them would have to operate at temperatures below 350°C, with correspondingly reduced efficiency in the steam turbines. Improved selective coatings may allow planar collectors—which Meinel and his co-workers believe, in principle, to be the most effective in areas of the United States other than the cloudless Southwest—to be used. But most initial designs are based on the assumption that concentration of the sunlight will be necessary, and in these systems the fabrication, cost, and durability of the concentrators are the major concern.

The trade-offs between different types of collectors are not the only feature of the design of solar thermal plants still open to debate. Even with concentrating collectors, it may prove advantageous to operate the system at a reduced temperature, according to the Minnesota team. Their analysis shows increasing efficiency of the collectors, but decreasing efficiency of the thermodynamic cycle of the turbines as the operating temperatures are reduced, with the optimum temperature dependent on detailed design of the system and on the heat storage medium chosen. Heat pipes of the size envisioned have never been built, and other hardware details remain to be considered.

Both groups of investigators believe that the cost of solar-thermal plants will be not more than two or three times what fossil-fueled or nuclear-generating plants cost now, and that rising fuel costs will eventually tip the balance in favor of solar-thermal plants whose fuel is "free." Before accurate estimates of costs can be made, they agree, more detailed engineering studies and some additional research are necessary. But Meinel, at least, believes that full-scale solar-thermal power plants could be built as early as 1985 with an adequate research effort. Other estimates are somewhat less optimistic, but a group of western utility companies is considering the development of a small solar-powered facility that could serve as a prototype for peak load applications.

Although solar energy has probably the fewest potential environmental problems associated with its use of any of the major sources of energy, some problems, none of which appear to be insuperable, do exist. Collecting surfaces absorb more sunlight than the earth does, and while this is not likely to alter the local thermal balance in household or other small-scale use, the larger expanse of collecting surface in a central power plant might. Thermal pollution will also be a problem if water-cooled turbines are used—indeed, more so than with nuclear power plants because solar installations are expected to have even lower thermal efficiencies. If waste heat is returned to the atmosphere, it could help to restore the local thermal balance. The effects of small changes in the thermal balance would depend on the local meteorological conditions, but are expected to be small. The lack of particulate emissions or radiation hazards might allow solar-thermal power plants to be built close enough to towns or industrial sites so that their waste heat could be put to use. Finally, like other industrial facilities, large-scale plants would also carry some risk of accidents, with the attendant possibility of leaking heat transfer or storage media into the environment.

Yet another option for generating electricity with sunlight is direct conversion by means of photovoltaic cells. But the cells available now—which were developed for space applications—are relatively inefficient and very expensive to manufacture. As a long-term prospect, however, both cadmium sulfide and silicon cells are attracting considerable attention. This option, and the bioconversion of sunlight to fuels, will be discussed in future articles.

Space heating and cooling with solar energy are not available today. Solar-thermal power plants have yet to be built on any but the smallest scale, and key elements of the necessary technology have not been adequately demonstrated. But both options appear to be close enough to practical tests of their economic feasibility to warrant increased efforts. The ancient dream of power from the sun may not, after all, turn out to be impossible.

—ALLEN L. HAMMOND

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Air Pollution Instrumentation (II): The Glamour of Lasers

The development of the laser has revitalized—some would say revolutionized—the optical sciences: holography and optical communications are but two of the many subject areas in which the laser has precipitated an unprecedented rate of development. Now a growing number of scientists are arguing that laser techniques will engender an even greater revolution in the detection and measurement of air pollutants. The narrow spectral width and high intensity of laser radiation, they contend, offer exceptionally high resolution when combined with conventional spectroscopic techniques. The low divergence of laser beams and their ability to transfer large amounts of electromagnetic energy over great distances, furthermore, suggest a tremendous potential for the measurement of the average concentration of pollutants over a long distance or from a remote location.

For the present, however, laser spectrometers remain little more than a promise, their development hindered by a variety of problems including the need for more sensitive photodetectors and for simple, tunable lasers. The apparent glamour of laser instruments and the inordinate attention devoted to their application in remote monitoring, moreover, have largely overshadowed two other developments that may prove far more significant—the use of lasers in point-monitoring applications, and refinements in correlation and Fourier transform spectroscopy.

