Analysis of Air and Air Pollutants

- **Additional Sources of Information**
- **Keywords**
- **Questions and Problems**

ANALYTIC MEASUREMENTS FORM THE FOUNDATION ON WHICH OUR UNDERSTANDING OF THE ATMOSPHERE IS BUILT. New measurement capability has often resulted in a significant expansion or revision of our understanding of atmospheric chemistry. Experimental measurements provide the information for testing theoretical models. In atmospheric chemistry, one of the most fundamental measurements is the most difficult: What is the composition of the atmosphere? Nitrogen gas represents more than 78% of the atmosphere, whereas reactive species, such as ozone, are present in parts per million (ppm) concentrations. The range in concentration of atmospheric constituents is extremely wide, as large as 10^{14}.

Measurements to determine the concentration of atmospheric constituents may be made in two different ways: **in situ**, which means the sample of the atmospheric gases must be placed inside the device (spectrometer) that is making the measurement, and **remotely** (remote-sensing technique), by passing a beam of energy that originates on a satellite, an aircraft, the space shuttle, or the ground through a portion of the atmosphere that is to be studied. Although these measurement techniques involve different instrumentation, the underlying principles are the same.

Automobile and smokestack emissions are the major sources of anthropogenic pollutants into the atmosphere, both of which

the Environmental Protection Agency (EPA) regulates. Measurements of the gases emitted from automobiles and smokestacks are difficult to make because the exhaust gases are hot and are traveling at a high velocity. The most common methods used to measure automobile exhaust and some of the EPA methods used for monitoring smokestack emissions are discussed.

■ In Situ Absorption Measurements

Spectroscopic measurements rely on the fact that different chemical compounds absorb electromagnetic radiation at different wavelengths. When a molecule absorbs a photon of electromagnetic radiation, the energy of the molecule increases. Figure 6.1 shows the interaction that occurs when a molecule absorbs electromagnetic radiation of different frequencies. For example, when a molecule absorbs microwave radiation, which is electromagnetic radiation of a relatively low energy, it only stimulates the rotational motion of the molecule. Infrared radiation (IR), which has higher energy than microwaves, stimulates the vibrations of molecules that absorb it. Ultraviolet (UV) radiation, which has even more energy than infrared, causes electrons in the molecules absorbing it to be promoted into higher energy orbitals; the molecule is said to be in the excited state. The lowest energy state of a molecule

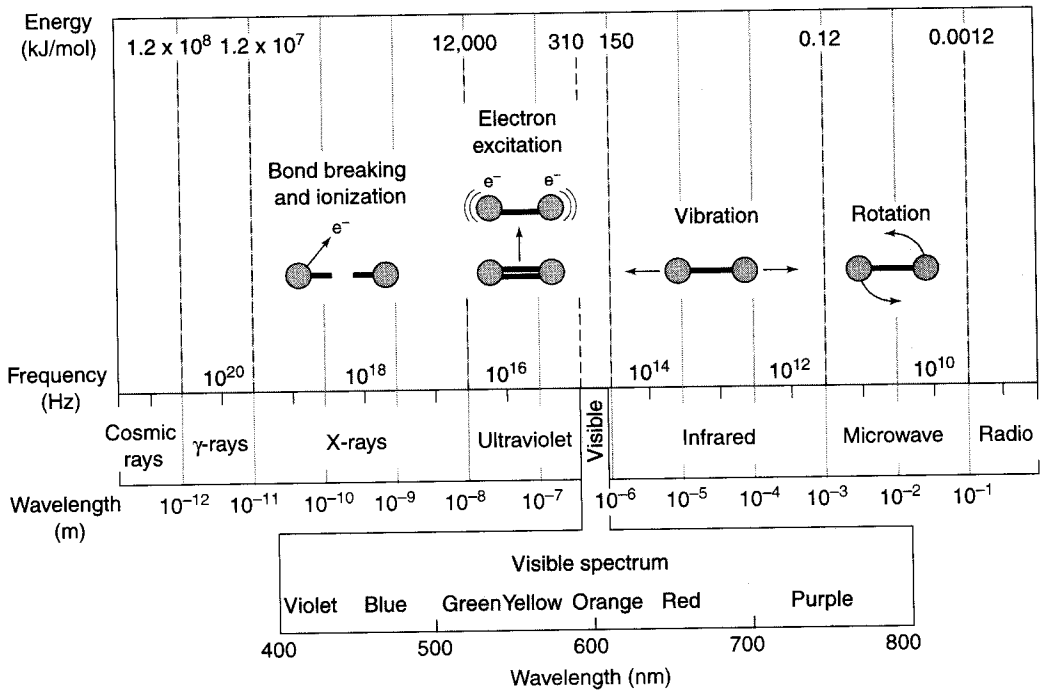

Figure 6.1 An electromagnetic spectrum showing the type of interaction that occurs when electromagnetic radiation in each energy region is absorbed by a molecule.

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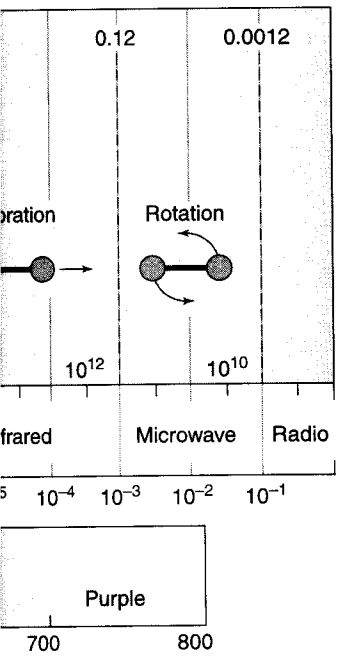

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is called the **ground state.** Very high-energy electromagnetic radiation, such as an X-ray, has enough energy to break chemical bonds and ionize molecules.

When the sample absorbs a beam of electromagnetic radiation, the **irradiance** of the beam is decreased. Irradiance (P), which is sometimes referred to as intensity or radiant power, is the energy per second per unit area of the light beam. A spectrophotometric measurement is illustrated in Figure 6.2. Electromagnetic radiation is passed through a monochromator (a prism, grating or filter) to select one wavelength of electromagnetic radiation. The light of a single wavelength is said to be monochromatic, which means "one color." The monochromatic light, with irradiance P_0, passes into a sample of length b. The irradiance of the beam emerging form the other side of the sample is P. Some of the light may be absorbed by the sample, and thus, $P \leq P_0$.

Transmittance (T) is defined as the fraction of the original light that has passed through the sample.

$$T = \frac{P}{P_0}$$

T has the range of 0 to 1. The percentage of transmittance is 100T and has a range from 0% to 100%. **Absorbance** (A) is defined as follows:

$$A = \log\left(\frac{P_0}{P}\right) = -\log T$$

When no light is absorbed, $P = P_0$ and $A = 0$. Absorbance is important because it is directly proportional to concentration (c) of the absorbing molecules in the sample.

The relationship between the concentration of the absorbing molecule and absorbance has been described in the Beer-Lambert law or simply **Beer's law:**

$$A = \epsilon bc$$

Absorbance is dimensionless, and thus, all of the constants and variables on the right side of the equation must have units that cancel. The concentration of the sample can be expressed in many ways: moles per liter, ppm, parts per billion (ppb), or mg/m^3. The pathlength (b) can be very small (cm) or very large (km). The quantity ϵ (epsilon), called the **molar absorptivity** (or extinction coefficient), is the characteristic of a molecule that indicates how much light it will absorb at a particular wavelength. The ϵ can be expressed by using many different units. Depending how the concentration and pathlength are expressed, ϵ must have units that make the products of (ϵbc) dimensionless.

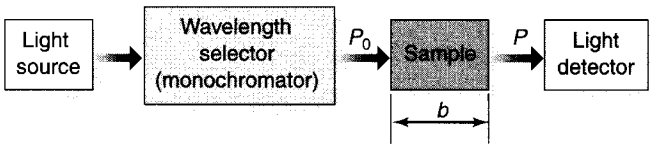


Figure 6.2 Diagram of single-beam spectrophotometric instrument. P_0, irradiance of beam entering sample; P, irradiance of beam emerging from sample; b, length of path through sample.

In Situ Ozone Measurements

UV absorption has been used to measure the concentration of ozone in stratospheric air. Figure 6.3 shows that ozone has a strong absorption in the UV region. Other atmospheric gases such as O_2, N_2, and H_2O do not absorb UV radiation and thus do not have to be removed from the air sample because they do not interfere with the ozone measurement. The concentration of ozone in the stratosphere is less than 10 ppm, and thus, the spectrophotometer that is used to make the measurement must be capable of measuring a small absorbance. This is most easily done by making the sample cell very long. Because Beer's law tells us that absorbance is proportional to the sample pathlength and because we can get a lot of sample easily, a long sample pathlength will greatly improve our ability to measure ppm levels of ozone.

A UV spectrometer has been designed to measure the amount of ozone present in stratospheric air. It is placed in a high-altitude aircraft, which is flown to the exact position where the measurement is to be made. Air that contains the ozone flows into the instrument through a tube (an in situ measurement). A schematic diagram of the instrument is shown in Figure 6.4. The UV spectrometer uses a low-pressure mercury lamp to produce the electromagnetic radiation. The output of the mercury lamp has a maximum at 254 nm, which is very near to the absorbance maxima for ozone (Figure 6.3). The tube carrying the air is split into two streams. In one stream there is an ozone scrubber that removes only ozone. The air passing through this side travels into the lower sample cell and acts as a reference. The other stream (which still contains ozone) travels into the upper sample cell. Each stream flows through one of the 50-cm sample cells. Light from the mercury lamp is sent down each cell, and a silicon photodiode at the end of each cell detects the intensity at the end of the path. An ozone concentration of 1 ppm in the stratosphere produces an absorption of 0.2. By comparing the absorbance of sample with ozone to the absorption sample without ozone, the difference in the absorbance of the two cells gives the ozone absorption independent of lamp intensity.

