEVICES*

Dynamic transmission is a form of opacity measurement where the light transmission value is averaged over a long period (up to several hours) and measures dynamic variations in light intensity. The method works by measuring small variations in opacity caused by changes in mass loading, incomplete mixing of particles, turbulence-induced inhomogeneity in particle distribution and pressure/temperature variations in the flowing gas. These monitors are able to achieve much better sensitivities than transmissometers over short path lengths, typically 1 mg/m$^3$ at 1 metre, but are not as sensitive as light scattering devices. The averaged transmission level is used to perform continuous zero offsets to compensate for material on the lenses or misalignment of the heads. This procedure makes the instruments relatively immune to the effects of window and lens contamination.

### *10.4.3 LIGHT SCATTER DEVICES*

When light is directed toward a particle, the particle may both absorb and scatter the light. If the wavelength of the light is large with respect to the size of the particle, a type of scattering called "Rayleigh" scattering occurs. If the wavelength of the light is approximately the same as the radius of the particle, a type of scattering called "Mie" scattering will occur (originally described by Gustav Mie in 1908). Analyzers have been developed to take advantage of scattering effects. They can be designed to measure either back-scattered light, forward scattered light, or light scattered toward the side, at a specified angle. A side-scattering instrument is illustrated in Figure 40. In this side-scattering device, infrared light is focused on a sample volume. Instead of measuring the backscattered radiation, the device locates a sensor above the lamp such that side-scattered light is detected. A reference measurement is made by monitoring the lamp intensity through a tube passing from the lamp to the detector.

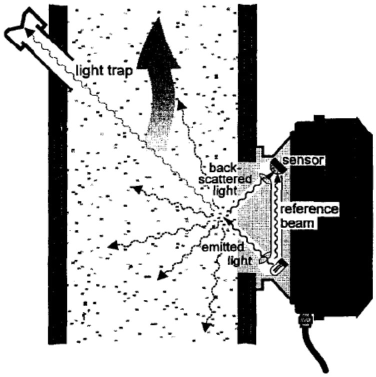


FIGURE 40 A side-scattering continuous mass emission monitor.

A light scatter instrument measures the amount of light scattered in a particular direction (i.e. forward, side or back) and outputs a signal proportional to the amount of scattering material (e.g. particulate matter) in the sample stream. As with transmissometers, mass concentration can only be derived by applying a transfer function, derived from a series of isokinetic tests. Because light scatter instruments achieve higher sensitivities than transmissometers, they are normally used for measuring low particle mass concentrations in smaller ducts (typically less than 2 metre diameter).

### *10.4.4BETA (B) GAUGE DEVICES*

When beta rays pass through a material, they can be absorbed or reflected by that material. The transmission of the beta rays is therefore attenuated and the reduction in beam intensity can be correlated to the amount of material present. By using a radioisotope for the beta source (e.g. $Kr^{85}$, $C^{14}$), "beta gauges" have been developed that can monitor particulate mass continuously. In this device, the flue gas is drawn isokinetically through a probe. The sample may then be diluted to reduce the dew point to the levels where condensation of flue gas moisture will not occur in the instrument. The gas is filtered through a glass fiber filter to produce a spot of collected particulate matter, which is moved between the beta source and detector for a determination of the beta ray attenuation. In practice, a moving filter tape allows the intermittent collection and measurement of one data point to produce a semi-continuous measurement (Fig. 41).

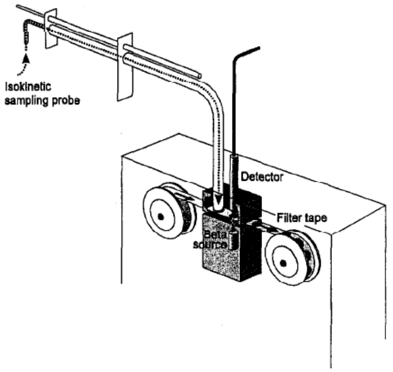


FIGURE 41 Typical beta gauge paper tape monitor.

The reduction of the beta ray beam intensity through the spot depends upon the electron density of the collected material and the amount of material present. To produce consistent measurements, a constant relationship must exist between the number of electrons per molecule and the molecular weight. This ratio is essentially the same for most particulate matter found in coal and oil combustion sources. In this method, the sample gas volume is controlled to provide a value for the particulate matter concentration. The range of the instrument is typically from 2 to 4,000 mg/m3. The method does require that the sample is collected isokinetically. Problems may occur with particulate deposition in the sample probe and sampling lines. Spot collection efficiency, particle composition, and gas volumes and dilution ratios are all factors that may produce error. These problems may be minimized in some applications by first diluting the sample, using high transport velocities, or pulsating flow. Beta (β) gauge are not continuous monitors and there are periods when they are not monitoring. The output they give is not a real-time determination of mass concentration, rather a series of discrete time weighted averages. Because the cross sectional area of the sampling nozzle is very small in comparison to the total area of the duct, there is a strong possibility that the sample is unrepresentative of the average mass concentration within the duct. In consequence, these systems are used more for ambient air applications than stack emissions.

### 10.4.5 TRIBO-ELECTRIC PROBE

The instrument is simple, consisting of a metal surface probe inserted into the stack. A probe is located in the stream of flowing dust. The electrical charge is generated in this device. The intensity of the current flowing from the probe to the grounded input of the measuring relay depends on the dust concentration. These devices are inherently reliable as they have no moving parts and use electronic systems to check their performance. Their sensitivity is a function of the gain employed to amplify very small signals and the length of the probe. Tribo-electric CEMs can achieve similar sensitivities to scatter devices but are affected to some extent by gas velocity variation. Tribo-electric monitors measure total mass flow directly and accurately at very low cost without the need for separate velocity measurements. It has been qualitatively successful as a bag-house particulate alarm monitor. The instrument, however, lacks a method of probe calibration and has shown problems for monitoring after electrostatic precipitators because of static electrical charges on the particles. Also, small particles may follow the gas streamlines around the probe and never make contact for the measurement.