Conventional optical spectrometers typically monitor gaseous pollutants by measuring attenuation of ultraviolet or infrared energy at a wavelength that is absorbed by the pollutant and comparing the attenuation to that observed at an adjacent wavelength where absorption is minimized. This simple technique is highly susceptible to interference, however: absorption bands are seldom unique, and it is generally quite difficult to find an acceptable reference wavelength.

This interference problem can be overcome very effectively if one obtains the complete absorption spectrum of the sample within a suitable wavelength interval and compares (correlates) this spectrum with that of the pollutant being measured. Correlation spectrometers based on this principle are generally divided into two classifications depending on whether or not the spectrum of the incident light is dispersed before the comparison is performed. A good example of dispersive instruments is the Cospec spectrometer developed and manufactured by Barringer Research Limited, Toronto, Ontario, Canada.

In the Cospec, incident ultraviolet light from the sun or from a xenon arc lamp is collected with a telescope, dispersed by a grating, and focused on an exit mask. This mask is a photographic reproduction of the spectrum of the pollutant etched in aluminum on transparent quartz. The spectrum of the incident light is compared to that of the pollutant by oscillating the spectrum across the mask while measuring the intensity of the transmitted light with a photodetector. If the pollutant is in the sample, the transmitted light will fluctuate in intensity at the oscillation frequency; the magnitude of the fluctuation is proportional to the concentration of pollutant.

Correlation spectrometers are highly specific, small, and very portable. Measurements can be made not only from fixed locations but also from moving vehicles and from airplanes. The chief disadvantage is cost; one Cospec, for example, costs several times as much as wet chemical systems for monitoring the same pollutants. Other limitations include the inability of most instruments to monitor more than one or two pollutants at a time, noise arising from scintillation of the air, and the fact that only a small number of pollutants have an ultraviolet spectrum.

Infrared Requires Higher Throughput

The restriction to ultraviolet spectroscopy results in part from the relative insensitivity of infrared detectors. Spectral measurements at infrared frequencies therefore require a greater efficiency of use of the incident light or higher throughput. In nondispersive correlation spectrometers this higher throughput is achieved by elimination of the narrow entrance slits required for dispersion of the spectrum, thereby allowing a greater amount of light to enter the instrument and enabling the entire incident spectrum to be focused on the detector.

Correlation is generally accomplished in nondispersive instruments by use of a cell containing a sample of the pollutant; this filter performs the same function as the replica mask in dispersive instruments. Incident light passes alternately through the filter and a transparent cell to the photocell. Fluctuations in the transmitted intensity then reveal the presence and concentration of the pollutant in the same manner as in the dispersive instrument.

The infrared sensitivity of such spectrometers is of the same magnitude as the ultraviolet sensitivity of dispersive spectrometers. Specificity and cost are also similar, but nondispersive instruments have greater potential versatility because nearly all pollutants have an infrared spectrum. One example of such an instrument is a prototype spectrometer developed for the National Aeronautics and Space Administration (NASA) by the Convair division of General Dynamics Corporation, San Diego, California. This spectrometer, which contains filter cells for three different pollutants, is designed for in-flight detection of pollutants with the earth's thermal infrared radiation used as a source. An improved model will be orbited by NASA.

The greatest degree of optical efficiency and the greatest amount of spectral information, however, are obtained with the use of Fourier transform spectroscopy (interferometry) with a Michelson interferometer. Interferometry, says Philip L. Hanst, chief of the Environmental Protection Agency's atmospheric chemistry and physics branch, is the most powerful research tool now available to atmospheric scientists. Interferometers deliver as much spectral information in seconds as the highest quality scanning spectrophotometers produce in hours. Using an interferometer with a 1-km path in a 9-m cell, Hanst adds, EPA scientists have measured pollutant concentrations of less than 1 part per billion (ppb).

The Michelson interferometer is physically—but perhaps not conceptually—simple. Incident light is divided into two beams of equal intensity by a 50 percent–silvered mirror. One beam is directed to a fixed mirror, the other to a movable mirror; these mirrors reflect the beams back to the beam-splitter where they are combined and directed to a detector. The combined beams produce an interference pattern that is characteristic of both the spectrum of the incident light and the difference in the distance from the beam-splitter to the two mirrors.

