

DOE/MC/32087-96/C0700

CONF-9604143-1

**An Advanced Open-Path Atmospheric Monitor Design**

**Author:**

L. Taylor  
D. Suhre  
S. Mech

**RECEIVED**

**MAY 21 1996**

**OSTI**

**Contractor:**

Westinghouse STC  
1310 Beulah Road  
Pittsburgh, Pennsylvania 15231

**Contract Number:**

DE-AR21-95MC32087

**Conference Title:**

41st Annual Analysis Division Spring Symposium

**Conference Location:**

Framingham, Massachusetts

**DISCLAIMER**

**Conference Dates:**

April 21-24, 1996

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**Conference Sponsor:**

Instrument Society of America

**Contracting Officer Representative (COR):**

J. Malhotra, E06

**MASTER**

**DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED**

## **DISCLAIMER**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, 175 Oak Ridge Turnpike, Oak Ridge, TN 37831; prices available at (615) 576-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22161; phone orders accepted at (703) 487-4650.

# AN ADVANCED OPEN-PATH ATMOSPHERIC MONITOR DESIGN

L. H. Taylor and D. R. Suhre  
Northrop Grumman Science & Technology Center  
1310 Beulah Road, Pittsburgh, PA 15235

S. J. Mech  
Westinghouse Hanford Company, P.O. Box 1970, L5-55, Richland, WA 99352

## KEYWORDS

Atmosphere, Derivatives, Design, Filter, Infrared, Laser, Monitor, Pollutants, Spectra

## ABSTRACT

The conceptual design of an open-path atmospheric monitor combines an acousto-optic tunable filter for emission spectroscopy (3-14  $\mu\text{m}$ ) with a mid-IR (4.6-5.4  $\mu\text{m}$ ) and far-IR laser (9.2-10.9  $\mu\text{m}$ ) for absorption spectroscopy. It utilizes mostly commercially available components, covers a large area (~4 km radius), measures the distance to any reflecting object, can take measurements along any line-of-sight, and is eye safe. Of twenty test pollutants it is to detect, the concentrations of all twenty will be measurable via emission spectroscopy and ten by the more sensitive absorption spectroscopy.

## INTRODUCTION

In the process of manufacturing nuclear reactor fuel, large amounts of toxic and radioactive waste materials have been generated and stored in hundreds of large underground tanks at DOE sites. These tanks are grouped together into a few areas call "tank farms". Over 50 dangerous gases have been identified or suspected of being present in the vapor head space of these tanks [1]. Near real-time continuous broad area atmospheric monitoring with automatic alarming if dangerous gases are released to the tank farm environment is needed to prevent exposing workers to unsafe conditions.

For long open-path remote sensing and quantitative measurements of atmospheric concentrations of trace vapors, differential-absorption lidar (DIAL) is the best technique. Furthermore, *infrared* DIAL systems are preferred because they are highly sensitive to the laser energy, are relatively "eye safe", and, most importantly, are in the spectral region (8-14  $\mu\text{m}$ ) where most molecule-specific absorption lines

occur (the 3-5  $\mu\text{m}$  band is useful for detection but contains so many lines that identification is difficult) [2]. Of the available infrared lasers,  $\text{CO}_2$  lasers are the best suited for long-path atmospheric monitoring because they have the highest efficiencies and powers, are easily tuned, and cover the 9.2-10.9  $\mu\text{m}$  region, i.e., their lines lie within the 8-14  $\mu\text{m}$  molecular fingerprint region. Furthermore, their wavelengths can be extended by second harmonic generation to cover the 4.6-5.4  $\mu\text{m}$  region [3].

However, all laser systems have limited wavelength coverage. Thus, a DIAL system should be complemented with a broader wavelength system. An Acousto-Optic Tunable Filter (AOTF) is a good choice for the complementary system because it is easily integrated into a DIAL system, it monitors emission spectra passively, it can be quickly tuned to any wavelength, its sensitivity to narrow lines is easily increased by measuring derivatives of spectra lines, and it covers the entire 3-14  $\mu\text{m}$  region [4].