In Situ Carbon Dioxide Measurements

Since 1958, a measurement of atmospheric carbon dioxide (CO_2) concentration has been made at the Mauna Loa Observatory on the island of Hawaii. Figure 6.5 shows that this observatory is located at a site that is far from major population centers. At an elevation of 3350 m

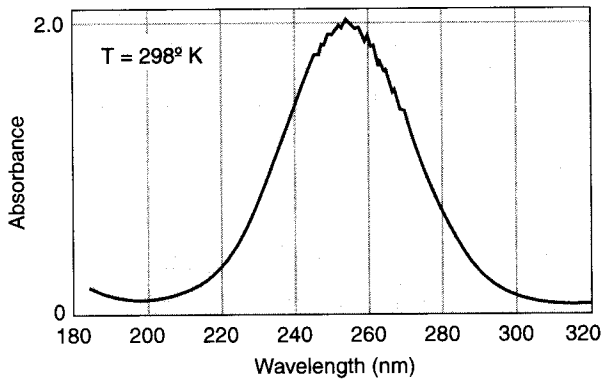
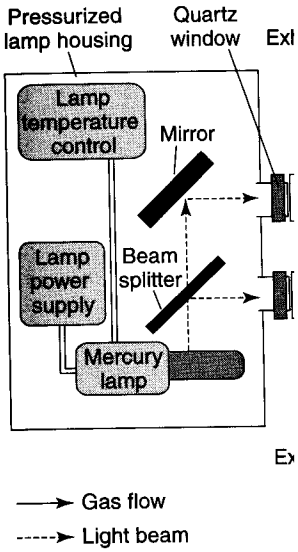


Figure 6.3 UV absorption spectrum of ozone. Adapted from L. T. Molina and M. J. Molina, 1986. Absolute absorption cross sections of ozone in the 185- to 350-nm wavelength range. *J. Geophys. Res.* 91 (D13): 14501–14508.



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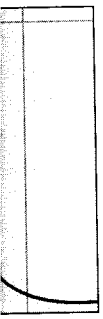

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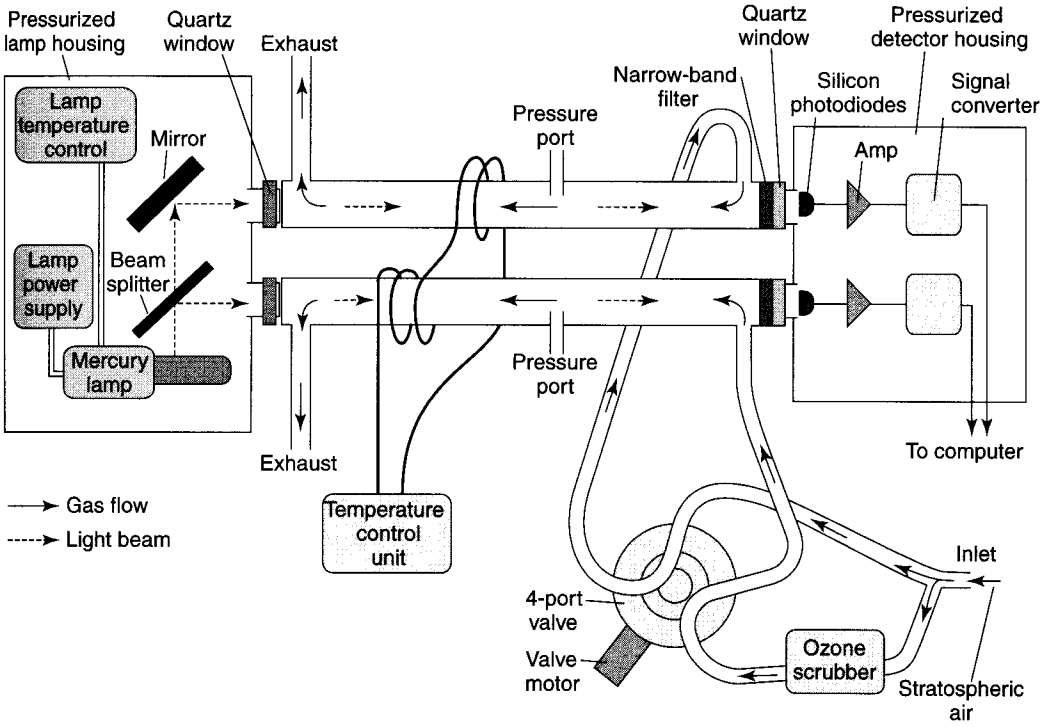


Figure 6.4 UV spectrometer that has been used to measure the ozone concentration. Adapted from M. H. Proffitt and R. J. McLaughlin, 1983. Fast response dual-beam UV-absorption photometer suitable for use on stratospheric balloons, *Rev. Sci. Instrum.* 54: 1719–1728.

on the flank of Mauna Loa volcano, it is an ideal site for making atmospheric CO_2 measurements. No nearby vegetation exists, and the prevailing nighttime, down-slope winds give a representative sampling of midtropospheric air from the central North Pacific Ocean. The record of CO_2 concentration is taken as a reliable index of long-term CO_2 growth.

The concentration of CO_2 in the atmosphere has been presented in a graphic form (Figure 6.6) that is widely known as the "Keeling curve." The Mauna Loa atmospheric CO_2 concentration measurements, taken since 1958 and now extending through the present, constitute the longest continuous record of atmospheric CO_2 concentrations available in the world and are considered to be reliable indicators of the regional trend in the concentration of atmospheric CO_2 in the middle layers of the troposphere. The methods and equipment used to obtain these measurements have remained essentially unchanged during the 40-year monitoring program.

The CO_2 concentrations taken at Mauna Loa Observatory are obtained using a **nondispersive, dual-detector, infrared (NDIR) detector**. The components and operational principles of the NDIR detector are discussed later in this chapter. Air samples at Mauna Loa are collected continuously from air intakes at the top of four 7-m towers and one 27-m tower. Four air samples are collected each hour for the purpose of determining the CO_2 concentration. This analyzer registers the concentration of CO_2 in a stream of air flowing at approximately 0.5 L hr/min. Every 20 minutes the flow is replaced by a stream of calibrating gas or "working

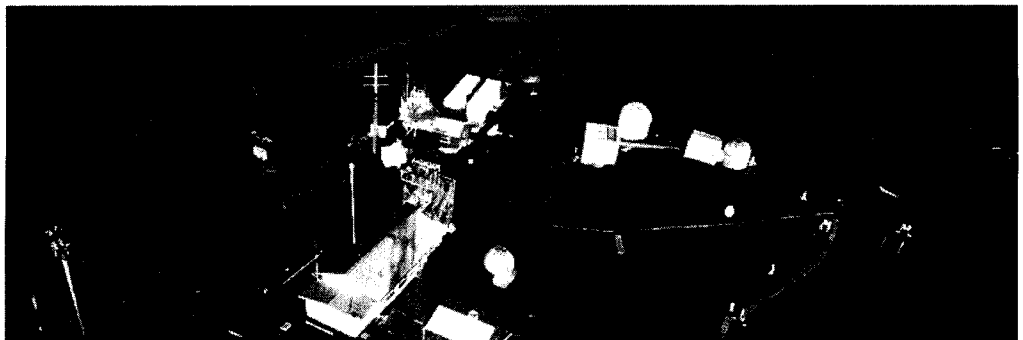
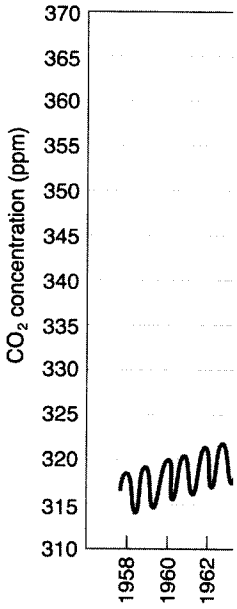


Figure 6.5 Picture of the Mauna Loa Observatory (a) and the Mauna Loa Observatory from the air (b).

reference gas." These calibration gases and other reference gases are compared periodically to determine the instrument sensitivity and to check for possible contamination in the air-handling system.

Because virtually all molecules (except inert gases and homonuclear diatomic molecules such as N_2 and H_2) absorb infrared radiation at specific wavelengths, infrared spectroscopy should be a useful technique for measuring atmospheric constituents. Infrared spectroscopy is relatively insensitive, and IR spectrometers require very long sample cells (10 to 100 meters) to detect ppb concentrations of atmospheric gases. An IR spectrometer that is more than 100 meters long is impractical, and because of this, IR is not used to make in situ measurements.



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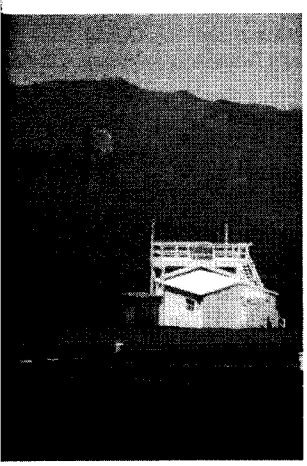