If the movable mirror oscillates toward and away from the splitter at a constant rate, the detector and its electronics will produce a plot of intensity versus time (an interferogram). In simplest terms, optical radiation is converted to signals in the audio range in much the same manner that electromagnetic radiation is converted to sound by a heterodyne radio. The sensitivity of interferometers is proportional to the size of the mirror; the resolution is proportional to the distance the mirror moves. It is also possible to improve the sensitivity of such instruments by averaging a large number of repetitive scans.

The spectrum of the incident light and the interferogram are complementary and constitute a Fourier pair. By performing a mathematical analysis of the interferogram with a digital computer, one can reconstruct the spectrum of the incident light. Reconstruction is not necessary for pollutant monitoring, however: the interferogram is just as unique as the incident spectrum. The interferogram of the sample can thus be correlated with a stored replica of the interferogram of the pollutant, although in this case the correlation is performed by a digital computer.

Correlation from Space

A simple example of such an instrument is the correlation interferometer being developed by Barringer Research and General Electric Company, Valley Forge, Pennsylvania, for NASA's carbon monoxide pollution experiment (COPE), in which atmospheric carbon monoxide concentrations will be measured from an orbiting satellite. To keep the COPE instrument as simple as possible, filters will remove all incident light except for two narrow spectral regions where carbon monoxide absorbs. An onboard minicomputer accumulates as many as 500 scans for each data point and compares the averaged interferogram to a stored replica of that of carbon monoxide, providing sensitivity of about 10 ppb.

A more ambitious instrument has been developed and is now being sold by the Digilab division of Block Engineering Inc., Cambridge, Massachusetts. This instrument can scan the entire infrared region and is thus capable of identifying and quantifying any gaseous pollutant whose interferogram is stored in the computer memory. The Block instrument and a somewhat similar prototype developed by the Electro Dynamics division of General Dynamics Corporation, Pomona, California, are currently being field tested by EPA.

Measurements with these instruments can be made in a variety of fashions. Vertical measurements of pollutant concentrations can be made from an airplane with the earth's thermal radiation as a source. Long-path monitoring of pollutants in urban areas can be accomplished over distances as great as 6000 m with a high-temperature, broadband infrared source. Exhaust gases from industrial facilities can be monitored with use of the self-emission of the heated pollutants, thus obviating the need for a separate light source.

This versatility, however, does not come cheaply. The Block interferometer and its associated computer costs about $65,000; the General Dynamics spectrometer costs about $50,000 without a computer. Both systems thus appear impractical for most applications except research. The one application in which they might find extensive use, according to J. Morris Weinberg, head of Block's advanced technology department, is in city- or statewide monitoring systems. In volume production, he suggests, the price of the interferometer assembly could be reduced from the current $25,000 to about $10,000. A large number of interferometers could then be linked to a central computer at a more reasonable system cost.

Laser-based systems are currently no less expensive than those incorporating interferometers, but a great deal of work has been expended on them in the expectation that new types of lasers will produce dramatic reductions in cost. This laser research can be divided into three classifications:

- Raman scattering, in which part of the incident light is scattered back to the receiver, but with its wavelength displaced by an amount characteristic of the vibrational frequencies of the pollutant.
- Resonance Raman scattering and fluorescence, in which the pollutant absorbs light of a characteristic wavelength and reemits it at a different wavelength.
- Resonance absorption, in which the pollutant absorbs light at characteristic frequencies and converts it to molecular vibrations.

Raman spectroscopy has several advantages for air pollution monitoring, including high specificity, low susceptibility to interference, the ability to measure the actual number of pollutant molecules in a sample volume, and the ability to provide range resolution and three-dimensional mapping of a pollutant cloud. Equally important, it is not necessary to have a coincidence of the laser emission wavelength and a pollutant absorption wavelength: light of any wavelength produces Raman scattering for all pollutants.

