the noise thermometer is an ideal instrument for calibrating a secondary thermometer, such as a pressure thermometer, whose calibration can readily and accurately be transferred from one laboratory to another. Further instrumental development for millidegree applications seems unnecessary at present. Rather the major problems in millikelvin noise thermometry that require attention in the immediate future involve establishing thermal contact to the thermometer and reducing its thermal response time.

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Air Pollution Monitoring by Advanced Spectroscopic Techniques

A variety of spectroscopic methods are being used to detect air pollutants in the gas phase.

J. A. Hodgeson, W. A. McClenny, P. L. Hanst

Pursuant to the Clean Air Act of 1970, the Environmental Protection Agency (EPA) published national ambient air quality standards which established maximum acceptable concentrations of certain air pollutants in the various states and regions (*1*). Table 1 lists the primary ambient air quality standards for gaseous pollutants (*1*). Implementation plans to meet the air quality standards are required of the various states. Measurements to determine ambient pollutant concentrations are inherently required in this scheme for achieving air quality. Air pollution measurements are also required in determining the effectiveness of control technology to limit pollutant emissions, for the determination of long-term trends in pollutant concentrations, in studies of the effects of pollutants on health, and in studies of pollutant transformations in the atmosphere. In this article we survey the current and future role of spectroscopic methods in meeting the requirements for the measurement of air pollutants. Detection methods must be sufficiently sensitive and interference-free to permit the investigator to determine whether these standards are met.

Before 1970, requirements for the measurement of gaseous pollutants were largely met by the use of instruments which were automated versions of standard wet chemical procedures. Such instruments were complex and were characterized by high maintenance requirements and marginal sensitivity and specificity. Spectroscopic techniques, whether in emission or absorption, offer means for the direct and continuous detection of the pollutant in the gas phase. The absorption or emission characteristics can serve to identify a pollutant and to measure its ambient concentrations. Furthermore, spectroscopy offers means for the direct observation of pollutants at a point or over an extended path without the need for any intervening sampling apparatus.

Spectroscopic techniques were used quite early to identify molecular pollutants in the atmosphere. The earliest studies were of the transmission spectra of solar radiation through the earth's atmosphere (*2*). Characteristic spectra of molecules in the atmosphere appear as absorption bands in the solar spectrum. Infrared absorption, in combination with a multipass cell, was used in early laboratory studies to identify compounds present during the photochemical irradiation of auto exhaust (*3*). The same technique applied by Scott *et al.* (*4*) yielded the first spectroscopic confirmation of ozone (O_3) and the first evidence of peroxyacetyl nitrate (PAN) in the Los Angeles atmosphere.

These early studies were qualitative rather than quantitative in nature and were carried out by researchers using rather complex equipment. Yet they amply demonstrated the power of spectroscopic techniques for the study of polluted atmospheres. Although the potential of spectroscopic techniques was recognized during the 1950's and

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early 1960's, the techniques and instrumentation had not advanced to the point that would make possible the design of simple, specific, and sensitive spectroscopic sensors.

In more recent times, there has been a virtual renaissance in spectroscopic measurements of atmospheric pollutants. This revival of interest was instigated in part by the impending legislation and monitoring needs of the 1970's. Other major factors, however, have been the development of new spectroscopic techniques and the evolution of advanced optical components suitable for use in routine monitoring instruments. Gas-phase chemiluminescent techniques have evolved to meet certain specific and critical monitoring needs, for example, the atmospheric monitoring of O_3 and the oxides of nitrogen [nitric oxide (NO) + nitrogen dioxide (NO_2) = NO_x]. Infrared detectors and nondispersive infrared techniques have reached a high degree of sophistication. The availability of tunable visible and infrared lasers has opened up new possibilities for the remote sensing of pollutants. The miniaturization of electric components, for example, solid-state amplifiers and detectors, has made possible the development of compact and inexpensive optical monitors.

These new developments have had their greatest impact in the areas of chemiluminescence detection, infrared absorption techniques, and the remote sensing of pollutants over a long optical path. In the sections that follow we present a discussion of each of these techniques. The final section deals with recent developments in ultraviolet-visible fluorescence and absorption and microwave absorption techniques.

Chemiluminescence Techniques

Chemiluminescent reactions. The glow of the firefly is a familiar example of the chemiluminescence phenomenon, which now finds practical application in air pollution measurements. Chemiluminescence usually occurs during an exothermic chemical reaction in which some of the excess energy causes the excited electronic and vibrational states of reaction products to become populated. The decay of these products to the ground state may occur with the emission of radiation, $h\nu$.

Since the chemiluminescence emission spectrum is characteristic of reaction products or excited intermediates, chemiluminescence has long been used to study reaction mechanisms and reaction kinetics. Although the use of chemiluminescence in kinetics is a kind of analytical application, chemiluminescence techniques have only recently been used in conventional analytical problems such as atmospheric monitoring. Extensive analytical applications have appeared only during the past 5 years (*5, 6*).

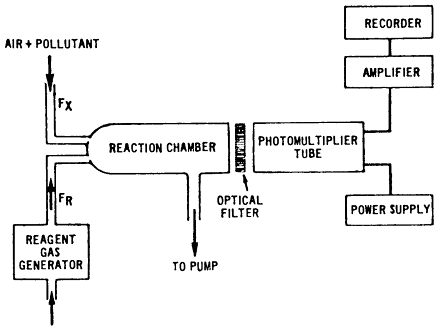

Fig. 1. Chemiluminescence detector; F_X, flow of pollutant; F_R, flow of reagent gas.

Our discussion of techniques below is limited to those involving ambient temperature chemiluminescent reactions between gas-phase species. This type of reaction has found the most widespread applicability in atmospheric monitoring. We do not include any discussion on flame chemiluminescence techniques, which are at present limited to the measurement of atmospheric sulfur compounds (*7*).

Chemiluminescence as an analytical technique. Chemiluminescence techniques for different molecules have some common characteristics in design and operation. Air containing the pollutant molecule of interest (X) is mixed in a flow reactor with an excess of a reagent gas (R), which reacts with X to yield an excited product, P:

$$X + R = P^*$$
$$P^* = P + h\nu$$

The intensity I of the chemiluminescence is directly proportional to the product of the reagent and pollutant concentrations, and is directly proportional to the pollutant concentration when the reagent concentration is constant and in excess:

$$I = k\,[R][X]$$
$$I = k'[X]$$

where $k' = k\,[R]$.

The integral components of a typical chemiluminescence detector are shown in Fig. 1. The reagent gas is often a reactive species, such as O_3 or atomic oxygen, which must be generated internally. Such species may be generated by electrical discharges or photochemical techniques. The optimum size and geometry of the reaction vessel depend on the reaction rate, the chamber pressure, and the sample flow rate. These parameters vary with different applications.

Interference or color filters are used to isolate a given spectral region and to prevent interferences from other chemiluminescent reactions of the reagent gas. Reagent gas is usually added to the chamber at a positive pressure from a cylinder. Chemiluminescent reactions involving atomic species as reagent must be operated at chamber pressures of a few torr, and mechanical vacuum pumps are required. Other chemiluminescent reactions may be studied at much higher pressures (100 torr to 1 atmosphere), and small, diaphragm type air pumps are adequate.