## SYSTEM DESCRIPTION

The conceptual design of the remote monitor, shown in Figure 1, is comprised of seven key elements: a  $\text{CO}_2$  laser, a harmonic generator, optics, an AOTF, detectors, a computer, and a gas calibration cell (not shown). The commercial  $\text{CO}_2$  laser envisioned for this monitor is tunable over 87 lines in the 9.2-10.9  $\mu\text{m}$  region and operates at 10 pulses/s with 1 to 250 mJ/pulse, depending on the line. The pulse width of the linearly polarized beam is 100 ns which allows the range to any reflecting object, e.g., the tree in Figure 1, to be measured to within  $\pm 15$  m. The range is needed to determine the average concentration of the vapor from the measured absorption or emission spectra.

An optional enhancement is a  $\text{Tl}_3\text{AsSe}_3$  (TAS) harmonic generator which would double the  $\text{CO}_2$  laser frequency, thereby adding to the system's capabilities a few trace vapors which have absorption lines around 5  $\mu\text{m}$  but none in the 9-11  $\mu\text{m}$  region. TAS harmonic generators, see Figure 2, are completely passive and are very efficient, having obtained 57% in the far infrared [3]. The harmonic generator will produce pulse energies from 1 to 15 mJ on 68 lines in the 4.6-5.4  $\mu\text{m}$  region. The transmitter optics then enlarges the laser beam to 40 cm diameter to make it eye safe and directs it into the atmosphere with a Newtonian telescope.

The receiver optics collects the reflected laser beam or atmospheric emission radiation with a 40 cm diameter Newtonian telescope. As shown in Figure 3, the range to the reflecting object is measured by directing the received beam, via a two-position stepping mirror, through matching optics to a fast HgCdTe detector, cooled to 200 K and optimized for  $\text{CO}_2$  lasers. Otherwise, the received radiation is collimated with matching optics and directed through the AOTF. The output of the AOTF is split by a dichroic beam splitter which sends the 6-14  $\mu\text{m}$  radiation to a HgCdTe detector and the 3-6  $\mu\text{m}$  radiation to an InSb detector. Two detectors are used for maximum sensitivity and both are cooled to 77 K.

The system is calibrated periodically by measuring the known concentrations of gases contained in a sealed gas cell. During calibration the left-most turning mirror in Figure 3 is turned  $45^\circ$  by a two-position stepping motor. The rotated position reflects externally produced radiation back onto itself while radiation from the gas cell goes to the detectors along the same optical path as the external radiation when the mirror is in the other position.

The optical head, excluding the computer and laser power supply, could be assembled in a bistatic configuration as shown in Figure 4 in which the components are shown to scale and the "tripod" represents a maneuverable optical bench. Located adjacent to the laser is an enclosure for the AOTF, electronics, detectors, and receiver beam directing optics. The actual design is in progress with the Los Alamos National Laboratory designing the laser subsystem.

## SYSTEM OPERATION

The CO<sub>2</sub> laser wavelengths are switched in a predetermined pattern, typically staying on each wavelength for one second. Electronically activated two-position mirrors direct the CO<sub>2</sub> laser beam through the harmonic generator crystal for short wavelength operation and around the crystal for long wavelength operation. A maneuverable telescope directs the beam to any target in real time. Thus, large areas can be quickly monitored via several beam paths and the beam paths quickly changed to respond to fugitive emissions wherever they may occur.

The AOTF is fabricated from a single crystal of TAS and operates as shown in Figure 5 (The design shown is a noncollinear AOTF whereas, for clarity in presentation, the AOTF shown in Figure 3 is a collinear configuration in which the optic and acoustic beams are parallel). 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,  $\sim 2 \text{ cm}^{-1}$ , will be phase matched to the acoustic beam and diffracted out of the main beam, with its plane of polarization rotated 90° since TAS is a birefringent crystal. The fraction of the input beam polarized in the direction orthogonal to that shown in Figure 5 is not affected by acoustic beam, passing straight through the crystal. The noncollinear TAS AOTF designed for this monitor is shown in Figure 6 as it appeared after fabrication.

The AOTF has two main functions. First, during absorption measurements the AOTF increases the signal-to-noise ratio by restricting radiation from the atmosphere to a narrow spectral range,  $\sim 2 \text{ cm}^{-1}$ , around the absorption line. Second, during emission measurements the AOTF is operated from 3-14  $\mu\text{m}$  as a narrow band filter. 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 7.