### *10.4.6 THE TAPERED ELEMENT OSCILLATING MICROBALANCE*

The tapered element oscillating microbalance (TEOM) generates stack particulate mass concentration information in real-time using a direct mass measurement approach. The instrument collects particulate matter from the flue gas using a dynamic isokinetic sampling system that continually adjusts to reflect changing stack velocity conditions. The instrument contains a unique system for measuring the stack gas moisture content in real time, along with the flue gas velocity. With the addition of flue gas $O_2$ and $CO_2$ data, the instrument computes the molecular weight of the stack gas. Stack particulate mass concentration values are generated on a dry, standard volume, basis.

## 10.5 CEMS FOR METALS

Either extractive or in-situ sampling methods can be used for monitoring metals. However, measurement problems develop when a metal is present in the flue gas in both the vapor and solid phases. Mercury is a typical example, where most of the total mercury is present as a vapor, although some may be bound in the form of mercuric chloride or other compounds in the particulate matter. Simple optical instrumentation can detect the mercury vapor, but not the other mercury compounds. To obtain a value for total mercury, either an extractive technique must be employed to reduce these compounds for subsequent measurement, or the particles and vapor alike can be heated to extremely high temperatures (as in an electric arc, a plasma torch, or a focused high energy laser beam) to emit characteristic spectra. In extractive metals monitoring systems, metal amalgamation and deposition in the probe and sampling lines present a significant problem. Here, close coupled systems or very short sampling lines may be necessary to obtain reproducible results.

Commercial systems are available for monitoring mercury on a continuous basis. In most mercury monitoring methods, mercury vapor is analyzed by light in the ultraviolet region of the spectrum. The simplest method is to merely project a UV light into the stack as in an in-situ instrument and monitor the absorption of light by the elemental mercury vapor. However, if mercury is present in other molecular forms, such as mercuric chloride ($HgCl_2$), total mercury will not be measured. Although in many incineration facilities elemental mercury comprises greater than 90% of the total mercury emitted, interest remains to measure total mercury. As a result, various stratagems have been devised to reduce the mercury compounds to elemental mercury, vaporize the elemental mercury, and measure the vapor through UV light absorption techniques. In one method, an isokinetically extracted continuous sample is heated in an infrared oven to volatilize particulate bound mercury and a sodium hydroboron solution is used to reduce all mercury compounds to elemental mercury. Elemental mercury then is measured using a UV photometer. In another method, mercury compounds are reduced chemically using stannous chloride and the elemental mercury is amalgamated with gold, which then is heated to release the mercury as vapor to be measured using a UV photometer. In a new microsensor technology, mercury vapor adsorbs on the surface of a thin noble-metal film. The electrical properties of the film change quantitatively to give a measurement of the amount of mercury present. Although mercury monitoring methods are commercially available, to measure total mercury adsorbed or bound on particulate matter, a continuous isokinetic sample must be obtained and the sample reduced to elemental mercury. However, chemical systems and ovens used in the various system designs require frequent periodic maintenance. These maintenance demands are typically greater than for traditional criteria pollutant monitoring systems.

## 10.6 FLOW RATE CONTINUOUS MONITORING SYSTEMS IN STATIONARY SOURCES

Some regulations require continuous measurement of stack gas velocity. Pollutant mass emission rates are estimated from the measured velocity from a stack or duct. A number of techniques are currently available to monitor flue gas volumetric flow rate. The methods vary in complexity from the use of Pitot tubes to transmitting ultrasonic signals across the stack.

# 11 SYSTEMS FOR AMBIENT AIR QUALITY DETERMINATION

Monitoring of air quality has become an increasingly important function of all air pollution control agencies. Air quality monitoring is carried out to assess the extent of pollution, ensure compliance with national legislation, evaluate control options, and provide data for air quality modeling. There are a number of different methods to measure any given pollutant, varying in complexity, reliability, and detail of data. These range from simple passive sampling techniques to highly sophisticated remote sensing devices. A monitoring strategy should carefully examine the options to determine which methodology is most appropriate, taking into account initial investment costs, operating costs, reliability of systems, and easiness of operation. Automatic methods are the most appropriate for continuous, in real-time measurements. This form of air pollution monitoring is a complex technical task, requiring not only direct measurements, but also measurement standards and quality assurance to ensure that the information provides a correct understanding of air quality. Nowadays, automatic measurement systems produce high resolution measurements (typically hourly averages or better) at a single point for pollutants such as $O_3$, $NO_x$, $SO_2$, CO, total organic compounds, benzene, 1,3-butadiene and other speciated hydrocarbon concentrations, $PM_{10}$ or $PM_{2.5}$. Methods used include a variety of sophisticated techniques such as infrared or UV absorption, UV fluorescence, chemiluminescence, chromatography. To ensure that the recorded data is accurate and reliable, a high standard of maintenance, calibration, operational and QA/QC procedures is required as well as sophisticated data recording devices to record, process, analyze and present the information.

## 11.1 MONITORING STATION

Automatic measurements are usually performed by using monitoring stations (Fig. 42). They provide data about air pollution levels at specific time and site of sampling. A monitoring station contains equipment for:

- sampling;
- measurements;
- calibration;
- data collection;
- data transmission and control.

Instruments in monitoring stations are generally placed inside special shelters.

FIGURE 42 Different types of monitoring stations.

## 11.2 THE SAMPLING PART

The sampling part of the monitoring station is the most important units in the whole measuring system. The validity of the final data depends on the correct location of this element. Local peculiarities that could invalidate the sampling results must be avoided: for example, localized windfields and the absorption or adsorption of pollutants on nearby surfaces such as walls or the ground. Acts of vandalism must also be guarded against. These criteria indicate that the air intake should, if possible, be freely exposed to winds from all directions. The inlet should therefore be at least 1m from any vertical surface (e.g. wall, buildings, vegetation) and elevated 3-4 metres above ground level and about 1m from any horizontal surface (e.g. hut roof) for samplers installed within a hut or container.