The basic electronics of the system consists of a photomultiplier tube, a high-voltage supply for the photomultiplier, an amplifier for the output current, and a recorder. The photomultiplier is a high-gain, low-dark-current tube, which should be selected to have good quantum efficiency over the region of spectral emission. Cooling of the photocathode by thermoelectric means is often used to obtain a low-dark-current background. At the present state of the art, solid-state detectors have insufficient sensitivity for the measurement of ambient concentrations of air pollutants. The amplifier is usually a d-c device capable of measuring anode cur-

Table 1. Primary ambient air quality standards.

Air quality standard	Concentration (in parts per million by volume)				
	NO_2	SO_2	O_3	CO	Hydrocarbons
Annual arithmetic mean	0.05	0.03			
Maximum 24-hour concentration*		0.14			
Maximum 8-hour concentration*				9.0	
Maximum 3-hour concentration*					0.24
Maximum 1-hour concentration*			0.08	35	

* Concentration not to be exceeded more than once per year.

rents in the range from 10^{-6} to 10^{-10} ampere. For most chemiluminescent reactions of present interest, the sensitivity is sufficient so that more sophisticated techniques, such as light chopping with synchronous detection or photon counting, are not warranted.

Chemiluminescence monitors have certain advantages and limitations. They inherently possess a high degree of sensitivity, specificity, and simplicity. With the use of high-gain, low-dark-current photomultiplier tubes, extremely low levels of chemiluminescence emission can be detected. In order for another molecule to be a positive interference in the chemiluminescence detection of X, it must react with the reagent gas, this reaction must be exothermic and produce chemiluminescence, and the chemiluminescence must overlap considerably with the spectral region in which X produces emission. Room-temperature chemiluminescent reactions are few, and, under the constraints above, interfering reactions are even more rare. A third component which quenches the excited state responsible for emission is a potential negative interference. In trace atmospheric detection, however, the predominant quenching agents are molecular oxygen (O_2) and molecular nitrogen (N_2), which do not vary in concentration. Chemiluminescence monitors can be simple and compact and can be constructed from commercially available components.

One limitation of chemiluminescence detection is a lack of general applicability. Although the list of applications to date is extensive, all molecules do not participate in chemiluminescent reactions. In common with most optical techniques, chemiluminescence detection is a nonabsolute method of measurement. In order to calibrate the output of any given detector, known concentrations of sample must be introduced.

Present applications. Gas-phase chemiluminescence techniques for the detection of O_3 and NO_x have been developed to an advanced stage. Detectors for these species are now commercially available and are being commonly used for routine monitoring. Although the currently available techniques are limited to the detection of O_3 and NO_x, this is a most important application. Early wet chemical analyzers for these pollutants were quite unsatisfactory. Furthermore, national ambient air quality standards (*1*) have been established for O_3 and NO_2, and routine monitoring of these pollutants is required in the states and regions.

The gas-phase chemiluminescence technique now used for O_3 was first described by Nederbragt *et al.* (*8*) and later by Warren and Babcock (*9*) for the measurement of O_3 in the vicinity of linear accelerators. In this technique a gas-phase reaction between O_3 and ethylene occurs at atmospheric pressure. The emission is a broad continuum centered at 435 nanometers (*10, 11*), which results from an emitting species believed to contain an excited carbonyl group (*10, 12*). Prototype "Nederbragt" detectors were constructed and evaluated by the EPA and were shown to have more than adequate sensitivity and specificity for ambient O_3 measurements (*10*). The Nederbragt method has been successfully applied in field applications and has been designated as the reference method for routine O_3 measurements required under recent federal air quality standards (*1*).

The simplicity of a typical Nederbragt detector is illustrated by the basic design shown in Fig. 1. A small-volume reactor (< 50 cubic centimeters) is used for mixing sample and reagent gas near the photocathode. The atmospheric pressure is maintained in the chamber. The sample flow used is about 10^3 cubic centimeters per minute, and the ethylene flow is approximately 10 cubic centimeters per minute. A filter is not required since no emission has been observed from the reaction of ethylene with other atmospheric pollutants. The photomultiplier response obtained is a linear function of the O_3 concentration over the range from 0.001 to 100 parts per million (ppm) [2 to (2×10^5) micrograms per cubic meter)].

The reaction between NO and O_3 produces near-infrared chemiluminescence:

$$NO + O_3 = NO_2^* + O_2$$

$$NO_2^* = NO_2 + h\nu$$

(spectral region, 0.6 to 3.0 μm)

This reaction may be used to detect either component when the other is present as excess reagent. The primary application has been for the detection of NO. The feasibility of building an NO detector based upon this reaction was initially demonstrated by Fontijn *et al.* (*13*). The NO chemiluminescence detector subsequently proved so successful in laboratory and field evaluations (*14*) that this detector has been applied to the measurement of total NO_x and NO_2 by means of a prior conversion of NO_2 to NO. Various techniques have now been devised whereby NO_2 may be quantitatively reduced to NO in a converter operated at elevated temperature (*15, 16*). The initial NO detectors operated at a reaction chamber pressure of a few torr and required mechanical vacuum pumps. In a recent development, ambient concentrations of NO were detected in a reactor cell operated at atmospheric pressure (*16*). Several commercial chemiluminescence NO_x models are being sold today, all of which operate at pressures of 200 torr or more and employ small diaphragm type air pumps. Chemiluminescence is now the reference method cited by the EPA for measuring NO_x in automotive emissions (*1*).

The typical commercial detector operates in a cyclic mode in which the incoming air sample alternately passes at 30-second intervals through the converter or a converter bypass line. Electronic subtraction of the NO signal from the preceding NO_x signal is used to generate an NO_2 output. One converter commonly used contains a carbon-based substrate maintained at 200° to 300°C. The O_3 generator is an electrical discharge unit which produces an O_3 concentration of about 0.5 percent (by volume). Sample flow rates for various units vary over the range from 10^2 to 10^3 cubic centimeters per minute. Chamber pressures range from 0.1 to 1 atmosphere. A cooled, infrared-sensitive photomultiplier must be used for the measurement of ambient concentrations. A cutoff filter is required to eliminate interfering emissions below 600 nanometers. The detector responds linearly to NO concentrations over the range from 0.001 to 10^4 ppm (1.3 to 1.3×10^7 micrograms per cubic meter).

Other potential applications. Many other chemiluminescent reactions are known that might be of potential use in air pollution monitoring. Techniques recently evaluated include the following: the photofragment detection of NO_2 (defined below); oxygen atom chemiluminescence for the detection of NO, sulfur dioxide (SO_2), carbon monoxide (CO), and hydrocarbons; and the detection of PAN with amines. Other chemiluminescent reactions of potential interest in air pollution monitoring are also suggested below.

The photofragment technique involves the detection of NO_2 by photolysis and the chemiluminescence detection of the resultant oxygen atom with NO used as reagent gas (*17*):

$$NO_2 + h\nu \text{ (310 to 400 nm)} = NO + O$$

$$O + NO + M = NO_2^* + M$$

$$NO_2^* = NO_2 + h\nu \text{ (400 to 1400 nm)}$$

where M represents a third component necessary in order that the reaction occur. This technique is of considerable interest since it makes possible direct NO_2 analysis as compared to the differential analysis discussed above.

A schematic of the experimental system used in the initial response studies is shown in Fig. 2. This is similar to the basic detector of Fig. 1 with the addition of a photolysis chamber upstream of the reaction chamber. A reduced chamber pressure of approximately 10 torr is used. The minimum detectable limit of NO_2 is 0.001 ppm (about 2 micrograms per cubic meter); the response is linear to greater than 1 ppm (about 2000 micrograms per cubic meter), and the response time is about 1 second. The potential interference from O_3 may be avoided by proper filtering of both the photolysis source and the photomultiplier.

