Air Pollution Instrumentation: A Trend toward Physical Methods

The political phase of the battle against air pollution has largely ended. Adequate legislation, particularly the milestone Clean Air Act of 1970, has been enacted to define permissible concentrations of pollutants in emissions from key sources and to establish acceptable levels of air pollutants for regions, states, and cities. The principal problems now are the development of new or refined technologies to limit emissions and the enforcement of the standards. Implicit in each of these problems is the need for suitable instruments to measure pollutant concentrations.

The production of air pollution instrumentation is a rapidly growing, ill-defined, and surprisingly complex sphere of interest that is attracting a surfeit of instrument companies, noninstrument companies, newly formed companies, and university and federal laboratories. Lured by a market that the Environmental Protection Agency (EPA) predicts will total more than $500 million during the 1970's, and bolstered by research funds from such sources as EPA, the National Aeronautics and Space Administration, the National Science Foundation, and the Department of Defense, these groups are refining instruments originally developed for other applications and are exploring a variety of alternative—and sometimes problematic—approaches. Overall, air pollution measurement appears to be characterized by an abundance of promising ideas for new monitoring techniques, a modicum of laboratory work toward development of these techniques, and a dearth of field work to prove the effectiveness of the instruments in use.

Air pollution instruments can be divided into two classes: those for measuring pollutant concentrations in the immediate proximity of the instrument, and those for measuring concentrations over a long path length or at locations remote from the instrument. With few exceptions, the latter category comprises laser-based instruments that are still in early stages of development. This category will be covered in a second article.

Nearly 200 different instruments utilizing at least a dozen different techniques for monitoring gaseous pollutants are now commercially available, and new ones are appearing regularly. These instruments have two common characteristics: few have received sufficient testing by EPA and independent laboratories to ensure their accuracy and reliability, and most will undoubtedly become obsolete before the end of the decade. For perhaps the single clearcut trend within this field is a growing shift away from the complexity of chemical techniques and toward the simplicity of physical methods of measurement that monitor many pollutants simultaneously.

The most widely used instruments currently, however, are based on wet chemical techniques, which were among the first to be developed and whose capabilities are thus most clearly defined by experimental data. Such instruments generally depend on colorimetric, coulometric, or conductimetric procedures to measure the concentration of a pollutant in a collection liquid through which the sample has been passed. In the standard reference method for nitrogen dioxide, for example, the gaseous sample is bubbled through a solution of sodium hydroxide, where the NO_2 is converted to stable sodium nitrate. After collection, the nitrate is diazotized with phosphoric acid sulfanilamide and coupled to *N*-1-naphthylethylenediamine; the concentration of the resulting chromophore is then determined colorimetrically.

Many Problems with Wet Chemicals

Wet chemical techniques readily lend themselves to automation and yield highly reproducible results. They are also sensitive, simple to operate, and inexpensive. These advantages are, however, largely offset by many drawbacks, including interference by other pollutants, instability of reagents, generalized problems associated with the complicated plumbing required, the need for different reagents for each species monitored, and the amount of time required for sampling and quantification.

Further problems arise in sampling. Earlier this summer, for example, EPA deputy administrator Robert W. Fri disclosed that average NO_2 concentrations determined in several areas of the United States were erroneous because of technical errors in sample collection. Using newly developed devices to generate known concentrations of NO_2, EPA investigators found that the efficiency of collection of NO_2 in sodium hydroxide varies with the concentration of NO_2 in the sample. The collection efficiency is less than 15 percent at NO_2 concentrations greater than 300 parts per billion (ppb), about 35 percent at concentrations near 60 ppb, and rises to at least 60 percent at concentrations less than 25 ppb; EPA had previously assumed that the efficiency was constant. It is, of course, possible to establish a calibration curve for sampling efficiency, but sharp fluctuations of NO_2 concentration during the sampling period make accurate calculation of the average concentration exceptionally difficult, if not impossible.

