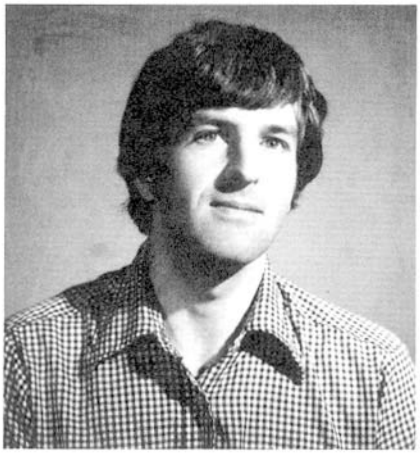
Laser Fluorosensors for Remote Environmental Monitoring



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INTRODUCTION

Fluorescence spectroscopy is used in a wide range of disciplines as both a qualitative and a quantitative analytical technique. The development of the laser has now allowed this method to be adapted to the remote-sensing role of monitoring environmental parameters from the air. Many environmental pollutants have been shown to have characteristic fluorescence properties lending them to possible detection and identification by a laser fluorosensor.[1-6]

The basic concept of a laser fluorosensor is shown in Fig. 1. A laser and receiver are situated on a remote sensing platform, usually an aircraft. The laser beam illuminates a small area at the surface. Any fluorescence induced by the absorption of the laser light is detected and analyzed by the receiver. From the strength and spectral distribution of the fluorescence signal, conclusions can be made about the nature of the target and the presence of a particular pollutant.

Oil-spill monitoring has been a primary target of fluorosensor development programs. The remote assessment of chlorophyll concentration as an indicator of water quality is also under study. These applications are discussed in this presentation, along with some more-speculative ones. First we will discuss in more detail the design concepts of fluorosensors.

FLUOROSENSOR DESIGN

The Laser

Fluorescence, the emission of light from photo-excited molecules, is observed mostly in the visible and near-ultraviolet regions of the spectrum. As the exciting light must be at higher energy than the emitted light, the laser for a fluorosensor must operate in the visible or ultraviolet. The optimum excitation wavelength varies depending on the pollutant to be monitored. Prototype sensors have been built using nitrogen lasers (337 nm), quadrupled and doubled Nd:YAG lasers (266 and 532 nm), flash-pumped dye lasers (400–500 nm), and an He-Cd laser (442 nm). We will discuss the fluorescence properties of possible targets in a later section, but, in general, the

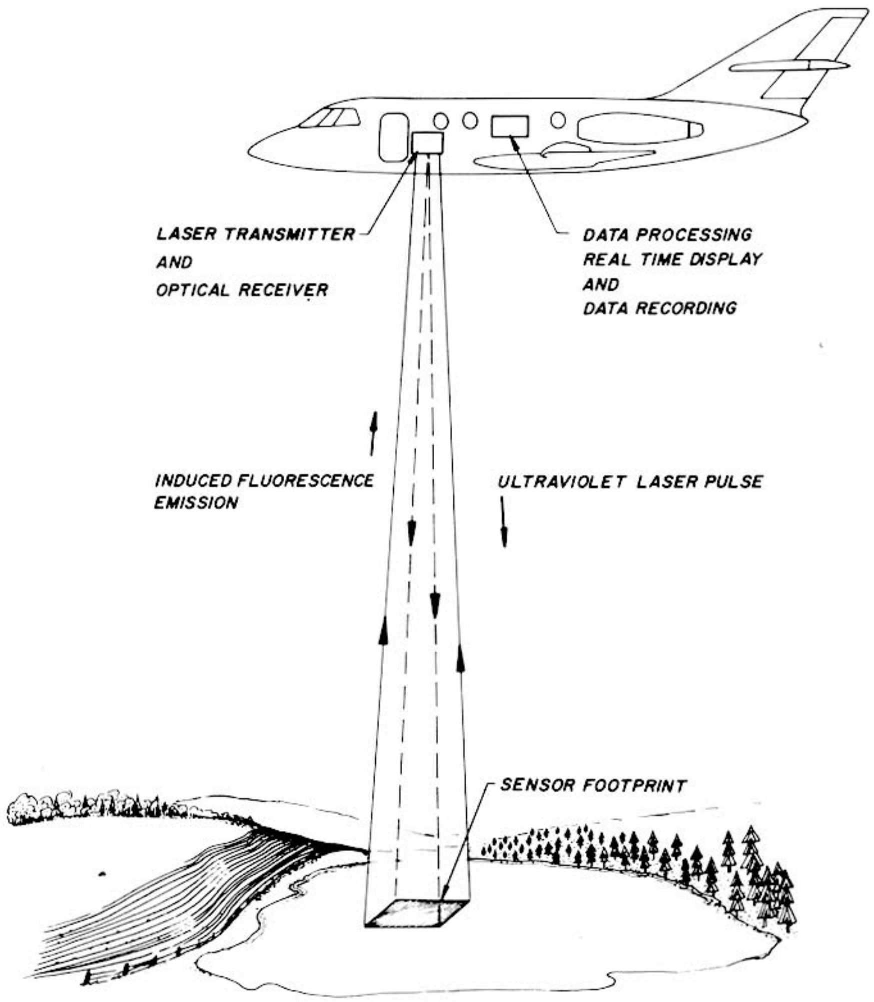

Fig. 1 The basic concept of a laser fluorosensor.