Many atomic oxygen reactions produce chemiluminescence. The use of oxygen atoms as reagent for multipollutant detection was investigated by Snyder and Wooten (*18*). In addition to NO_x, CO and SO_2 were detected on the basis of their reactions with oxygen atoms:

$$O + O + SO_2 = SO_2^* + O_2$$
$$SO_2^* = SO_2 + h\nu \ (\lambda_{max} = 280 \text{ nm})$$
$$O + CO + M = CO_2^* + M$$
$$CO_2^* = CO_2 + h\nu \ (\lambda_{max} \simeq 400 \text{ nm})$$

In the detection of NO_x, any NO_2 present is rapidly converted to NO by the rapid gas-phase reaction

$$O + NO_2 = NO + O_2$$

Thus NO_2 is converted in situ to NO, and the emission intensity is proportional to the total NO_x concentration.

In the feasibility study, a microwave discharge of O_2 in argon was used as a high-concentration source of atomic oxygen. The minimum detectable limits obtained were approximately 0.005 ppm (about 10 micrograms per cubic meter) for NO_x, 0.001 ppm (3 micrograms per cubic meter) for SO_2, and 100 ppm (10^5 micrograms per cubic meter) for CO. The sensitivity obtained for CO was inadequate for atmospheric monitoring. The sensitivities obtained for NO_x and SO_2 are quite promising. Applications have not yet been pursued, primarily because of problems attendant with the long-term operation of currently available atomic oxygen sources (*6*).

Hydrocarbons react with oxygen atoms to produce chemiluminescence from the ultraviolet region to the near-infrared (*19, 20*). The emission results from excited radicals such as OH, CH, C_2, and HCO, which are produced by complex paths which are not fully known. The emission obtained with hydrocarbons is probably too general to be useful for the detection of individual hydrocarbons or even classes of hydrocarbons. Krieger *et al.* (*20*) have suggested that the intensity of the Meinel bands (near-infrared OH emission) may provide a useful index of photochemically reactive hydrocarbons in the atmosphere. The rationale was that the emission intensity depends upon the rate of attack of oxygen atoms on hydrocarbons and that the intensity would therefore provide a useful index of the hydrocarbon reactivity in photochemical smog systems. Although this is certainly a novel suggestion, more effort will be required to correlate such an index with other classical measures of hydrocarbon reactivity.

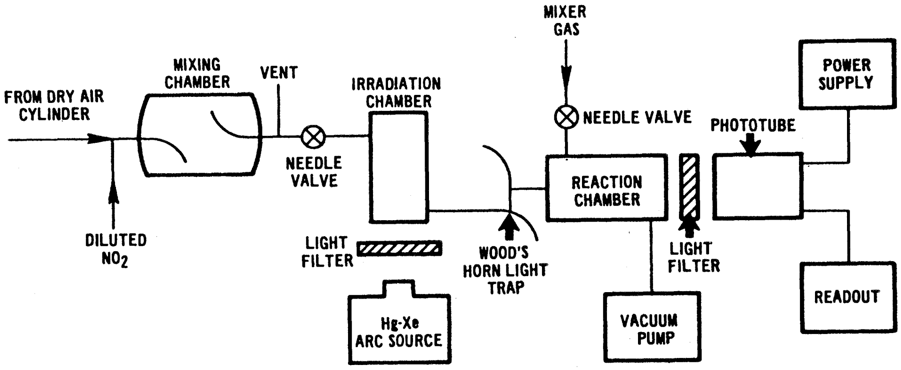

Fig. 2. Photofragment NO_2 detector.

In a recent publication, Pitts *et al.* (*21*) reported a new chemiluminescent reaction between PAN and triethylamine. The reaction yields a broad-band emission with a peak at 665 nanometers. The mechanism of the reaction is unknown, but the analytical potential is certainly evident. With a laboratory detector, Pitts *et al.* reported an initial sensitivity for PAN detection of 0.006 ppm (3 micrograms per cubic meter).

Kummer and his co-workers have also observed chemiluminescence from the gas-phase reactions of O_3 with a variety of compounds, including hydrogen sulfide (H_2S) and organic sulfides, and have suggested that this chemiluminescent reaction be used for measuring atmospheric sulfur compounds (*11*). The emission observed in their experiments from both H_2S and organic sulfides was due to electronically excited SO_2. Therefore, the use of O_3 as reactant gas should lead to a nonspecific detector for gas-phase sulfur compounds.

Zare and his co-workers (*22*) have observed chemiluminescence in crossed molecular beam experiments involving group II alkali metal atoms and some molecules of interest, for example,

$$Ba + NO_2 = BaO^* + NO$$
$$BaO^* + NO = BaO + NO + h\nu$$
$$Ba + Cl_2 = BaCl_2^* = BaCl_2 + h\nu$$
$$BaCl_2^* = BaCl^* + Cl = BaCl + Cl + h\nu$$

Intense emission is obtained in the visible region which may be useful for detecting NO_2 and molecular chlorine (Cl_2). However, the requirements for reactive alkali metal vapor and high vacuum operation would complicate routine applications of this type of reaction.

Detailed general reports on chemiluminescence (*6, 23*) have appeared which describe many reactions that may be of potential interest. Hydrogen atoms produce near-infrared chemiluminescence in the reaction with NO_x by a mechanism analogous to the $O + NO_x$ chemiluminescence:

$$H + NO_2 = NO + HO$$
$$H + NO + M = HNO^* + M = HNO + M + h\nu \ (650 \text{ to } 760 \text{ nm})$$

Hydrogen atoms also quite efficiently produce vibrationally excited products and infrared chemiluminescence upon reaction with molecules such as O_3 or Cl_2:

$$H + O_3 = OH^* + O_2$$
$$H + Cl_2 = HCl^* + Cl$$

Solid-state detectors would be required to observe the HCl emission, and sensitivity may be a problem. "Active" nitrogen from an electrical discharge contains atomic nitrogen and electronically and vibrationally excited N_2. This is another potential reagent gas which commonly produces chemiluminescence upon reaction with hydrocarbons and halogenated compounds.

The above list of reactions is by no means inclusive and is intended only to illustrate the potential scope of chemiluminescence techniques in air pollution monitoring. Furthermore, in the above discussion we have considered only gas-phase chemiluminescence. In liquid- and solid-phase media, numerous chemiluminescence reactions are available which may provide solutions to other environmental monitoring problems.

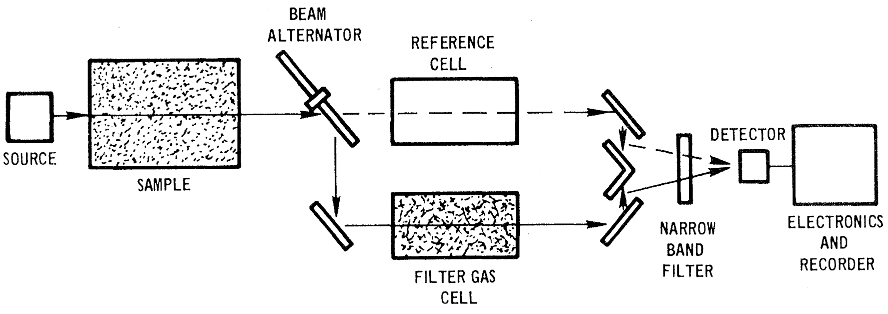

Fig. 3. Nondispersive analyzer.