The AOTF has the added benefit in that spectral derivatives are easily obtained for lines much narrower than the AOTF passband. This feature is obtained, as shown in Figure 8, by modulating the acoustic frequency at a fixed frequency,  $\sim 1 \text{ kHz}$ . 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 narrow emission lines. 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 [4].

## SYSTEM PERFORMANCE

The CO<sub>2</sub> laser power is sufficiently large that the signal-to-noise ratio 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 high sensitivity due to its high power and very narrow line width compared with the absorption lines of the vapors. However, the finite number, 87, of laser lines limits the number of gases which can be detected to some value less than 87.

On the other hand, when operating in the passive mode, the monitor is capable of measuring the emission spectra of literally hundreds of gases due to the large wavelength coverage. 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 the modulation of the AOTF passband to increase the signal-to-background ratio (SBR) by obtaining first and second derivatives of the spectra. This enhancement is shown in Figure 9 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. The potential sensitivity improvement of this modulation technique is larger at shorter wavelengths due to the falloff of the blackbody, as seen from the theoretical results in Table I [4]. Not included in these results is the reduction in the signal-to-noise ratio which accompanies the taking of derivatives.

**Table I. Derivative spectroscopy increases the SBR of narrow lines.**

Wavelength, $\mu\text{m}$	SBR 1st Derivative	SBR 2nd Derivative
2.8	1300	12000
3.7	75	4700
5.3	36	1100
10.6	9	68

In developing any monitor it is important to know the specific vapors which must be monitored since no monitor can effectively detect all gases and all gases are not equally dangerous. For this purpose a list of sixteen vapors has been compiled [5]. This list is given in Table II with the list ordered according to priority with Benzene having the highest priority. The table specifies which vapors can be detected by absorption spectra with the CO<sub>2</sub> laser and which vapors can be detected by emission spectra with the AOTF. Of the sixteen vapors, nine can be detected in the very sensitive laser absorption mode and all sixteen can be detected in the thermal emission mode.

### ACKNOWLEDGEMENTS

The development of the monitor concept described above is being funded by the DOE Morgantown Energy Technology Center under contract DE-AR21-95M32087. The contract monitor, Darren Mollot, has been most helpful in the early stages of this contract.

Table II. Vapors to be monitored ordered by priority.

Vapor	Detection by Thermal Emission	Detection by Laser Absorption
Benzene	yes	yes
Vinylidene chloride	yes	yes
Nitrogen dioxide	yes	
Carbon tetrachloride	yes	
Butadiene	yes	yes
Chloroform	yes	
Methylene chloride	yes	
Carbon monoxide	yes	
Ammonia	yes	yes
Nitric oxide	yes	
n-Hexane	yes	yes
Trichlorofluoromethane	yes	yes
2-Hexanone	yes	
Toluene	yes	yes
Acetonitrile	yes	yes
Pentane	yes	yes

### REFERENCES

1. "Radioactive Tank Waste Remediation Focus Area," Report DOE/EM-0255, U.S. Dept. Commerce, Technology Administration, NTIS (1995).
2. D. K. Killinger and N. Menyuk, "Remote Probing of the Atmosphere Using a CO<sub>2</sub> DIAL System," IEEE J. Quantum Electron. QE-17: 1917 (1981).
3. D. R. Suhre, "Efficient Second Harmonic Generation in Tl<sub>3</sub>AsSe<sub>3</sub> Using Focussed CO<sub>2</sub> Laser LRadiation," J. Appl. Phys. B52: 367 (1991).
4. M. Gottlieb, "Acousto-Optic Tunable Filters," Chap. 4, Design and Fabrication of Acousto-Optic Devices, A. P. Goutzoulis and D. R. Pape, Eds., Marcel-Dekker, New York (1994).
5. L. H. Taylor and S. J. Mech, "Gaseous Analytes of Concern at Hanford Tank Farms," Report in preparation (1996).