most versatile fluorosensor uses ultraviolet excitation. Only in the special case of chlorophyll is there an advantage to exciting in the visible.

Both pulsed and cw lasers have been incorporated into fluorosensors. There are, however, advantages in using a pulsed source. With a pulsed source one can employ gating techniques in the detector that result in a significant drop in the background and prevent overloading of the detector. This background is due to the scattering of ambient light by the surface and the atmosphere into the receiver and is of sufficient intensity to restrict the use of a cw or nongated pulsed system to nighttime operation. In a pulsed-laser-gated detection system the detector is gated on for the duration of the return fluorescence signal, which is also of a pulsed nature, as fluorescence decay times are generally less than 30 nsec. The detector is then gated on again between laser pulses, giving a measure of the background that can be subtracted from the signal pulse. If the laser repetition rate is 100 Hz and the gate width 50 nsec, the reduction in background gained by employing this method is 2×10^5 times.

The advantages of a pulsed system are outweighed if the laser repetition rate is too slow to give adequate resolution on the ground. For airplane operation at 320 km/h, a rate of 100 Hz gives a ground resolution of ~1 m. Operation from a helicopter or stationary platform allows the use of lower rates. For most remote-sensing applications a resolution of 10 m is adequate.

In order to take maximum advantage of the background reduction, the laser pulse width should be less than the fluorescence lifetime of the species under study allowing the use of the smallest gate width. One only gains advantage in having the pulse width very much smaller than the fluorescence decay time if one intends to measure the decay time. This fluorescence property has been shown in some cases to give additional information on the target.[5]

The strength of the fluorescence signal induced by the laser is directly proportional to the power of the laser. The signal-to-noise ratio (SN) is, in the shot-noise limit, proportional to the square of the power. SN and hence lower detection limits are therefore raised by increasing the laser power. One can also increase SN by averaging over several consecutive laser shots at the expense of ground resolution.

In summary, the ideal laser for fluorosensing is a high-peak-power ultraviolet laser giving pulses of 10-nsec width at a repetition rate of 10 to 100 Hz. Finally, the laser must be compact, light, safe, and self-sufficient enough to be operated in an aircraft in flight.

The Receiver

Depending on the application, receivers can cover a wide range of complexity, but all can have their operation broken down, as in Fig. 2. The light collector is universally a telescope, typically Cassegranian. The requirements are that the telescope be as fast and efficient as possible within the constraints of weight and size set by airborne operation. The telescope is field stopped to view just that area of the ground illuminated by the laser. At its simplest the wavelength selector can be a single filter to block out reflected laser light. Other filters can then be used to determine the detector

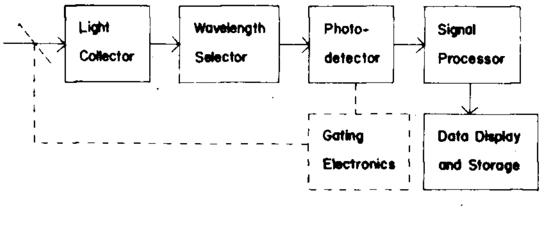

Fig. 2. Laser fluorosensor receiver operation.

bandpass. If spectral resolution is required, then the selector must be a fast spectrograph. In the simplest sensor the photodetector is a single photomultiplier, the signal processor is merely an amplifier, and the data display and storage system is a strip chart recorder. For pulsed-laser-gated detector operation of this type of system, the gating electronics must be triggered by the outgoing laser pulse and a suitable delay added to allow the laser pulse to reach the target and the fluorescence pulse to return before gating the tube. The delay can be set from the aircraft altimeter or, better, inferred from the time of flight of the previous pulse. It is the tube itself that must be gated, not the anode signal, if detector overloading is to be avoided. One must either use a specialized tube with a gating electrode or devise a method of pulsing an ordinary tube. In pulsed operation the signal processor is best a dual-channel boxcar integrator, which, with suitable signal routing and gating, will perform the background subtraction and integrate the required number of pulses.