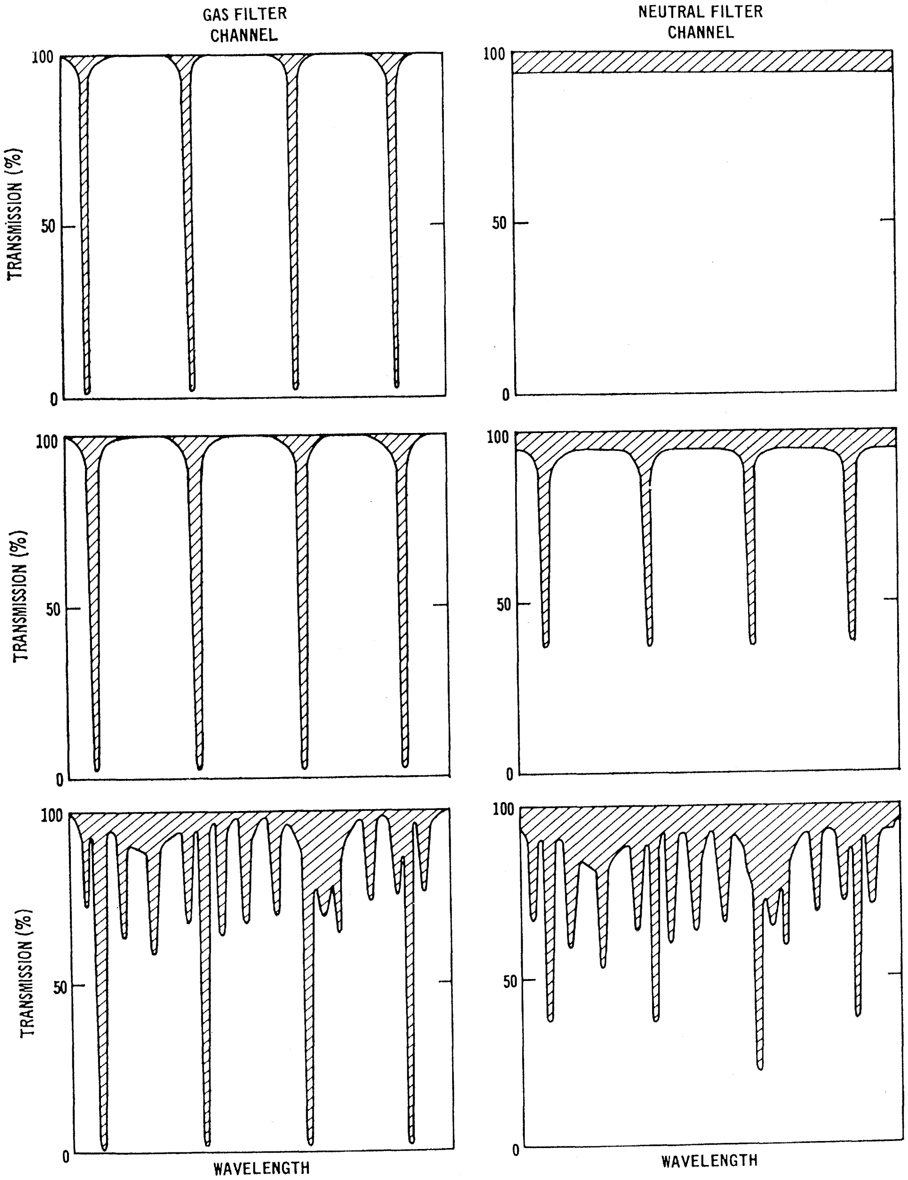

Fig. 4. Absorption in two channels of a nondispersive analyzer. (Top spectra) Balance when absorbing sample is absent. (Center spectra) Unbalance due to the introduction of matching absorption lines by the sample. (Bottom spectra) Retention of unbalance when nonmatching spectral lines are added.

Infrared Absorption Techniques

The infrared vibration-rotation spectrum includes one distinctive band or more for nearly every significant gaseous air pollutant. This region of the spectrum has been used in pollution research by many groups of experimenters during the past 20 years (*4, 24, 25*). During that time, improvements in the instrumentation have made possible a great increase in the sensitivity of the laboratory infrared methods. In a recent article on the use of the Fourier transform spectrometer in pollution studies Hanst *et al.* have discussed many of the recent improvements (*25*). The incorporation of new developments into instruments for routine monitoring has been slow, but the effects of new developments are being felt now and should be more pronounced in the near future.

For ambient air monitoring, the most promising type of infrared instrument appears to be the nondispersive analyzer. Several new types of such analyzers have been developed. The Andros instrument for CO detection monitors the effect of atmospheric CO absorption on the ratio of transmitted infrared fluorescence from CO absorption cells containing two different isotopic species (*26*). The UNOR instrument for CO, NO, and other gases uses a new configuration of pneumatic detector, which observes the ratio between the absorption in the wings of the spectral lines and the absorption in the centers of the lines (*27*). An instrument being built by JRB, Inc., for the National Aeronautics and Space Administration can detect several pollutants by a gas-filter correlation technique based on the spectral fine structure of a number of compounds in filter cells (*28*). An instrument proposed by Goody would use a pressure-modulated, gas-filled cell to produce alternations in the absorption of the spectral lines (*29*). All of these new techniques show gains in selectivity and sensitivity by comparison with older types of nondispersive analyzers.

The principal problems limiting the use of nondispersive methods have previously been the requirement for multiple-reflection cells to measure ambient concentrations and the water vapor interference in the detection of several pollutants. These difficulties are being ameliorated by improvements in the optical, mechanical, and electronic aspects of instrument design. Further improvements are easily foreseen.

Operating principles of nondispersive analyzers. A nondispersive correlation method is diagrammed in Fig. 3. In the laboratory, the radiation source would be a hot wire or other thermal emitter. The sample could be enclosed in a single-pass cell or a multiple-pass, long-path cell. In the field, the radiation source could be the sun and the sample could be the open atmosphere. After the radiation has passed through the sample, it is directed alternately through the filter gas cell and the reference cell and then through the band-pass filter to the detection system. The only moving part in the system is the beam alternator, such as a rotating chopper, a vibrating tuning fork, or an electro-optic switch.

The operating principle of the system is illustrated by the drawing of a typical portion of spectrum in Fig. 4. The absorption spectra of the two filter channels are shown at the top. The left channel contains the gas filter that introduces the absorption lines into the continuum. The right channel contains a neutral filter that has been adjusted to yield the same total absorption as the left channel. As the detection system alternates between channels, it "sees" constant intensity. The center spectra in Fig. 4 show the absorption changes that occur when matching spectral lines appear in the incident radiation. The intensity transmitted by the left channel is not changed appreciably, whereas the intensity transmitted by the right channel is decreased. The detection system now "sees" unequal intensities that appear as an alternating signal at the channel-switching frequency. The lower spectra in Fig. 4 show the intensity changes that occur when the nonmatching spectral lines of a second compound appear in the spectrum. These lines reduce the energy by the same proportion to each side, and the second compound is not seen. Continuum absorption, scattering by particles, or soiling of the sample cell windows will likewise leave the balance between the two channels undisturbed. The band-pass filter passes a spectral region chosen for maximum detection sensitivity and discrimination against interferences and blocks all unwanted light.

