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**An Advanced Open-Path Atmospheric Pollution Monitor for Large Areas**

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## An Advanced Open-Path Atmospheric Pollution Monitor for Large Areas

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### Need

Large amounts of toxic waste materials, generated in manufacturing fuel for nuclear reactors, are stored in tanks buried over large areas at DOE sites. Flammable and hazardous gases are continually generated by chemical reactions in the waste materials. To prevent explosive concentrations of these gases, the gases are automatically vented to the atmosphere when the pressure exceeds a preset value. Real-time monitoring of the atmosphere above the tanks with automatic alarming is needed to prevent exposing workers to unsafe conditions when venting occurs.

### Objectives

This project is to design, develop, and test an atmospheric pollution monitor which can measure concentrations of DOE-specified and EPA-specified hazardous gases over ranges as long as 4 km. A tentative list of the 14 most dangerous DOE analytes is given in Table 1 with their required detection limits. This list was provided in 1994 by the Hanford Research Laboratory and is updated periodically.

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**Table 1. Analytes of Concern**

Chemical	Detection Limit ppm
Acetone	25.00
Ammonia	2.50
n-Butanol	50.00
Butyronitril	0.80
Dodecane	10.00
Hexanone	0.10
Methylene Chloride	0.05
Nitrogen Dioxide	0.10
Nitrogen Oxide	0.10
Nitrogen Trioxide	0.10
Toluene	5.00
Tributyl Phosphate	0.40
Vinyl Acetate	0.40
Vinylidene Chloride	0.40

### Approach

A CO<sub>2</sub> laser (1) to measure absorption spectra in the 9-11 μm region and (2) to determine the distance over which the measurements are made, is combined with an acousto-optic tunable filter (AOTF) to measure thermal emission spectra in the 2-14 μm region.

More explicitly, for long open-path remote sensing and quantitative measurements of atmospheric concentrations of trace vapors, differential-absorption lidar (DIAL) is the best

technique in which the laser is tuned to the absorption peak of a pollutant gas and then to a nearby wavelength at which the pollutant does not absorb. Furthermore, *infrared* DIAL systems are preferred because they are highly sensitive to the laser energy, are relatively “eye safe”, and, most importantly, can cover the spectral range where most molecule-specific absorption lines occur, that is, the infrared “fingerprint region” of 8-12  $\mu\text{m}$ .<sup>1</sup> These systems can also measure the distance over which the measurements are made -- without the use of retroreflectors.

However, all laser systems have limited wavelength coverage. Thus, a DIAL system must be complemented with a system which covers a broader range of wavelengths. An AOTF is a good choice for the complementary system because it (1) is easily integrated into a DIAL system, (2) covers a broad wavelength region of 2-14  $\mu\text{m}$ , (3) monitors emission spectra passively, (4) can be quickly tuned to any desired wavelength, (5) has high sensitivity to narrow lines via derivative spectroscopy, (6) does not have moving mechanical parts, and (7) provides complete images which can be used with focal plane array detectors.

## Project Description

### System Description

The remote monitor, shown in Figure 1, is comprised of seven key elements: a CO<sub>2</sub> laser, a harmonic generator crystal, optics, an AOTF, detectors, a computer, and a gas calibration cell (not shown).<sup>2</sup> The pulsed commercial CO<sub>2</sub> laser has ~60 lines which, due to the laser lines being very narrow, provides high spectral selectivity in the 9.2-10.9  $\mu\text{m}$  region. The laser operates at 10 pulses/s with 1 to 250 mJ/pulse and a 100 ns pulse width.

An optional harmonic generator (not included in the contract) doubles the laser frequency and provides 1 to 15 mJ/pulse for detecting molecules with absorption spectra in the 4.6-5.4  $\mu\text{m}$  region. The harmonic generator would be fabricated from internally grown thallium arsenic selenide (TAS) crystals which have produced the highest efficiency<sup>3</sup> (57%) and the highest laser power<sup>4</sup> (6 W) in the mid-infrared at 4.6  $\mu\text{m}$ . Figure 2 shows a TAS harmonic generator.

