Optical Environmental Monitoring in Industry

By Robert L. Spellicy

Title I of the Clean Air Act (CAA) amendments of 1990[1] imposes upon industry and government the responsibility to gather data vital to the development of appropriate control strategies as well as to demonstrate compliance with the National Ambient Air Quality Standards (NAAQS). Title III of the Act requires ongoing programs to assess, reduce, and control hazardous air pollutants, while Title V requires the reduction, control, and monitoring of gases contributing to acidic aerosol production. One of the significant aspects of the CAA is its attention to multiple hazardous air pollutants (HAPS) rather than the more traditional focus on a limited number of so-called criteria pollutants. The Act imposes challenging air monitoring requirements, and it appears that traditional technologies may not be adequate to meet them.

Because of the limitations of traditional monitoring, the CAA amendments have spawned keen interest in the development of reliable, cost-effective monitoring methods with enhanced capabilities. In this development, optical methods appear to be playing a key role because they can monitor for multiple compounds simultaneously, monitor through the ambient air, and provide real-time data. These capabilities have been lacking in traditional monitors for these new compounds of interest.

Both industry and government have taken initiatives that have accelerated the development and deployment of new monitoring technologies. Industry, driven by an immediate need for monitoring, has installed, and in some cases even developed, prototype monitoring systems for their facilities without direct regulatory pressure to do so. Government has provided a much more cooperative environment: Encouraging the use of new technologies; assisting with the testing and validation of new methods; and establishing means for industry to achieve rapid regulatory acceptance of new technologies (*e.g.*, EPA Method 301[2]). Presently, new technologies are applied to stationary source or stack monitoring, mobile source (vehicle) monitoring, and fence-line or industrial perimeter monitoring.

To provide an overview of optical monitoring today, I offer: (1) an outline of currently used optical monitoring techniques, particularly infrared and ultraviolet spectroscopic methods, (2) two specific examples of industrial applications of new emerging technologies, and (3) a look at what the future may hold for optical techniques in environmental monitoring.

Emerging optical monitoring systems

Optical monitoring has been in use for decades in one form or another. Thermal or multispectral imagery has been a key monitoring technique for military applications, while spectrometers or interferometers have long been the cornerstone in analytical laboratories worldwide. The basic science has been in hand. However, while powerful, these systems have been expensive, delicate, and inappropriate for unattended use in industrial environments. The challenge has been to develop rugged, reliable, and cost-effective systems that can be operated by non-scientific personnel. This has been accomplished in a limited way today, and it appears that many more systems will be commercially viable in the next few years.

Figure 1. Photograph of the beam path for a fence-line FTIR monitoring system operated by Radian Corp. at a petrochemical plant in Houston, Texas. The plant is to the right and the residential area to the left. The prevailing wind is off the plant and into the residential area.

The systems that have been developed to date can be grouped into two general categories: those that use a broadband source and hence cover a large spectral range, and those that use laser or spectrally narrow sources and consequently cover only a small range of wavelengths. Examples of broadband systems are infrared and ultraviolet spectrometers that typically operate with grating monochromators and single detectors or

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arrays of detectors. The most common, in the UV, is the ultraviolet differential optical absorption spectrometer (UV-DOAS). A specific infrared system that is extensively used today is the Fourier transform infrared (FTIR) interferometer. The most common of the laser systems is the diode laser sensor. Diodes are either 1) ambient temperature (as developed initially for communications), which emit in the near infrared or 2) cryogenic, which emit throughout the infrared. A unique laser application is lidar (light detection and ranging), which operates at one or more fixed laser wavelengths. Lidar is unique in that it provides spatial information as well as compound detection.

The role of new techniques

Both laser-based and broadband systems have their own advantages and disadvantages. Broadband systems like FTIR or UV-DOAS can monitor many compounds simultaneously. In fact, these systems can be used to determine what compounds are present in an unknown mixture. However, systems with broad spectral coverage usually have finite spectral resolution. This means that while they can "see" many compounds, they may lack the resolution to differentiate them in a complex mixture. Also, the finite resolution, if it is low compared to fine features that need to be observed in the spectrum, may make it impossible to observe the true absorption peaks. This can limit the minimum gas concentration that can be observed. In contrast to this, laser-based systems have very high resolution and in some cases narrow scanning ranges. The resolution of these devices provides for very high sensitivity and specificity, but they must have a spectral output that matches the absorption features of a compound of interest. Because of their fixed wavelength (or very limited scanning range), they are usually limited to single compound detection, and a separate device is required for each compound to be monitored.