Discrimination against interferences. The degree of interference from other components depends on the distribution of absorption lines across the spectrum and the width of the spectral region under study. If a spectral line of the interfering gas falls on top of one of the lines of the compound to be measured, the interference is positive. If the interfering line falls between the lines of the compound to be measured, the interference is negative. Over a wide enough spectral region, positive and negative interferences may cancel. Systems of the type shown in Fig. 3 have been used to measure atmospheric CO, carbon dioxide (CO_2), and methane in the presence of each other along with water and nitrous oxide (N_2O). One can measure NO_2 and formaldehyde in the region from 2700 to 2900 cm^{-1} using bands which are overlapped by the hydrocarbon C–H band. The system diagrammed might *not* have sufficient discrimination to deal with more serious cases of interference such as those between water and NO in the region from 1800 to 2000 cm^{-1} or water and sulfur dioxide in the region from 1330 to 1390 cm^{-1}. For these cases there are several ways of obtaining a higher degree of discrimination against interference.

The discrimination is higher when there is more fine-line structure in the spectra. By pressure reduction, individual absorption lines are made narrower and stronger at the center; but the extent to which the overall absorption band changes depends on the spacing of the individual absorption lines. When there are hundreds of lines per wave number, as with larger pollutant molecules, the fine-line structure is obtained only at a pressure of a few hundredths of an atmosphere. When there are few lines per wave number, as with some lighter pollutant molecules, the spectrum may be continuous at a pressure of 1 atmosphere but will break into individual lines when the pressure is reduced to 0.25 atmosphere. This effect is illustrated in Fig. 5 for a pollutant with seven lines spaced 0.1 wave number apart. Pressure reduction will fail to yield fine structure only when the lines are closer together than their Doppler width, which in the infrared vibration-rotation spectrum is on the order of 0.001 wave number. Pressure reduction reduces molecular concentration. Thus, while the discrimination is being increased, the detection sensitivity is being reduced and longer optical paths are required.

Another way of increasing the discrimination between the gas being measured and the interfering gases is to use gas-filled filter cells at two different pressures and path lengths. The lower pressure cell (longer path length) has narrower but more intense absorption lines than the higher pressure cell. Detecting the gas under study involves a comparison of the line wing absorption to the line center absorption. The spectral regions between the lines then do not contribute to the measurement, and the number of interfering lines is greatly reduced.

Still another way of increasing the discrimination is to use as a radiation source a heated sample of the species of gas to be measured. Since the emission spectrum matches the absorption spectrum very closely, the spaces between the lines are again removed from consideration. A further advantage of the heated gas as a source is that the

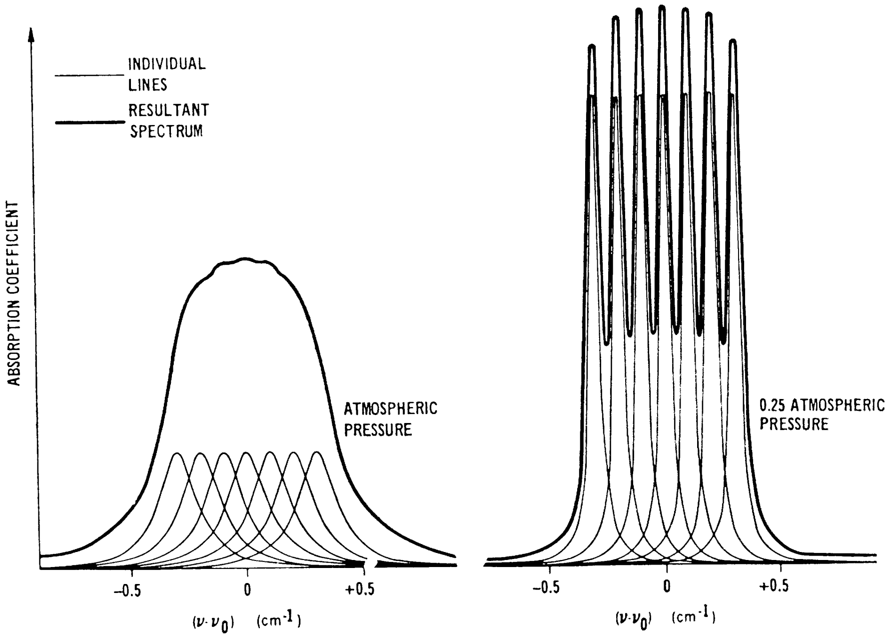

Fig. 5. Effect of pressure reduction on band fine structure.

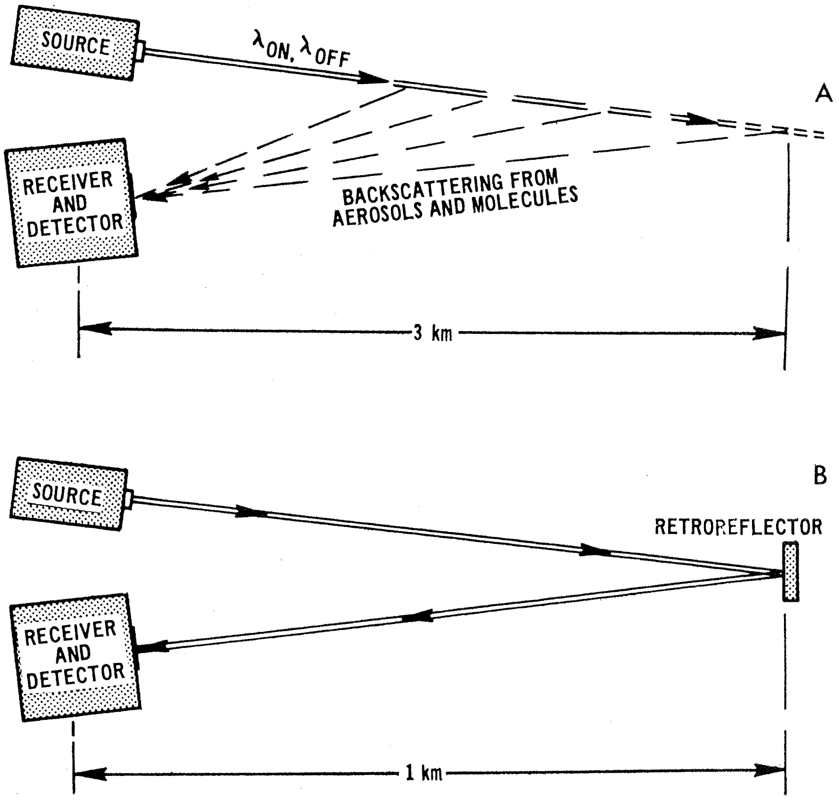

Fig. 6. (A) Differential absorption and scattering configuration. (B) Direct absorption configuration.

apparent absorption coefficient becomes much higher as a result of the good spectral match.

The use of heated gas as a source should also make it possible to conduct a nondispersive analysis even in those cases when the spectrum is only an envelope of many overlapping lines. For example, formic acid has a band centered at about 1100 cm^{-1}, which has no serious interferences, and a high degree of discrimination is not required. If the characteristic shape of the band appears both in the source and in the filter medium, the system should have a high enough degree of discrimination to permit measurements at atmospheric pressure. Similarly, nitric acid may be detected by means of its band at 880 cm^{-1} and so may other large molecules which do not have spectral fine structure at useful pressures.