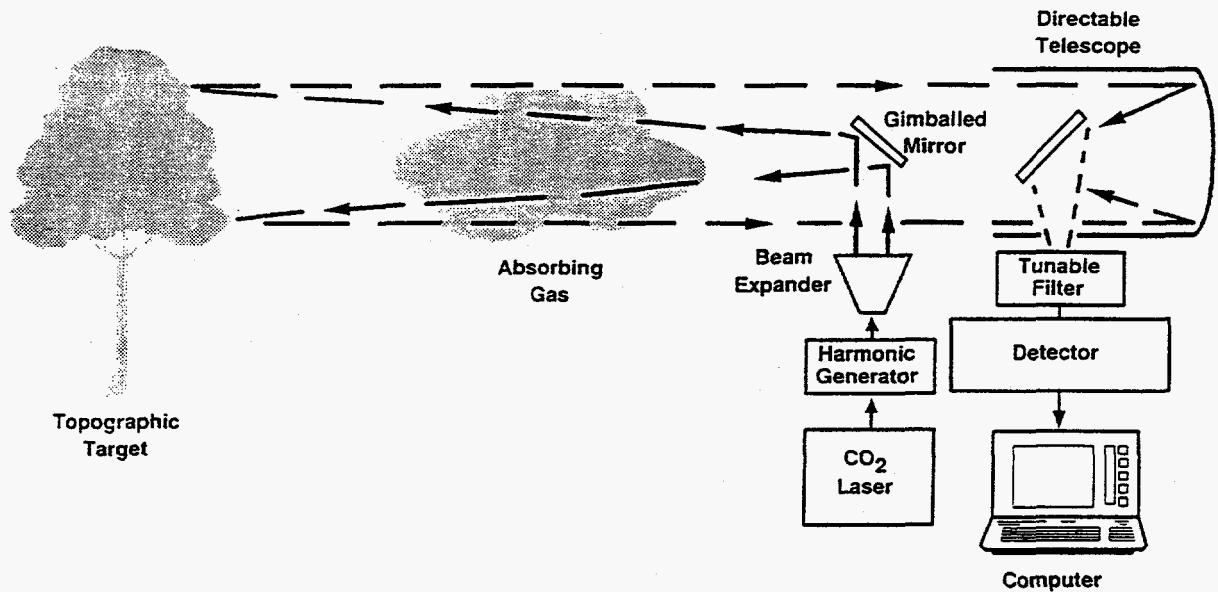


FIG. 1 — THE REMOTE ATMOSPHERIC MONITOR COMBINES A NARROW WAVELENGTH LASER TO PROVIDE RANGE AND SENSITIVE DETECTION VIA ABSORPTION SPECTROSCOPY WITH AN AOTF TO PROVIDE WIDE WAVELENGTH MEASUREMENTS VIA EMISSION SPECTROSCOPY.



Westinghouse Science & Technology Center

FIG. 2 — THE TAS HARMONIC GENERATOR IS A SMALL SOLID-STATE COMPONENT.



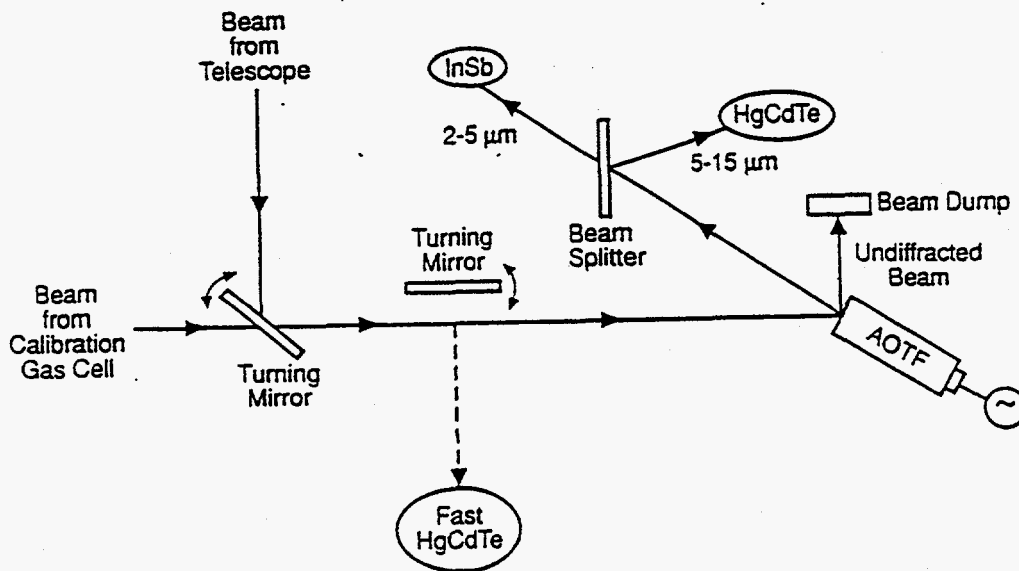


FIG. 3 — THE RECEIVER'S OPTICS AFTER THE TELESCOPE DIRECTS RADIATION FROM EITHER THE ATMOSPHERE BEING MEASURED OR A CALIBRATION GAS CELL TO ONE OF THREE DETECTORS.