In current environmental monitoring, each of these types of systems has a role. For example, FTIR systems provide the coverage of compounds important in monitoring for accidental releases in an industrial complex. In this application, detection limit is not as important as sensitivity to all possible hazardous compounds at the site. For continuous monitoring of emissions by a limited number of compounds either in stationary sources (stacks) or in the ambient air, immunity to interference by other compounds and low detection limit are overriding factors. Here the UV-DOAS and diode laser systems are ideal. The special case of lidar also has its strength, that of spatial resolution. It, like other laser-based systems, is limited in species coverage but it is the only technique today that provides for spatial mapping. Clearly, lidar has application to tracing pollutants to their origin, mapping atmospheric phenomenon such as ozone depletion in the upper atmosphere, or providing for vertical profiling of molecular constituents to better understand atmospheric transport and diffusion.

Today, optical methods are used in many monitoring tasks and their use is accelerating. Two specific examples are presented here to give a flavor for the current state-of-the-art: open path monitoring at an industrial fence line and extractive monitoring of industrial stacks and vents.

Open air monitoring

Open air monitoring, as its name implies, is performed through the ambient air. It is normally applied to monitoring around chemical storage areas, along the property line of a facility between the plant and the public, or around Superfund sites during remediation.[3-5] In this mode of operation, a set of telescopes (or a single coaxial telescope) is used to transmit and receive the light. These are arranged so the infrared or ultraviolet beam passes through the region to be monitored before being received. The telescopes can be placed at opposite ends of the open-air path (a bistatic configuration) or both can be placed together at one end (the monostatic mode). In the monostatic case, a mirror must be placed at the end of the path opposite to the transmitter and receiver to return the beam to the receiver. This is typically done using a corner cube reflector or an array of corner cubes. A corner cube returns an input beam directly back upon itself regardless of how the cube is pointing. Consequently, it provides insensitivity to vibration or motion of the mirror or its platform. This is critical for use of these systems in industrial environments.

Figure 1 shows the path of a currently operational fence-line monitoring system at a petrochemical plant in Houston, Texas. The plant is visible to the right, and just behind the tree line on the left is a residential area. The dominant wind direction is from left to right in the photograph, coming off the plant and into the residential area. The system installed at the site is an FTIR operating at 0.5 cm^{-1} resolution. It monitors continuously for some 30 compounds and collects data once per second while averaging the results over five minutes before reporting it. All data are provided in real time to the plant local area network. Once on the network, the plant manager, safety officers, and security guards have access to both real time and historical data via small programs on their local personal computers.

Each compound being monitored also has a defined alarm threshold, and these are usually specified as some fraction of health risk levels. If any compound exceeds its threshold, the monitoring system triggers an alarm or initiates a prescribed sequence of events. In most cases, an actual alarm is triggered in the plant manager's office to alert the office to an event. In some cases, other monitoring equipment is also triggered, such as collection of actual air samples in canisters for subsequent analysis. Plant managers can view one of several displays that help them determine what has happened and what action may be necessary. The most fundamental display is simply a tabulation of gas concentrations in which any compound exceeding its threshold is printed in red. However, tabulations are hard to comprehend quickly, so plots of data are also available. These display the time history of gas concentrations for each monitored compound. An example of such a plot is shown in Figure 2. In this plot, the time history of an ammonia release is shown from midnight through 2:45 p.m. In the afternoon a sustained release is seen although its peak concentration is only at 60 parts per billion (ppb).

Plots like this allow the plant manager to determine immediately whether the alarm was caused by a very short duration, low-level "spike," which may be of no health consequence, or by a sustained or high-level release, which could cause health risks. In addition to these time series plots, plots correlating observed concentrations with the wind are also available. For the ammonia release of Figure 2, the wind correlation plot is shown in Figure 3. This plot is a polar plot with the angle representing the direction from which the wind was coming when the concentration was measured and the distance the point is plotted from center being the actual gas concentration. This type of plot immediately shows the direction from which the emissions are coming. The distribution acts like a "finger" pointing in the direction of the source. In the plot shown here, the ammonia clearly came from 150° or south-southeast. Information like this allows the plant manager to determine where in the plant the emissions are coming from and, based on knowledge of the plant processes, make a judgment on what action if any is necessary.

