17

Ambient Air Pollutants: Analysis and Measurement

I. ANALYSIS AND MEASUREMENT OF GASEOUS POLLUTANTS

The samples gathered according to the protocols described in the previous chapter must be analyzed for their physical and chemical properties. The two major goals of testing for air pollutants are identification and quantification of a sample of ambient air. Air pollution measurement techniques generally pass through evolutionary stages. The first is the qualitative identification stage. This is followed by separate collection and quantification stages. The last stage is the concurrent collection and quantification of a given pollutant.

Gaseous SO_2 is an example. Very early procedures detected the presence of SO_2 in ambient air by exposing a lead peroxide candle for a period of time and then measuring the amount of lead sulfate formed. Because the volume of air in contact with the candle was not measured, the technique could not quantify the amount of SO_2 per unit volume of air.

The next stage involved passing a known volume of ambient air through an absorbing solution in a container in the field and then returning this container to the laboratory for a quantitative determination of the amount of absorbed SO_2. The United Nations Environmental Program–World Health Organization's worldwide air sampling and analysis network used this

method for SO_2, the only gaseous pollutant measured by the network. The final evolutionary step has been the concurrent collection and quantification of SO_2. An example of this is the flame photometric SO_2 analyzer, in which SO_2-laden air is fed into an H_2 flame, and light emissions from electronically excited combustion products are detected by a photomultiplier tube. Prior calibration of the analyzer permits the rapid determination of SO_2. This is but one of the many methods available for the measurement of SO_2.

Hundreds of chemical species are present in urban atmospheres. The gaseous air pollutants most commonly monitored are CO, O_3, NO_2, SO_2, and nonmethane volatile organic compounds (NMVOCs). Measurement of specific hydrocarbon compounds is becoming routine in the United States for two reasons: (1) their potential role as air toxics and (2) the need for detailed hydrocarbon data for control of urban ozone concentrations. Hydrochloric acid (HCl), ammonia (NH_3), and hydrogen fluoride (HF) are occasionally measured. Calibration standards and procedures are available for all of these analytic techniques, ensuring the quality of the analytical results. See Table 17.1 for a summary of emission limits for one particular source class, incinerators.

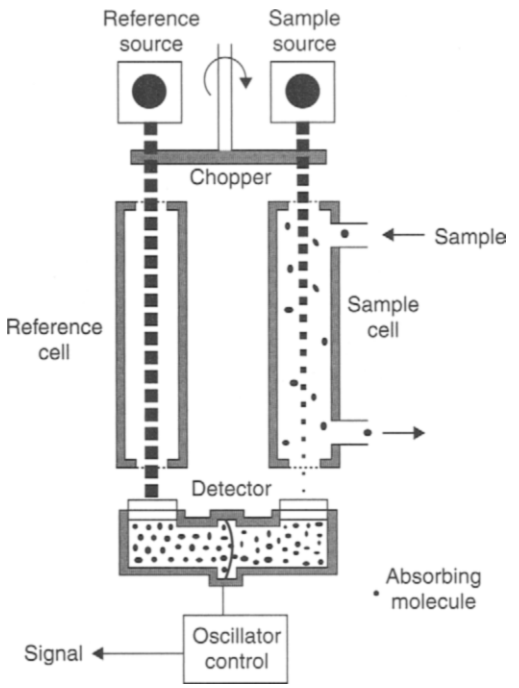


Fig. 17.1. NDIR analyzer. *Source*: Bryan, R. J., Ambient air quality surveillance, in *Air Pollution*, 3rd ed., Vol. III (Stern, A. C., ed.), p. 375. Academic Press, New York, 1976.

A. Carbon Monoxide

The primary reference method used for measuring carbon monoxide in the United States is based on nondispersive infrared (NDIR) photometry [1, 2]. The principle involved is the preferential absorption of infrared radiation by carbon monoxide. Figure 17.1 is a schematic representation of an NDIR analyzer. The analyzer has a hot filament source of infrared radiation, a chopper, a sample cell, reference cell, and a detector. The reference cell is filled with a non-infrared-absorbing gas, and the sample cell is continuously flushed with ambient air containing an unknown amount of CO. The detector cell is divided into two compartments by a flexible membrane, with each compartment filled with CO. Movement of the membrane causes a change in electrical capacitance in a control circuit whose signal is processed and fed to a recorder.

The chopper intermittently exposes the two cells to infrared radiation. The reference cell is exposed to a constant amount of infrared energy which is transmitted to one compartment of the detector cell. The sample cell, which contains varying amounts of infrared-absorbing CO, transmits to the detector cell a reduced amount of infrared energy that is inversely proportional to the CO concentration in the air sample. The unequal amounts of energy received by the two compartments in the detector cell cause the membrane to move, producing an alternating current (AC) electrical signal whose frequency is established by the chopper spacing and the speed of chopper rotation.

Water vapor is a serious interfering substance in this technique. A moisture trap such as a drying agent or a water vapor condenser is required to remove water vapor from the air to be analyzed.

Instruments based on other techniques are available which meet the performance specifications outlined in Table 17.1.

TABLE 17.1

Sampling Required to Demonstrate Compliance with Emission Limits for the New Source Performance Standards (NSPS) for Hospital/Medical/Infectious Waste Incinerators (HMIWI), Pursuant to the US Court of Appeals for the District of Columbia Circuit Ruling of March 2, 1999, Remanding the Rule to the US EPA for Further Explanation of the Agency's Reasoning In Determining the Minimum Regulatory "Floors" for New and Existing HMIWI

Pollutant (units)	Unit size[a]	Proposed remand limit for existing HMIWI[b]	Proposed remand limit for new HMIWI[b]
HCl (ppmv)	L, M, S	78 or 93% reduction[c]	15[c] or 99% reduction[c]
	SR	3100[c]	N/A[d]
CO (ppmv)	L, M, S	40[c]	32
	SR	40[c]	N/A[d]
Pb (mg/dscm)	L, M	0.78 or 71% reduction	0.060 or 98% reduction[c]
	S	0.78 or 71% reduction	0.78 or 71% reduction
	SR	8.9	N/A[d]

(*continued*)

TABLE 17.1 (*Continued*)

Pollutant (units)	Unit size[a]	Proposed remand limit for existing HMIWI[b]	Proposed remand limit for new HMIWI[b]
Cd (mg/dscm)	L, M	0.11 or 66% reduction[c]	0.030 or 93% reduction
	S	0.11 or 66% reduction[c]	0.11 or 66% reduction[c]
	SR	4[c]	N/A[d]
Hg (mg/dscm)	L, M	0.55[c] or 87% reduction	0.45 or 87% reduction
	S	0.55[c] or 87% reduction	0.47 or 87% reduction
	SR	6.6	N/A[d]
PM (gr/dscf)	L	0.015[c]	0.009
	M	0.030[c]	0.009
	S	0.050[c]	0.018
	SR	0.086[c]	N/A[d]
CDD/CDF, total (ng $dscm^{-1}$)	L, M	115	20
	S	115	111
	SR	800[c]	N/A[d]
CDD/CDF, TEQ (ng $dscm^{-1}$)	L, M	2.2	0.53
	S	2.2	2.1
	SR	15[c]	N/A[d]
NO_x (ppmv)	L, M, S	250[c]	225
	SR	250[c]	N/A[d]
SO_2 (ppmv)	L, M, S	55[c]	46
	SR	55[c]	N/A[d]

[a] L: large; M: medium; S: small; SR: small rural.
[b] All emission limits are measured at 7% oxygen.
[c] No change proposed.
[d] Not applicable.
Source: 40 *Code of Federal Regulations*, Part 60, Standards of Performance for New Stationary Sources and Emission Guidelines for Existing Sources: Hospital/Medical/Infectious Waste Incinerators; Proposed Rule, February 7, 2007.

B. Ozone

The principal method used for measuring ozone is based on chemiluminescence [3]. When ozone and ethylene react chemically, products are formed which are in an excited electronic state. These products fluoresce, releasing light. The principal components are a constant source of ethylene, an inlet sample line for ambient air, a reaction chamber, a photomultiplier tube, and signal-processing circuitry. The rate at which light is received by the photomultiplier tube is dependent on the concentrations of O_3 and ethylene. If the concentration of ethylene is made much higher than the ozone concentration to be measured, the light emitted is proportional only to the ozone concentration.