Apart from the correct siting of the air intake, it is important that the whole sampling system should be constructed in such a way that data from stations measuring the same parameters are comparable. Air sample inlet probe construction materials along with the design of the inlet manifold are important in obtaining representative air samples and conserving the integrity of the contaminant concentrations. The design of the inlet manifold should minimize the effects of moisture condensation, pressure drop, dust settlement and air sample residence time in the inlet. A high capacity sampling manifold should be used. The aim should be to achieve uniformity in the sampling volume and velocity, the number of possible connections for different monitors, the material used for the construction of the manifold, and protection against the effects of external temperature and pressure changes, with particular regard to condensation within the sampling system. On account of the different requirements, separate sampling probes should be used for gaseous pollutants and suspended particles (aerosols). If possible, automatic controls signaling and correcting deviations from the desired performances of the monitors should be built into the sampling system. Regular maintenance of the whole sampling system at intervals of 3-6 months, with careful cleaning of the manifold, is necessary for avoiding inaccuracies due to the contamination of the walls. Some important variables affecting the sampling manifold design are the diameter, length, flow rate, pressure drop, and materials of construction. A borosilicate glass (which includes Pyrex®), FEP Teflon® or their equivalent must be the only material in the sampling train (from inlet probe to the back of the analyzer) that can be in contact with the ambient air sample. For volatile organic compound (VOC), FEP Teflon® is unacceptable as the probe material because of VOC adsorption and desorption reactions on the FEP Teflon®. Borosilicate glass, stainless steel, or its equivalents are the acceptable probe materials for VOC and carbonyl sampling. Care must be taken to ensure that the sample residence time is kept to 20 seconds or less. No matter how nonreactive the sampling probe material may be, after a period of use, reactive particulate matter is deposited on the probe walls. Therefore, the time it takes the gas to transfer from the probe inlet to the sampling device is also critical. Ozone, in the presence of nitrogen oxide (NO), will show significant losses even in the most inert probe material when the residence time exceeds 20 seconds. Other studies indicate that a 10-second or less residence time is easily achievable. Residence time is defined as the amount of time that it takes for a sample of air to travel from the opening of the cane to the inlet of the instrument and is required to be less than 20 seconds for reactive gas monitors. The residence time of pollutants within the sampling manifold is also critical. It is recommended that the residence time within the manifold and sample lines to the instruments is less than 10 seconds (of the total allowable 20 seconds). If the volume of the manifold does not allow this to occur, then a blower motor or other device (vacuum pump) can be used to decrease the residence time.

## 11.3 MEASURING INSTRUMENTS

Although a large number of measuring instruments have recently become available, only a small number are suitable for use in automated monitoring systems. They fulfill several requirements related to:

1. functional characteristics-measuring ranges, measuring interval, accuracy, repeatability, selectivity;
2. operational characteristics-behaviour with respect to external conditions such as temperature and humidity, and energy and maintenance requirements;
3. dimensions of instruments and associated equipment;
4. control of the correct functioning of the instruments ("status" signals);
5. reference measurements and determination of zero drift (zero check) ;
6. signals indicating need for maintenance and repair.

Analyzers and samplers for the following pollutants are usually contained in monitoring station:

- sulfur dioxide (principle: pulsed UV fluorescent);
- itrogen oxide/ principle: oxides of nitrogen/nitrogen dioxide (principle: chemiluminescence);
- carbon monoxide (principle: Non-Dispersive Infrared Photometry – Gas Filter Correlation);
- ozone (principle: UV photometry);
- volatile organic compounds (principle: automated gas chromatographic/PID analysis of up to eight (8) VOC compounds including benzene, toluene, ethyl benzene, m-, o- and p- xylene. 1-3 butadiene using a microprocessor);
- ambient particulate (both PM10 and PM2.5, continuous measurements, principle: true micro-weighing, separate inlets PM10 & PM2.5);
- ammonia (principle: $NH_3$ conversion to NO by oxidation. $NO_2$ in the air stream is also converted to NO. The difference obtained by measuring NO in the output of the two sample streams is equal to the $NH_3$ concentration);
- High Volume PM-10 particulate samplers;
- Low Volume PM-2.5 particulate samplers.

The integral part of air quality monitoring station is meteorological instrumentation. To meet the best exposure criteria, sensors to measure meteorological parameters are usually mounted on towers or masts. If sensors are mounted improperly, errors due to the influence of nearby obstacles and possibly of the tower itself will be introduced into the measurements. Meteorological instrumentation includes sensors for: wind speed (the anemometer), wind direction, air pressure, ambient temperature, precipitation, solar radiation (the detector should be able to measure short-wave radiation, which is comprised of the direct component of sunlight and the diffuse component of skylight) and relative humidity at air quality monitoring stations. It has been recommended that the standard height at which surface wind measurements should be taken is 10 metres (however measurements at a height of 2 metres are acceptable for tripod-mounted sensors). The temperature and humidity sensors must be housed in a ventilated radiation shield (aspiration velocity should exceed 3m/s) to protect the sensor from thermal radiation. The WMO standard for ambient air temperature measurements is 2 metres above ground. The environmental protection agencies recommend that the sensor be located at least 2 metres above ground, up to a maximum of 10 metres. Vandalism and security need to be considered in the placement of these sensors. Pyranometers used for measuring incoming solar radiation should be located with an unrestricted view of the sky in all directions during all seasons, with the lowest solar elevation angle possible. Sensor height is not critical for these units. A tall platform or a rooftop is a desirable location. Net radiometers should be mounted about 1 metre above ground and in such a fashion as to avoid obstructions to the field of view both upward and downward. The ground cover should be representative of the general site area. The monitoring objective will govern the collection of solar or net radiation data.