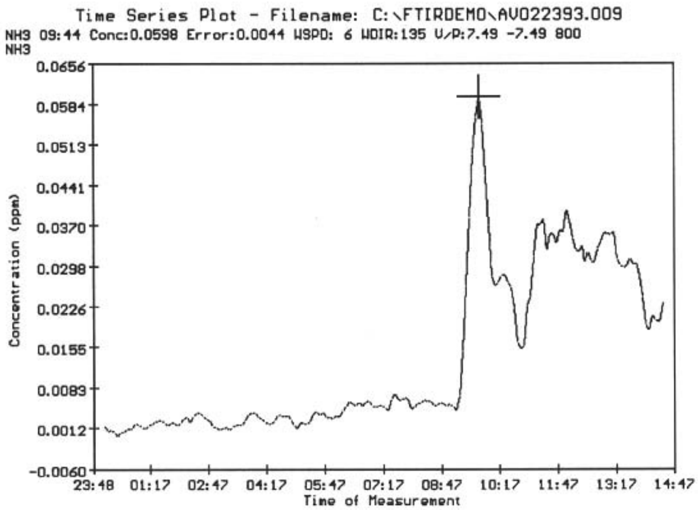

Figure 2. A time history plot of ammonia (NH_3) at the fence line of a petrochemical facility detected by the FTIR monitoring system shown in Figure 1. The rapid increase at roughly 9:30 a.m. is a release detected by the system. The cross hair at the peak shows the concentration (0.059 ppm) and error (±0.004 ppm) listed at the top of the plot.

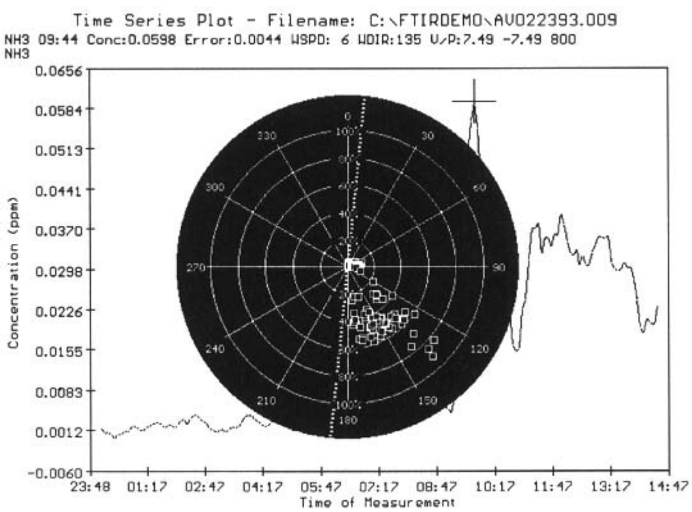

Figure 3. The correlation of wind direction with the observed gas concentrations of Figure 2. This plot allows the direction of the release to be detected. In this case, the emissions are coming from 150° or from the south-southeast.

Open path systems also provide historical data on fugitive emissions, which are low-level emissions arising from very small leaks in flanges, valves, or piping. These releases are also important if they exceed long-term exposure guidelines because of the health risk they can represent. Specific concerns are usually for carcinogenic compounds, and great attention is being given to development of systems capable of fenceline or wide area monitoring of these compounds on a continuous basis.

Industrial stack monitoring

Industrial stack monitoring has become critical to industry since the advent of the Clean Air Act Amendments. This is because industry must determine, on its own, what significant compounds its facility emits and submit this information as part of its application for an operating permit. In-stack monitoring is critical for (1) determining significant emissions from the stacks, (2) continuously demonstrating compliance with emissions regulations, and (3) monitoring for reductions of emissions as process modifications or controls are implemented.