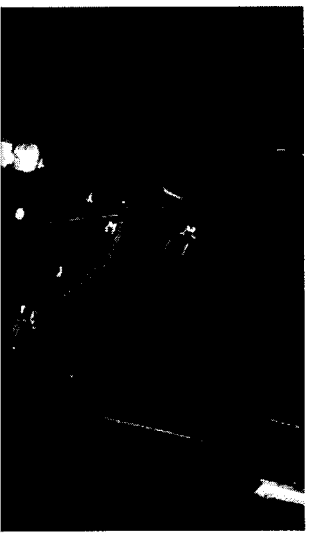

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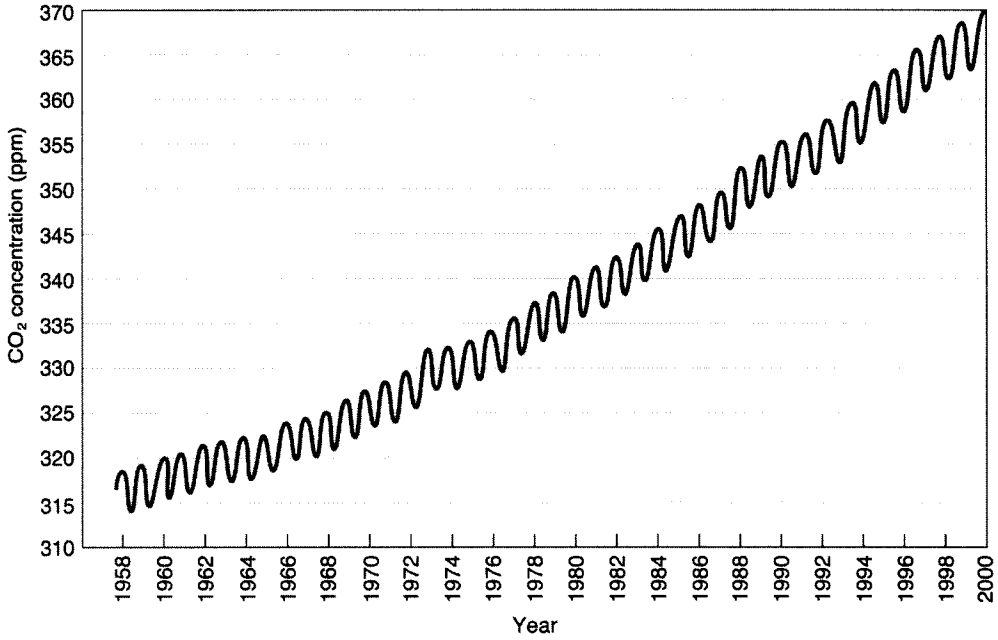


Figure 6.6 Since the first the measurements were made at Mauna Loa, Hawaii, in 1958, CO_2 concentrations in the atmosphere have risen dramatically. The yearly seasonal variations are caused by the removal of CO_2 from the atmosphere by growing plants in the summer and the return of CO_2 to the atmosphere in the winter when plants decay.

■ IR Spectrometry

Molecules selectively absorb specific IR frequencies that correspond to the frequencies of the vibrational oscillations of the atoms, which are connected by covalent bonds. When a molecule absorbs IR radiation, the amplitudes of these vibrations increase. The absorption corresponding to these oscillations appears in certain definite wavelength regions of the spectrum.

The frequency (ν) at which a characteristic IR absorption occurs depends on the mass of the atoms involved in the vibration and the strength of the bond connecting the atoms. Planck's equation relates the energy (E) of the absorbed radiation to its frequency.

$$E = h\nu \qquad h = 6.626 \times 10^{-34}\ \text{Js, Planck's constant}$$

Frequency is inversely proportional to the wavelength (λ) of the absorbed radiation.

$$E = hc(1/\lambda)$$

The quantity ($1/\lambda$) is called the wavenumber, $\bar{\nu}$, and is usually expressed in units of cm^{-1}.

$$E = hc\bar{\nu}$$

An IR band is normally reported as a position of maximum absorption in wavenumbers ($\bar{\nu}$) in units of reciprocal centimeters (cm^{-1}). Figure 6.7 shows the infrared absorption bands for the

atmospheric gases water and CO_2 and Figure 6.8 for the pollutant gas N_2O. Figure 6.7 shows that the most intense IR band for CO_2 is between 2200 to 2400 cm^{-1}, and Figure 6.8 shows that for N_2O the most intense IR bands lie in the region of 2100 to 2400 cm^{-1}. The absorbance of the pollutant CFC-12, which can be seen in Figure 3.17, has an intense absorbance in the 1200 to 800 cm^{-1} region.

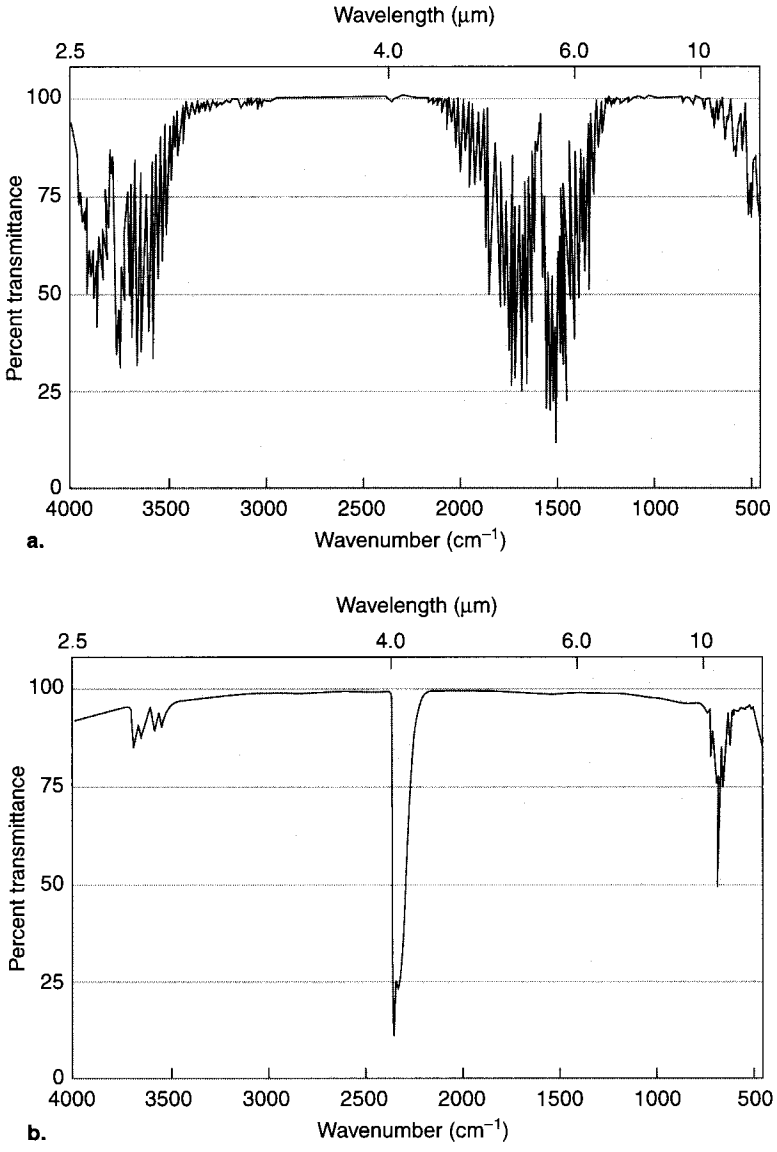
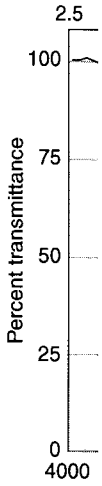


Figure 6.7 Infrared spectrum of the atmospheric gases water (a) and CO_2 (b). ©BIO-RAD Laboratories, Sadtler Division, 2000.



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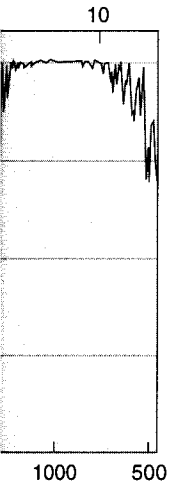

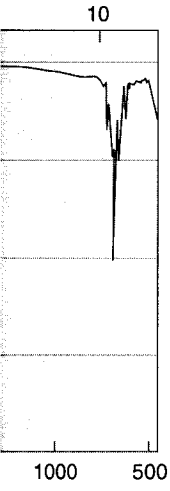

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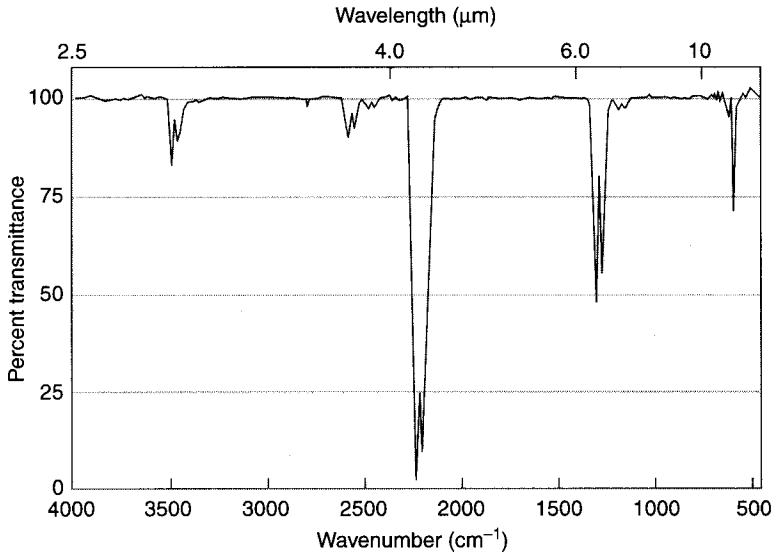


Figure 6.8 Infrared spectrum of pollutant gas N_2O. ©BIO-RAD Laboratories, Sadtler Division, 2000.

■ Infrared Vibrational Frequencies

The absorption that is observed in the infrared region can be described by using a very simple model that calls for the atoms in the molecule to be considered balls and the bonds that connect them to be springs. As can be seen in Figure 6.9, for a diatomic molecule, the two atoms have masses (M_1 and M_2), and the spring has a force constant (k).

Two atoms that are connected by a spring would naturally settle into a specific motion when disturbed. The masses vibrate with a frequency that depends on the masses and the strength of the spring. Such vibrations, which occur at characteristic frequencies, are what we measure in vibrational spectra.

For diatomic molecules, the frequency of the vibration can be described as a harmonic oscillator and $\bar{\nu}$ by the following equation:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12}\sqrt{\frac{k}{\mu}}$$

Where

$\bar{\nu}$ is the wavenumber of an absorption peak in cm^{-1}.

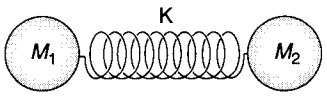
k is the force constant of the bond in Newtons per meter (N/m).

5×10^2 N/m is the average for single bonds.

1×10^3 N/m is the average for double bonds.

1.5×10^3 N/m is the average for triple bonds.

c is the velocity of light in cm/sec.



K is the force constant of the spring

Figure 6.9 Molecular vibrations of two atoms connected by a bond.