Instruments based on this principle may be calibrated by a two-step process shown in Fig. 17.2 [4]. A test atmosphere with a known source of ozone is produced by an ozone generator, a device capable of generating stable levels of O_3. Step 1 involves establishing the concentration of ozone in the

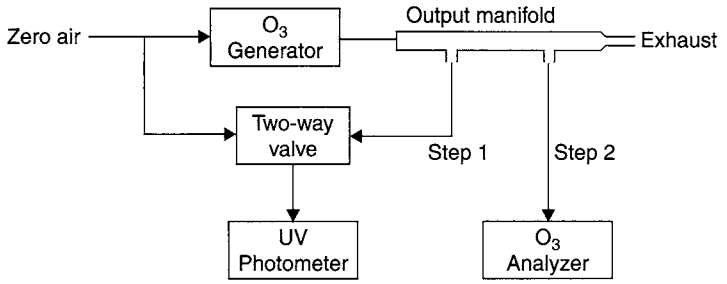


Fig. 17.2. Calibration apparatus for ozone analyzer (UV).

test atmosphere by ultraviolet (UV) photometry. This is followed by step 2, calibration of the instrument's response to the known concentration of ozone in the test atmosphere.

C. Nitrogen Dioxide

The principal method used for measuring NO_2 is also based on chemiluminescence (Fig. 17.3) [5]. NO_2 concentrations are determined indirectly from the difference between the NO and NO_x (NO + NO_2) concentrations in the atmosphere. These concentrations are determined by measuring the light emitted from the chemiluminescent reaction of NO with O_3 (similar to the reaction of O_3 with ethylene noted for the measurement of O_3), except that O_3 is supplied at a high constant concentration, and the light output is proportional to the concentration of NO present in the ambient air stream.

Figure 17.4 illustrates the analytical technique based on this principle. To determine the NO_2 concentration, the NO and NO_x (NO + NO_2) concentrations are measured. The block diagram shows a dual pathway through the instrument, one to measure NO and the other to measure NO_x. The NO pathway has an ambient air stream containing NO (as well as NO_2), an ozone stream from the ozone generator, a reaction chamber, a photomultiplier tube, and signal-processing circuitry. The NO_x pathway has the same components, plus a converter for quantitatively reducing NO_2 to NO. The instrument can also electronically subtract the NO from NO_x and yield as output the resultant NO_2.

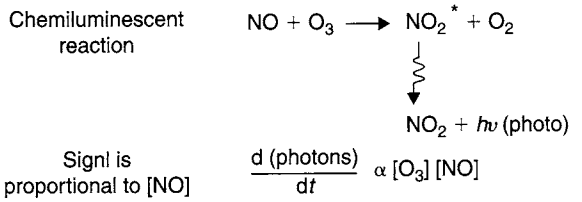


Fig. 17.3. NO_2 chemiluminescent detection principle based on the reaction of NO with O_3.

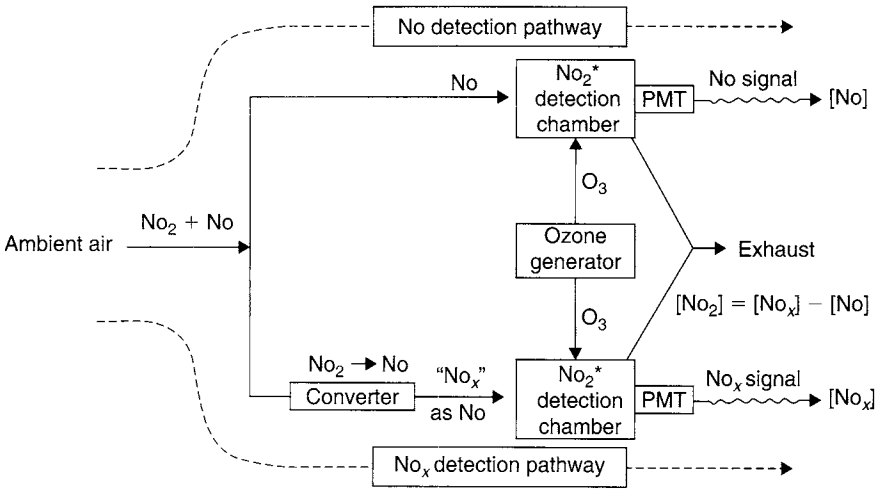


Fig. 17.4. Schematic diagram of chemiluminescent detector for NO_2 and NO. PMT: photomultiplier tube.

Air passing through the NO pathway enters the reaction chamber, where the NO present reacts with the ozone. The light produced is measured by the photomultiplier tube and converted to an NO concentration. The NO_2 in the air stream in this pathway is unchanged. In the NO_x pathway, the NO- and NO_2-laden air enters the converter, where the NO_2 is reduced to form NO; all of the NO_x exits the converter as NO and enters the reaction chamber. The NO reacts with O_3 and the output signal is the total NO_x concentration. The NO_2 concentration in the original air stream is the difference between NO_x and NO. Calibration techniques use gas-phase titration of an NO standard with O_3 or an NO_2 permeation device.

D. Sulfur Dioxide

Several manual and continuous analytical techniques are used to measure SO_2 in the atmosphere. The manual techniques involve two-stage sample collection and measurement. Samples are collected by bubbling a known volume of gas through a liquid collection medium. Collection efficiency is dependent on the gas–liquid contact time, bubble size, SO_2 concentration, and SO_2 solubility in the collection medium. The liquid medium contains chemicals which stabilize SO_2 in solution by either complexation or oxidation to a more stable form. Field samples must be handled carefully to prevent losses from exposure to high temperatures. Samples are analyzed at a central laboratory by an appropriate method.

The West–Gaeke manual method is the basis for the US Environmental Protection Agency (EPA) reference method for measurement of SO_2 [6]. The method uses the colorimetric principle; i.e., the amount of SO_2 collected is

proportional to the amount of light absorbed by a solution. The collection medium is an aqueous solution of sodium or potassium tetrachloromercurate (TCM). Absorbed SO_2 forms a stable complex with TCM. This enhanced stability permits the collection, transport, and short-term storage of samples at a central laboratory. The analysis proceeds by adding bleached pararosaniline dye and formaldehyde to form red-purple pararosaniline methylsulfonic acid. Optical absorption at 548 nm is linearly proportional to the SO_2 concentration. Procedures are followed to minimize interference by O_3, oxides of nitrogen, and heavy metals.

The continuous methods combine sample collection and the measurement technique in one automated process. The measurement methods used for continuous analyzers include conductometric, colorimetric, coulometric, and amperometric techniques for the determination of SO_2 collected in a liquid medium [7]. Other continuous methods utilize physicochemical techniques for detection of SO_2 in a gas stream. These include flame photometric detection (described earlier) and fluorescence spectroscopy [8]. Instruments based on all of these principles are available which meet standard performance specifications.

E. Nonmethane Volatile Organic Compounds

The large number of individual hydrocarbons in the atmosphere and the many different hydrocarbon classes make ambient air monitoring a very difficult task. The ambient atmosphere contains a ubiquitous concentration of methane (CH_4) at approximately 1.6 ppm worldwide [9]. The concentration of all other hydrocarbons in ambient air can range from 100 times less to 10 times greater than the methane concentration for a rural versus an urban location. The terminology of the concentration of hydrocarbon compounds is potentially confusing. Hydrocarbon concentrations are referred to by two units—parts per million by volume (ppmV) and parts per million by carbon (ppmC). Thus, 1 μL of gas in 1 L of air is 1 ppmV, so the following is true:

Mixing ratio	ppmV	ppmC
$\frac{1\,\mu L \text{ of } O_3}{1\,L \text{ of air}} =$	1 ppm ozone	—
$\frac{1\,\mu L \text{ of } SO_2}{1\,L \text{ of air}} =$	1 ppmV SO_2	—
$\frac{1\,\mu L \text{ of } CH_4}{1\,L \text{ of air}} =$	1 ppmV CH_4	1 ppmC CH_4
$\frac{1\,\mu L \text{ of } C_2H_6}{1\,L \text{ of air}} =$	1 ppmV C_2H_6	2 ppmC C_2H_6

The unit ppmC takes into account the number of carbon atoms contained in a specific hydrocarbon and is the generally accepted way to report ambient hydrocarbons. This unit is used for three reasons: (1) the number of carbons atoms is a very crude indicator of the total reactivity of a group of hydrocarbon compounds; (2) historically, analytical techniques have expressed results in this unit; and (3) considerable information has been developed on the role of hydrocarbons in the atmosphere in terms of concentrations determined as ppmC.