There is really only one problem associated with Raman spectroscopy, but it is a very serious problem. Only an extremely small amount of radiation is returned by Raman scattering, typically less than 1 percent. Even with the very high radiation intensities available with modern lasers, therefore, only minute quantities of light are returned to the detector, thus necessitating extremely efficient light collection systems and photodetectors.

The difficulties of overcoming this problem can be illustrated with a Raman spectrometer developed jointly by Harvey Tannenbaum and his associates at Edgewood Arsenal, Maryland, and the research department at Block Engineering. In this instrument, a pulsed ruby or neodymium : yttrium-aluminum-garnet (Nd : YAG) laser emitting in the ultraviolet region is the light source. Scattered light is collected with a 91.5-cm telescope and transmitted to a fixed grating spectrophotometer. Two or more movable photon counters can be located at the wavelengths corresponding to the Raman shift of the desired pollutants, and a third is fixed permanently at the wavelength characteristic of nitrogen.

Nitrogen Provides Internal Standard

The amount of light collected by each detector is then compared to the amount collected by the nitrogen detector to determine the absolute concentration of the pollutants. But even with this massive instrument, which costs more than $300,000 to develop and build, the maximum sensitivity is only about 0.2 ppm for sulfur dioxide (less for other pollutants), making its use impractical for monitoring ambient concentrations of pollutants.

The light source, rather than the detector, is the major problem associated with resonance scattering and resonance absorption spectroscopy. In both cases, it is imperative that the wavelength of the emitted light be near or identical with a wavelength corresponding to an electronic excitation or molecular vibration of the pollutant molecule. This can be accomplished in one of two ways: by finding a laser emission wavelength that fortuitously coincides with the absorption wavelength of the pollutant, or by using a tunable laser.

Resonance scattering (of which fluorescence is a special case) should be considerably more sensitive than Raman scattering because the amount of light returned to the detector is much greater. Little published experimental work seems to have been done on laser fluorescence, however, and almost none on the use of fluorescence in remote monitoring. Some of the problems which may have hindered such work include the unavailability of lasers emitting at suitable wavelengths, the great cost of systems for remote monitoring, collisional broadening of fluorescence spectra at atmospheric pressures, and the difficulty of measuring absolute concentrations of pollutants.

Some laboratory work has been done, though. Milton Birnbaum and Jerry A. Gelbwachs of the Aerospace Corporation, Los Angeles, California, for example, have used a photodetector placed at a 90° angle to radiation from a helium : cadmium or argon ion laser to detect fluorescence from nitrogen dioxide at concentrations as low as 1 ppb.

A far greater amount of labor has been expended on the application of lasers to absorption spectroscopy, perhaps because of the relative simplicity and lower cost of this technique. A good example of this approach is a prototype spectrometer developed by C. Kumar N. Patel and Lloyd B. Kreuzer of Bell Telephone Laboratories, Murray Hill, New Jersey. In their instrument, 19 different emission wavelengths from carbon dioxide and carbon monoxide lasers have been used to detect ten gaseous pollutants at concentrations of a few parts per billion.

The Bell instrument is similar to nondispersive infrared spectrometers in that the detector is a microphone located inside the sample cell. Intermittent laser radiation at an appropriate wavelength is absorbed by the pollutant, producing intermittent heating and expansion and a cyclic pressure increase, which is detected by the microphone. Comparison of the audio energy to the total energy transmitted by the cell then reveals the pollutant concentration. Only one pollutant can be measured at a time, however (although different pollutants can be monitored sequentially), and the instrument cannot be used for long-path monitoring.

An instrument that is capable of long-path monitoring is the infrared laser atmospheric monitoring system (ILAMS) developed by L. R. Snowman of the General Electric Company, Pittsfield, Massachusetts. ILAMS is based on spectral scanning—rapid sequential transmission of individual wavelengths—with four laser emission wavelengths chosen from among the more than 70 available in a $^{12}C^{16}O_2$-filled plasma

Fig. 1. Monitoring emissions from a distant smokestack with Block Engineering's remote laser Raman spectrometer.

tube. The four wavelengths are chosen by a computer program which maximizes resolution of the pollutants.