μ is the reduced mass in kilograms, which can be computed by

$$\mu = \frac{M_1 M_2}{M_1 + M_2}$$

EXAMPLE 6.1

Calculate where in the IR the characteristic absorption of the C≡O bond in carbon monoxide (CO) would occur.

1. Compute the reduced mass:

   for carbon

$$M_1 = \frac{12 \times 10^{-3}\ \text{kg/mol}}{6.02 \times 10^{23}\ \text{atoms/mol}} = 2.0 \times 10^{-26}\ \text{kg}$$

   for oxygen

$$M_2 = \frac{16 \times 10^{-3}\ \text{kg/mol}}{6.02 \times 10^{23}\ \text{atoms/mol}} = 2.7 \times 10^{-26}\ \text{kg}$$

$$\mu = \frac{(2.0 \times 10^{-26}\ \text{kg})(2.7 \times 10^{-26}\ \text{kg})}{(2.0 + 2.7) \times 10^{-26}\ \text{kg}} = 1.1 \times 10^{-26}\ \text{kg}$$

2. Substitute into the equation the following:

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} = 5.3 \times 10^{-12}\sqrt{\frac{k}{\mu}}$$

$$= 5.3 \times 10^{-12}\sqrt{\frac{1.5 \times 10^{3}\ \text{N/m}}{1.1 \times 10^{-26}\ \text{kg}}}$$

$$= 1.96 \times 10^{3}\ \text{cm}^{-1} = 1960\ \text{cm}^{-1}$$

This is a good approximation for the absorbance. CO (C≡O) experimentally shows an absorbance between 1900 to 2250.

■ Remote Measurements of Atmospheric Composition

A variety of spectroscopic techniques have been used to measure the Earth's atmosphere from space. Spectroscopic instruments look along the edge of the Earth's stratosphere (**limb paths**), downward (**nadir**) paths, or a combination of viewing geometry for occultation, emis-

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sion, and scattering experiments. In an **occultation experiment**, the sun or a bright star is observed as the line of sight from the object to the viewing instrument passes through the atmosphere. In an **emission experiment**, the radiation emitted by the atmosphere is observed. In a **scattering experiment**, solar radiation, which is scattered as it passes through the atmosphere, is observed. Space-based instruments have probed the atmosphere using UV, visible, infrared, and microwave radiation.

The geographic coverage of a satellite instrument depends on the orbit as well as the orientation of the satellite instrument with respect to the orbital plane. By adjusting the plane of the orbit, the period of precession can be made to be 1 year; in this way, the precession keeps up with the movement of the Earth in its orbit around the sun, and the orbit maintains a constant relationship to the sun. In this sun-synchronous mode, the observations can be made at, for example, local noon and local midnight around the orbit. Many of the atmospheric experiments use this mode so that geographic variation can be distinguished for diurnal (daily) variation. Figure 6.10 illustrates how satellites and Earth-based instruments are deployed to make measurements of atmospheric gases.

Atmospheric Trace Molecular Spectroscopy

Atmospheric trace molecular spectroscopy (ATMOS) was first flown on the Spacelab 3 Shuttle mission in 1985. On that first flight, 40 different gases were detected, and a database was constructed of trace gases in the stratosphere. The instrument was also able to detect and measure wind patterns in the mesosphere and troposphere. ATMOS has since flown several more shuttle missions. In 1992, ATMOS provided information about the Mount Pinatubo volcanic eruption and its effect on the atmosphere. On later flights, ATMOS detected dramatic increases in CFC gases that occurred in the stratosphere since its first flight in 1985.

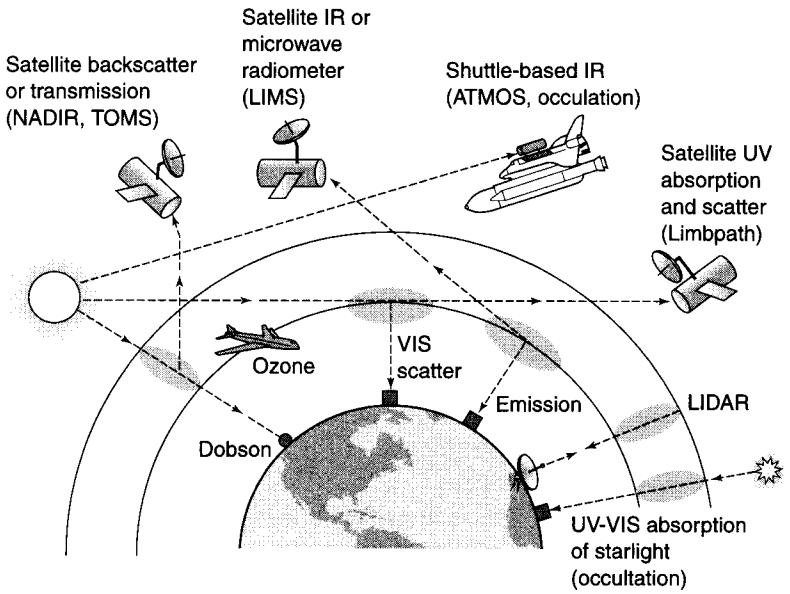

Figure 6.10 Some spectrometers are based on the Earth, and others are positioned on satellites.

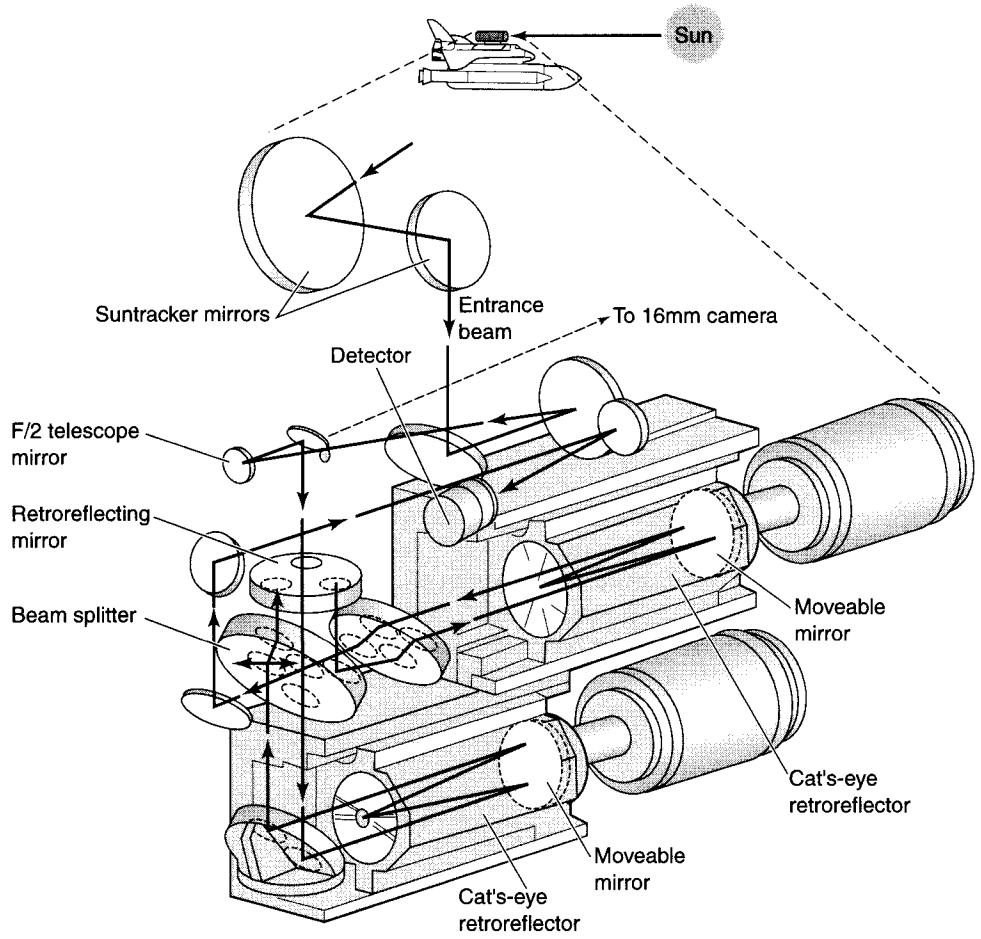

Figure 6.11 Schematic of the ATMOS IR spectrometer flown on the space shuttle. This spectrometer measures high-resolution atmospheric transmission spectra by observing sunlight that has passed through the atmosphere. Adapted from R. Zander, et al., 1996. Increase of stratospheric carbon tetrafluoride (CF_4) based on ATMOS observations from space. *Geophys. Res. Lett.* 23:2353.

Figure 6.11 shows a schematic of the ATMOS instrument, which is a high-resolution Fourier Transform IR spectrometer. The ATMOS has a sun tracker, which keeps the instrument's field of view on the sun, and a telescope, which collects the IR radiation to be processed by the spectrometer. The spectrometer simultaneously measures the concentrations of gases in the stratosphere at altitudes of between 10 and 150 km (6 to 96 miles). Because gas molecules absorb specific wavelengths of incoming solar radiation by determining the wavelengths that have been absorbed, the composition of the stratosphere can be determined. Because ATMOS has the ability to detect gases in concentrations lower than 1 ppb, its data have been used to test theoretical models that describe the chemistry of the stratosphere.

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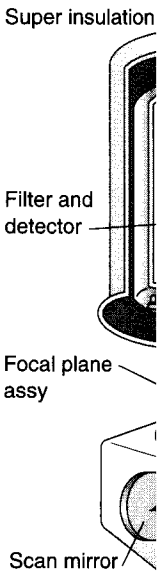

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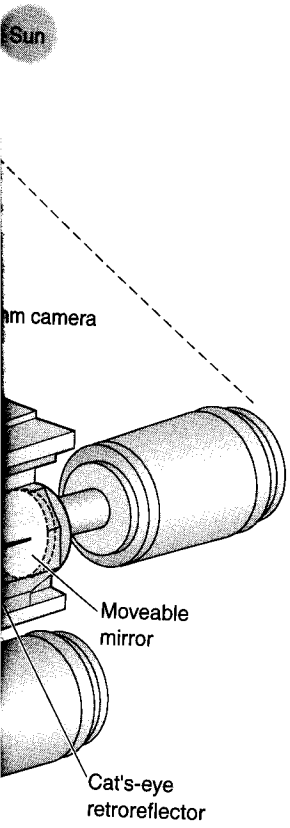

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The principal disadvantage of ATMOS for the study of stratospheric chemistry is the fact that it can make measurements at only sunrise and sunset. This means that at most 24 sunrises and sunsets are observed each day and that the measurement is local, not global. Many gases have diurnal variation because their production is dependent on photolysis by sunlight.