Historically, measurements have classified ambient hydrocarbons into two classes: methane (CH_4) and all other NMVOCs. Analyzing hydrocarbons in the atmosphere involves a three-step process: collection, separation, and quantification. Collection involves obtaining an aliquot of air, e.g., with an evacuated canister. The principal separation process is gas chromatography (GC), and the principal quantification technique is with a calibrated flame ionization detector (FID). Mass spectroscopy (MS) is used along with GC to identify individual hydrocarbon compounds.

A simple schematic diagram of the GC/FID principle is shown in Fig. 17.5. Air containing CH_4 and other hydrocarbons classified as NMVOCs pass through a GC column and the air, CH_4, and NMVOC molecules are clustered into groups because of different absorption/desorption rates. As CH_4 and NMVOC groups exit the column, they are "counted" by the FID. The signal output of the detector is proportional to the two groups and may be quantified when compared with standard concentrations of gases. This simplified procedure has been used extensively to collect hydrocarbon concentration data for the ambient atmosphere. A major disadvantage of this technique is the grouping of all hydrocarbons other than CH_4 into one class. Hydrocarbon compounds with similar structures are detected by an FID in a proportional manner, but for compounds with significantly different structures the response may be different. This difference in sensitivity results in errors in measurements of NMVOC mixtures.

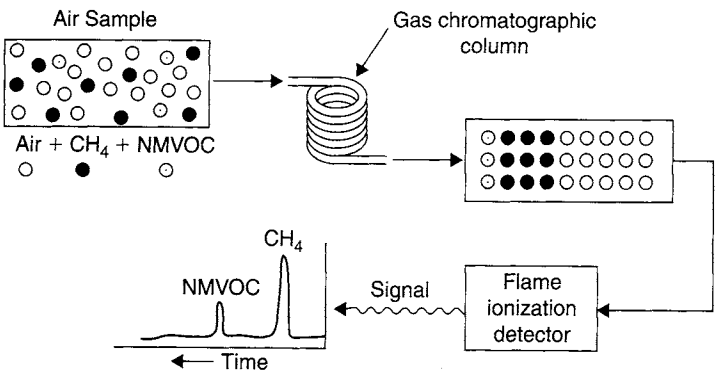


Fig. 17.5. Schematic diagram of hydrocarbon detection by GC. NMVOC: nonmethane volatile organic carbon.

More sophisticated GC columns and techniques perform more detailed separations of mixtures of hydrocarbons into discrete groups. Table 7.14 lists individual hydrocarbons measured in ambient air by advanced GC techniques.

Other types of detectors include the flame photometric detector (FPD) and the electron capture detector (ECD). The FID is composed of an H_2 flame through which the hydrocarbon gases are burned, forming charged carbon atoms, and an electrometer grid which generates a signal current proportional to the number of carbon atoms in the flame. The example of 1 ppmV methane (CH_4) and 1 ppmV (but 2 ppmC) ethane (C_2H_6) is related to this detection principle. One ppmV of CH_4 and 1 ppmV of C_2H_6 in air have the same number of molecules of hydrocarbon in a given volume of air, but if an aliquot of each mixture were run through an FID, the signal for ethane would be nearly twice the methane signal: 2 ppmC ethane compared to 1 ppmC methane.

The FPD is also used to measure sulfur-containing compounds and therefore is useful for measurement of sulfur-containing hydrocarbons such as dimethylsulfide or furan. The FPD has an H_2 flame in which sulfur-containing gases are burned. In the combustion process, electronically excited S_2* is formed. A photomultiplier tube detects light emitted from the excited sulfur at ~395 nm. The ECD is preferred for measuring nitrogen-containing compounds such as PAN and other peroxyacyl nitrate compounds. The ECD contains a radioactive source which establishes a stable ion field. Nitrogen-containing compounds capture electrons in passing through the field. Alterations in the electronic signal are related to the concentration of the nitrogen species.

F. Laboratory Analysis of Air Pollutant Samples

When the sample arrives at the laboratory, the next step may be "extraction." The pollutant of concern on the environmental sample may be sorbed to particles on the filter or may be trapped on substrate and must be freed for analysis to take place. So, to analyze the sample, the chemicals must first be freed from the sorbant matrix. Dioxins provide an example. Under environmental conditions, dioxins are fat soluble and have low vapor pressures, so they may be found on particles, in the gas phase, or suspended to colloids. Therefore, to collect the gas-phase dioxins, the standard method calls for trapping it on polyurethane foam (PUF). These properties have influenced the design of the PS-1 monitor, which is used to collect semivolatile organic compounds (SVOCs) like the dioxins. It has both a filter and a polyurethane foam (PUF) trap to collect both particle and gas phases, respectively. Thus, to analyze dioxins in the air, the PUF and particle matter must first be extracted, and to analyze dioxins on filters, those particles that have been collected must also be extracted.

Extraction makes use of physics and chemistry. For example, many compounds can be simply extracted with solvents, usually at elevated temperatures. A common solvent extraction is the Soxhlet extractor, named after the German food chemist, Franz Soxhlet (1848–1913). The Soxhlet extractor (the US EPA Method 3540) removes sorbed chemicals by passing a boiling solvent through the media. Cooling water condenses the heated solvent and the extract is collected over an extended period, usually several hours. Other automated techniques apply some of the same principals as solvent extraction, but allow for more precise and consistent extraction, especially when large volumes of samples are involved. For example, supercritical fluid extraction (SFE) brings a solvent, usually carbon dioxide to the pressure and temperature near its critical point, where the solvent's properties are rapidly altered with very slight variations of pressure.[1] Solid phase extraction (SPE), which uses a solid and a liquid phase to isolate a chemical from a solution, is often used to clean up a sample before analysis. Combinations of various extraction methods can enhance the extraction efficiencies, depending on the chemical and the media in which it is found. Ultrasonic and microwave extractions may be used alone or in combination with solvent extraction. For example, the US EPA Method 3546 provides a procedure for extracting hydrophobic (that is, not soluble in water) or slightly water soluble organic compounds from particles such as soils, sediments, sludges, and solid wastes. In this method, microwave energy elevates the temperature and pressure conditions (i.e., 100–115°C and 50–175 psi) in a closed extraction vessel containing the sample and solvent(s). This combination can improve recoveries of chemical analytes and can reduce the time needed compared to the Soxhlet procedure alone.

Not every sample needs to be extracted. For example, air monitoring using canisters and bags allows the air to flow directly into the analyzer. Surface methods of particle matter, such as fluorescence, sputtering, and atomic absorption (AA), require only that the sample be mounted on specific media (e.g. filters). Also, continuous monitors like the chemiluminescent system mentioned earlier provide ongoing measurements.

Chromatography consists of separation and detection. Separation makes use of the chemicals' different affinities for certain surfaces under various temperature and pressure conditions. The first step, injection, introduces the extract to a "column." The term column is derived from the time when columns were packed with sorbents of varying characteristics, sometimes meters in length, and the extract was poured down the packed column to separate the various analytes. Today, columns are of two major types, gas and liquid. GC makes use of hollow tubes ("columns") coated inside with compounds that hold organic

[1] See Ekhtera, M., Mansoori, G., Mensinger, M., Rehmat, A., and Deville, B., Supercritical fluid extraction for remediation of contaminated soil, in *Supercritical Fluids: Extraction and Pollution Prevention* (Abraham, M., and Sunol, A., eds.), ACSSS, Vol. 670, pp. 280–298. American Chemical Society, Washington, DC, 1997.

chemicals. The columns are in an oven, so that after the extract is injected into the column, the temperature is increased, as well as the pressure, and the various organic compounds in the extract are released from the interior column surface differentially, whereupon they are collected by a carrier gas (e.g. helium) and transported to the detector. Generally, the more volatile compounds are released first (they have the shortest retention times), followed by the semi-volatile organic compounds. So, boiling point is often a very useful indicator as to when a compound will come off a column. This is not always the case, since other characteristics such as polarity can greatly influence a compound's resistance to be freed from the column surface. For this reason, numerous GC columns are available to the chromatographer (different coatings, interior diameters, and lengths). Rather than coated columns, liquid chromatography (LC) makes use of columns packed with different sorbing materials with differing affinities for compounds. Also, instead of a carrier gas, LC uses a solvent or blend of solvents to carry the compounds to the detector. In the high-performance LC (HPLC), pressures are also varied.

