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ABSTRACT

Spectroscopy provides a fast sensitive method for chemical analysis. Lasers are high intensity narrow bandwidth, collimated light sources in the infrared, visible, and ultraviolet spectral regions. Wavelength tunable lasers can be used for spectroscopic chemical identification by means of techniques such as opto-acoustic spectroscopy, thermal lensing, and fluorescence excitation. These methods all share the useful characteristic that their detection sensitivity to small quantities of chemicals improves with higher laser intensity. We have developed apparatuses to use these techniques for trace chemical identification and detection. In addition, a useful improvement to thermal lensing, which we designate thermal deflection spectroscopy, has been developed.

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Light absorption methods for chemical detection have been used for many years since they offer some real advantages over other methods. Optical absorption can be used as a probe for chemicals at a distance from the detector, thus preventing exposure of the operator to toxic or hazardous materials. The advent of laser light sources enhances the utility of traditional absorption techniques. Thus, the beam-like nature of laser light provides remote detection at much larger distances; the high intensity provides greater sensitivity for real time detection, and the narrow linewidths and tunability provide selectivity and specificity in identifying the toxic chemical in a complex environmental sample.

In traditional absorption spectroscopy light is passed through a sample and the ratio of light intensity transmitted to light intensity incident on the sample, I/I_0 , is measured. Beer's law is used to relate this measurement to the quantity of absorbing material present in the sample. Increasing the intensity of the incident light does not affect this ratio nor does it appreciably affect the accuracy of the measurement if the amount of light absorbed is small. The reason is that one is measuring the effect of a small number of molecules on a large amount of light and trying to observe small changes in a large quantity.

Fortunately, a group of techniques which are collectively termed excitation spectroscopy have been developed over the last century or so and have been much less used until the advent of lasers. These methods

include fluorescence spectroscopy^{1,2} and the opto-acoustic effect.³ Their common characteristic is that they follow the effects of the light absorbed rather than the light transmitted. Fluorescence spectroscopy, for instance, measures the light emitted from the sample at a different wavelength following absorption. For a small sample there may be very little fluorescent light emitted, but the amount of fluorescence is proportional to the incident light intensity. Thus, the sensitivity of this method for trace chemical detection is greatly enhanced by the use of powerful lasers. The emitted light may be distinguished from the incident light by its different wavelength and by the difference in propagation direction. Laser-induced fluorescence has been used to detect compounds in the part-per-trillion range.¹

In the opto-acoustic effect a microphone is used to detect a pressure pulse following deposition of the absorbed light energy in the sample. This method shares with fluorescence the same characteristic of having a detection sensitivity that improves with increasing laser light intensity. The opto-acoustic effect has been used to detect compounds in the sub-part-per-billion range.⁴

In a complex environmental sample there may be many different chemicals present; in order to prevent false alarms a toxic chemical detection method must also be an identification method. One needs to have a "fingerprint" pattern of peaks and valleys in the optical absorption spectrum of the compound of interest so that as the laser is scanned in wavelength, the excitation of fluorescence (or acoustic energy) mirrors that pattern of peaks and valleys, i.e. where there is no absorption there can be no fluorescence. This pattern can then be used to specifically identify the compound. In fluorescence spectroscopy it is also

possible to measure the set of wavelengths emitted from the sample for a fixed excitation wavelength and thus obtain a two dimensional pattern for even better identification.

Since the requirement for a wavelength tunable laser light source is so important, Fig. 1 shows the range of various laser tuning techniques. Most methods begin with powerful, efficient driver lasers shown on the bottom of the figure. The driver lasers often are limited in tuning range, but these driver outputs can be shifted to new wavelengths by means of the techniques shown in the upper part of the figure. Sometimes the shift is fixed as in Raman shifting;⁵ sometimes the shift is continuously tunable as in dye lasers⁶ or optical parametric oscillators.⁷ These methods cover the ultraviolet, visible, and infrared regions of the spectrum.

In Fig. 2 are shown the chemical agents of interest on the left side of the figure and the simulants with which we have worked on the right side. They are similar in that all of them are phosphonate esters. In Fig. 3 is shown an infrared absorption spectrum of pure liquid OSP along with assignments of the absorption peaks to specific bond stretching frequencies.⁸ These bonds are present in both the chemical agents as well as our simulants. Superimposed on the graph in dashed lines are the wavelengths of some CO₂ laser lines. A CO₂ laser could be rapidly tuned from one line to another to provide the kind of spectral signature previously discussed.

Figure 4 shows a concept of how opto-acoustic detection could be used for point monitoring. An amplitude modulated laser beam, if it is absorbed in the duct, deposits energy in the air and produces a pattern of pressure waves which are detected by the microphone. The sound

intensity is greatly increased if the modulation frequency corresponds to a resonant mode of the duct. Slots allow fresh air sample to flow through the device for a quick response to contamination. While similar devices already exist, it would be useful if opto-acoustic detection could be used for remote monitoring, and more specifically, as single-ended remote monitoring devices where both the detector and the laser are in the same place. Such a concept is depicted in Fig. 5. Using a 300-watt CO₂ laser and a cloud of Freon 12, we have generated sound intensities of over 100 decibels.