These disadvantages can be overcome by measuring atmospheric emission rather than absorption. Emission measurements may be made at any point on Earth and at any time of day.

Limb Infrared Monitor of the Stratosphere

The Nimbus 7 satellite, which was first used in 1978, used a **limb infrared monitor of the stratosphere** (LIMS) to measure the IR emission of the Earth. This polar-orbiting satellite is able to complete a picture of the entire stratosphere in 1 day. The IR emission depends on atmospheric temperature as well as on the composition of the atmosphere. The temperature is determined by measurement of the emission from a gas of known concentration, such as CO_2. The radiance of the thermal emission of the Earth's atmosphere is much less than that of the sun; therefore, it is necessary to use broader spectral bands for the measurement rather than a high-resolution spectrum.

A schematic of the LIMS instrument is illustrated in Figure 6.12. It used a telescope to collect infrared radiation from a limb view (at the edge) of the stratosphere. The IR radiation from five spectral bands was measured. This enabled LIMS to measure global distributions of trace gases with concentrations in the ppb range for the first time. The five gases measured were CO_2, O_3, H_2O, HNO_3, and NO_2.

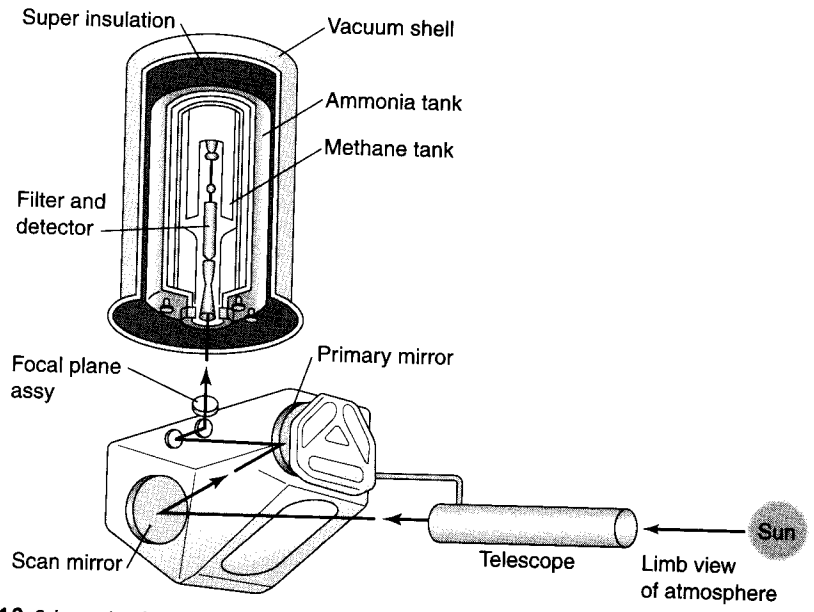

Figure 6.12 Schematic of the LIMS instrument flown on the Nimbus 7 satellite. This instrument measures the emission from the atmosphere in six infrared bands. From J. C. Gille and J. M. Russell III, 1984. The limb infrared monitor of the stratosphere: Experimental description, performance, and results. *J. Geophys. Res.* 89: 5125–5140.

Total Ozone Mapping Spectrometer

Unlike the previous two instruments, which operate in the infrared, the **total ozone mapping spectrometer** (TOMS) measures the total atmospheric ozone column by measuring the UV region in a range in which few other atmospheric molecules absorb strongly. The atmosphere scatters the UV radiation from the sun strongly; the combination of scattering and absorption allows the instrument to determine the concentration of ozone from the spectrum of the radiation reflected back into space.

The TOMS instrument (Figure 6.13) is a UV instrument that measures the albedo of the Earth at six wavelengths between 213 and 380 nm; a comparison of the radiation scattered back from the atmosphere with the incident solar radiation permits measurement of the ozone column.

The original TOMS gave the most complete global picture of the distribution of ozone and its change in concentration in the years from 1979 until its failure in 1992. Subsequent TOMS instruments are maintaining the long-term ozone record. Another important atmospheric gas (sulfur dioxide, SO_2) also has strong absorption in the UV region. TOMS has successfully tracked stratospheric clouds containing SO_2 from several volcanic eruptions.

Light Detection and Ranging

Light detection and ranging (LIDAR) is similar to radar. A radar transmitter sends radio waves, and the radar detector measures the time that it takes for them to bounce (scatter) off

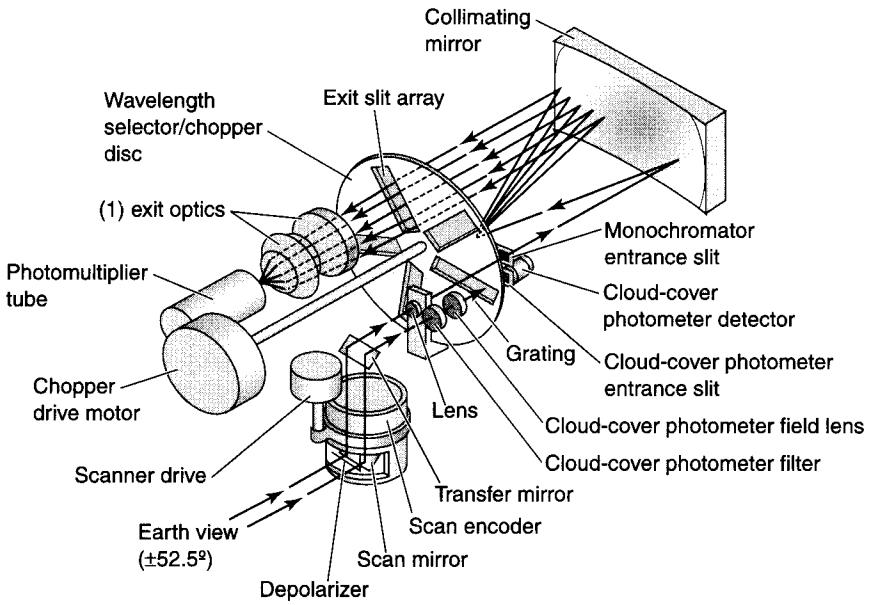

Figure 6.13 The TOMS UV photometer used to measure global distribution of ozone from the Nimbus 7 satellite. From D. F. Heath, A. J. Krueger, H. R. Roeder, and B. D. Henderson, 1975. The solar backscatter ultraviolet and total ozone mapping spectrometers (SBUV/TOMS) for Nimbus G. *Opt. Eng.* 14: 323–331.

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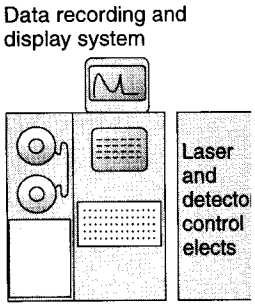

Figure 6.14 The LIDAR s
Proc. IEEE. 77: 419.

an object and return to the detector. LIDAR operates in the visible and infrared regions. Different types of physical processes in the atmosphere are related to different types of light scattering. The LIDAR system is usually Earth based, although a LIDAR system has been taken into space and has been operated on the space shuttle.

A simplified block diagram of a LIDAR system is shown in Figure 6.14. The LIDAR transmitter is a laser, and the receiver is an optical telescope that is focused on an extremely sensitive photomultiplier detector. This detector records the photons that reach it and converts the response to an electronic signal that is many times stronger. Some LIDAR systems use multiple lasers that operate at several different wavelengths simultaneously. The laser beam is shot into the atmosphere, and the detector measures the light that is scattered back. In one type of experiment called differential absorption LIDAR, a technique that is used to measure atmospheric ozone, the laser is sequentially shot into the atmosphere at two different wavelengths. The first laser pulse is at a wavelength at which ozone absorbs weakly. In the second wavelength, ozone absorbs strongly. The difference in the absorption of light at the two wavelengths can be used to determine the amount of ozone.

One of the most common applications of LIDAR is to detect aerosol particles in the atmosphere. Particles have a much larger scattering cross-section than do molecules, and if there are a substantial number of airborne particles, then the fraction of light scattered back to the detector is much larger than the return from gas molecules alone. In regions with high concentrations of particles, LIDAR determines the "backscatter ratio" or the ratio of observed backscattered signal to what would have been obtained from molecular scattering alone. Conversely, at altitudes in which the aerosol concentration is negligible, the variation of backscatter can be used for measurements of temperatures in the upper stratosphere and

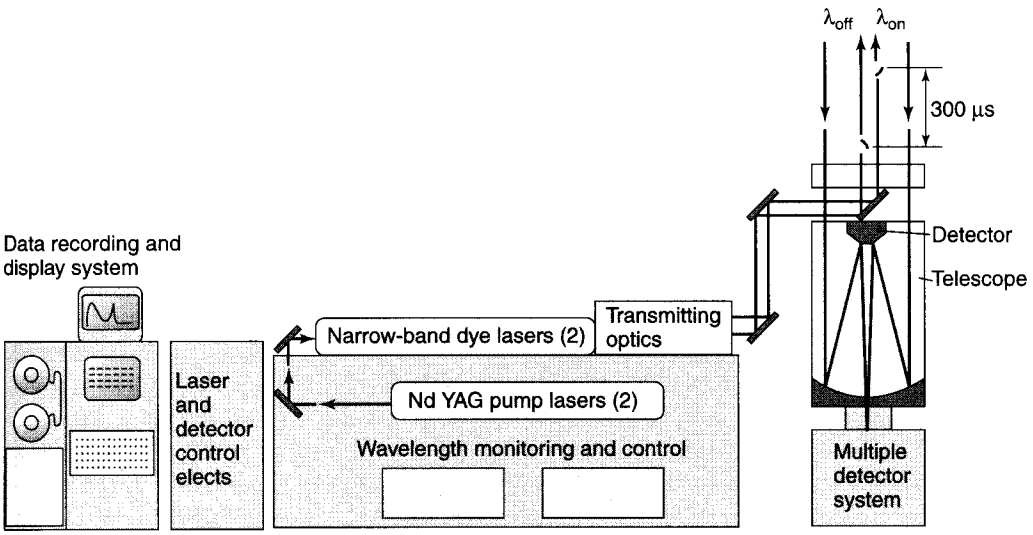

Figure 6.14 The LIDAR system. From E. V. Browell, 1989. Differential absorption LIDAR sensing of ozone. *Proc. IEEE.* 77: 419.

mesosphere, a height that weather balloons cannot reach. Measurement of the Doppler shift between the transmitted and received signals permits the measurement of wind velocity along the path of the laser beam.