Detection is the final step for quantifying the chemicals in a sample. The type of detector needed depends on the kinds of pollutants of interest. Detection gives the "peaks" that are used to identify compounds (see Fig. 17.6). For example, if hydrocarbons are of concern, GC with FID may be used. GC–FID gives a count of the number of carbons, so for example, long chains can be distinguished from short chains. The short chains come off the column

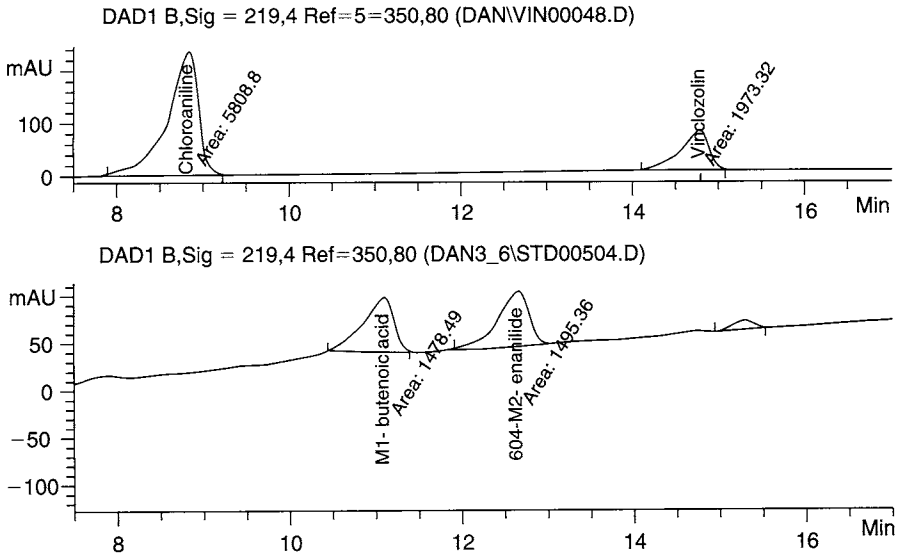


Fig. 17.6. High-performance liquid chromatograph/UV detection peaks for standard acetonitrile solutions: 9 mg L^{-1} 3,5-dichloroaniline and 8 mg L^{-1} the fungicide vinclozolin (top); and 7 mg L^{-1} M1 and 9 mg L^{-1} M2 (bottom). *Source*: Vallero, D., *Engineering the Risks of Hazardous Wastes*, Butterworth-Heinemann, Boston, MA, 2003.

first and have peaks that appear before the long-chain peaks. However, if pesticides or other halogenated compounds are of concern, ECD is a better choice.

A number of detection approaches are also available for LC. Probably the most common is absorption. Chemical compounds absorb energy at various levels, depending on their size, shape, bonds, and other structural characteristics. Chemicals also vary in whether they will absorb light or how much light they can absorb depending on wavelength. Some absorb very well in the UV range, while others do not. Diode arrays help to identify compounds by giving a number of absorption ranges in the same scan. Some molecules can be excited and will fluoresce. The Beer–Lambert law tells us that energy absorption is proportional to chemical concentration:

$$A = eb[C] \tag{17.1}$$

where, A is the absorbency of the molecule, e is the molar absorptivity (proportionality constant for the molecule), b is the light's path length, and $[C]$ is the chemical concentration of the molecule. Thus, the concentration of the chemical can be ascertained by measuring the light absorbed.

One of the most popular detection methods is mass spectroscopy (MS), which can be used with either GC or LC separation. The MS detection is highly sensitive for organic compounds and works by using a stream of electrons to consistently break apart compounds into fragments. The positive ions resulting from the fragmentation are separated according to their masses. This is referred to as the "mass to charge ratio" or m/z. No matter which detection device is used, software is used to decipher the peaks and to perform the quantitation of the amount of each contaminant in the sample.

For inorganic substances and metals, the additional extraction step may not be necessary. The actual measured media (e.g. collected airborne particles) may be measured by surface techniques like AA, X-ray fluorescence (XRF), inductively coupled plasma (ICP), or sputtering. As for organic compounds, the detection approaches can vary. For example, ICP may be used with absorption or MS. If all one needs to know is elemental information, for example to determine total lead or nickel in a sample, AA or XRF may be sufficient. However, if it is speciation (i.e. knowing the various compounds of a metal), then significant sample preparation is needed, including a process known as "derivatization." Derivatizing a sample is performed by adding a chemical agent that transforms the compound in question into one that can be recognized by the detector. This is done for both organic and inorganic compounds, for example, when the compound in question is too polar to be recognized by MS.

The physical and chemical characteristics of the compounds being analyzed must be considered before visiting the field and throughout all the steps in the laboratory. Also, the quality of results generated about contamination depends on the sensitivity and selectivity of the analytical equipment. Table 17.2 defines some of the most important analytical chemistry threshold values.

TABLE 17.2

Expressions of Chemical Analytical Limits

Type of limit	Description
Limit of detection (LOD)	Lowest concentration or mass that can be differentiated from a blank with statistical confidence. This is a function of sample handling and preparation, sample extraction efficiencies, chemical separation efficiencies, and capacity and specifications of all analytical equipments being used (see IDL below).
Instrument detection limit (IDL)	The minimum signal greater than noise detectable by an instrument. The IDL is an expression of the piece of equipment, not the chemical of concern. It is expressed as a signal to noise (S:N) ratio. This is mainly important to the analytical chemists, but the engineer should be aware of the different IDLs for various instruments measuring the same compounds, so as to provide professional judgment in contracting or selecting laboratories and deciding on procuring for appropriate instrumentation for all phases of remediation.
Limit of quantitation (LOQ)	The concentration or mass above which the amount can be quantified with statistical confidence. This is an important limit because it goes beyond the "presence–absence" of the LOD and allows for calculating chemical concentration or mass gradients in the environmental media (air, water, soil, sediment, and biota).
Practical quantitation limit (PQL)	The combination of LOQ and the precision and accuracy limits of a specific laboratory, as expressed in the laboratory's quality assurance/quality control (QA/QC) plans and standard operating procedures (SOPs) for routine runs. The PQL is the concentration or mass that the engineer can consistently expect to have reported reliably.

Source: Vallero, D., *Engineering the Risks of Hazardous Wastes*. Butterworth-Heinemann, Boston, MA, 2003.

G. Semivolatile Organic Compounds

For sampling and analyzing SVOCs, a good place to start is US EPA "Method 1613," Tetra-through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS (Rev. B), Office of Water, Engineering and Analysis Division, Washington, DC (1994), as well as "RCRA SW846 Method 8290," polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) by high-resolution gas chromatograph/high-resolution mass spectrometry (HRGC/HRMS), Office of Solid Waste, US EPA (September 1994). For air, the best method is the PS-1 high-volume sampler system described in US EPA "Method TO-9A" in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* [24].

As mentioned, the extraction can be made by solvent extraction, by SFE, or by other techniques depending on the compound and the sorbant used to

collect it. The procedure to analyze SVOCs begins with preparation of the sample for analysis by GC/MS using the appropriate sample preparation (e.g. EPA Method 3500) and, if necessary, sample cleanup procedures (i.e. EPA Method 3600). Next, the extract is introduced into the GC/MS by injecting the sample extract into a GC with a narrow-bore fused-silica capillary column. The GC column is temperature programmed to separate the analytes, which are then detected with MS. This is usually preferred. However, sometimes certain analytes cannot be detected directly with MS (e.g. highly polar compounds must first be derivatized). Thus, other detection systems, such as UV light, may need to be employed. The drawback is that the detection limits are often higher than that of MS.

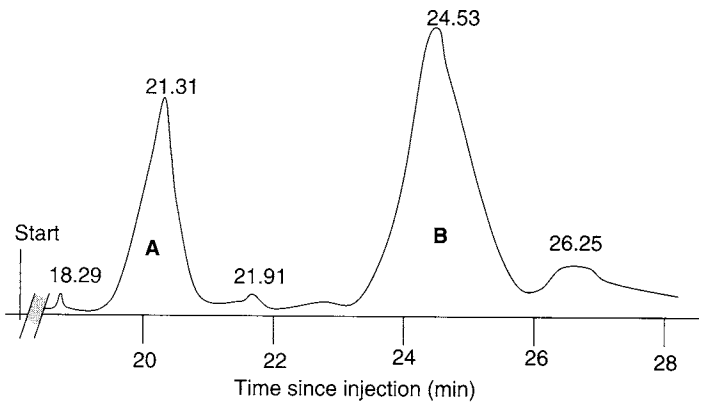
Analytes eluted from the capillary column are introduced into the mass spectrometer using a jet separator or a direct connection. Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards (i.e. by the mass to charge [m/z] ratios of the molecular fragments). The column is selected based on the retention time (RT) of the particular SVOC. However, the most commonly used column for SVOCs is 30 m × 0.25 mm ID (or 0.32 mm ID) 1 μm film thickness silicone-coated fused-silica capillary column (J&W Scientific DB-5 or equivalent).

Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve that has been prepared in a solvent of known concentrations of the target SVOC.

Interference is a problem since SVOCs are ubiquitous in the environment (e.g. phthalates are used as platicizers even in laboratory settings). Thus, GC/MS data from all blanks, samples, and spikes must be evaluated for such interferences.

1. Air Pollution Chromatography Example

Consider the situation where an analytical laboratory has generated the following chromatogram and table from an HPLC/UV at 254 nm using a 5 μm, C_{18}, 4.6 × 250 mm column from a sample you submitted:



Retention time	Area	Type	Area/Height	Area (%)
18.29	NA	NA	NA	0.1
21.31	NA	NA	NA	31.4
21.91	NA	NA	NA	0.2
24.53	NA	NA	NA	67.2
26.25	NA	NA	NA	1.1

Even with the missing entries in the table, one can still ascertain certain information. What are the retention times of compounds A and B? Which compound is present in a larger amount? Which compound has the higher boiling point? What would happen to the retention times of compounds A and B if the column temperature were raised? You suspect that compound B is benzo(a)pyrene (B(a)p). How would you find out whether this is the case?

The retention time of compound A is 21.31 min, shown above of the peak and in the table's retention time column. The retention time of compound B is 24.53 min. You cannot tell from this table or chromatogram which compound is present in a larger amount, since the only way to do so is to have calibration curve from known concentrations of compound A and compound B (at least three, but preferably five). For example, you would run the HPLC successively with injections of pure solutions of 0.01, 0.1, 1, 10, and 100 $\mu g\ L^{-1}$ concentrations of compound A, and again with pure solutions of the same concentrations of compound B. These concentrations would give peak areas associated with each known concentration. Then you could calculate (actually the HPLC software will calculate) the calibration curve. So, for example, if a peak with an area of 200 is associated with 1 $\mu g\ L^{-1}$ of compound A and a peak with an area of 2000 is associated with 10 $\mu g\ L^{-1}$ of compound A (i.e. a linear calibration curve) at 21.31 min after the aliquot is injected into the HPLC, then when you run your unknown sample, a peak at 21.31 min with an area of 1000 would mean you have about 5 $\mu g\ L^{-1}$ concentration of compound A in your sample. The same procedure would be followed to draw a calibration curve for compound B at a retention time of 24.53 min.

The reason it is not sufficient to look at the percent area is that each compound is physically and chemically different, and recall from the Beer–Lambert law (Eq. 17.1) that the amount of energy absorbed (in this case, the UV light) is what gives us the peak. If a molecule of compound A absorbs UV at this wavelength (i.e. 254 nm) at only 25% as that of compound B, compound A's concentration would be higher than that of compound B (because even though compound B has twice the percent area, its absorbance is 4 times that of compound B).

Compound A likely has the lower boiling point since it comes off the column first. As mentioned, this is only true if other factors, especially polarity, are about the same. For example, if compound B has about the same polarity as the column being used, but compound A has a very different polarity, compound A will have a greater tendency to leave the column. Generally,

however, retention time is a good indicator of boiling point; i.e., shorter retention times mean lower boiling points.

If the column temperature were raised, both compounds A and B would come off the column in shorter times. Thus, the retention times of both compounds A and B would be shorter than before the temperature was raised.

To determine whether the peak at 24.53 min is B(a)p, you must first obtain a true sample of pure B(a)p to place in a standard solution. This is the same process as you used to develop the calibration curve above. That is, you would inject this standard of known B(a)p into the same HPLC and the same volume of injection. If the standard gives a peak at a retention time of about 25 min, there is a good chance it is B(a)p. As it turns out, B(a)p absorbs UV at 254 nm and does come off an HPLC column at about 25 min.

The column type also affects retention time and peak area. The one used by the laboratory is commonly used for polycyclic aromatic hydrocarbons, includingB(a)p. However, numerous columns can be used for semivolatile organic compounds, so both the retention time and peak area will vary somewhat. Another concern is co-elution, i.e. two distinct compounds that have nearly the same retention times. One means of reducing the likelihood of co-elution is to target the wavelength of the UV detector. For example, the recommended wavelength for B(a)p is 254 nm, but 295 nm is preferred by environmental chromatographers because the interference peak in the B(a)p window is decreased at 295 nm. Another way to improve detection is to use a diode array detection system with the UV detector. This gives a number of different chromatograms simultaneously at various wavelengths. Finally, there are times when certain detectors do not work at all. For example, if a molecule does not absorb UV light (i.e. it lacks a group of atoms in a molecule responsible for absorbing the UV radiation, known as chromophores), there is no way to use any UV detector. In this case another detector, e.g. mass spectrometry, must be used.

H. General

The methods that have been discussed require specially designed instruments. Laboratories without such instruments can measure these gases using general-purpose chemical analytical equipment. A compendium of methods for these laboratories is the *Manual on Methods of Air Sampling and Analysis* [10].

II. ANALYSIS AND MEASUREMENT OF PARTICULATE POLLUTANTS

The three major characteristics of particulate pollutants in the ambient atmosphere are total mass concentration, size distribution, and chemical composition. In the United States, the $PM_{2.5}$ concentration, particulate matter

with an aerodynamic diameter $< 2.5\,\mu m$, is the quantity measured for an air quality standard to protect human health from effects caused by inhalation of suspended particulate matter. However, there remains a strong interest in the course fraction (PM_{10}) because it may be linked with certain diseases (e.g. asthma) and because it often has toxic components (e.g. sorbed metals and semivolatile organic compounds like dioxin). As shown in Chapter 11, the size distribution of particulate pollutants is very important in understanding the transport and removal of particles in the atmosphere and their deposition behavior in the human respiratory system. Their chemical composition may determine the type of effects caused by particulate matter on humans, vegetation, and materials.

Mass concentration units for ambient measurements are mass (μg) per unit volume (m^3). Size classification involves the use of specially designed inlet configurations, e.g., $PM_{2.5}$ sampling. To determine mass concentration, all the particles are removed from a known volume of air and their total mass is measured. This removal is accomplished by two techniques, filtration and impaction, described in Chapter 16. Mass measurements are made by pre- and postweighing of filters or impaction surfaces. To account for the absorption of water vapor, the filters are generally equilibrated at standard conditions ($T = 20°C$ and 50% relative humidity).

Size distributions are determined by classifying airborne particles by aerodynamic diameter, electrical mobility, or light-scattering properties. The most common technique is the use of multistage impactors, each stage of which removes particles of progressively smaller diameter. Figure 17.7

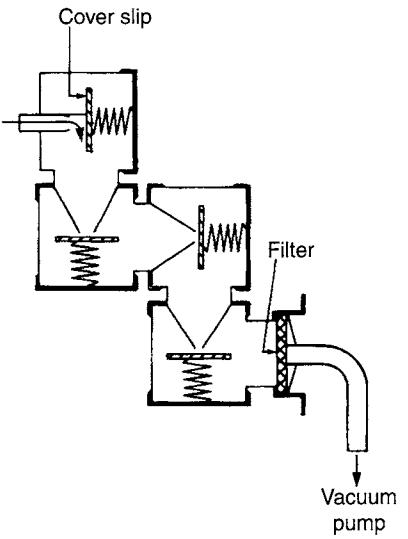


Fig. 17.7. Schematic diagram of a four-stage cascade impactor. *Source*: Giever, P. M., Particulate matter sampling and sizing, in *Air Pollution*, 3rd ed., Vol. III (Stern, A. C., ed.), p. 41. Academic Press, New York, 1976.

shows a four-stage impactor. The particulate matter collected on each stage is weighed to yield a mass size distribution or is subjected to chemical analysis to obtain data on its chemical size distribution. Impactors are used to determine size distributions for particle diameters of ~0.1 μm and larger.

Electrical mobility is utilized to obtain size distribution information in the 0.01–1.0 μm diameter range. This measurement method requires unipolar charging of particles and their separation by passage through an electrical field [11]. By incrementing the electrical field strength progressively, larger charged particles may be removed from a flowing air stream. The change in the amount of charge collected by an electrometer grid is then related to the number of particles present in a particular size increment. Instruments based on this principle yield a number size distribution.