## 11.4 CALIBRATION EQUIPMENTS

Calibration equipments should be provided for the calibration of the air quality analyzers, particulate samplers, meteorological equipment, data acquisition system. The calibration system for the air monitoring equipment should incorporate an automatic gas dilution calibrator, a calibrator based on internal permeation oven, an ozone generator, calibration gas standards, a high performance zero air generator to calibrate all of the analyzers in the system. The calibration materials/gases and measurement devices, such as flow meters and pressure gauges, must be certified for accuracy against a reference or transfer standard traceable to a primary reference standard. This is to ensure consistency across the province and reproducibility. There are many models and makes of calibrators designed for dynamic calibration of ambient air analyzers. Gas cylinders, permeation devices or a combination of both can be used as calibration source materials. The calibration cycles should be configurable through the Data Acquisition System at any specific time during the day or night. The dilution calibrator should be able to perform mixing of source gas (from the calibration gas bottles or tubes) with zero air (from the zero air generator) in order to generate a wide range of calibration gas concentrations and minimizing the number of calibration gas standards required.

Meteorological, flow, and electronics calibration should include e.g.:

- wind direction calibrator (degree wheel);
- telescopic orientation sight;

- wind speed sensor accuracy (synchronous motors);
- temperature (precision resistors and thermometers);
- portable aneroid pressure calibrator;
- relative humidity calibrator;
- data acquisition system (voltage, frequency, resistor standards and calibrated multi-meters);
- calibrator flow (traceable bubble meter and flow with water manometer).

All stations must be equipped with zero-air generators and span gas dilution systems that can be activated by the DAS system. The gas dilution calibrator must provide a simple means of obtaining precise gas dilution calibrations for each of the instruments at the station. If an ozone analyzer is at the station, the calibrator must provide gases for precision checks and gas phase titration.

## 11.5 DATA ACQUISITION SYSTEM

For continuous monitoring of air contaminants and meteorological parameters, a real-time data acquisition system (DAS) to collect, display and report the data is required. DASs have a wide range of capabilities (e.g. telephone, wireless, radio link, satellite communications, editing and reporting software, etc.) and emitters/site operators should select systems that suit their needs and also meet the specified requirements. The data acquisition system (DAS) should provide full control over the entire system enabling automatic calibration cycles to be performed and system errors to be detected and reported. The data acquisition system should feature automatic data validation software complete with data capture percentage. The system should preferably collect data directly from the instruments in digital format. The Data Acquisition System should be able to collect and store meteorological data and air quality data from instruments. The DAS should be a low-powered data logger designed to be used for recording and storing data. In the station should be installed data collection, evaluation and, reporting systems (including required remote connections, hardware and software) to interrogate and control each station's data acquisition system and collect data into a centrally-located computer at local and at national level. These collection systems should simplify the tasks of automatically and manually retrieving and viewing measurement data, collating and storing data into a central database at city and national level, and evaluating and summarizing data into comprehensive reports. It should be capable of real-time viewing of measurement and diagnostic data and control calibration sequences and other system functions. The system should also be able to retrieve information directly from the station's data acquisition system following validation and support remote communication. It should compute and report concentrations of all pollutants which exceed ambient air quality standards, the time of day that the exceedence occurred and the number of times within the preceding twenty-four (24) hour period that the standard(s) were exceeded. The system shall also calculate and report the air quality index. The software should be able to generate graphs and reports in the standard Windows format in definable periodic categories including hourly, daily, weekly, monthly and yearly.

## 11.6 SHELTER

Continuous analyzers must be housed inside secured buildings or shelters with restricted and/or controlled public access. The stations should provide proper shelter for monitoring equipment and include air-conditioning for temperature control at 20-30 °C, internal ventilation systems, electrical supply protection and conditioning, monitoring of electrical supply upset events, calibrations systems and zero air generators, security systems, rack cabinets, computerized data acquisition and data processing systems. Therefore, the shelter should be equipped as follows:

- gas bottle rack for securing expendable gas cylinders;
- meteorological tower;
- 220 VAC, 50Hz power supply;
- power conditioning capacity sufficient to assure uninterrupted power of sufficient quality to avoid data loss and meet instrument requirements;
- working bench and storage shelves and filing cabinet with desk light;
- interior lighting, smoke detector, fire extinguisher and telephone jacks for the work desk;
- instrumentation rack;
- lockable, heavy duty tamper proof door;
- high quality vinyl flooring with wood paneling on the walls;
- insulated walls, ceiling, and floor;
- gas sample inlet probe, heated eight (8) port glass sample manifold/handling system with blower;
- PVC exhaust manifold;
- the shelter roof shall be constructed as a sampling platform suitable for frequent station operator use with non-skid materials. A safety railing shall extend around the roof and an exterior ladder will be provided from the ground to the roof;
- uninterrupted power supply (UPS) with battery backup for monitors, data logger, and inlet pumps for continuous operation of minimum 1 hour (220V input) shall be provided.

The shelter should be rugged enough to withstand local weather condition extremes. It is recommended that monitoring stations be housed in the shelters that are fairly secure from intrusion or vandalism. Consideration should be given to the use of an intrusion alarm and/or a chain link fence around the shelter and adequate exterior lighting to secure the facility and protect it against vandalism. Generally, all sites should be located in fenced or secure areas with access only through locked gates or secure pathways (Fig. 43). All structures should be secured to their foundations and protected from damage during natural disasters. It is recommended that an appropriate fire extinguisher and a first aid kit be furnished for emergency situations. Every attempt should be made to reduce the environmental footprint of shelters to make them as energy-efficient as possible.

It is recommended that the shelter should contain two rooms separated by a door. The reasons for this are twofold. The entry and access should be into the computer/data review area. This allows access to the site without having to open the room that houses the equipment. It also isolates the equipment from cold/hot air that can come into the shelter when someone enters. Also, the Data Acquisition System (DAS)/data review area is isolated from the noise and vibration of the equipment. This area can be a place where the operator can print data, and prepare samples for the laboratory. This also gives the operator an area where cursory data review can take place. If something is observed during this initial review then possible problems can be corrected or investigated at that time. The DAS can be linked through cables that travel through conduit into the equipment area. The conduit is attached to the ceiling or walls and then dropped down to the instrument rack. Communications service should be available for data transmission telemetry.