When the modulated CO₂ laser is absorbed in a gas sample, both acoustic pressure waves and transient temperature increases are produced. We have discussed the detection of the pressure pulses; the temperature increase produces a decrease in the refractive index of the air. This effect has been used as a chemical detection technique and is called thermal lensing spectroscopy. In our modification, the gradient in refractive index at the CO₂ laser beam can be used to deflect a second probe laser beam such as a helium neon laser, and the deflection can be measured with a dual photodiode.¹⁰ A device to accomplish this is shown in Fig. 6. A CO₂ laser is modulated by a slotted wheel, 1. A helium neon laser beam travels parallel and adjacent to the CO₂ following the germanium beam combiner, 2. A 15-cm cell filled with air and varying partial pressures of absorber causes deflection of the helium neon beam with a lever arm, L, of 2 meters. A beam stop, 3, of pyrex prevents the CO₂ laser from damaging the photodiode. The dual photodiode has two silicon photodiodes with a narrow gap between them and balanced so that a small motion of the HeNe spot off of center will produce a signal in the differential amplifier. A spot motion of 10⁻³ spot diameters can be detected.

In Fig. 7 is seen the deflection signal observed for a CO₂ laser input to the cell as shown. The average CO₂ power at a repetition rate of 20 Hz is 0.1 watt. The absorber is DMMP at its room temperature vapor pressure of approximately 1 torr, mixed with 680 torr of air.

Varying the partial pressure of absorber by successive dilutions is difficult because of absorption on the cell walls, however, Fig. 8 can be obtained using Freon 12 as the absorber gas mixed with N₂ gas at 760 torr. Signal is determined from the peak of plots such as Fig. 7. Focusing the lasers into the cell gives a larger signal than the collimated beams. The latter measurements have been multiplied by a factor of 3 to place them on the same scale.

In order to test the effect of higher power CO₂ lasers on the signal, Fig. 9 was plotted. The good straight line behavior suggests that the sensitivity of the technique will improve with higher power lasers.

This experiment can be extended to a single-ended remote detection method if one realizes that the deflected image of the HeNe spot can be at a target and monitored by means of a telescope with a dual photodiode at the focus. Such a device is shown in Fig. 10. The modulation of the CO₂ laser appears as a modulated motion of the HeNe laser spot on the rock. This experiment has been performed in a lab and proves to be remarkably insensitive to the surface roughness of the rock. Fortunately, CO₂ lasers operate in a window in the atmospheric transmission spectrum where there are few interfering absorbers naturally present,^{11,12} and they are line tunable over a wide range and are also efficient.

As part of a contract, we have also developed an apparatus for measuring laser-induced fluorescence. The machine is, at present, a

research instrument built for maximum flexibility and is shown in Fig. 11. It consists of a pulsed nitrogen laser at 3371 Å which pumps a tunable dye laser in the green to orange region of the spectrum. The dye laser is frequency doubled in a nonlinear crystal to provide a source of tunable ultraviolet light, which excited the sample. The fluorescence is picked off from the side and focused into a monochromator. A photomultiplier tube detects the pulses of light, and a boxcar amplifier averages the resulting electrical pulses for a stripchart recorder to display. Data is displayed as a function of either the excitation wavelength (determined by the dye laser) or the emission wavelength (determined by the monochromator setting). Because of the extreme sensitivity of this apparatus, even part-per-million impurities in the liquid samples have been shown to give erroneous results.

In summary, both the opto-acoustic and thermal deflection techniques show high potential for use as point or remote detection methods at the part-per-million level. The next steps in the program will be to extend the work to the chemical agents and to develop an optimal set of wavelengths for agent identification in a real world environment. The laser-induced fluorescence technique requires further testing on purified samples.

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Figure Captions

- Fig. 1. A survey of various techniques for producing tunable lasers.
- Fig. 2. Chemical agents and simulants.
- Fig. 3. The infrared absorption spectrum of neat liquid OSP, and CO₂ laser emission lines which could be used to fingerprint the presence of OSP.
- Fig. 4. A conceptual design of an opto-acoustic cell for chemical detection.
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- Fig. 7. The time-resolved thermal deflection signal as observed on an oscilloscope.
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- Fig. 9. A plot of thermal deflection signal strength versus CO₂ laser power incident on the cell.
- Fig. 10. The apparatus used for quasi-single ended remote detection by thermal deflection. At the focus of the telescope is the dual photodiode which monitors deflection of the Helium Neon spot on the rock. In lab tests the sensitivity is similar to the apparatus of Fig. 6.
- Fig. 11. The laser apparatus for producing and detecting fluorescence. Spectra may be taken as a function of excitation wavelength or as a function of emission wavelength.