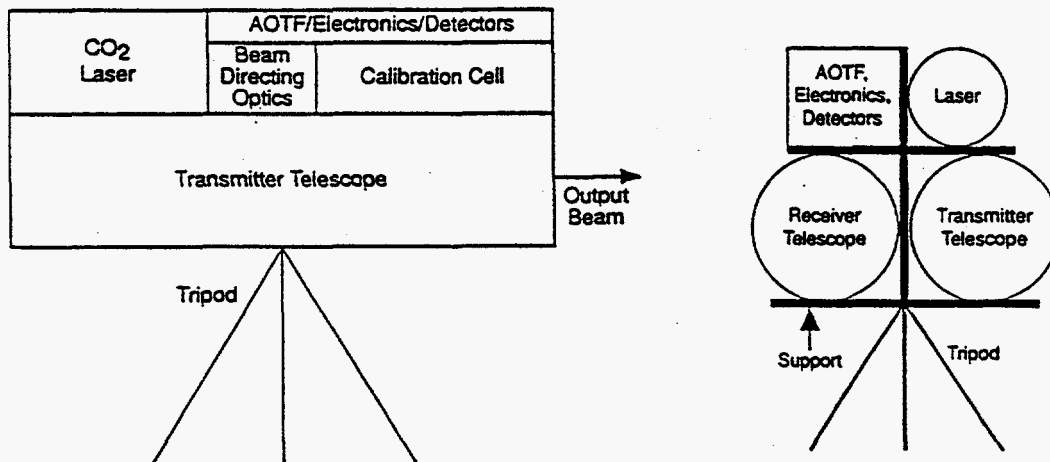


FIG. 4 — THE KEY COMPONENTS, SHOWN TO SCALE, ARE GROUPED TOGETHER INTO A COMPACT UNIT.

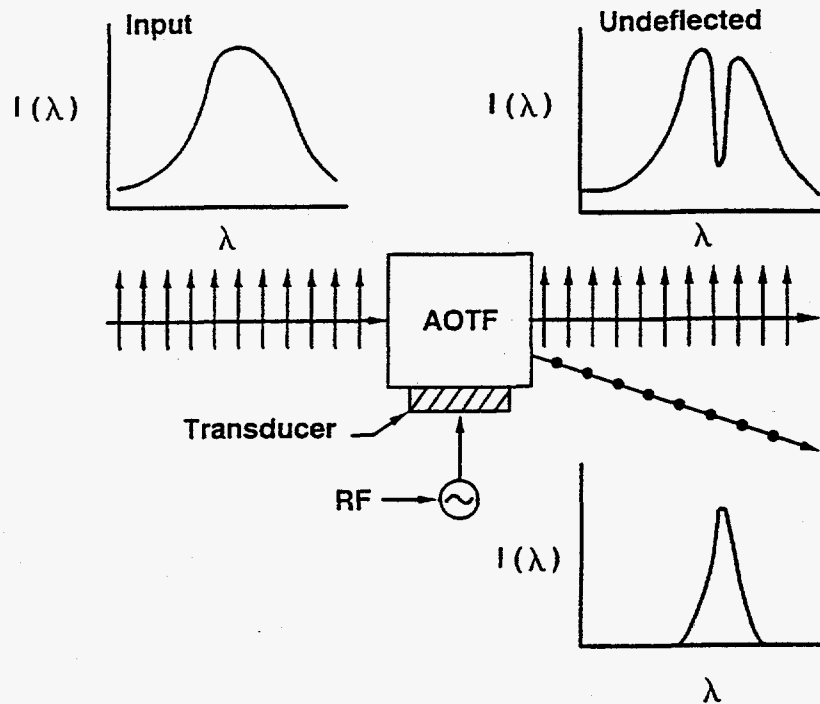


FIG. 5 — A NONCOLLINEAR BIREFRINGENT AOTF DIFFRACTS A SMALL WAVELENGTH SLICE OUT OF THE INPUT SPECTRUM. THE DIFFRACTED BEAM IS PUT INTO A DIFFERENT ANGLE AND ITS PLANE OF POLARIZATION ROTATED 90°, SIMPLIFYING THE SEPARATION OF THE TWO BEAMS.