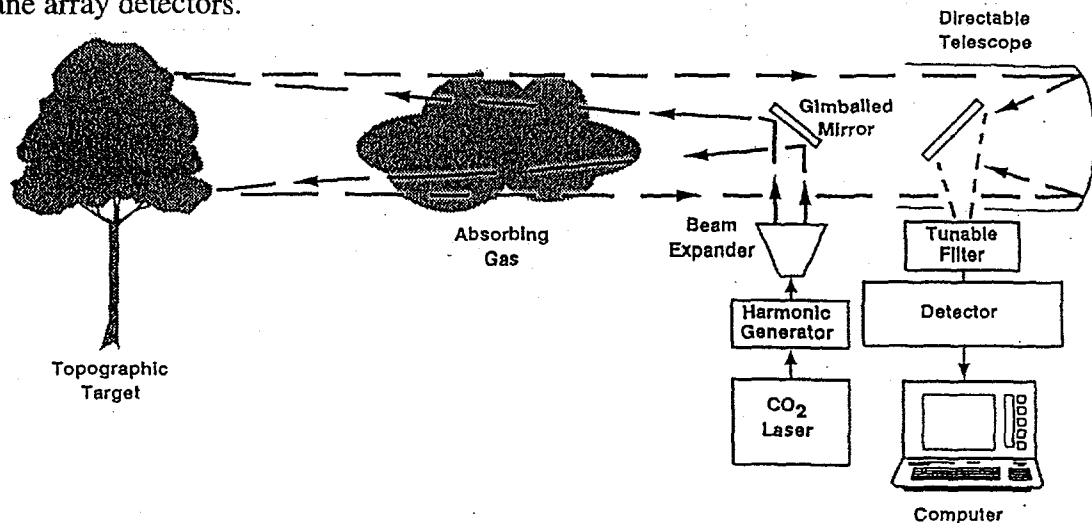
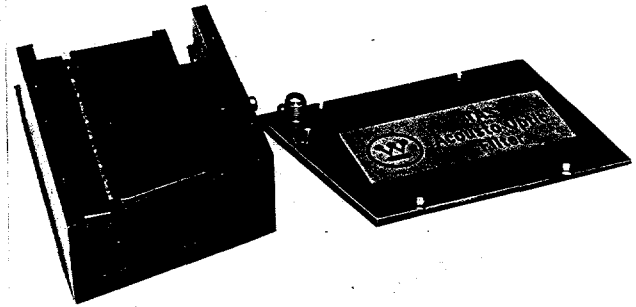
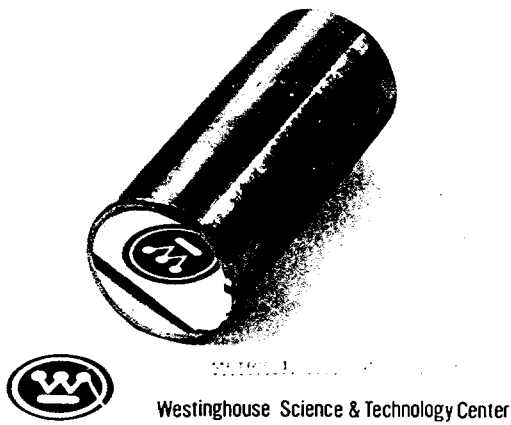


Figure 1 - Basic Configuration of Remote Monitor



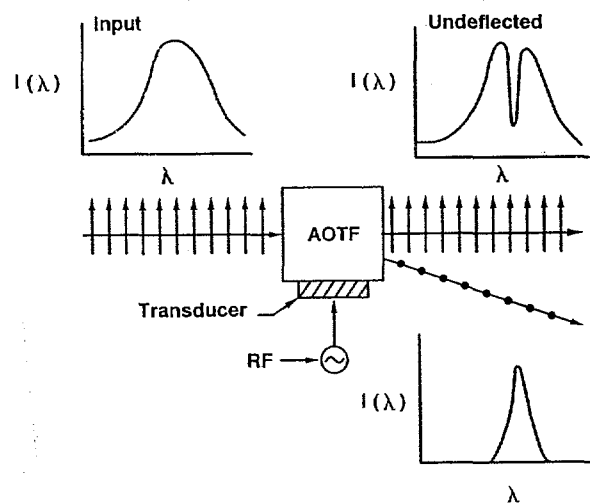
**Figure 2 - Harmonic Generator and AOTF are Small Solid-State Components**