Light-scattering properties of particles are also utilized to determine a number size distribution [12]. Individual particles interact with a light beam and scatter light at an angle to the original direction of the beam. The intensity of the scattered light is a function of the diameter and the refractive index of the particle. Inlet systems are designed to dilute a particle-laden air stream sufficiently to permit only one particle in the beam at a time. The intensity of the scattered light, as measured by a photomultiplier tube, is proportional to particle size. The number of electrical pulses of each magnitude is accumulated in a multichannel analyzer. By sampling at a known flow rate, the number of particles of different diameters are counted with this type of instrument.

The chemical composition of particulate pollutants is determined in two forms: specific elements, or specific compounds or ions. Knowledge of their chemical composition is useful in determining the sources of airborne particles and in understanding the fate of particles in the atmosphere. Elemental analysis yields results in terms of the individual elements present in a sample such as a given quantity of sulfur, S. From elemental analysis techniques we do not obtain direct information about the chemical form of S in a sample such as sulfate (SO_4^{2-}) or sulfide. Two nondestructive techniques used for direct elemental analysis of particulate samples are X-ray fluorescence (XRF) spectroscopy and neutron activation analysis (NAA).

XRF is a technique in which a sample is bombarded by X-rays [13]. Inner shell electrons are excited to higher energy levels. As these excited electrons return to their original state, energy with wavelengths characteristic of each element present in the sample is emitted. These high-energy photons are detected and analyzed to give the type and quantity of the elements present in the sample. The technique is applicable to all elements with an atomic number of 11 (sodium) or higher. In principle, complex mixtures may be analyzed with this technique. Difficulties arise from a matrix effect, so that care must be taken to use appropriate standards containing a similar matrix of elements. This technique requires relatively expensive equipment and highly trained personnel.

NAA involves the bombardment of the sample with neutrons, which interact with the sample to form different isotopes of the elements in the

sample [14]. Many of these isotopes are radioactive and may be identified by comparing their radioactivity with standards. This technique is not quite as versatile as XRF and requires a neutron source.

Pretreatment of the collected particulate matter may be required for chemical analysis. Pretreatment generally involves extraction of the particulate matter into a liquid. The solution may be further treated to transform the material into a form suitable for analysis. Trace metals may be determined by AA spectroscopy, emission spectroscopy, polarography, and anodic stripping voltammetry. Analysis of anions is possible by colorimetric techniques and ion chromatography. Sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), nitrate (NO_3^-), chloride (Cl^-), and fluoride (F^-) may be determined by ion chromatography [15].

Analytical methods available to laboratories with only general-purpose analytical equipment may be found in the *Methods of Air Sampling and Analysis* cited at the end of the previous section.

III. ANALYSIS AND MEASUREMENT OF ODORS

Odorants are chemical compounds such as H_2S, which smells like rotten eggs, and may be measured by chemical or organoleptic methods. Organoleptic methods are those which rely on the response to odor of the human nose. Although chemical methods may be useful in identifying and quantifying specific odorants, human response is the only way to assess the degree of acceptability of odorants in the atmosphere. This is due to several factors: the nonlinear relationship between odorant concentration and human response, the variability of individual responses to a given odorant concentration, and the sensory attributes of odor.

Four characteristics of odor are subject to measurement by sensory techniques: intensity, detectability, character (quality), and hedonic tone (pleasantness–unpleasantness) [16]. Odor intensity is the magnitude of the perceived sensation and is classified by a descriptive scale, e.g., faint–moderate–strong, or a 1–10 numerical scale. The detectability of an odor or threshold limit is not an absolute level but depends on how the odorant is present, e.g., alone or in a mixture. Odor character or quality is the characteristic which permits its description or classification by comparison to other odors, i.e., sweet or sour, or like that of a skunk. The last characteristic is the hedonic type, which refers to the acceptability of an odorant. For the infrequent visitor, the smell of a large commercial bread bakery may be of high intensity but pleasant. For the nearby resident, the smell may be less acceptable.

The sensory technique used for assessing human perception of odors is called *olfactometry*. The basic technique is to present odorants at different concentrations to a panel of subjects and assess their response. The process favored by the US National Academy of Sciences is dynamic olfactometry [16]. This technique involves a sample dilution method in which a flow of clean, nonodorous air is mixed with the odorant under dynamic or constant

flow conditions. With this type of apparatus and standard operating conditions, it is possible to determine the detection threshold and the recognition threshold. At high dilution, the panel will be able to tell only whether an odorant is present or absent. Only at higher concentrations, typically by a factor of 2–10, will the subjects be able to identify the odorant.

The olfactometric procedure contains the following elements:

1. Dynamic dilution.
2. Delivery of diluted odorant for smelling through a mask or port.
3. Schedule of presentation of various dilutions and blanks.
4. Obtaining responses from the panelists.
5. Calculation of a panel threshold from experimental data.
6. Panelist selection criteria.

The first element, dynamic dilution, provides a reproducible sample for each panelist. The system must minimize the loss of the odorant to the walls of the delivery apparatus, provide clean dilution air of odor-free quality, maintain a constant dilution ratio for the duration of a given test, and have no memory effect when going from high to low concentrations or switching between odorants of different characters. The type of mask or port and the delivery flow rate have been found to influence the response of panelists in determining odor threshold and intensity.

The schedule of presentation may influence the results. The sensory effects are judgment criterion, anticipation, and adaptation. The judgment criterion determines how the panelist will respond when asked whether or not an odor is sensed. Individuals differ in their readiness to be positive or negative. The anticipation effect is a tendency to expect an odor over a given series of trials. Subjects show some positive response when no odorant is present. The adaptation effect is the temporary desensitization after smelling an odorant. This is also called olfactory fatigue and often occurs in occupational settings. Because of olfactory fatigue, investigators evaluating odor concentration in the field must breathe air deodorized by passage through an activated carbon canister before and after sniffing the ambient air being evaluated.

Individuals differ in their sensitivity to odor. Figure 17.8 shows a typical distribution of sensitivities to ethylsulfide vapor [17]. There are currently no guidelines on inclusion or exclusion of individuals with abnormally high or low sensitivity. This variability of response complicates the data treatment procedure. In many instances, the goal is to determine some mean value for the threshold representative of the panel as a whole. The small size of panels (generally fewer than 10 people) and the distribution of individual sensitivities require sophisticated statistical procedures to find the threshold from the responses.

Thresholds may also be determined by extrapolation of dose–response plots. In this approach, the perceived odor intensity is measured at several dilutions using some intensity rating method (Fig. 17.8). The threshold value may be selected at some value (e.g., zero intensity) and the concentration determined with the dilution ratio.

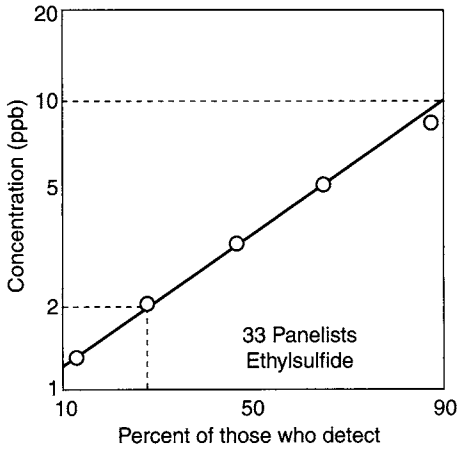


Fig. 17.8. Distribution of sensitivity to ethylene sulfide odor in 33 individuals. The abscissa is the percentage of the individuals who detected the presence of ethylene sulfide at various levels. *Source*: Dravnicks, A., and Jarke, F., *J. Air Pollut. Control Assoc.* **30**, 1284–1289 (1980).

IV. ANALYSIS AND MEASUREMENT OF VISIBILITY

Impairment of visibility is a degradation of our ability to perceive objects through the atmosphere. As discussed in Chapter 14, several components influence our concept of visibility: the characteristics of the source, the human observer, the object, and the degree of pollution in the atmosphere. Our attempts to measure visibility at a given location can take two approaches: human observations and optical measurements. In pristine locations such as national parks, use of human observers has permitted us to gain an understanding of the public's concept of visibility impairment. Although it is difficult to quantify the elements of human observations, this type of research, when coupled with optical measurements, provides a better measure of visibility at a given location [18].

Optical measurements permit the quantification of visibility degradation under different conditions. Several instruments are capable of measuring visual air quality, e.g., cameras, photometers, telephotometers, transmissometers, and scattering instruments.