FIGURE 43 Monitoring station located in fenced area.

The shelter should have good lighting, and must have an adequate electrical power supply. They should be designed to provide 220 VAC voltage throughout the year. The shelter should be equipped with enough electrical circuits for the current load of equipment plus other instruments that may be added later or audit equipment.

The shelter must be ventilated, heated and cooled to maintain an inside temperature in the range of 20°C and 30°C throughout the year to meet the specifications of the housed instrumentation. The air conditioning/heating unit should be mounted to heat and cool the equipment room. The shelter's design dictates that they are insulated to prevent temperature extremes within the shelter. Some possibilities include venting of excess heat of monitoring instruments to the outside in summer months and ensuring that the amount of space devoted to the monitors is not excessive. For QA/QC purposes, temperature and relative humidity sensors should be installed inside all monitoring stations. A proper sampling environment demands control of all physical parameters external to the samples that might affect sample stability, chemical reactions within the sampler, or the function of sampler components. With respect to environmental temperature for designated analyzers, most such analyzers have been tested and qualified over a temperature range of 20°C to 30°C; few are qualified over a wider range. This temperature range specifies both the range of acceptable operating temperatures and the range of temperature change which the analyzer can accommodate without excessive drift. The latter, the range of temperature change that may occur between zero and span adjustments, is the most important. When one is outfitting a shelter with monitoring equipment, it is important to recognize and accommodate the instrument with the most sensitive temperature requirement. To accommodate energy conservation regulations or guidelines specifying lower thermostat settings, designated analyzers located in facilities subject to these restrictions may be operated at temperatures down to 18°C, provided the analyzer temperature does not fluctuate by more than 10°C between zero and span adjustments. Operators should be alert to situations where environmental temperatures might fall below 18°C, such as during night hours or weekends. Temperatures below 18°C may necessitate additional temperature control equipment or rejection of the area as a sampling site. Shelter temperatures above 30°C also occur, due to temperature control equipment that is malfunctioning, lack of adequate power capacity, or shelters of inadequate design for the environmental conditions. Occasional fluctuations above 30°C may require additional assurances that data quality is maintained. Sites that continually have problems maintaining adequate temperatures may necessitate additional temperature control equipment or rejection of the area as a sampling site. In order to detect and correct temperature fluctuations, a 24-hour temperature recorder at the analyzer site is suggested. These recorders can be connected to data loggers and should be considered official documentation that should be filed. Many vendors offer these types of devices. Usually they are thermocouple/thermistor devices of simple design and are generally very sturdy. Reasons for using electronic shelter temperature devices are two-fold: 1) through remote interrogation of the DAS, the agency can tell if values collected by air quality instruments are valid, and 2) that the shelter temperature is within a safe operating range if the air conditioning/heating system fails.

All monitoring shelters should be designed to control excessive vibrations and external light falling on the instruments. Air quality instrumentation should be located in an instrument rack or equivalent (Fig. 44). The instruments and their support equipment are placed on sliding trays or rails. In the past, small utility trailers were the norm in monitoring shelters. However, in some areas, this will not suffice. Recently, steel and aluminum storage containers are gaining wide acceptance as monitoring shelters. By placing the racks away from the wall, the rear of the instruments are accessible. The trays or rails allow the site operators access to the instruments without removing them from the racks.

FIGURE 44 “19-Racks” inside the “standard” station for the analyzers and devices.

# 12 REMOTE SYSTEMS

Remote measurements can be based on different analytical methods and instrumentation. Remote sensing of air pollutants is usually based on electromagnetic radiation. There is a number of advantages and disadvantages of optical remote sensing over traditional point monitoring. Remote, optical sensing is particularly advantageous for monitoring of air pollutants in distinct, inaccessible, large areas. Of course, the line of measurement has to be unobstructed. The horizontal ranges much beyond a few kilometers become very difficult to achieve. The point measurements provide more spatial resolution information than the remote sensing. Typically, detection limit of the remote optical systems is at the level of $\mu g/m^3$. The concentrations of air pollutants normally lie in the ppb to ppm range but exhibit large fluctuations. The trace species present in the atmosphere range from as low as 0,1 ppt to several ppb. Therefore, the lowest detection limit of remote instruments may not be sufficient for the desired application. The spectral range and resolution of these instruments is sufficient to distinguish different constituents. But water vapor, $CO_2$, CO, $O_3$, hydrocarbons and many other compounds may preclude both qualitative and quantitative analysis of gases that are of interest. Remote sensing provides continuous, rapid, in near-real time data. These methods are based on the direct, non-intrusive, contactless measurements. Therefore, any potential influence on the air under investigation is excluded. For some instruments, several gases can be measured simultaneously. A serious problem is the calibration of the remote systems. The traditional calibration method cannot be applied because a gas standard cannot be introduced into a fixed path length gas cell. The results of measurements depend on atmospheric conditions. Fog and rain can preclude data collection. The data acquisition and transmission are affected by temperature. The analysis of spectroscopic data is rather complicated, but has progressed greatly in recent years. Remote, optical systems still require skilled operating staff. These systems are expensive. These instruments do not exist in a portable form. They are used in stationary or transportable form.

The optical remote systems can be split into two categories:

- the instruments with a long-open optical path;
- LIDAR systems.

## 12.1 INSTRUMENTS WITH THE LONG-OPEN OPTICAL PATH

The instruments with the long-open optical path measure the absorption of electromagnetic radiation by pollutants over the optical monitoring path of a few hundred meters. The extended path that the beam traverses is fully open to the air so that pollutants can move across the path under the influence of wind or diffusion. Long-open path absorption techniques are based on the same principles as spectrophotometry. However, by using well-collimated normal light beams or laser beams, it is possible to use a path length of several kilometers, instead of the 1 cm cuvette typically applied in the chemical laboratory.