■ Monitoring Automotive Emissions

Mobile sources of air pollution have a very large impact on our nation's air quality. For example, nationwide, highway motor vehicles contribute one quarter of all volatile organic compound emissions (but in some cities, such as Washington, DC, the contribution is even higher, approximately one half of all volatile organic compounds). Motor vehicles also contribute almost one third of the nitrogen oxide (NO_x) emissions nationwide and up to 62% of the CO emissions. It is clear that successful strategies for controlling mobile sources are essential to achieving clean air.

One of the major challenges that we are facing is that more cars are on the road today and are being driven more miles every year. Vehicle miles traveled (VMT) doubled from 1- to 2-trillion miles between 1970 and 1990. Also, according to a recent government study, over 25% of all trips are less than 1 mile, suggesting that many of us are becoming even more dependent on cars.

Looking into the future, according to EPA modeling, if we simply hold steady with the emission control programs in place today, in the year 2005, emissions will begin to rise again as VMT increases. Figure 6.15 shows that VMT will overtake current control technologies in the year 2005.

The second major challenge that we are facing is the problem of in-use deterioration. Although all new vehicles offered for sale must be designed and produced to meet emissions standards, actual in-use performance is not as good. Broken or malfunctioning parts or simply a lack of proper maintenance or repair too often results in vehicle emissions that are sig-

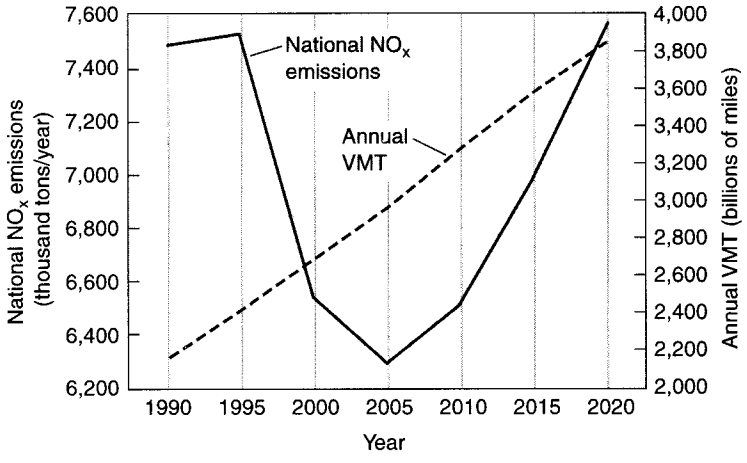

Figure 6.15 Growth in VMT and NO_x emissions.

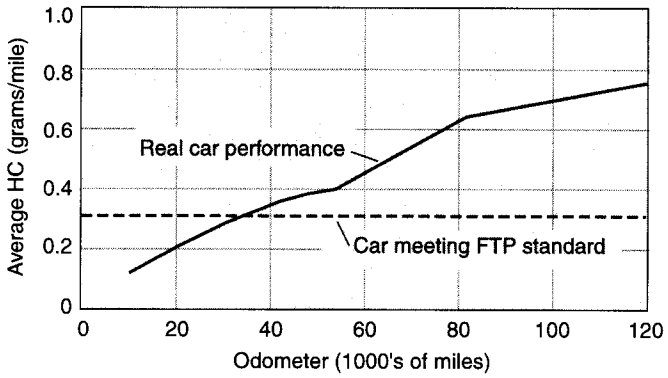

Figure 6.16 Emissions of HCs as an automobile ages.

nificantly above the standards. As can be seen in Figure 6.16, data show that hydrocarbon (HCs) emissions increase approximately 77% as a car is driven more miles. This type of increase is seen for other pollutants as well, demonstrating that in-use emission increases are responsible for more than 50% of total mobile source emissions.

The 1990 Clean Air Act called for enhanced inspection and maintenance programs in the most polluted areas of the country and has effectively improved the quality of air that we breathe. A 1996 study in Colorado of roadside emissions showed some interesting trends that were not evident. Emissions from old cars, which were expected to be the most polluting group, were often not as great as some new cars. As can be seen in Figure 6.17, the worst 20% of new cars pollute more than the best 40% of 20-year-old cars. Later inspection of these new car polluters showed that 41% had deliberately tampered with their emission control equipment and that 25% had defective or missing emission control equipment.

The techniques and equipment used to measure automotive emissions must be able to provide accurate, rapid analyses at a relatively low cost. The monitoring equipment must be extremely durable because it is housed in automotive garages and must be easily calibrated and remain stable for long periods. Although the operators performing the tests are trained, it is the instrument that is calibrating itself, making the measurements, and writing the test reports.

Automobile HCs

Internal combustion engines used in automobiles and trucks produce a complex mixture of organic molecules. The designs of the four-cycle internal combustion engine and the catalytic converter were discussed in Chapter 4. Depending on the air/fuel ratio of the engine and the compression ratio, more or less HCs are produced. The emissions contain saturated and unsaturated hydrocarbons, aromatic hydrocarbons, polynuclear aromatic hydrocarbons, as well as alcohols, aldehydes, ketones, and ethers.

A detector that will respond to almost all organic compounds that contain carbon–hydrogen bonds is the **flame ionization detector**, which uses a hydrogen/air flame to burn organic molecules in a sample, and as a result, it produces a current that is proportional to

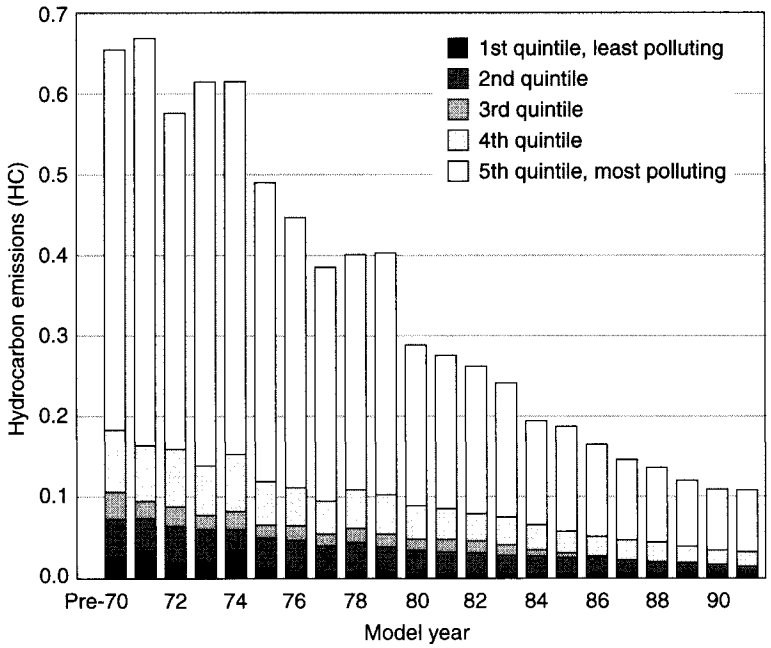

Figure 6.17 HC emissions from vehicles in California in 1991. From G. A. Bishop and D. H. Stedman, 1996. Measuring the emissions of passing cars. *Acc. Chem. Res.* 29: 489.

the carbon mass flow into the flame. A schematic diagram of the hydrogen flame detector can be seen in Figure 6.18. The dominant reaction that takes place in the hydrogen flame is as follows:

$$CH^{\bullet} + O^{\bullet} \rightarrow CHO^{+} + e^{-}$$

$$CHO^{+} + H_2O \rightarrow H_3O^{+} + CO$$

The most stable ion in a hydrocarbon flame is H_3O^+. The current generated by the detector is carried from the burner nozzle to the ion collector plate. There is an opposing recombination reaction that reduces signal output:

$$H_3O^{+} + e^{-} \rightarrow H_2O + H^{\bullet}$$

The applied voltage between the collector plate and the burner nozzle must be large enough so that the ions do not recombine before reaching the collector. When HC molecules enter the flame ionization detector, they are burned, and the current between the burner nozzle and the ion collector plate increases proportionally to the amount of HC that is present.