Photography can provide a permanent record of visibility conditions at a particular place and time. This type of record can preserve a scene in a photograph in a form similar to the way it is seen. Photometers measure light intensity by converting brightness to representative electric signals with a photodetector. Different lenses and filters may be used to determine color and other optical properties. When used in combination with long-range lenses, photometers become telephotometers. This type of instrument may

view distant objects with a much smaller viewing angle. The output of the photodetector is closely related to the perceived optical properties of distant targets. Telephotometers are often used to measure the contrast between a distant object and its surroundings, a measurement much closer to the human observer's perception of objects.

A transmissometer is similar to a telephotometer except that the target is a known light source. If we know the characteristics of the source, the average extinction coefficient over the path of the beam may be calculated. Transmissometers are not very portable in terms of looking at a scene from several directions. They are also very sensitive to atmospheric turbulence, which limits the length of the light beam.

Scattering instruments are also used to measure visibility degradation. The most common instrument is the integrating nephelometer, which measures the light scattered over a range of angles. The physical design of the instrument, as shown in Fig. 17.9, permits a point determination of the scattering coefficient of extinction, b_{ext} [19]. In clean areas, b_{ext} is dominated by scattering, so that the integrating nephelometer yields a measure of the extinction coefficient. As noted in Chapter 14, b_{ext} can be related to visual range through the Koschmieder relationship.

Other measurements important to visual air quality are pollutant related, i.e., the size distribution, mass concentration, and number concentration of airborne particles and their chemical composition. From the size distribution, the Mie theory of light scattering can be used to calculate the scattering coefficient [20]. Table 17.3 summarizes the different types of visual monitoring methods [21].

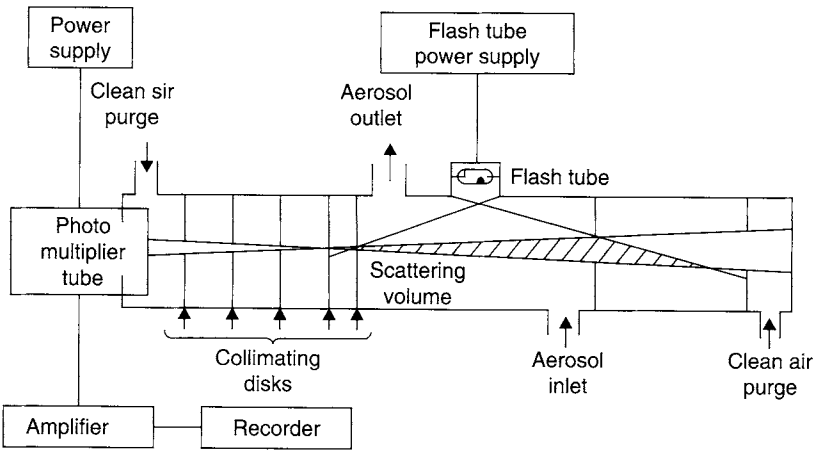


Fig. 17.9. Schematic diagram of the integrating nephelometer. *Source*: Ahliquist, N. C., and Charlson, R. J., *J. Air Pollut. Control Assoc.* **17**, 467 (1967).

TABLE 17.3

Visibility Monitoring Methods

Method	Parameters measured	Advantages	Limitations	Preferred use
Human observer	Perceived visual quality, atmospheric color, plume blight, visual range	Flexibility, judgment; large existing database (airport visual range)	Labor intensive; variability in observer perception; suitable targets for visual range not generally available	Complement to instrumental observations; areas with frequent plume blight, discoloration; visual ranges with available target distances
Integrating nephelometer	Scattering coefficient (b_{scat}) at site	Continuous readings; unaffected by clouds, night; b_{scat} directly relatable to fine aerosol concentration at a point; semiportable; used in a number of previous studies; sensitive models available; automated	Point measurement, requires assumption of homogeneous distribution of particles; neglects extinction from absorption, coarse particles (> 3–$10\,\mu m$; must consider humidity effects at high relative humidity	Areas experiencing periodic, well-mixed general haze; medium to short viewing distances; small absorption coefficient (b_{abs}); relating to point composition measurements
Multiwavelength telephotometer	Sky and/or target radiance, contrast at various wavelengths	Measurement over long view path (up to 100 km) with suitable illumination and target, contrast transmittance, total extinction, and chromaticity over sight path can be determined; includes scattering and absorption from all sources; can detect plume blight; automated	Sensitive to illumination conditions; useful only in daylight; relationship to extinction, aerosol relationship possible only under cloudless skys; requires large, uniform targets	Areas experiencing mixed or inhomogeneous haze, significant fugitive dust; medium to long viewing distances (one-fourth of visual range); areas with frequent discoloration; horizontal sight path

Transmissometer	Long path extinction coefficient (b_{ext})	Measurement over medium view path (10–25 km); measures total extinction, scattering and absorption; unaffected by clouds, night	Calibration problems; single wavelength; equivalent to point measurement in areas with long view paths (50–100 km); limited applications to date still under development	Areas experiencing periodic mixed general haze, medium to short viewing distance areas with significant absorption (b_{abs})
Photography	Visual quality, plume blight, color, contrast (limited)	Related to perception of visual quality; documentation of vista conditions	Sensitive to lighting conditions; degradation in storage; contrast measurement from film subject to significant errors	Complement to human observation, instrumental methods; areas with frequent plume blight, discoloration
Particle samplers	Particles	Permit evaluation of causes of impairment	Not always relatable to visual air quality; point measurement	Complement to visibility measurements
Hi vol.	TSP	Large database, amenable to chemical analysis; coarse particle analysis	Does not separate sizes; sampling artifacts for nitrate, sulfate; not automated	Not useful for visibility sites
Cascade impactor	Size-segregated particles (more than two stages)	Detailed chemical, size evaluation	Particle bounce, wall losses; labor intensive	Detailed studies of scattering by particles <2 μm
Dichotomous and fine particle samplers (several fundamentally different types)	Fine particles (<2.5 μm) coarse particles (2.5–15 μm) inhalable particles (0–15 μm)	Size cut enhances resolution, optically important aerosol analysis, low artifact potential, particle bounce; amenable to automated compositional analysis; automated versions available; large networks under development	Some large-particle penetration; 24 h or longer sample required in clean areas for mass measurement; automated version relatively untested in remote locations	Complement to visibility measurement, source assessment for general haze, ground-level plumes

Source: US EPA. *Protecting Visibility*, EPA 450/5-79-008. Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1979.

V. ANALYSIS AND MEASUREMENT OF ACIDIC DEPOSITION

The two components of acidic deposition described in Chapter 14 are wet deposition and dry deposition. The collection and subsequent analysis of wet deposition are intuitively straightforward. A sample collector opens to collect rainwater at the beginning of a rainstorm and closes when the rain stops. The water is then analyzed for pH, anions (negative ions), and cations (positive ions). The situation for dry deposition is much more difficult [22].

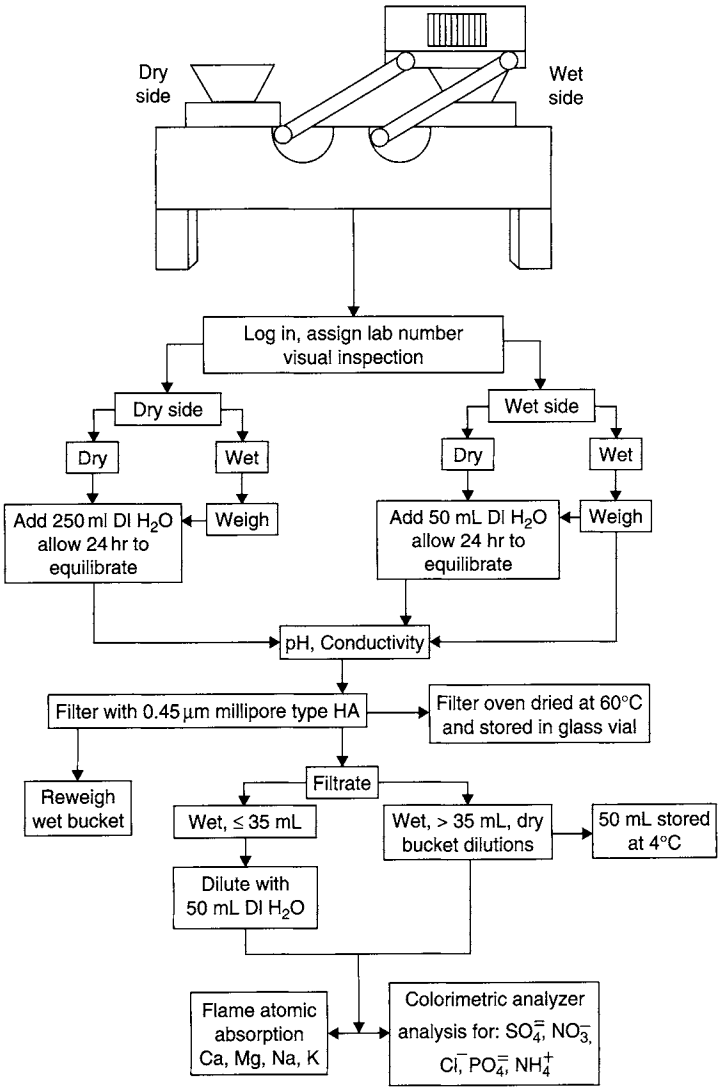


Fig. 17.10. Wet/dry precipitation collector and flow chart for analysis of samples. (DI H_2O: distilled water). *Source*: NADP Quality Assurance Report, Central Analytical Laboratory, Illinois Institute of Natural Resources, Champaign, III, March 1980.