When a spectrograph is used to obtain spectral resolution, its output must be sliced to give the required number of channels. Two approaches have been used: the image can be sliced directly, using light pipes to convey the light to an array of photomultipliers, or an image-intensifier tube can be used to amplify the light signal, which is then sliced and conveyed by fiber optics to a diode array. In the former case the photomultipliers themselves are gated separately; in the latter case the image-intensifier tube is gated. Both these systems have been used to give spectral resolution of $\sim$20 nm in the 350–700-nm range. A commercial optical multichannel analyzer has also been tested in the laboratory for these purposes.[7]

Once spectral resolution is incorporated in a fluorosensor it is worthwhile to use a microprocessor-based data-acquisition system to control the display and storage of the data. Such a system can be also capable of limited real-time correlation procedures, the output of which can trigger a pollutant-detection alarm.

FLUOROSENSOR APPLICATIONS

The Detection and Characterization of Oil Spills

A major effort in laser fluorosensor development has been directed toward applications in the remote detection and characterization of oil spills. Figure 3 shows the fluorescence spectra of three oil samples measured in our laboratory. They are representative of the three main classes of mineral oil, namely, crude, light refined, and heavy refined or residual. Oils fall into these classes because of their physical properties, such as density and viscosity, and their fluorescence properties are no exception.[5] For excitation at 337 nm, the crude oils show broad unstructured emission with a maximum at wavelength λ_{max} between 480 and 570 nm and with a fluorescence quantum efficiency at λ_{max}, η_{max} between 4×10^{-5} and 4×10^{-4} nm^{-1} Light refined petroleum products, such as diesel and furnace fuel oil, show partly structured emission with λ_{max} less than 455 nm and typically about 440 nm and with η_{max} between 2.4×10^{-4} and 6×10^{-4} nm^{-1}. Heavy refined petroleum products, such as bunker fuel oil, show weaker, broad, unstructured emission with λ_{max} between 525 and 600 nm and with η_{max} between 1×10^{-5} and 6×10^{-5} nm^{-1}.

To take full advantage of these fluorescence spectral properties, one requires a fluorosensor with a spectral resolution of about 20 nm. A single-channel instrument will detect oil fluorescence, but added resolution makes spectral correlation possible, avoiding ambiguity between oil and other environmental fluors. It is this specificity that makes laser fluorsensors attractive for oil-spill detection. Most other sensors, particularly those of imaging type, recognize oil slicks by the appearance of an anomalous area that may be suggestive of but is not unique to oil. Effective policing and subsequent conviction obviously require the positive identification of oil.

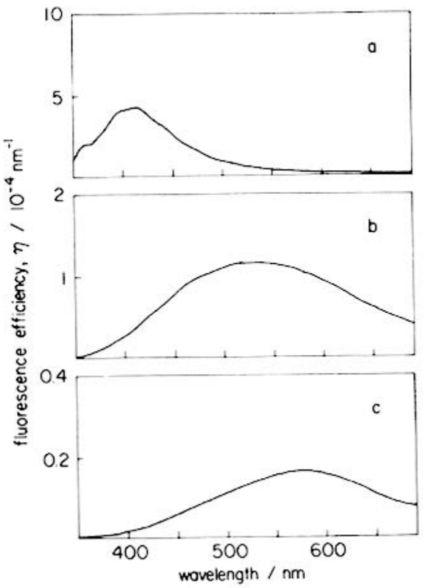

Fig. 3. Fluorescence spectra of oils, typical of their type; a, marine diesel oil, a light refined petroleum product; b, Arabian crude oil; c, bunker 6C, a heavy or residential petroleum product. Excitation wavelength, 337 nm.

In theory a fluorosensor could also measure the fluorescence decay times of the oil. These have been shown to be characteristic of the particular oil.[5,8] In the laboratory, using complex analysis of the decay curves, one can distinguish between samples of oil in a particular group. However, to make such a characterization, SN has to be much better than that currently possible with a remote fluorosensor. At SN levels attainable by current fluorosensors, oil fluorescence decays can be fitted to one-exponential functions giving single decay times. This decay time is dependent on the oil and on the detection wavelength. All oils show longer decay times in the red than in the blue. The heavier the oil the shorter its decay time at any particular wavelength, typical decay times at $\sim$500 nm varying between 30 nsec for a light diesel oil to 1 nsec for a heavy bunker oil and at $\sim$380 nm between 13 and $<$1 nsec for the same two oils. Taken by themselves, such decay-time measurements give no classification of the oil beyond that possible when using spectral measurements. They do offer an extra parameter for distinguishing between oil and targets, such as dyes, that do not show decay-time wavelength dependence.

Advantage can also be taken of the Raman scattering of the laser light by water. In the absence of oil this is quite strong because of the relatively long penetration depth and is easily detected by a fluorosensor. The presence of oil results in less, if any, light penetrating into the water and consequent suppression of the Raman signal. By devoting a fluorosensor channel to the Raman wavelength, added discrimination can be gained.