The different optical methods are applied in long-open path instruments, e.g.:

- FTIR spectroscopy;
- gas correlation spectroscopy;
- photo-acoustic spectroscopy;
- tunable diode laser absorption spectroscopy;
- differential optical absorption spectroscopy.

The differential optical absorption spectroscopy (DOAS) has been very successful during recent years. It is routinely used to monitor the air quality in many urban and industrial areas. The DOAS is commercially available in the OPSIS system. It consists of a transmitter, receiver, spectrometer, computer. The transmitter with a high pressure xenon lamp generates a concentrated beam of light that includes wavelengths from short-wave UV to long-wave IR. The beam of light is sent along a chosen, monitoring path. The receiver captures this light and sends it through an optical fibre to the Czarny-Turner spectrometer, in which the radiation is broken up into spectra by a grating. The optical grating can be adjusted so that an optimum range of wavelengths is detected. The light is transformed into an electrical signal. In this form, chemical information is sent to the computer. It collects more than a hundred spectra per second. The absorption spectrum registered from the light path is compared with a pre-calibrated reference spectrum. The calculations carried out by the computer are based on library spectra recorded under controlled laboratory conditions. The measured result is an average concentration of the gas component detected between the transmitter and receiver. The OPSIS system can monitor more than 20 pollutants such as: $SO_2$, $NO_2$, $NH_3$, HCl, $O_3$, formaldehyde, mercury, vapors and several hydrocarbons including methane, styrene, benzene, toluene and xylene.

## 12.2 LIDAR

The long-open path systems can only give the mean pollutant concentration over a fixed path. Three-dimensional measurements can be performed with the lidar (**li**ght **d**etection **a**nd **r**anging) systems. These instruments work similar to radar (**ra**dio **d**etection **a**nd **r**anging). In general, the lidar system consists of a pulsed laser and an optical receiver collecting and detecting the scattered light (Fig. 45).

The laser beam sent into the atmosphere is scattered in every direction by the molecules and particles (e.g. dust, water droplets) in the atmosphere. A part of the beam is scattered backward to the receiver. It is possible to collect and detect this radiation by an optical telescope and special detectors. The backscattered light is measured as a function of the return time, which is equivalent to the distance.

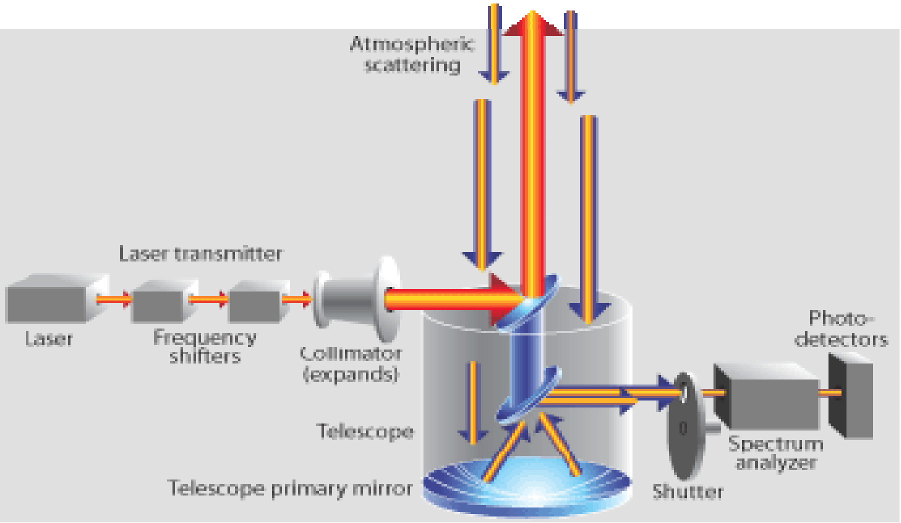


FIGURE 45 LIDAR

The LIDAR work can be described by the following features.

1. Optical in situ technique that enables trace gas concentration measurements over an open-path, or free air environment.
2. Real time measurements can be performed and documented directly in the field.
3. Solid state Raman-shifted laser technology provides a very spectrally narrow optical output pulse. This enables specific trace gas species to be quantitatively measured.
4. Performing a differential absorption measurement provides corrections due to atmospheric aerosols, atmospheric turbulence and competing atmospheric trace gas constituents such as water vapor, etc.
5. Reflectivity of the Object. Highly reflective objects may saturate some laser

detectors, while the return signal from low-reflectivity objects may occasionally be too weak to register as valid.

6. Laser lidar is an "active illumination" technique that, unlike photography, does not depend on ambient illumination. It works during day or at night.
7. A strong sunlight reflection off a highly reflective target may "saturate" a receiver, producing an invalid or less accurate reading. However, laser measurements are not usually affected by other reflections.
8. Laser measurements can be weakened by interacting with dust and vapor particles, which scatter the laser beam and the signal returning from the target. However, using last-pulse measurements can reduce or eliminate this interference.
9. Laser measurements can be made to targets at any angle.
10. The laser is not affected by background noise.
11. Laser measurements are based on the speed of light and are unaffected by temperature variations.
12. The laser is unaffected by pressure or vacuum variations, or off-gas layers.

There are different types of the lidar systems e.g. differential absorption lidar (DIAL). This system is based on a pulsed laser which uses two beams of different wavelengths instead of a single one. If one wavelength is selected to be at the absorption maximum of the gas of interest and the second is at a non-absorbing wavelength then the differential absorption between the two returned beams is proportional to the amount of absorbing gas in the beam. The difference directly reflects the concentration of the pollutant (via Beer`s Law), and provides a range resolved measurement of the specific pollutant. By scanning the field of investigation, two or three-dimensional concentration profiles (mappings) are easily obtained. DIAL monitoring of $SO_2$, $O_3$, $NO_2$, NO hydrocarbons and other pollutants has been reported. Remote sensing techniques tend to be expensive and/or difficult to operate over extended periods, so their main function has tended to be validation or development of plume rise and dispersion models and/or pollutant-reaction models. It is possible to use remote systems to monitor emissions as an alternative, or a supplement, to plant monitoring systems.