The 250 mJ/pulse laser energy is sufficiently high that topological objects such as trees or buildings can be used as a back-reflectors, but the laser intensity is sufficiently low, due to the 20 cm diameter output beam diameter, that the laser beam is eye-safe. The use of topological objects is a major convenience in operation and allows fugitive releases to be monitored anywhere within the monitor's operational radius.

The reflected laser beam is collected with a 40 cm diameter mirror. The large mirror diameter reduces the effects of laser speckle. The laser power is pulsed to allow a convenient time-of-flight measurement of the distance to any topological back-reflector. This distance is needed to determine the average concentration of any gas along the optical path.

The received laser beam or thermal emission radiation is focused through the AOTF onto the detectors. The AOTF is fabricated from a TAS crystal, as shown in Figure 2, and operates as shown in Figure 3. The received beam, linearly polarized as

indicated by the arrows, enters the crystal and interacts with a periodically varying spatial distribution of indices of refraction set up by an acoustic beam inserted via the transducer. Only a narrow spectral band,  $\sim 10 \text{ cm}^{-1}$ , will be phase matched to the acoustic beam and diffracted out of the main beam, with its plane of polarization rotated  $90^\circ$  since TAS is a birefringent crystal. The center wavelength of the diffracted beam is uniquely determined by the frequency of the acoustic beam.



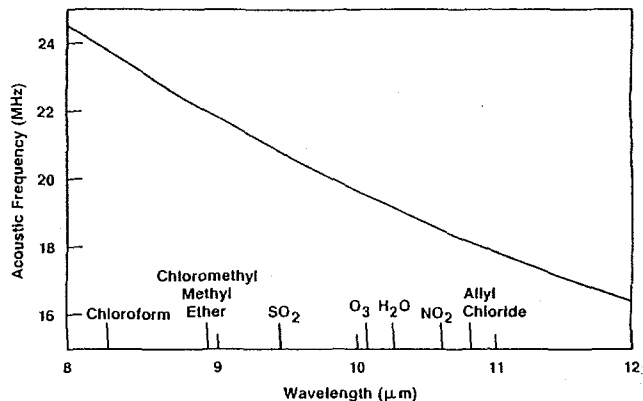
**Figure 3 - AOTFs are Electronically Tuned**

Two point detectors are used for improved sensitivity. One detector operates from 2 to 6  $\mu\text{m}$  and one operates from 6 to 14  $\mu\text{m}$ . The AOTF directs the received radiation to the two detectors by using one transducer for the 2-6  $\mu\text{m}$  and a second transducer for the 6-14  $\mu\text{m}$  portion. The transducers are placed on different faces of the crystal and diffract the two portions of the beam into two different directions. The detector signals are then analyzed by the computer to obtain path-averaged concentrations from the emission intensity and laser-determined range.

### System Operation

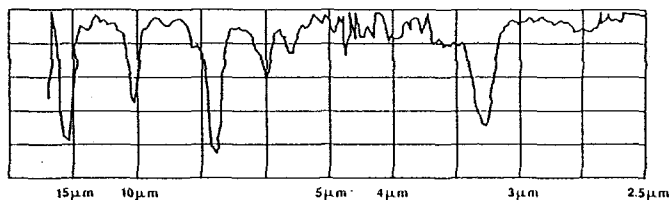
The  $\text{CO}_2$  laser wavelengths are switched in a predetermined pattern, typically staying on each wavelength for one second. An electronically controlled gimbaled telescope directs the beam to any target in real time. Thus, large areas can be quickly monitored via several beam paths.