Most hydrocarbons (saturated, unsaturated, and aromatic) give the same relative response. Alcohols do not respond as well as hydrocarbons, and direct comparisons cannot be made for oxygenated fuels. A correction factor is incorporated for oxygenated fuels. Propane is used

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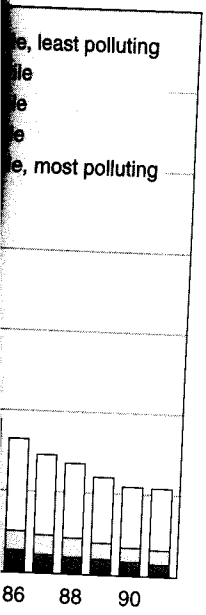

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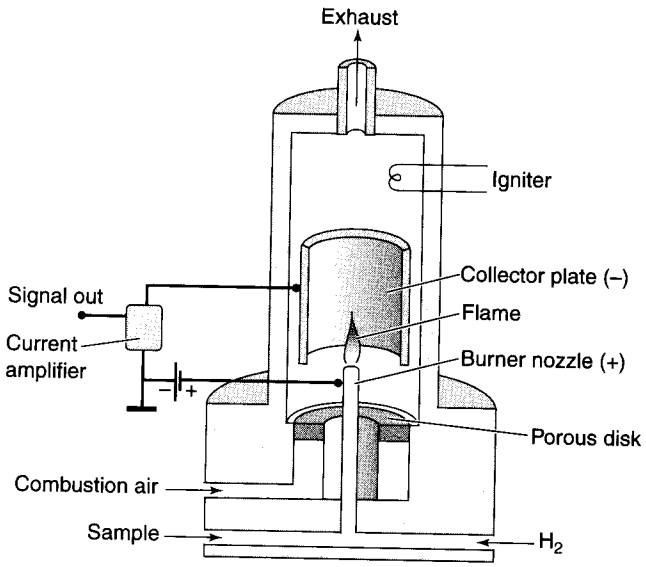

Figure 6.18 The flame ionization detector for measurement of hydrocarbons in auto tailpipe emissions. Courtesy of Horiba International Corp.

as a calibration gas. Because they do not burn, there is no direct interference from the other tailpipe gases: CO, CO_2, NO_x, and H_2O.

Automobile NO_x Emissions

The NO_x in automobile tailpipe emissions are measured by the use of **chemiluminescence**, chemical reactions that release energy produced by emitting light rather than heat. Fireflies use chemiluminescent reactions to produce light.

In this case, the NO in the tailpipe emissions is reacted with ozone. The energy produced in this reaction is released as light rather than as heat. The reaction is a two-step process. In the first step, the ozone reacts with the NO to produce an excited-state nitrogen dioxide molecule (NO_2*). The electrons in the NO_2* are not in the lowest energy state but are in an excited state. In the second step of the reaction, the NO_2* loses excess energy as the excited electrons return to ground state and emit the excess energy as a photon of light (hν). The reactions can be written as follows:

$$NO + O_3 \rightarrow NO_2^* + O_2 \text{ (chemical activation)}$$

$$NO_2^* \rightarrow NO_2 + h\nu \text{ (emission of light)}$$

Not all of the NO_x in the tailpipe is NO. Significant amounts of NO_2 are usually present as well. If the tailpipe sample is passed through a heated-activated carbon catalyst, the NO_2 can be converted to NO. The reaction is as follows:

$$NO_2 + C \rightarrow NO + CO$$

An analysis of tailpipe emissions that have been treated this way gives the amount of NO_x, which is the sum of NO and NO_2 present. To measure the amount of NO in the tail pipe gas stream, the carbon catalyst is removed from the stream. The difference between the two results gives the NO_2 present.

The NO_2* loses energy and gives off electromagnetic radiation in the 600- to 2500-nm range, with a maximum absorption at 1200 nm. The emitted light is measured by a photomultiplier; the intensity of light is proportional to the concentration of NO. An optical filter is placed between the reaction chamber and the photomultiplier to ensure that only light in the 600- to 2500-nm range reaches the detector. A diagram of the **chemiluminescent analyzer** (CLA) for NO_x is shown in Figure 6.19. The ozone used in the reaction is produced in a chamber just before the NO_x detector. In the ozone generator, air is irradiated with UV light to produce O_3.

The CLA is very dependable, has no moving parts, and is an ideal detector for continuous, rapid monitoring. There is no direct interference from the other tailpipe gases: CO, CO_2, HC, or H_2O.

Automobile CO Emissions

CO in tailpipe emissions is monitored by infrared spectrometry. The IR region is from 400 to 4000 cm^{-1}. Some of the gases, such as O_2 and N_2, which are present in tailpipe emissions do not absorb in the IR region. The wavelength of maximum absorption of the other individual tailpipe gases that do absorb in the IR is listed in Table 6.1.

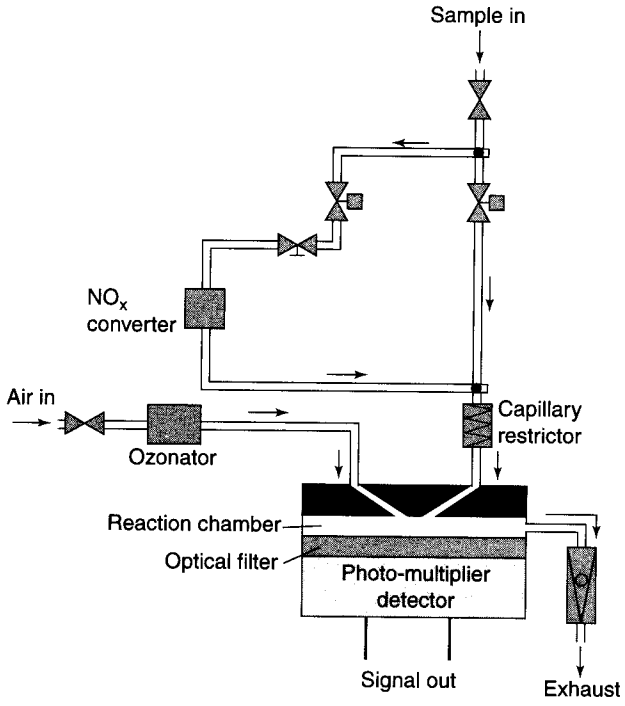

Figure 6.19 The CLA for NO_x emissions. Courtesy of Horiba International Corp.

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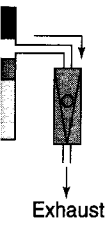

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Table 6.1

Wavelength of Maximum Absorbance of Tailpipe Gases

Molecule	λ (cm^{-1})
CO	2170
NO	1940
H_2O	3756, 1595
CO_2	2349, 1343, 667
NO_2	1665, 1358, 757
CH_4	3019, 2916, 1534, 1306

In a dispersive IR, the IR radiation from the source, which emits radiation across the 400- to 4000-cm^{-1} range, is dispersed by a grating into narrow bands of IR radiation. The instrument sequentially scans the IR recording absorption at each wavelength. After the data are recorded (approximately 20 minutes), it is presented as a spectrum, which is a graph of the absorbance versus wavelength. A dispersive IR is not used for measuring tailpipe emissions because it would take a dispersive IR too long to record the spectrum of a tailpipe sample.

CO emission monitoring uses a nondispersive infrared analyzer, NDIR. An NDIR analyzer differs from the dispersive IR spectrometer in that the radiation from the source is not dispersed by a grating. The NDIR analyzer is constructed for a specific analysis. A diagram of the NDIR instrument is shown in Figure 6.20.

The NDIR analyzer uses a heated tungsten filament, which is a broad-band source that emits across the IR region. The reference cell is filled with nitrogen, and the sample to be measured flows through the sample cell. A flexible diaphragm separates the two sides of the detector. Optical filters are placed between the IR source and the sample and reference cell to remove IR wavelengths that would be absorbed by CO_2 in the sample.

When a sample containing CO is present in the sample cell, IR energy from the source will be absorbed, and less IR energy will reach the sample side of the detector cell. The difference in IR energy reaching the two halves of the detector causes a small pressure imbalance between the detector cells, which causes the diaphragm between the cells to bend. A constant voltage applied between the detector plate and the diaphragm causes a current to flow when the distance changes.

The voltage output of the NDIR is nonlinear because of the absorption characteristics of gases. The cell absorption is related to cell length by Beer's law. A 30-cm pathlength is needed for measurement of ppm levels of CO. The speed of the response is limited by the flow rate and sample cell volume. As the cell pathlength is increased to give more sensitivity, the cell volume increases. Because the flow rate is kept constant, this means that the time it takes to measure each car (cycle time) must increase.

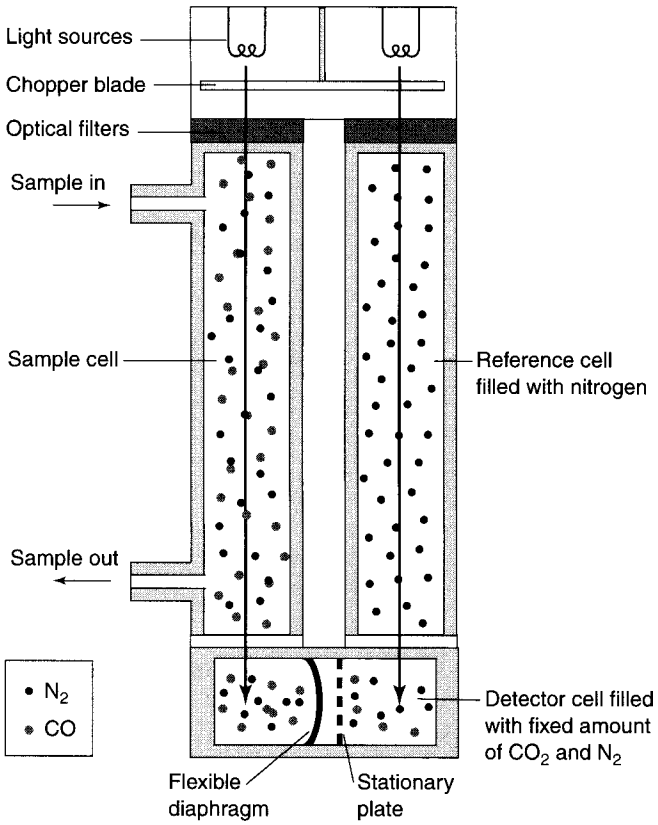
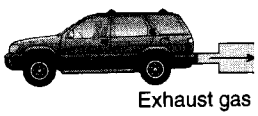


Figure 6.20 NDIR for the analysis of CO in automobile emissions. Courtesy of Horiba International Corp.