# 13 SENSORY ANALYSIS

Sensory analysis (or sensory evaluation) is a scientific discipline that applies principles of experimental design and statistical analysis to the use of human senses for the purposes of evaluating first of all consumer products. An examination using one or more of the senses: sight, smell, taste, smell, hearing, vision (Fig. 46).

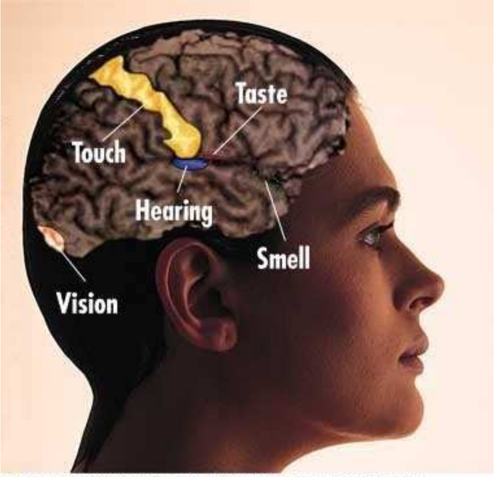


Photo of head-Michael Freeman; MRI scan of head-John Belliveau, NMR Center, Massachusetts General Hospital

FIGURE 46 Human senses.

## 13.1 ODOURS

Odours play an important role in today's densely populated world. There are several definitions which describe this problem. Odour is an organoleptic attribute perceptible by the olfactory organ on sniffing certain volatile substances. Odorant is a substance which stimulates a human olfactory system so that an odour is perceived. Odorous gas is a gas that contains odorants.

In certain cases, the odorous gases given off may annoy the neighbouring populations. The industrialist responsible for the odours emissions may therefore control odorous gases spontaneously or under pressure of the surrounding population and/or the administration. In all industrial processes, exact odour concentration determination provides valuable process management indicators. For example, in the wastewater industry a noticeable increase in odour yield may indicate a biological process becoming inefficient. Similarly, in the composting of organic materials, an increase in the strength of odour may indicate inefficient ventilation of the material. Therefore, the analysis of the gaseous effluents is required for the checking of the odorous gases emissions as well as the odour control. Two approaches are possible:

- physico-chemical analysis;
- sensory analysis (olfactometry).

Physico-chemical analysis can identify the composition of the odours mixture both qualitatively and quantitatively. This method is based on analytical chemistry. Gas chromatography and gas chromatography/mass spectrometry is especially often used in this type of analysis.

## 13.2 OLFACTOMETRY

The measurement of olfactory acuity and the characteristics of odours is called olfactometry or odorimetry (Olfactometry odour analysis - CEN 13725). In other words, sensory analysis (olfactometry) is used to quantify odours. Olfactometry is based on the measurement of the response of assessors to olfactory stimuli. This method provides a global understanding of the odour since it takes into account the chemical molecules at the origin of the odour as well as the physiological system without which this odour would not be perceived. Physico-chemical analysis and olfactometry are complementary since one provides knowledge of the composition of the mixture studied while the other answers the question: “is an odour being off and, if so, how much”. The properties of the human olfactory sense organs are so complex that no sensor is currently able to exactly reproduce them. This is why the only operational measurement “device” for odours is still a human nose.

The principle of olfactometry measurement is determining odour concentration of a gaseous sample by presenting a panel of selected and screened human subjects with that sample and varying the concentration by diluting the sample with neutral gas (normally fresh air), in order to determine the dilution factor at the 50% detection threshold. Olfactometry requires panels of human assessors (panellists), on whom the objects are tested, and recording the responses made by them. By applying statistical techniques to the results, it is possible to evaluate the object under test. In olfactometry, measurement results are always based on two items of information:

- a mean value;
- a standard deviation which is the reflection of inter-individual differences in perception for the gaseous mixture studied.

In practice, two types of olfactometries are used: direct or delayed.

### *13.2.1 DIRECT OLFACTOMETRY*

Direct olfactometry is defined as a measurement of odour concentration without any time-lag between the sampling (operation) and the measurements, equivalent to dynamic sampling or on-line olfactometry. It is used for constant odorous emissions. The advantage of direct olfactometry is that the short time elapsing between sample and measurement effectively reduces the risks of a modification in the composition of the gaseous sample through chemical reactions or adsorption. The disadvantage of this method is that it requires the use of ventilated measuring room in order to isolate the panel members from the ambient environment, which is always odorous to some extent. Such equipment is difficult to implement and often requires very long sampling lines liable to disturb the sample (condensation, adsorption, admission of air). The disadvantage is also the need to send the team of experts to the site as this is expensive.

### *13.2.2 DELAYED OLFACTOMETRY*

The measurement of an odour with a time-lag between sampling and measurement is classified as a delayed olfactometry. The sampled gas is stored (preserved) in an appropriate container, e.g. sampling bags. This is used for constant or non-constant odorous emissions. Delayed olfactometry improves measurement accuracy by placing the assessors in the best possible laboratory conditions without additional cost since the experts are in the spot. The disadvantage lies in the time between sampling and analysis, which is limited to 30 hours.

## 13.3 FACTORS DETERMINING QUALITY OF ODOUR MEASUREMENTS

There are some important aspects that affect the accuracy (repeatability and reproducibility) of odour measurements (odour strength and odour concentration):

- ensure the suitable sampling;
- keep testing environment odour-free;
- calibrate dynamic olfactometer regularly;
- ensure the panelists are trained and screened.

### *13.3.1 SAMPLING*

The sampling of odorants is an important part in measuring the odour. It conditions the quality and reliability of the results of the measurement. Usually, standards describe different gas sampling procedures according to:

- the source and analysis;
- the conditions of storage and transport.

The choice of a sampling method depends also on the type of olfactometry that is to be applied. Two types of sampling can be considered:

- dynamic sampling;
- sampling for delayed olfactometry.