Operation of ILAMS is simple. The spectrally scanning laser emits radiation which is returned to the detector by a distant retroreflector. The detector output is sent through signal-processing electronics which compensate for changes in laser output power and which apply computer-calculated linear weights to the signal at each wavelength to cancel interference. The weighted signals are then summed to produce an output voltage proportional to pollutant concentration. The current ILAMS, Snowman says, can detect average concentrations of 14 ppb of ethylene and 19 ppb of ammonia over a 6100-m path with virtually no interference from rain, haze, or snow.

The system can be readily modified to monitor other pollutants, he points out, by changing the filter system to select other wavelengths and by using other types of lasers to provide the necessary wavelengths. The discrimination of the system can also be improved by increasing the number of transmitted wavelengths, but 8 to 12 seems to be the maximum useful number because of the complexity of the filter system. The ideal ILAMS, Snowman indicates, would be based on a continuously tunable laser in which all wavelengths could be chosen electronically.

The tunable laser, in fact, appears to be the Holy Grail of atmospheric scientists investigating remote or long-path monitoring. There are currently at least five promising approaches to tunable lasers that are finding some experimental use in air pollution detection. The "spin flip" Raman laser developed by Bell's Patel incorporates a carbon monoxide laser focused on a sample of InSb in a variable magnetic field to generate tunable Raman radiation at infrared wavelengths. Patel and Kreuzer have used this laser in the experimental configuration described earlier to detect nitric oxide concentrations of about 10 ppb. This laser is a cumbersome, complex, expensive piece of equipment, however, and seems unlikely to find wide use.

Magnetic fields can also be used to tune lasers by the Zeeman effect. Gary J. Linford of Hughes Aircraft Company, Culver City, California, has found, for example, that magnetic fields as great as 5500 gauss split each emission wavelength (or line) of xenon lasers into two new lines centered on the original emission wavelength but displaced by as much as 10 Å. The two new laser lines are equal in intensity, but are circularly polarized with opposite helicities.

If one of the new laser lines is brought into coincidence with an absorption wavelength of a pollutant, the other can then serve as a reference beam. Polarized filters are used to allow the detector to receive radiation alternately from each beam; the concentration of the pollutant is then determined from the ratio of the transmitted intensities of the two beams. Pollutant concentrations much less than 1 ppb should be readily detectable with this apparatus incorporating a 15-km optical path, Linford suggests.

A third approach is the use of organic dye lasers, which emit over a wide spectral region, combined with a rotatable diffraction grating that allows wavelength selection. Such lasers, however, do not emit a narrow enough spectral line for truly high-resolution absorption spectroscopy, and a precise setting of the emission wavelength is difficult to achieve and to maintain.

A more promising approach is the optical parametric oscillator. In a crystal, the fundamental emission frequency of a laser can be divided into two new frequencies whose sum must equal the original frequency, but whose relative values can be varied by rotation of the crystal or by heating it. Such oscillators require very intense bursts of laser radiation, however, and carefully selected and controlled crystals. They are currently also complex and expensive, but nonetheless seem destined to find at least some use in air pollution spectroscopy.

By far the simplest and most promising tunable lasers are diode lasers such as those developed by Everett D. Hinkley and his associates at Massachusetts Institute of Technology's Lincoln Laboratory, Lexington, Massachusetts. A diode laser is a single semiconducting crystal processed so that one side is an *n*-type semiconductor in which electrons carry the current and the other is a *p*-type in which holes (or electron vacancies) carry the current. Under an applied current, recombination of electrons and holes occurs at the interface with the emission of light.

Hinkley has found that lead-tin-telluride diodes of the form $Pb_{1-x}Sn_xTe$ can be constructed to emit radiation at any wavelength between 6.5 and 32 micrometers by varying the relative stoichiometric concentrations of lead and tin. Furthermore, the emission wavelength of any such crystal can be varied over several wave numbers by applying pressure, by applying an external magnetic field, or by varying the current applied to the diode. The small size and potentially low cost of such diodes suggest that several could be incorporated in one instrument to provide tuning across a broad spectral region. This type of device, atmospheric scientists agree, will undoubtedly be the basis for much future air pollution instrumentation.—THOMAS H. MAUGH II

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