Infrared and ultraviolet spectroscopic systems have been applied to this problem very successfully. For stack monitoring there are two approaches: *in situ* (or cross stack monitoring) and extractive monitoring. *In situ* monitoring, much like open-path monitoring, propagates the IR or UV beam through the stack itself. Also like open-path work, this can be done either in a single pass mode—(transmitting from one side and receiving at the other) or in a double pass mode—(transmitting to a corner cube on the far side and receiving it after its return). The detection limits possible in this case are dictated by the path length provided by the stack. *In situ* monitoring is most common in UV systems. Monitoring of this type is ideal for situations requiring continuous monitoring of compounds that are present in the stack at moderate levels (*e.g.*, ppm levels) because the modest path length of the stack can provide adequate detectivity. *In situ* monitoring is also ideal for detection of unstable compounds that cannot be reliably removed from the stack for analysis. In contrast to *in situ* monitoring, extractive monitoring, which is most common for IR systems, pulls a sample from the stack into an external instrument for analysis. Extractive monitoring is usually conducted using a heated extraction line and heated cell to avoid condensation of volatile compounds and to minimize possible adsorption of compounds on the walls of the cell or extraction line. To achieve low enough detection limits in an extractive system, a moderate path through the sample is required. This is usually accomplished using a multiple pass cell. Figure 4 shows such a cell for an FTIR extractive system. The cells used are frequently White cells,[6] which use three spherical mirrors internally to re-image the light back and forth, allowing for 30 passes or more. Typical cells 30 cm in length can provide 8–10 m of optical path while cells on the order of one to two meters in length can provide paths up to 100 m. Because detection goes as the product as concentration times path length, this longer path translates into proportionally lower minimum detectable concentrations.

An important, and very recent, application of extractive monitoring is for acid gases in semiconductor manufacturing. Here FTIR systems have been applied, and are ideal because of the number of acids and organics that need to be monitored in typical stacks. In semiconductor manufacturing, acids such as nitric, hydrofluoric, sulfuric, and hydrochloric are used regularly. Also, these are frequently present in the stack along with significant concentrations of ammonia. No good monitoring method exists for this situation. Standard monitoring techniques detect total chlorine or total fluorine but in the presence of ammonia much of the acid is converted to ammonium salts. Traditional methods cannot differentiate between salts and acid, and in practice, the total is taken as the acid emissions, a number that is almost two or three times too high.

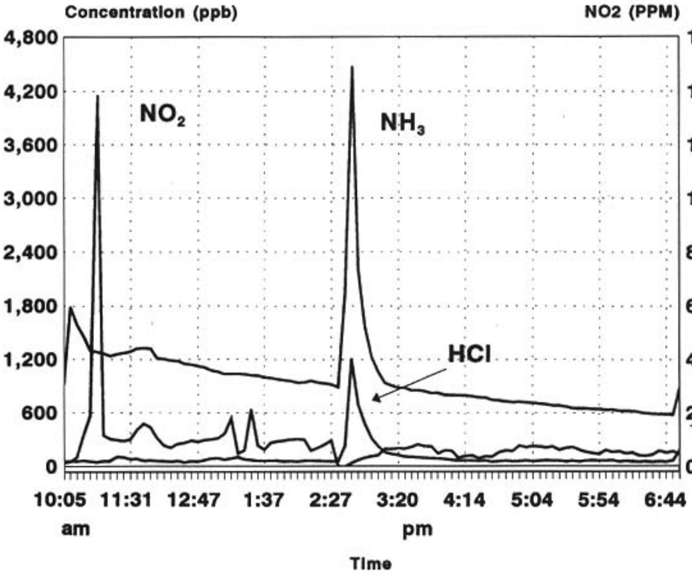

Figure 5. A time history plot of gas concentration observed in a semiconductor scrubber exhaust. The spikes of NO_2, NH_3, and HCl are correlated with activities of the batch manufacturing process. Real-time monitoring of these and other acid gases is a powerful capability of FTIR.

Optical methods are one of the few approaches that can detect all acids of interest and can "see" them independently of the salts. In using FTIR, however, one complication arises. Because they have a strong affinity for water, the acids usually form mists in the stack. The FTIR will only detect gaseous compounds and therefore will not detect the mist (just like it will not detect aerosols or salts). To assure a proper measurement of the acids, a high temperature (185° C) extraction line and cell are used to totally vaporize the water and leave the acids as molecular vapor. Another challenge for IR-based systems is that wet scrubbers are almost universally used to strip out much of the acid in the exhaust before it is emitted to the atmosphere. This produces a saturated air stream. Unfortunately, water interferes (spectrally) with the detection of many of the acids and organics of interest. To circumvent this, care must be taken in developing analysis methods on the FTIR, which use regions minimally influenced by water. Careful correction for unavoidable water interference is imperative. Given appropriate methods development, however, FTIR has been used very successfully for continuous monitoring of these stacks.