**Dynamic sampling**

The gas is directly ducted from the place of sampling to the olfactometer without storage in a sample container. This method shall only be applied to emissions with a constant concentration level throughout the duration of sampling. This sampling technique applies to cases of odorous atmospheres arising from the sources that are, or could be channelled (stack release, breathing of storage tanks, biofilters, mixed liquid volumes such as in water collection stations). In this type of sampling, a sample is collected and transferred into a sample container for analysis by delayed olfactometry. This sampling technique shall be applied if the odour room conditions required for assessors cannot be maintained on site, or for the sources where odour concentration can vary with time, which is typically the case.

### Sampling for delayed olfactometry

Sampling for delayed olfactometry can be applied to all sources emitting odorants, whether diffused, channelled or those that can be channelled for sampling. It is recommended that one of the following two methods of sample collection is used:

- direct pumping;
- sampling on the base of the "lung principle".

In direct pumping, the sample is pumped directly into the sample bag. This method has to be used with caution in order that the sample being collected is not contaminated by odours previously adsorbed onto the pump and the sample tube being desorbed into the sample. Sampling lines have to be replaced between samples and the pump flushed with neutral gas until all contamination is removed.

Sampling on the base of the "lung principle" uses the sample bag which is placed in a rigid container. The air is removed from the container using a vacuum pump. The under pressure in the container causes that the bag is filled with a volume of sample equal to that which has been removed from the container.

Appropriate materials shall be used for those parts of sampling equipment that are in contact with the odorant sample. Inappropriate materials:

- silicone rubber;
- natural rubber.

The following materials are appropriate:

- polytetrafluoroethylene (PTFE);
- tetrafluoroethylene hexafluoropropylene copolymer (FEP);
- polyethyleneterephalate (PET, Nalophan);
- stainless steel;
- glass.

Samples should be analysed as soon as possible after sampling. The interval between sampling and measurement shall not exceed 30 h.

### *13.3.2 ODOUR LABORATORY*

An odour-free testing environment is required for odour measurement. Contamination or disturbance of background odours can be avoided in an odour-free testing room. To keep a testing laboratory odour-free, the following efforts are useful:

- renovation materials should not have any kind of smell;
- the furniture and equipments inside the room should not release any odour;
- no odorous compounds or chemicals should be stored in the laboratory;
- an effective activated carbon filter should be installed at the inlet of air-conditioning system;
- the ventilation rate of the laboratory should be kept higher than the

minimum requirement.

## **Olfactometers**

Olfactometer is an apparatus in which a sample of odorous gas is diluted with neutral gas (air or nitrogen) in a defined ratio and presented to panelists (assessors). These instruments can be divided in two groups: static and dynamic. The first one dilutes by mixing two known volumes of gas, an odorous sample and a neutral gas, respectively. The rate of dilution is calculated from the volumes. It delivers a flow of mixtures of odorous and neutral gas with known dilution factors in a common outlet and presents to panelists (Fig. 47). Among different instruments (techniques), dynamic olfactometers are preferred.

FIGURE 47 Dynamic olfactometer.[odour.unsw.edu.au]

### *13.3.3 THE DYNAMIC OLFACTOMETRIC PROCEDURE*

The dynamic olfactometric procedure contains the following elements:

- dynamic dilution;
- delivery of diluted odorant for smelling through a mask or port;
- schedule of presentation of various dilutions and blanks;
- obtaining responses from the panelists;
- calculation of a panel threshold from experimental data;
- panelist selection criteria.

### *13.3.4 INSTRUMENT CALIBRATION*

The calibration of olfactometer needs to be done regularly using a tracer gas such as carbon monoxide (CO). In addition to accuracy and precision, the instability is determined. The statistics of calibrated results of olfactometer should comply with the quality criteria as defined in the standard.

### *13.3.5 PANELISTS*

Panelist (assessor) is somebody who participates in odour testing. Reliable panelists (assessors) are important to ensure the accuracy of olfactometry measurement. Panel is a group of panel members. Panel member is an assessor who is qualified to judge samples of odorous gas, using dynamic olfactometry within the scope of this standard. Panelists should be trained and screened from normal people before they are qualified to be panelists. Panelist screening tests uses standard odorous gas (such as n-butanol) to check the performance of each panelist candidate and select those whose responses statistically meet the defined criteria to be panelists for real odour tests. The individuals included on a panel have to be selected in order to verify that their olfactory perception is representative of standard population. The aim of the selection is to detect and remove from the panel people that have been found to suffer from anosmia (lack of sensitivity to olfactory stimuli) or who are hyper-sensitive to certain chemical substances. In fact, these individuals are rare in the general population (several percent).

## 13.4 THE USE OF OLFACTOMETRY

Olfactometry is used to measure three variables:

- odour concentration,
- odour intensity,
- odour annoyance.

The odour measurement results can be used to calculate odour emission rates from the sources where the samples were collected. With the calculated odour emission rates, odour dispersion modeling and odour impact assessment can be performed. Olfactometric sampling and analysis provide directly comparable data for different odour types and a reliable measurement of odour concentration, thereby providing valuable data from which to make reasonable odour management decisions. Quantifying ambient odour is often needed for the following purposes:

- monitoring daily operations (i.e. management performance evaluations);
- comparison of operating practices (i.e. evaluating alternatives);
- documenting specific events or episodes (i.e. defensible, credible evidence);
- monitoring compliance (i.e. compliance assurance for permits);
- determination of compliance (i.e. permit renewal);
- determination of status (i.e. baseline data for expansion planning);
- investigation of odour control effectiveness (i.e. scientific testing);
- verification of odour dispersion modeling (i.e. model calibration);
- determination of specific odour sources (i.e. investigation of complaints);
- verification of complaints (i.e. notice of violation).

Olfactometry offers a great number of applications in the field of air pollution by odours of industrial origin. It allows for the study of complex gaseous effluents and provides objective results taking into account the differences in olfactory perception that naturally exist among individuals.

# 14 LITERATURE

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