Collection of particles settling from the air is very dependent on the surface material and configuration. The surfaces of trees, plants, and grasses are considerably different from that of the round, open-top canister often used to collect dry deposited particles. After collection, the material must be suspended or dissolved in pure water for subsequent analysis.

An overview of acid rain monitoring activities in North America shows several national and regional programs in operation in the United States, Canada, and Mexico [23]. The National Atmospheric Deposition Program has established the nationwide sampling network of ~100 stations in the United States. The sampler is shown in Fig. 17.10 with a wet collection container. The wet collection bucket is covered with a lid when it is not raining. A sensor for rain moves the lid to open the wet collector bucket and cover the dry bucket at the beginning of a rainstorm. This process is reversed when the rain stops.

The primary constituents to be measured are the pH of precipitation, sulfates, nitrates, ammonia, chloride ions, metal ions, phosphates, and specific conductivity. The pH measurements help to establish reliable long-term trends in patterns of acidic precipitation. The sulfate and nitrate information is related to anthropogenic sources where possible. The measurements of chloride ions, metal ions, and phosphates are related to sea spray and windblown dust sources. Specific conductivity is related to the level of dissolved salts in precipitation.

Figure 17.10 also shows a flowchart for analysis of wet and dry precipitation. The process involves weight determinations, followed by pH and conductivity measurements, and finally chemical analysis for anions and cations. The pH measurements are made with a well-calibrated pH meter, with extreme care taken to avoid contaminating the sample. The metal ions Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+} are determined by flame photometry, which involves absorption of radiation by metal ions in a hot flame. Ammonia and the anions Cl^{-}, SO_4^{2-}, NO_3^{-}, and PO_4^{3-} are measured by automated colorimetric techniques.

Air pollution analytical methods continue to evolve and to improve. A good way to stay up-to-date on current methods is to visit the website for the US EPA's Ambient Monitoring Technology Information Center: http://www.epa.gov/ttn/amtic.

REFERENCES

1. Dailey, W. V., and Fertig, G. H., *Anal. Instrum.* **77**, 79–82 (1978).
2. US Environmental Protection Agency, **40** CFR, Part 50, Appendix C, July 1992.
3. Stevens, R. K., and Hodgeson, J. A., *Anal. Chem.* **45**, 443A–447A (1973).
4. US Environmental Protection Agency, Transfer Standards for Calibration of Air Monitoring Analyzers for Ozone, EPA-600/4-79-056. Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1979.
5. US Environmental Protection Agency, *Fed. Regist.* **41**, 52686–52695 (1976).
6. US Environmental Protection Agency, **40** CFR, Part 50, Appendix A, July 1992.
7. Hollowell, C. D., Gee, G. Y., and McLaughlin, R. D., *Anal. Chem.* **45**, 63A–72A (1973).

8. Okake, H., Splitstone, P. L., and Ball, J. J., *J. Air Pollut. Control Assoc.* **23**, 514–516 (1973).
9. National Oceanic and Atmospheric Administration, *United States Standard Atmosphere*. US Government Printing Office, Washington, DC, 1976.
10. Lodge, J. P. (ed.), *Methods of Air Sampling and Analysis*, 3rd ed. American Public Health Association, CRC Press, Boca Raton, FL.
11. Liu, B. Y. H., Pui, D. Y. H., and Kapadia, A., Electrical aerosol analyzer, in *Aerosol Measurement* (Lundgren, D. A., Harris Jr., F. S., Marlow, W. H., Lippmann, M., Clark, W. E., and Durham, U. D., eds.), pp. 341–384. University Presses of Florida, Gainesville, FL, 1979.
12. Whitby, K. T., and Willeke, K., Single particle optical particle counters, in *Aerosol Measurement* (Lundgren, D. A., Harris Jr., F. S., Marlow, W. H., Lippmann, M., Clark, W. E., and Durham, U. D., eds.), pp. 241–284. University Presses of Florida, Gainesville, FL, 1979.
13. Dzubay, T. G., *X-ray Fluorescence Analysis of Environmental Samples*. Ann Arbor Science Publishers, Ann Arbor, MI, 1977.
14. Heindryckx, R., and Dams, R., *Prog. Nucl. Energy* **3**, 219–252 (1979).
15. Mulik, J. D., and Sawicki, E., *Ion Chromatographic Analysis of Environmental Pollutants*, Vol. 2. Ann Arbor Science Publishers, Ann Arbor, MI, 1979.
16. National Research Council, *Odors from Stationary and Mobile Sources*. National Academy of Sciences, Washington, DC, 1979.
17. Dravnicks, A., and Jarke, F., *J. Air Pollut. Control Assoc.* **30**, 1284–1289 (1980).
18. Malm, W., Kelley, K., Molenar, J., and Daniel, T., *Atmos. Environ.* **15**, 1875–1890 (1981).
19. Ahliquist, N. C., and Charlson, R. J., *J. Air Pollut. Control Assoc.* **17**, 467 (1967).
20. Twomey, S., *Atmospheric Aerosols*, pp. 200–216. Elsevier North-Holland, New York, 1977.
21. US Environmental Protection Agency, Protecting Visibility, EPA-450/5-79-008. Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1979.
22. Hicks, B. B., Wesely, M. L., and Durham, J. L., Critique of Methods to Measure Dry Deposition—Workshop Summary, EPA-600/9-80-050. Environmental Sciences Research Laboratory, Research Triangle Park, NC, 1980.
23. Wisniewski, J., and Kinsman, J. D., *Bull. Am. Meteorol. Soc.* **63**, 598–618 (1982).
24. US EPA, Method TO-9A in Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd ed. EPA/625/R-96/010b, 1999.

SUGGESTED READING

Harrison, R. M., and Young, R. J. (eds.), *Handbook of Air Pollution Analysis*, 2nd ed. Chapman & Hall, London, 1986.

Lundgren, D. A., Harris Jr., F. S., Marlow, W. H., Lippmann, M., Clark, W. E., and Durham, U. D. (eds.), *Aerosol Measurement*. University Presses of Florida, Gainesville, FL, 1979.

Newman, L. (ed.), *Measurement Challenges in Atmospheric Chemistry*. American Chemical Society, Washington, DC, 1993.

Sickles II, J. E., *Adv. Environ. Sci. Technol.* **24**, 51–128 (1992).

Winegar, E. D., and Keith, L.H., *Sampling and Analysis of Airborne Pollutants*. Lewis Publishers, Boca Raton, FL, 1993.

QUESTIONS

1. Describe the rationale for the US EPA's establishment of a standard reference method for measurement of National Ambient Air Quality Standard air pollutants.

2. Under what conditions can another method be substituted for a standard reference method?
3. Describe the potential interferences (a) in the NDIR method for measuring CO and (b) in the chemiluminescent method for measuring NO_2.
4. The electrical aerosol analyzer and the optical counter are used to measure particle size distributions. Describe the size range and resolution characteristics of each of these instruments.
5. How can human observers, optical measurements along a line of sight, and point measurements by nephelometry provide conflicting information about visual air quality in the same location?
6. Using the Code of Federal Regulations, list the current reference methods for measuring NO_2, O_3, SO_2, CO, total suspended particulate matter, and lead.
7. List two types of calibration sources for gas analyzers.
8. Review the air pollution literature and describe the difficulties in establishing a standard reference method for measuring NO_2.
9. Describe the deficiencies of a total suspended particulate measurement for relating ambient concentrations to potential human health effects.
10. Explain how one chemical compound can have a larger peak on a chromatogram than another compound, yet have a much lower concentration.
11. Why is extraction important in analyzing air pollutants? When is it not necessary?