The AOTF is computer controlled through the rf drive, thereby allowing the integration time and wavelength selection to be adjusted for optimum detection, either on a continual basis or whenever the need arises. The AOTF has two functions. During absorption measurements the AOTF increases the signal-to-background ratio by restricting radiation from the atmosphere to a narrow spectral range around the laser line. During emission measurements, the AOTF is operated from 2 to 14  $\mu\text{m}$ . By careful selection of the acoustic frequency, the wavelength of the diffracted beam can be centered on key emission lines of specific gases, such as shown in Figure 4. These key emission lines can be monitored when absorption measurements are not being taken, and if preset thresholds are exceeded the laser can be activated for more detailed measurements. Alternatively, the entire



**Figure 4 - AOTF Wavelength is Centered on Line by the Acoustic Frequency**

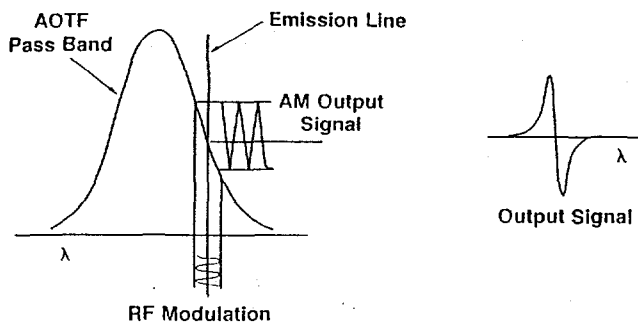
wavelength region can be scanned to obtain spectra such as the one for benzene shown in Figure 5.



**Figure 5 - Benzene Spectrum Generated by Scanning an AOTF**

The detectability of sharp emission lines is enhanced by dithering the acoustic frequency at a fixed modulation frequency,  $\sim 1$  kHz, as shown in Figure 6. This modulation sinusoidally shifts the AOTF passband. The modulation does not affect the radiation from sources which have relatively constant intensities over the AOTF passband, but modulates the intensity from emission lines narrower than the AOTF passband. A lock-in amplifier tuned to the modulation frequency gives the first derivative of the spectra within the AOTF passband. The second derivative is obtained in a similar manner.<sup>5</sup>

The computer calculates concentrations and the range to the reflecting target. It sounds



**Figure 6 - AOTF Derivative Detection is Very Sensitive to Narrow-Lines**

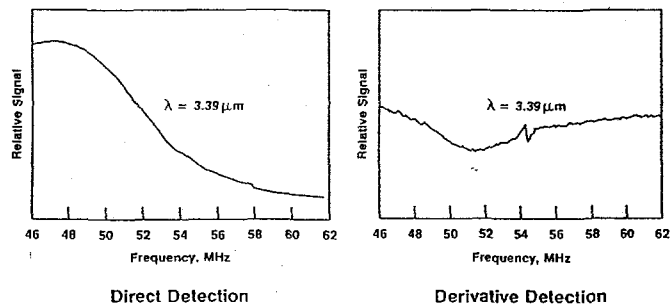
an alarm whenever any preset concentration level of a hazardous gas is exceeded anywhere within a radius of 4 km. It also stores the results, displays the results, controls the operation of the monitor, and periodically inserts, by optical means, the gas calibration cell into the optical path to calibrate both the absorption and emission measurements.

## Results

The laser power is sufficiently large that signal-to-noise ratios over 8 km path lengths is not a problem. In this mode of operation the monitor is essentially the same as other CO<sub>2</sub> DIAL systems and has the same sensitivities. In the 9.2-10.9 μm region, computed detection limits vary from 1 ppb for Freon 12 to 60 ppb for ethyl-mercaptan to 340 ppb for sulfur dioxide. In the 4.6-5.4 μm region, computed detection limits vary from 0.3 ppb for carbonyl sulfide to 21 ppb for nitrous oxide to 187 ppb for carbon monoxide.