Wet chemical techniques are thus losing favor with environmental scientists, notes Alfred Ellison of EPA's division of chemistry and physics, although the relatively low cost of such instruments ensures their continued use. Many users, he adds, are now switching to instruments based on such chemical techniques as chemiluminescence, electrochemical transducers, and flame ionization coupled with gas chromatography.

Chemiluminescence is based on the light-emitting reaction of the monitored pollutant with a gaseous reagent. Nitrogen oxide, for example, is measured by its reaction with ozone to form oxygen and electronically excited NO_2. Collapse of the excited molecule to the ground state produces light, and the intensity of the emitted light is proportional to the original concentration of NO. Atmospheric O_3 is monitored in the same fashion by its reaction with ethylene.

Chemiluminescence has many advantages in comparison to wet chemical techniques, and is now the standard reference method for measuring O_3 concentrations. The technique is sensitive and specific, and measurements are rapid and highly reproducible. The major disadvantages include the relatively large initial expense for the instrument, maintenance of the plumbing and the gaseous reagent, and the limited number of pollutants to which the technique is applicable.

Table 1. Minimum limits of detection (in parts per million) of selected gaseous pollutants with state-of-the-art, commercially available instruments.

Method	NO_2	SO_2	O_3	CO	Hydrocarbons
Wet chemistry	0.01	0.01	0.02		
Chemiluminescence	0.005	0.005	0.002	100	
Electrochemical transducers	0.05	0.05		20	
Gas chromatography	10	0.005		0.1	0.02
Nondispersive infrared				0.5	
Dispersive infrared*	0.025	0.025	0.1	0.1	
Dispersive ultraviolet†	0.05	0.003	0.17		

* Minimum concentration to give 1 percent absorption in a 100-meter cell. † Minimum concentration to give 1 percent absorption in a 20-meter cell. [Source: James Hodgeson, Environmental Protection Agency]

Electrochemical transducers would appear to represent a significant advance in pollutant detection. These devices depend on selective electrocatalytic oxidation (or reduction) of the pollutant in a cell that is very similar to a fuel cell. In a typical transducer, the sample gas flows past a semipermeable membrane that allows a small, constant fraction to enter the cell. Inside the cell, the sample diffuses through a thin liquid film to an electrocatalytic electrode, where a charge transfer reaction occurs. Bulk electrolyte and a reference electrode make up the rest of the cell. In operation, the cell produces an electrical potential that is directly proportional to the concentration of pollutant in the sample stream and, within reasonable limits, is independent of the sample flow rate.

Such transducers have a number of advantages, including low cost, ease of maintenance, simplicity of operation, and versatility. Several inexpensive cells, each specific for a different pollutant, can be linked to one instrument that contains the electronics assembly, thus providing multipollutant capability. Many problems are associated with their use, however.

Recent industrial tests, says Craig Hollowell of the environmental instrumentation group at Lawrence Berkeley Laboratory, indicate that problems of base-line drift and interference by other pollutants are greater with transducers than with any other type of commercial instrument. Other problems he cites include insufficient instrument stability, evaporation of the electrolyte, and reduced cell lifetime caused by clogging of the membrane in heavily polluted samples (although cells can be rejuvenated by the manufacturer). The low price of transducers makes them very popular for source monitoring applications, Hollowell points out, but without further refinements they will probably remain no more than a stopgap technique.

Gas chromatography is being used increasingly for pollutant monitoring because of its ability to separate similar pollutants before their concentrations are measured. Such a procedure is especially important in the measurement of hydrocarbon concentrations: federal standards establish maximum concentrations for all hydrocarbons except methane, which is generally considered innocuous and is thus left uncontrolled. Hydrocarbon monitoring techniques must therefore be able to exclude methane or to measure its concentration independently, and gas chromatography fills this need perfectly.

In a typical installation, the chromatograph separates methane, carbon monoxide, and other hydrocarbons. The concentration of each is then generally determined with a flame-ionization detector, in which the pollutant is burned in a hydrogen-rich flame. The method is sensitive, rapid, and highly specific, and has now been adapted for monitoring sulfur-containing pollutants.