Path length considerations. The length of the optical path required for the absorption experiment depends on the concentration of material to be detected, the absorption band strength, and the design of the optical system. To calculate the required path, the level of unbalance between the sample beam and the reference beam that the detection system can measure must be known. This detectable signal will clearly be a function of such factors as the source stability, the detectivity of the sensing element, and the amount of energy impinging on the sensing element. This latter factor is especially high for the nondispersive analyzers because of their large energy throughput. One can reasonably expect to observe a signal fluctuation, at the beam switching frequency, which is only one ten-thousandth of the total signal. The absorption equation,

$$\ln I_0/I = \alpha c \ell$$

then is expressed as:

$$10^{-4} = \alpha c \ell$$

If c is the concentration in fractions of 1 atmosphere, and ℓ is the sample path in centimeters, the effective absorption coefficient, α, might in a typical case have a value of 30 cm^{-1} atm^{-1}. For the limiting value of c to be 10^{-7} atmosphere, the required value of ℓ is then 30 centimeters. This illustrative calculation is reasonable in light of the commercially available Andros instrument for CO. That instrument can measure CO down to 10^{-7} atmosphere, using a path of 50 centimeters. The long sample paths needed for still greater sensitivity can be achieved by folding the light beam between mirrors (*2*).

Laser radiation. A laser can serve a a light source in a nondispersive analyzer if the laser emission line falls on one of the absorption lines of the compound to be measured. Preferably the laser should switch between two frequencies—one which is absorbed and one which is not. The presence of the compound to be detected will then change the ratio of intensity between the two laser lines. Such a system may not discriminate against interferences as well as a nondispersive analyzer which operates on a wide region of the spectrum.

The use of lasers also makes feasible a new technique for bringing out weak bands without requiring a long optical path. In this new method, one monitors the absorption per unit volume rather than the transmission. This technique has been outlined by Kerr and Atwood (*30*). They named their instrument the laser illuminated absorptivity spectrophone. By using a pulsed laser or by chopping a continuous laser beam at audio frequencies, a sound wave is created in the absorbing sample. This can be picked up by a microphone; the signal can be increased by raising the power of the source while holding the path length constant. With lasers of moderate size, one can measure absorptivities as small as one part in 10^7 per centimeter. A similar system has been used by Kreuzer and Patel to measure NO in an air sample (*31*).

Absorption Techniques for Remote Sensing

A remote-sensing technique pioneered by Schotland and his co-workers (*32*) has recently been predicted (*33, 34*) to be capable of measuring less than 1.0 ppm of NO_2, CO, and SO_2 with a spatial resolution of 15 meters and a range exceeding 1.0 kilometer. Called differential absorption and scattering (DAS), the technique operates as shown in Fig. 6A. A wavelength-tunable laser pulse (10 to 100 millijoules) is backscattered from atmospheric aerosols (Mie scattering) or atmospheric gases (Rayleigh scattering), or both. The backscattered radiation is collected with telescopic optics and monitored with a sensitive detector. The ratio, R, of this signal to the transmitted pulse signal is such that

$$R \sim \exp[-2(\alpha_0 L + \sum_m \alpha_m \int_{\ell=0}^{L} c_m d\ell)] \tag{1}$$

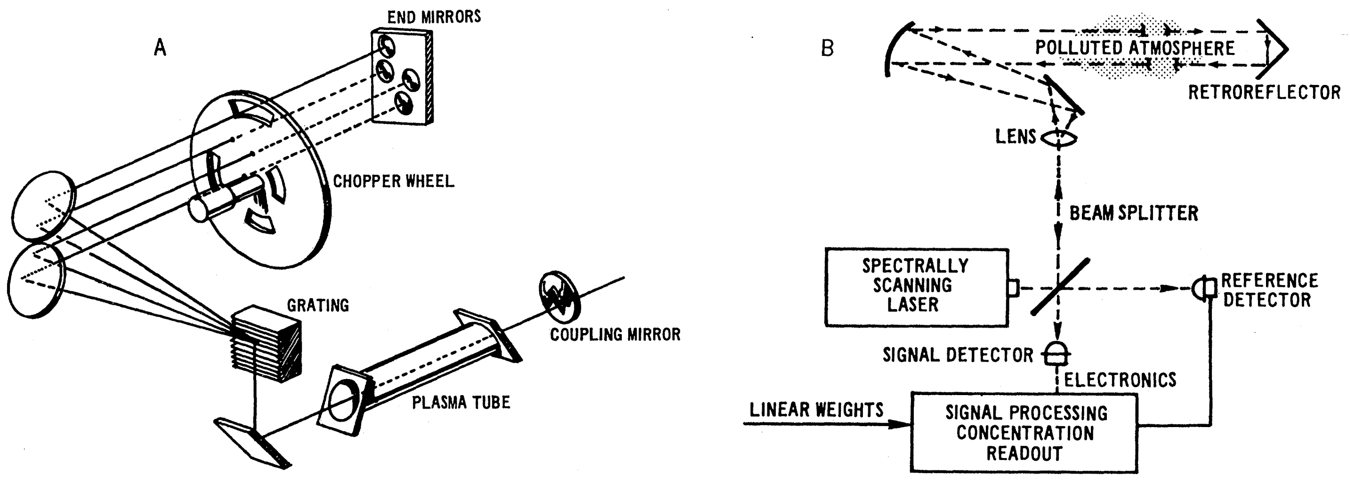

Fig. 7. (A) Spectrally scanning laser. (B) Direct absorption system incorporating spectrally scanning laser.

where L is the distance to the backscattering pulse, α_0 is the scattering coefficient, and α_m denotes the absorption coefficient of one of m molecular species. If no interferences are present, that is, if $m = 1$, and if α_0 is independent of wavelength, two wavelengths will be sufficient to determine the target gas density. One wavelength, λ_1, usually is chosen to coincide with an absorption maximum and the other, λ_2, with a minimum. The average density over distance ℓ is then

$$c \equiv L^{-1} \int_{\ell=0}^{L} c(\ell) d\ell = L^{-1} (\alpha_2 - \alpha_1)^{-1} \ln (R_1/R_2) \qquad (2)$$

where subscripts 1 and 2 refer to quantities associated with λ_1 and λ_2. By differentiating with respect to distance, the spatial profile of concentration is obtained.

For direct absorption methods, such as represented in Fig. 6B, a retroreflector is placed to reflect the source radiation. The average density over a total path L is identical in form to that given in Eq. 2. However, R now denotes the ratio of the transmitted to the received beam energies. Comparison of DAS and direct absorption methods shows that DAS provides ranging capability by time-of-flight measurement, spatial resolution, and a three-dimensional, single-ended measurement capability. The direct absorption method is simpler in that many of the low-power laser and broad-band sources presently available can be used.

Two other interesting techniques have been suggested. Zaromb (*35*) has proposed a technique similar to DAS in which the backscattered signal is due to Raman scattering from atmospheric N_2 and O_2. In this case the laser pulse generates a return at a number of wavelengths which are dispersed at the receiver prior to detection. If two of these wavelengths lie along a gradient in the absorption spectrum of the target gas, relative signal returns can be processed to give information equivalent to that with DAS. Byer and Garbuny (*34*) have conducted a detailed analysis to show the feasibility of using topological reflectors in direct absorption systems. Under typical visibility conditions, they predict that a uniformly dispersed NO_2 concentration of 0.1 ppm can be detected over a path length of 6 kilometers with no more than a 10-millijoule transmitted pulse. Surprisingly, DAS has not been used experimentally for the detection of trace gases, although a tunable source, an organic dye laser, is readily available for the detection of NO_2 with the use of visible absorption and makes such a demonstration an imminent possibility.