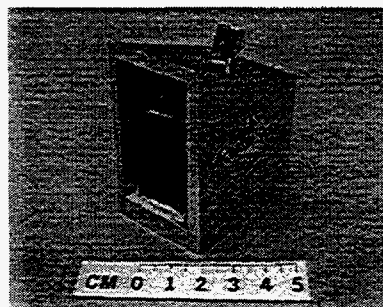


FIG. 6 — THE AOTF DESIGNED FOR THIS MONITOR IS ANOTHER SMALL SOLID-STATE COMPONENT.

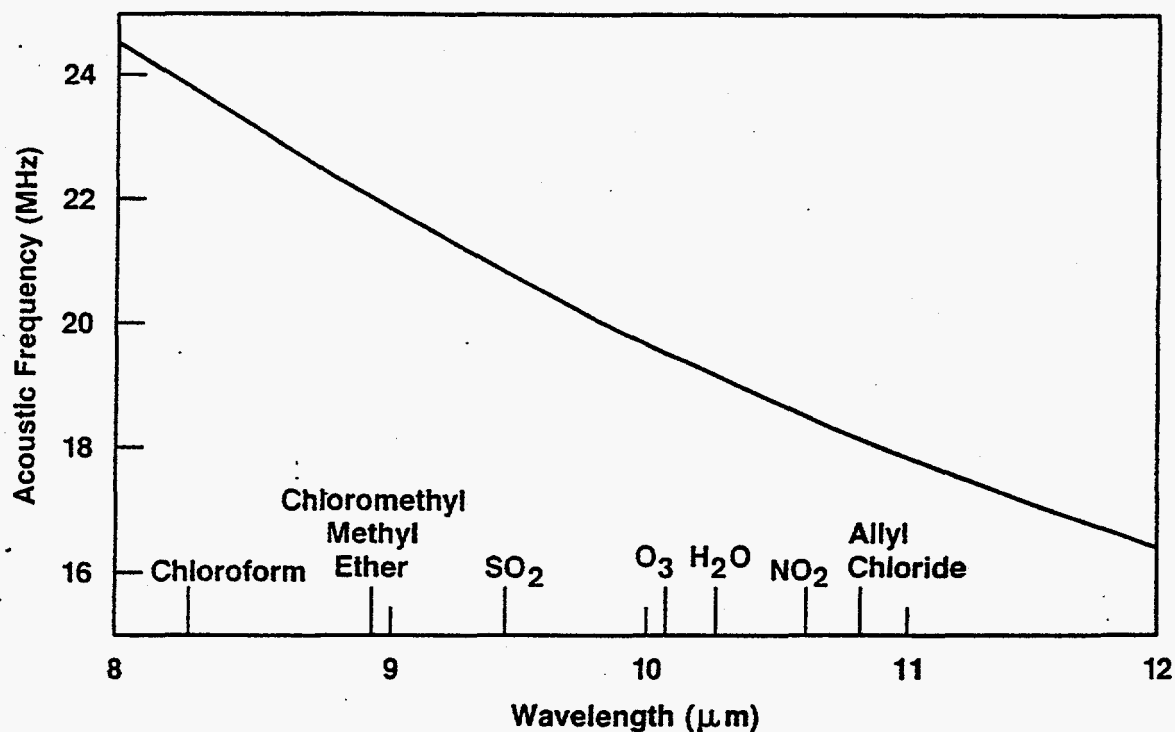


FIG. 7 — THE CENTER WAVELENGTH OF THE FILTERED BEAM FROM AN AOTF IS CENTERED ON THE EMISSION LINE OF A VAPOR BY ADJUSTING THE ACOUSTIC FREQUENCY.