Chromatographs Highly Automated

Modern air pollution chromatographs are highly automated instruments capable of unattended operation for extended periods, according to Larry Dworetsky of the reentry and environmental systems division of General Electric Company, Philadelphia, Pennsylvania. General Electric is thus using both sulfur and hydrocarbon chromatographs in a statewide pollution monitoring system that it is designing for Pennsylvania. An additional advantage of these instruments, he adds, is that they frequently can indicate the existence of pollutants whose presence is unknown or unexpected.

But gas chromatographs also have several drawbacks, points out Franz J. Burmann of EPA's air surveillance branch. They require extensive maintenance, he says, and their operators generally have to be technically trained. Other shortcomings include the need for a constant supply of carrier gas, the cycling time associated with operation of the chromatograph, and the length of time required for stabilization of the column when the instrument is turned on.

The general complexity of all the previously mentioned systems, the necessity for handling reagents, and the general lack of multipollutant capability are among the many factors mediating a growing trend toward physical methods of measurement. Environmental scientists, says EPA's Ellison, are now in the early stages of an extensive shift to optical detectors based on infrared or ultraviolet spectroscopy. Only a few such instruments are on the market now, notes Berkeley's Hollowell, but the number seems certain to grow as newly developed improvements are incorporated.

Such improvements are necessary to overcome many of the problems that have hindered the development of optical techniques for pollutant monitoring. Foremost among the problems is that of interference from other pollutants and, particularly, water vapor—a problem most often manifested as an inability to provide a suitable reference against which the sample can be compared. Others include susceptibility of the optics to vibrations, long-term instability of the associated electronics, and condensation of pollutants on the optics. Counterbalancing these problems, however, are high sensitivity, simplicity, portability, speed of measurement, and their potential for detecting many pollutants.

Optical techniques can be divided into two broad categories: nondispersive instruments, which transmit the complete spectrum through the sample and modify the detector for selectivity, and dispersive instruments, in which a prism or grating is used to disperse the spectrum into its component wavelengths either before or after the beam is transmitted through the sample. Nondispersive instruments, by their nature, are limited to monitoring only one pollutant, while dispersive instruments are capable of monitoring several.

Nondispersive infrared spectroscopy has found its greatest use in carbon monoxide monitors and is the standard reference method for that pollutant. In a typical application, radiation from a broad-band infrared source is passed simultaneously through a reference cell containing either CO-free air or nitrogen and through an atmospheric sample from which water vapor has been removed. Attenuation of infrared energy by CO in the sample chamber is detected by two CO-filled cells, one for each beam, coupled by a flexible diaphragm. Absorption of the infrared energy by the detector CO leads to heating and expansion, thereby creating a pressure differential proportional to the attenuation by the sample. The pressure differential is detected by the diaphragm and a microphone-like transducer that converts the differential into an electrical signal suitable for amplification and display.

Such an instrument is sufficiently sensitive for most applications and, with either infrared or ultraviolet sources, is readily adaptable to a variety of stable gases. It is, however, highly susceptible to interference by water vapor and strongly absorbing pollutants whose absorption is not canceled by the reference cell. The microphonic detector, furthermore, is extremely susceptible to mechanical vibrations and thus severely limits the portability of such instruments.

One solution to some of these problems is embodied in a unique CO monitor produced by Andros, Inc., Berkeley, California. The Andros instrument contains a broadband infrared source that stimulates fluorescence of $C^{16}O$ and $C^{18}O$ contained in a sealed cell. The stimulated radiation is passed first through a filter that alternately removes radiation from each isotopic source and then through the sample chamber to a solid state photocell. The wavelengths of the radiation emitted by the $C^{16}O$ and $C^{18}O$ are sufficiently close that their intensities are attenuated equally by moisture or other pollutants in the sample. But since some 99.8 percent of naturally occurring CO is $C^{16}O$, only the radiation produced by $C^{16}O$ will be absorbed by the sample. The concentration of CO is then determined from the ratio of transmitted light of each wavelength. Instruments of this type are currently being used by the U.S. Navy to monitor CO in nuclear submarines, and will also be used for the same purpose in NASA's Skylab orbiting laboratories.