Recent direct absorption experiments have involved coincidence absorption by trace gases of gas laser lines in double-ended experiments. The collimated beam and high power densities available with lasers make possible measurements over a more extended path length. Hanst and Morreal (*36*) and Jacobs and Snowman (*37*) recognized this possibility and placed emphasis on the coincidence of gas laser lines with characteristic "fingerprint" spectra of gases in the wavelength region from 2 to 15 micrometers. Snowman and Gillmeister (*38*) have discussed a system in which 4 of some 60 available lines from the $^{12}C^{16}O_2$ laser are used to monitor trace concentrations of ethylene and ammonia (NH_3). Their experimental arrangement is shown in Fig. 7A. The CO_2 lines were dispersed by an intracavity reflection grating. The four wavelengths were obtained by use of a mechanical chopper which sequentially exposed mirrors placed beyond the grating. These mirrors complete the resonant cavity of the laser. The system sensitivity to concentrations of ethylene and NH_3 was approximately 0.02 ppm (about 20 micrograms per cubic meter) as determined by calibration cells, which were placed to intercept a measurement path of approximately 4 kilometers. Measurements of dispersed pollutants at this concentration have not, however, been demonstrated. A system incorporating two frequency-stabilized CO_2 lasers measuring simultaneously is being tested by Hidalgo and Christy (*39*). They have measured the absorption coefficients of O_3 at CO_2 laser lines (00°1 to 02°0 band) P-10 → P-36 in the 9.5-micrometer spectral region. For a 1 percent absorption differential and no interferences, the values for the pair of lines P-14 and P-24 indicate a sensitivity for O_3 of 0.010 ppm (20 micrograms per cubic meter) over a total path length of 2.0 kilometers. Other gas lasers have coincidences with absorption bands of pollutant gases (*2*) or can be moved into coincidence by Zeeman splitting. This latter approach has been used successfully by Linford (*40*) to tune xenon laser wavelengths several angstroms through absorption gradients of formaldehyde.

Hinkley and Kelly (*41*) and Hinkley (*42*) have discussed the application of tunable diode lasers to air pollution problems, and direct absorption measurements of SO_2 across industrial stacks have been demonstrated (*43*). In this application, a $Pb_{1-x}Sn_xTe$ diode cooled to liquid helium temperatures operates in the region from 1120 to 1130 cm^{-1} corresponding to the ν_1 band of SO_2. Current passed through

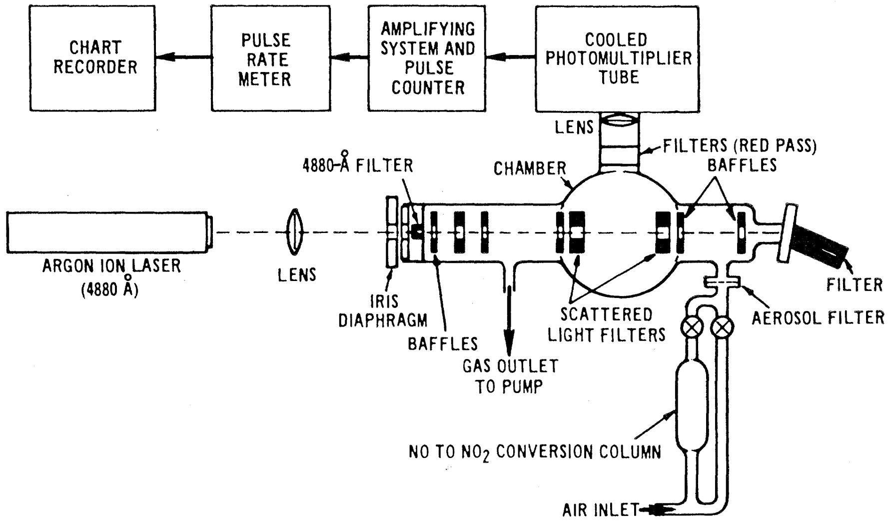

Fig. 8. Fluorescence NO_2 detector.

the diode controls its performance. A high current pulse causes laser emission at λ_1. This pulse is followed by a steady low current which resistively heats the diode to a higher temperature, thereby changing the refractive index of the diode and its optical length. A second high current pulse causes laser emission at λ_2. The pulsed outputs (typically 0.5 milliwatt) at λ_1 and λ_2 are used in a direct absorption system (Fig. 7B). An extension of the technique for path lengths on the order of a kilometer appears feasible.

Long path measurements of O_3 in which the ultraviolet output of arc sources is used have been reviewed by Stair (*44*). In these early experiments the absorption at wavelengths centered at 2500 angstroms was measured over distances of approximately 0.3 kilometer. More advanced systems employing correlation techniques have developed in recent years. One of these, the Barringer Cospec III (*45*), measures SO_2 and NO_2. The instrument consists of a telescope to collect radiation from a remotely placed source, a two-grating Ebert-Fastie spectrometer for dispersion of the incoming light, a disk-shaped, multiple-slit mask, and an electronics system. By rotating the mask two sets of narrow wavelength intervals are alternately passed to the detector by selective shielding of the exit plane of the spectrometer. One of the sets coincides with the absorption maxima of the gas to be measured, and the other is chosen to coincide with the absorption minima. The detection of a difference signal provides measurement of the average concentration of the target gas.

Another correlation method involves matching the periodic pass-bands of birefringent crystals with absorption spectra (*46*). High-energy throughput is obtained, although for NO_2 the absorption peaks are essentially periodic only over restricted wavelength intervals. Regardless of the type of correlation, the effective absorption for each set of wavelengths allows calculation of an average concentration. For a correlation type measurement, the initial source intensities are not measured and calibration must be carried out by placing cells containing the target gas in the light path.

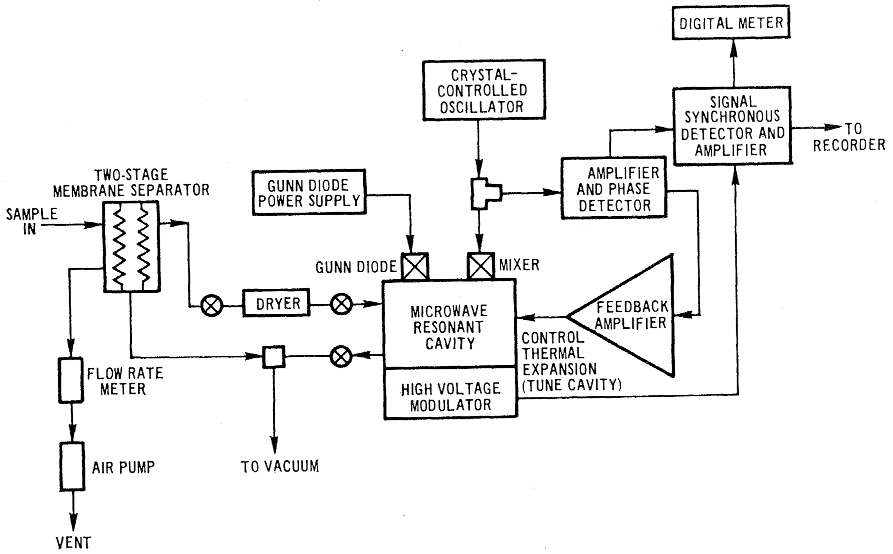

Fig. 9. Gunn-diode, microwave-cavity formaldehyde monitor.