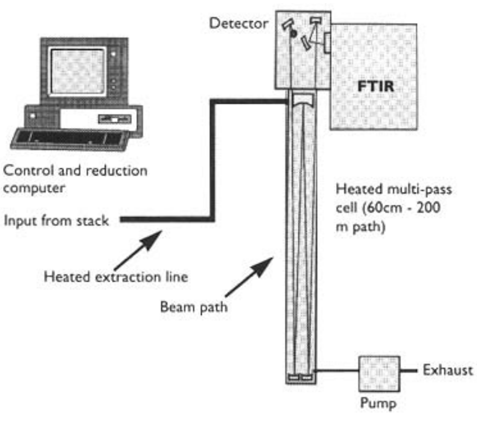

Figure 4. Schematic of an extractive FTIR monitor as used for stack monitoring. Heated input and output lines are used and the multipass cell provides long pathlengths by re-imaging the IR light repeatedly before allowing it to exit. Cells from 4 m to over 100 m are commercially available.

Cart-mounted FTIR systems have been developed specifically for semiconductor monitoring. Such a system was used to generate the gas concentration time trace shown in Figure 5. These data were gathered at the output of a scrubber operating at a chip manufacturing facility. In this case, we have shown hydrochloric acid (HCl), ammonia (NH_3), and nitrogen dioxide (NO_2). The rapid changes in these concentrations are typical for the batch processes used in semiconductor manufacturing. However, until the use of FTIR, it was not possible to directly observe this type of behavior or the correlations between the emissions of various compounds. The emissions shown here clearly indicate the tight correlation between NH_3 and HCl because of the process activity. There are also programs underway to look at the efficiency of wet scrubbers and to develop higher efficiency scrubbers for the removal of the acid gases. These programs are also using FTIR to provide continuous, real-time detection of a variety of acids at the output of prototype scrubbers. Rapid measurement of input and output concentrations is critical over at least a ten-fold span of concentrations. Here FTIR appears to provide the necessary breadth of compound coverage and measurement speed.

What the future holds

Optical and spectroscopic methods are seeing increased use in environmental monitoring as the demands for improved detection grow. These demands will certainly not diminish and the pressure to develop yet more sensitive systems as well as those with broader compound coverage will continue. Existing systems like UV-DOAS and FTIR will be used extensively, but their compound coverage and minimum detectable concentrations must improve. The most significant advances in these techniques will not be in hardware, which is already fairly advanced, but in analytical software. Current analytical methods work well but are limited in application and must know *a priori* what compounds to look for and what interferents may be present. Integration of expert systems and neural networks into the spectral analysis routines of FTIR and UV-DOAS could provide these systems with the ability to optimize their own detection methods while also being adaptable to a changing monitoring environment.

The next significant advancement in monitoring hardware may be in the development of wavelength agile sources. A laser-like source—but one that can be tuned throughout the infrared or ultraviolet—would provide the best of all "worlds." Several possibilities exist, including advanced diode lasers or arrays of diodes permitting continuous coverage of broad ranges of the infrared. Perhaps even more significant are the advancements in optical parametric oscillator lasers. These devices are already capable of being scanned over broad infrared regions but their instantaneous line width (spread) is poor. Advances in this technology to broaden the tuning range and bring its linewidth down (to perhaps the 0.1 to $0.01 cm^{-1}$ range) could provide a nearly ideal source. Such a source would integrate the best characteristics of broadly tuning systems like FTIR or UV-DOAS with the spectral resolution of lasers. A source of this type would clearly render obsolete many of the current approaches. If the tunability of lasers is indeed accomplished, lidars with multicomponent coverage also becomes possible. If the power can be achieved to provide good spatial coverage, these may well be the penultimate monitor.

Clearly, the field of optical environmental monitoring has a bright future. But, significant advancements of current technology will be required to meet the ever-increasing demands of industry and government.

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