Dispersive spectrophotometers generally rely on more conventional methods. Detection is typically accomplished by measuring attenuation at a wavelength that is strongly absorbed by the pollutant to be monitored. A reference is provided by alternating the absorbed wavelength with a nearby wavelength at which absorption of the monitored pollutant and of other species in the sample is minimized; pollutant concentrations are then calculated from the ratio of the transmitted intensities. The accuracy of the measurement depends greatly on the amount of absorption at the reference wavelength, and for many pollutants an appropriate reference is not available.

A solution to this problem is exhibited in an ultraviolet ozone detector manufactured by Dasibi Corporation, Glendale, California. In this instrument, the sample gas stream is divided into two portions, and the ozone in one stream is catalytically converted to oxygen. The ozone-free stream then becomes the reference gas, thereby minimizing interference by moisture and other pollutants. But this technique, like that of the Andros instrument, has not been successfully applied to other pollutants, so that its utility appears limited. A further drawback is that such techniques necessitate a separate instrument for each pollutant to be measured, and thus eliminate one of the most significant potential benefits of optical systems.

Microwaves More Promising

An alternative, and potentially more promising, physical method is microwave spectroscopy. Small, polar molecules convert microwave energy to rotational energy at discrete frequencies that are characteristic for each pollutant. Since there is very little overlap in these frequencies, a high degree of specificity can be obtained. The principal drawback to this technique is a lack of sensitivity, since absorption at microwave frequencies is considerably smaller than absorption in the infrared.

Microwave spectrometers are generally operated at low sample pressures —typically about 10^{-2} torr—to prevent collisional broadening of absorption bands. At such pressures, however, the absolute number of pollutant molecules is so reduced that detection of ambient concentrations of pollutants may require an unreasonably long microwave cavity or wave guide to provide a sufficiently large sample.

A partial solution to this problem is provided by Lawrence W. Hrubesh of Lawrence Livermore Laboratory, who has designed a 15-cm resonating cavity that achieves greater sensitivity by repeatedly passing the microwaves through a small sample. With this wave-guide and state-of-the-art instrumentation, he says, strongly absorbing pollutants such as sulfur dioxide, ammonia, and formaldehyde can be measured accurately in the 100 ppb range. Less polar pollutants, such as NO_2, can be measured at concentrations as small as 10 parts per million.

A further increase in sensitivity can be obtained by preconcentration of the atmospheric sample. One such approach being examined by Hrubesh and Lee Scharpen of Hewlett-Packard Corporation, Palo Alto, California, is the use of gas-permeable membranes. Dimethyl silicone membranes, for example, allow much greater permeation of organic and some inorganic gases than of the major constituents of air. Under appropriate pumping conditions, therefore, such membranes not only provide an approximately hundredfold enrichment in pollutant concentrations, but also produce the required reduced sample pressure. Multipollutant microwave spectrometers embodying such improvements could be on the commercial market in as little as 2 years, Scharpen says. The principal problem that must first be overcome, he adds, is to ensure that the permeation characteristics of the membrane remain constant throughout its lifetime.

A great number of other techniques for monitoring air pollution are also under investigation. One new research development deserves mention, however, for it is indicative of the types of instruments that may eventually be used. Earlier this summer, Bernard C. LaRoy and his associates at the Philip Morris Research Center, Richmond, Virginia, revealed a major breakthrough in the development of solid-state electrochemical transducers. They find that thin-film lanthanum fluoride electrolytes are able to transport ions formed by donation of electrons to such reducible gases as SO_2, NO_2, NO, and CO_2.

Miniature electrochemical cells constructed with this solid electrolyte exhibit a conductivity that, above a voltage threshold characteristic of each gas, varies linearly with gas concentration. (The only observed exception, NO_2, exhibits a logarithmic relation between conductivity and concentration.) Few air pollution experiments have been performed with such cells, LaRoy says, primarily because of the novelty of the technique. But, he contends, the properties of the solid electrolyte promise a great increase in reliability, simplicity, and longevity compared to current instruments of all types.

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