In measuring emission spectra the large wavelength coverage allows the monitoring of literally hundreds of gases. However, the sensitivity is lower because the emitting gas is at or near the same temperature as the atmosphere which is emitting as a blackbody. Fortunately, many atmospheric vapors have

narrow line widths which allows modulation of the AOTF to increase the sensitivity by obtaining first and second derivatives of the spectra. An example of this enhancement is shown in Figure 7 for a laser line with 1% of the spectral radiance of a glow bar in the background. The laser line cannot be seen in direct detection but when the first derivative is taken the laser line is clearly seen.



**Figure 7 - Measurements of HeNe Laser Line with 1% the Radiance of a Glow Bar**

The theoretical sensitivity of the spectral derivative technique can be in the ppb range but is wavelength dependent because of the atmospheric blackbody wavelength dependence. The signal (emission line) to background (atmospheric radiation) ratio is increased, by taking the first derivative, by a factor of 9 at 10.6 μm, by 36 at 5.3 μm, and by 75 at 3.7 μm. The second derivative increases are 68 at 10.6 μm, 1100 at 5.3 μm, and 4700 at 3.7 μm. However, the signal-to-noise ratio decreases with each higher derivative.<sup>5</sup>

Of the fourteen Analytes of Concern in Table 1, the system performance can be estimated for the nine Analytes for which we have spectra. Table 2 contains those estimates for dry air which are presented in the form of ranges between 0.2 km and 20 km over which the Analyte concentration can be measured at the detection limit given in Table 1.



**Table 2. Ranges in km over which detection limits in Table 1 can be measured.**

Analyte	Absorption		Emission
	Min.	Max.	Min.
Acetone	Cannot Measure		1
Ammonia	2.6	8.7	5
n-Butanol	Too Absorbing		1
Methylene Chlo.	Cannot Measure		80
Nitric Oxide	Interference		2073
Nitrogen Dioxide	7.0	20.	9608
Toulene	0.2	20.	3
Vinyl Acetate	0.2	20	855
Vinylidene Chlo.	0.2	20.	724

The laser absorption mode can measure concentrations for five of the nine Analytes. It cannot measure nitric oxide due to interference from normal atmospheric gases. It could however measure n-Butanol at much lower concentrations but at 50 ppm it completely absorbs the laser beam. Methylene Chloride and Acetone do not have spectra which overlap with any of the laser lines. These results are for a minimum measurable power difference at the detector of 5% and a topological reflector with a reflectivity of 6%.

For the thermal emission performance estimates in Table 2 it is assumed that the atmosphere is at 23 C and the background object is a concrete building at 25 C with an emissivity of 0.92. All nine Analytes can be detected but the shortest detection range, assuming a minimum detectable difference of 3% between the building and the atmosphere, varies widely. However, these results are for a single measurement at a medium temperature difference between the atmosphere and background. Monitor performance would be improved by averaging several measurements and/or by applying derivative spectroscopy.

The example results in Table 2 illustrate how the absorption and emission spectra complement each other. Laser absorption is useful at any time of day or night but is limited in the number of pollutants it can measure. In contrast, thermal emission is useful for all pollutants but it does not measure range and cannot be used at all times or for all ranges; there will always be times or geometries when the background radiance matches that of the intervening atmosphere, thereby rendering measurements impossible.

### Benefits

The open-path atmospheric pollution monitor will:

- reduce personnel exposure to harmful gases
- monitor inaccessible or dangerous regions
- reduce monitoring costs for large areas
- be easily setup in any location
- be easily pointed in any direction
- be manually or automatically operated
- be self-calibrating via a calibration gas cell
- be self-contained, except for electrical power

### Future Activities

The program is divided into a Base Program plus two options. The 13 month Base Program is to design, build, and bench test the complete pollution monitor within the Westinghouse laboratory. Furthermore, the list of Analytes of Concern will be updated and

absorption spectra will be measured for those Analytes which do not have digitized absorption spectra. The five month Option I is to support independent testing, under carefully controlled conditions, of the monitor at METC to determine the full range of its performance capabilities. The six month Option II is to support open-path atmospheric testing at the Hanford National Laboratory to determine atmospheric effects on system performance. Commercialization activities for this monitor will proceed in parallel with the options.

### Acknowledgments

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