Automobile Emissions: Sample Handling

As anyone who has had his or her car's emissions tested knows that tailpipe emissions testing must be completed rapidly. The results of the emissions test are only as reliable as the sample that is taken. Because tailpipe emissions are exiting from the automobile at a extremely high velocity and at an elevated temperature, manufacturers of testing equipment have developed a sampling system that would decrease the velocity of the emissions while maintaining an elevated temperature. Manufacturers, such as Horiba, have developed a **constant volume sampler** (Figure 6.21). The exhaust gas from the tailpipe is diluted with filtered ambient air. This system uses a critical flow venturi to establish the flow rate. A constant flow is established through the venturi by a turbo compressor blower. The blower reduces the outlet pressure such that a choked condition occurs at the venturi throat. As long as this pressure is equal to or less than "critical" and a constant temperature is maintained, the flow rate through the venturi is constant. Knowing the inlet pressure and temperature, flow at standard conditions can be computed; the data system uses this information to determine the dilution that has been made and to compute the final concentration of HC, CO, and NO_x.



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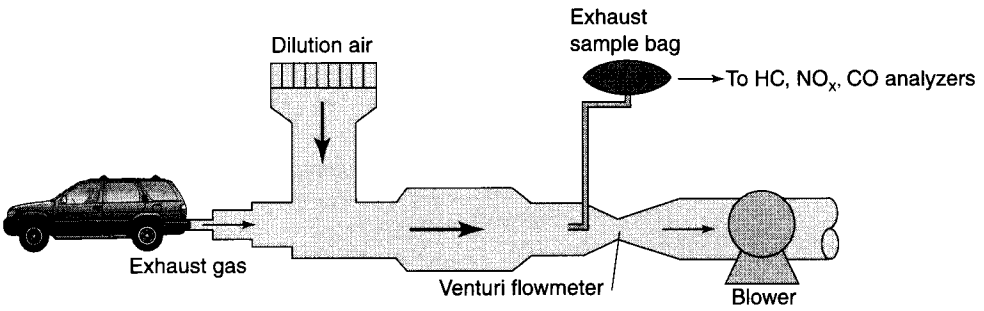

Figure 6.21 The Horiba constant volume sampler. Courtesy of Horiba International Corp.

■ Monitoring Emissions from Stationary Sources

The Clean Air Act of 1970 specified that the EPA design the National Ambient Air Quality Standards (NAAQSs) for criteria air pollutants. Criteria air pollutants are those whose permissible levels were based on health guidelines, or criteria, from air quality reports. NAAQSs were divided into primary standards, which were designed to protect the public health, particularly the people who were most susceptible to respiratory problems, such as those with asthma, the elderly, and infants. Secondary standards were designed to protect the public welfare (crops, visibility, and animals). The EPA was required to set primary standards based on health considerations alone, not on the cost of technology that would be required to meet the standard.

The six original criteria pollutants were CO, NO_2, SO_2, total suspended particulates (TSPs), HCs, and photochemical oxidants. Particulate lead was added to the list in 1976. O_3 replaced photochemical oxidants in 1979. HCs were removed from the list in 1983, and the TSP criteria were changed to include only particles with a diameter of 10 μm or less, which are called PM_{10}; a $PM_{2.5}$ standard (which is discussed later here) was added in 1997. Table 6.2 lists the current primary NAAQSs.

■ Monitoring SO_2 Emissions

The release of SO_2 to the atmosphere is the primary cause of acid rain in the United States. Fossil fuel combustion at electric power-generating plants accounts for nearly 75% of the SO_2 emissions; industrial sources contribute approximately 25%.

Coal frequently contains sulfur in the form of the mineral pyrite (FeS_2). Coal in the United States contains sulfur, typically between 1% and 4% by weight. When coal is burned, the sulfur is oxidized to SO_2.

The EPA method for analyzing the ambient air for SO_2 in determining compliance with the primary and secondary NAAQSs is described in the *Code of Federal Regulations*. The methods described in the *Code of Federal Regulations* have been shown to be useful for regulatory and legal purposes. When new methods are discovered, the EPA requires a careful examination of the performance of the new method by a carefully selected group of laboratories. A comparison of data obtained from the new method by each individual laboratory is made

Table 6.2

Current Primary Federal Air Quality Standards

Pollutant	NAAQSs
O_3	
1-Hour average	0.12 ppmv (235 μg/m³)
8-Hour average	0.08 ppmv (160 μg/m³)
CO_2	
1-Hour average	35 ppmv (40 mg/m³)
8-Hour average	9.5 ppmv (10.5 mg/m³)
NO_2	
Annual average	0.053 ppmv (100 μg/m³)
SO_2	
24-Hour average	0.14 ppmv (365 μg/m³)
PM_{10}	
24-Hour average	150 μg/m³
$PM_{2.5}$	
24-Hour average	65 μg/m³

against the results from the older existing method. Once the new method has been shown to be superior by giving lower detection limits, more precise results, or faster analysis, then the EPA proposes a modification of the method.

Pararosaniline Spectrophotometric Method for the Determination of SO_2

The EPA pararosaniline method will measure SO_2 concentrations between 0.01 to 5.00 ppm in ambient air. Figure 6.22 shows that an air pump with a constant flow rate pulls the air sample into an impinger and bubbles the air to be measured through a solution containing potassium tetrachloromercurate. The SO_2 present in the air stream reacts with the tetrachloromercurate solution to form a stable disulfitonatomercurate complex as follows:

$$HgCl_4^{2-} + 2\,SO_2 + 2\,H_2O \rightarrow Hg(SO_3)_2^{2-} + 4\,H^+ + 4\,Cl^-$$

The disulfitonatomercurate complex resists air oxidation and is stable in the presence of strong oxidants such as ozone and NO_x. During subsequent analysis, the complex is reacted with p-rosaniline dye and formaldehyde to form an intensely colored p-rosaniline methyl sulfonic acid. The concentration of this red-violet species is determined by measuring the absorbance at 548 nm. A Beer's law calibration curve is constructed by preparing standards with known concentrations of SO_2 and plotting absorbance versus concentration. The absorbance of an unknown sample is found by measuring its absorbance and by determining its corresponding concentration from the calibration curve. The absorbance is directly

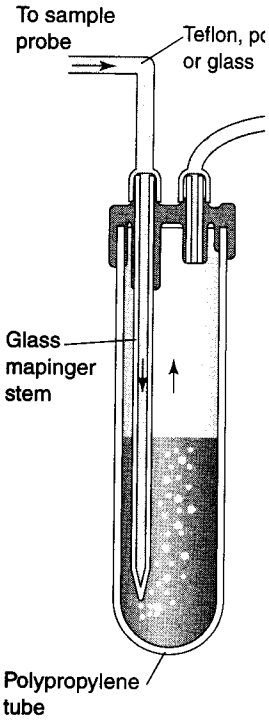

Figure 6.22 Collecting a sa

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■ Particulate

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The combustion of
was formed millions
The classes of coal are
to their heating value.
(FeS). These minerals

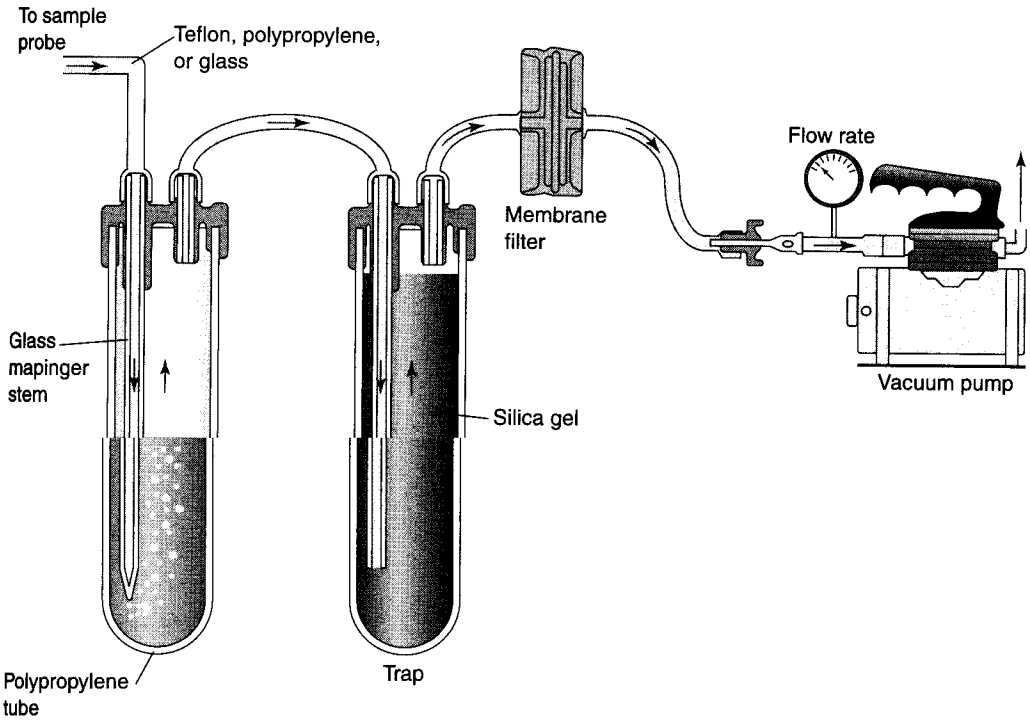

Figure 6.22 Collecting a sample for the pararosaniline spectrophotometric SO_2 method. Adapted from EPA. *CFR* 40.

related to the amount of SO_2 collected. The total volume of air sampled, corrected to EPA reference conditions (25°C, 760 mm), is determined from the measured flow rate and the sampling time. The concentration of SO_2 in the ambient air is expressed in micrograms per standard cubic meter ($\mu g/m^3$).

■ Particulate Emissions

Fossil Fuel Combustion

Fossil fuels are an anthropogenic source of particulate matter (PM). Coal, oil, natural gas, gasoline, and diesel fuel all produce some PM. Combustion of gasoline in an automobile engine emits particles of organic material (soot), Si, Fe, Zn, and S. Diesel-powered trucks emit 10 to 100 times more particulate material than do gasoline-powered vehicles; most of the PM is organic material from unburned fuel.

The combustion of coal releases soot, sulfate, and fly ash. Coal is a solid fossil fuel that was formed millions of years ago by compaction of partially decomposed plant material. The classes of coal are distinguished by their percentage of carbon, which is directly related to their heating value. Seams of coal also form with other natural minerals such as iron pyrite (FeS). These minerals are often occluded in the pieces of coal and are responsible for the