Scanning spectrometers with continuum sources and telescopic optics have been in use for many years. Investigators for the EPA are using one such instrument (*47*) to gather data on various pollution sources and to select optimum wavelength regions for the analysis of specific pollutants. Major system components are a 1700°K blackbody source, telescopic collimating and receiving optics 60 centimeters in diameter, a 0.25-meter grating monochromator, and a closed-cycle, cryogenically cooled mercury-germanium detector. In operation over a 4-kilometer path the instrument is capable of 1-cm^{-1} resolution in the 9-micrometer region and has been used to detect O_3 concentrations of 0.2 ppm (200 micrograms per cubic meter) (*48*).

A common limitation inherent in all the absorption techniques is a practical limit on the detection sensitivity caused by atmospheric turbulence. Turbulent transfer of heat from the earth to the atmosphere causes localized variations in the index of refraction of air. Collimated light passed through the atmosphere is subject to distortion by the attendant focusing-defocusing effect (*49*). Beam spreading, destructive interference within the beam cross section, and beam deflection can result. In remote measurements turbulence can cause the beam to overfill the receiver and can cause the energy received to vary as a function of time. Since fluctuations in the refractive index are observed to decrease with increasing frequency from 0 to 1 kilohertz (*50*), one way to avoid these problems is to complete a measurement in less than a millisecond (*38*). An alternative is signal-averaging over an appropriate time interval.

Long path techniques have many challenges to offer researchers over the next few years. Among the more important are the development of tunable sources and methods of tuning, the measurement of absorption coefficients with sources actually used in the remote-sensing system, and the thorough evaluation of systems to establish their sensitivity and accuracy under real measurement conditions. Once these challenges are met, the remote sensing of ambient air pollutants should become a useful tool to complement point monitors.

Other Spectroscopic Techniques

Molecular gas-phase fluorescence shows promise for the detection of several small pollutant molecules including NO_2, SO_2, NO, Cl_2, and formaldehyde. Each of these molecules possesses ultraviolet or visible absorption bands which may be used to excite the characteristic fluorescence of the molecule. The simplicity of fluorescence techniques is an especially attractive feature. Fluorescence, like chemiluminescence, is an emission technique but has the advantages of requiring no reagent and of being independent of the rate of sample flow.

Laser-induced fluorescence has been shown sufficient to give a direct, real-time measurement of ambient concentrations of NO_2. Gelwachs *et al.* (*51*) accomplished this by using a 100-milliwatt argon ion laser continuously operating at 488 nanometers in a system shown schematically in Fig. 8. Photon counting techniques were employed to detect the low fluorescence signals. A solution filter with a passband from 700 to 810 nanometers and a high rejection ratio for 488 nanometers established a low background against which small signals could be detected. Okabe *et al.* (*52*) have used a system with similar functional components to measure SO_2 fluorescence. The focused output of 15-watt resonance lamps of zinc (213.8 nanometers) and cadmium (228.8 nanometers) induces SO_2 fluorescence to allow detection of concentrations from 0.1 to 1600 ppm.

Virtually all pollutants of interest possess rotational absorption lines in the microwave region. The microwave spectrum provides an even more specific fingerprint of a molecule than the infrared spectrum because of the narrowness of the rotational line and the accuracy with which its frequency can be measured. Microwave spectroscopy has not been applied in earlier quantitative air pollution measurements because of the complex nature of present microwave systems, the low rotational absorption coefficients and resultant poor sensitivities, the low pressure requirements, and the high metallic surface area inherent with conventional microwave absorption cells.

Hrubesh (*53*) has recently developed a simplified microwave pollutant monitor which ameliorates the problems discussed above. A block diagram of his system is shown in Fig. 9 (*54*). A resonant cavity is coupled to a small solid-state, Gunn-diode microwave source. The resonant cavity provides a long effective path length at minimum volume and internal surface area. Thermal expansion is used in a feedback loop to control cavity dimensions and thus the resonant frequency. Conventional stark modulation of the sample and synchronous detection at the modulation frequency are used to measure small changes in microwave power due to sample absorption. A two-stage membrane separator is used on the inlet to preconcentrate the pollutant by more than two orders of magnitude for certain pollutants. Even without the separator this system has a sensitivity in the low parts-per-million range for pollutants such as SO_2, NH_3, NO_2, and formaldehyde.

The O_3 absorption of the 253.7-nanometer mercury resonance line was the first spectroscopic approach employed for monitoring pollutant concentration in the lower atmosphere (*55*). A commercial O_3 photometer was actually available in the mid-1950's from the Harold Kruger Instrument Company, San Gabriel, California. This instrument was marginally sensitive to ambient concentrations and was ultimately replaced by more stable colorimetric oxidant recorders.

The ultraviolet absorption approach has recently been revived in a commercial O_3 photometer offered by the DASIBI Corporation of Glendale, California. This unit employs updated electronic circuitry, including a stabilized mercury source, dual detectors with a unique internal reference system, digital electronics, and signal integration. The sensitivity and stability of this device are adequate for the measurement of ambient O_3 concentrations. The ultraviolet absorption technique has the advantages over chemiluminescence that it requires no reagent and may be internally calibrated on the basis of the known path length and the absorption coefficient of O_3. It has the disadvantage that high concentrations of certain hydrocarbons or mercury vapor may be interferences.

Ultraviolet absorption is also the approach employed in a multipollutant analyzer offered by Spectrometrics of St. Petersburg, Florida. Because of the overlapping nature of bands in the ultraviolet, the Spectrometrics analyzer measures the amplitude of the second derivative (*56*) of the absorption spectra as a means of extracting quantitative information in the presence of interferences. By this means a band, which is only a shoulder in the absorption curve, becomes a peak whose amplitude can be measured. The Spectrometrics unit uses a 20-meter, multipass cell for the measurement of ambient concentrations of molecules such as NO, SO_2, and NH_3.

Conclusions

The monitoring requirements related to air pollution are many and varied. The molecules of concern differ greatly in their chemical and physical properties, in the nature of their environment, and in their concentration ranges. Furthermore, the application may have specific requirements such as rapid response time, ultrasensitivity, multipollutant capability, or capability for remote measurements. For these reasons, no single spectroscopic technique appears to offer a panacea for all monitoring needs. Instead we have attempted to demonstrate in the above discussion that, regardless of the difficulty and complexity of the monitoring problems, spectroscopy offers many tools by which such problems may be solved.

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Meteorological Doppler Radar

R. Lhermitte

Conventional microwave radars have been widely used for the observation and study of precipitation systems since the early stages of their development. Indeed, microwave radars have become useful meteorological instruments for the observation of the three-dimensional structure of convective storms and for the monitoring of rainfall over large areas for hydrological studies. However, even though it provides continuous monitoring of the three-dimensional structure of storms and some estimate of their intensity from the observation of backscattered signal power, the conventional radar fails to reveal directly the kinematics of a convective storm. Since convective storms in the huge intertropical convergence zone contribute significantly to large-scale circulation and sometimes produce large damaging hail and tornadoes when occurring over land, the observation and study of their dynamics have been a very important goal to which continuous research efforts have been devoted in the past few years.

It was not until a decade ago that the application of Doppler techniques to meteorological radars was proposed. Doppler radars provide information on target movements, thereby allowing observation of particle velocities within storms. Since the horizontal velocity of precipitation particles is generally that of the surrounding air, it was expected that measurement of particulate motions would provide an effective means for observing horizontal winds inside convective storms.

The rate of change of the distance of a target from the radar produces variations of the backscattered signal phase, which can be interpreted as a

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