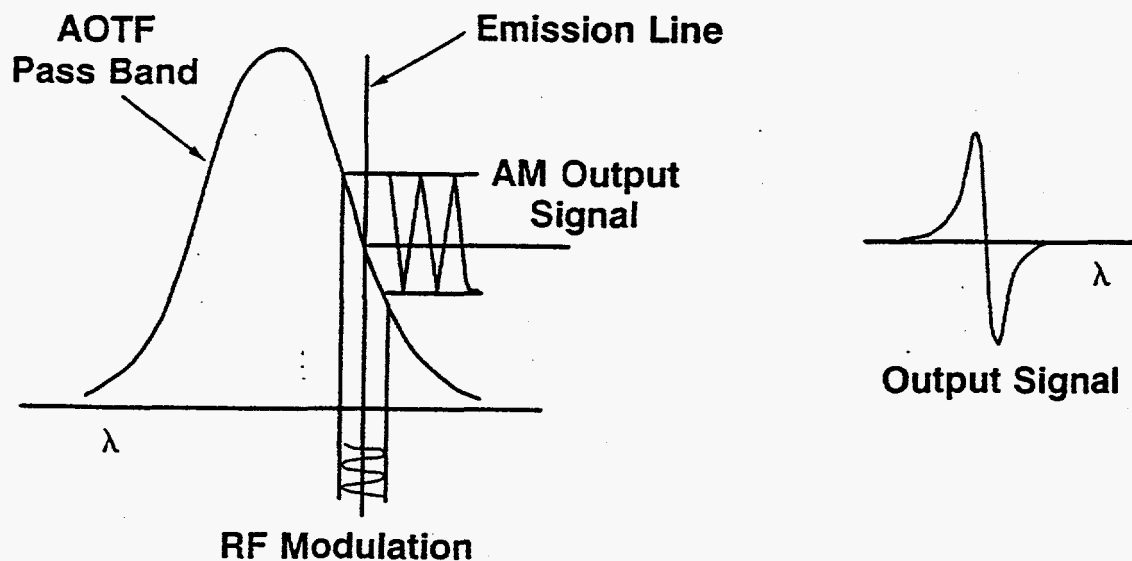
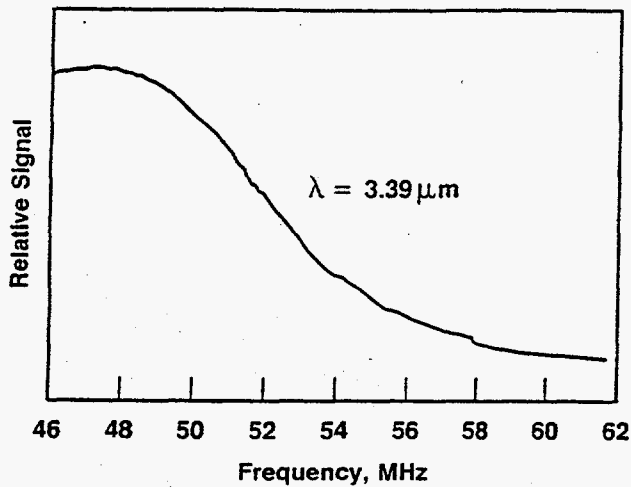
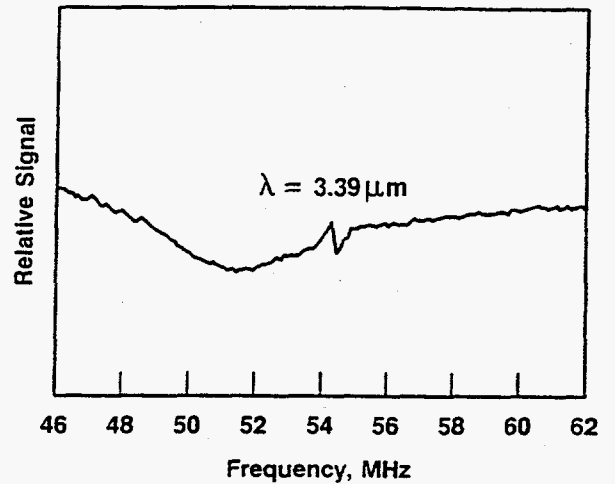


FIG. 8 — DERIVATIVE DETECTION WITH AN AOTF IS EASILY OBTAINED BY MODULATING THE FREQUENCY OF THE ACOUSTIC BEAM.



Direct Detection



Derivative Detection

FIG. 9 — DIRECT DETECTION OF A LASER LINE WITH A RADIANCE 1% OF THE BLACKBODY RADIANCE AT THE SAME WAVELENGTH SHOWS NO LINE, BUT DERIVATIVE DETECTION WITH AN AOTF SHOWS IT VERY CLEARLY.