The successful airborne operation of a multichannel laser fluorosensor in the detection and characterization of oil spills has recently been demonstrated. In a joint experiment involving NASA, the U.S. Coast Guard, the American Petroleum Institute, and the Canada Centre for Remote Sensing (CCRS), two fluorosensors were flown over spills of rhodamine WT dye, Merban crude oil, and LaRosa crude oil. The first sensor, built by Barringer Research Ltd. for CCRS, uses the gated-image-intensifier technique discussed earlier and has 16 channels, 20 nm wide, covering the range 380 to 680 nm.[9] The second sensor, built by Avco Everett Corporation for the National Aeronautics and Space Administration Wallops Flight Center, is of the multiple photomultiplier type, having a total of 40 spectral channels covering the wavelength interval from 350 to 800 nm. A rapidly scanning mirror directs the sensor footprint so that a fluorescence image of the terrain under the aircraft can be formed.[10] Observation of the real-time display of the CCRS sensor during these flights showed clear differences among the dye, the two types of crude oil, the ocean water, and a ship. Raman-scattering suppression was unique to the oils. Subsequent use of a technique for the correlation of the crude data with oil spectra measured in the laboratory showed that Merban crude oil, LaRosa crude oil both before and after application of the dispersant Corexit 9527, rhodamine dye, and ships can all be distinguished from one another and from the general fluorescence background of the ocean water.

An offshoot of the oil-spill surveillance role is the use of laser fluorosensors in oil exploration. Natural oil and gas seepages do occur and are an obvious indication of under-sea hydrocarbon deposits. A laser fluorosensor offers the possibility of arranging large-scale aerial surveys in search of such phenomena.

Chlorophyll Monitoring

Chlorophyll in green plants and algae fluoresces in the 650- to 750-nm range. Although chlorophyll is not a pollutant itself, its concentration is an indirect indicator of environmental conditions. For example, in water-quality studies, such parameters as the chemical oxygen demand can be related to chlorophyll concentration. Chlorophyll fluorescence is best excited by light of wavelength 400–500 nm. Current prototype laser fluorosensors for monitoring chlorophyll are based on flashlamp-pumped dye lasers operated in this range. Emission is monitored at 680 nm. The low repetition rate of these lasers means that they must be operated from a helicopter. A sensor has been built using a laser that sequentially scans four excitation wavelengths to give added discrimination of the chlorophyll fluorescence through its excitation spectrum.[11] A problem in these measurements is variability in penetration depth that is due to variations in the water turbidity. Proposals to correct this problem include measurement of the strength of the water Raman scatter and the degree of polarization of the backscattered excitation light, both of which can be related to the water turbidity.

Over land a similar sensor could also possibly be used to assess plant stress. The fluorescence from chlorophyll in plants is dependent on many factors, one of which is plant stress. This stress can be due, among other things, to lack of nutrients, reaction to pollutants and parasites, or disease. Diurnal changes in chlorophyll fluorescence will complicate measurements, but over large homogeneous tracts of vegetation, such as forests, anomalies in the general fluorescence return could be used to indicate plant stress before it became apparent to passive sensors, such as cameras and multispectral scanners. The technique would be used to monitor threatened areas, such as downwind from smokestacks and areas bordering known disease outbreaks.

Other Environmental-Monitoring Roles

Apart from oil-spill detection, several other environmental-monitoring roles could be performed by using a laser fluorosensor.

Several possible pollutants that lend themselves to direct monitoring by laser fluorosensors include pulp-mill effluent, coal-mine tailings, and aromatic solvents used in coal-liquifaction plants. There is a real need for a technique for mapping an accidental spill of the aromatic solvents.

Large-scale hydrographic studies using biodegradable dyes in much smaller quantities than needed for photographic surveys can be conducted with a laser fluorosensor.

One of the more suitable roles for laser fluorosensing is the monitoring of large-scale insecticide-spraying operations, such as those conducted against the spruce budworm, in which millions of acres are sprayed annually. Now monitoring is carried out at scattered ground stations. Insecticides are often sprayed in oil-based formulations that maintain the fluorescence properties of the oil. Where this is not the case, a fluorescent dye could be added to the formulation. Current fluorosensors using 337-nm N_2-laser excitation do not have the sensitivity to detect insecticides in the quantities in which they are sprayed. However, development of suitable lasers operating at ~240 nm (possibly excimer lasers) will allow advantage to be taken of the increased absorption of light by the oil in insecticide formulations at lower wavelengths.

FUTURE DEVELOPMENTS IN LASER FLUOROSENSING

The present generation of fluorosensors, which can still be regarded as prototypes, are just beginning to be demonstrated in the roles for which they were designed. Notable success has been obtained in the identification and classification of oil spills and in the mapping of the distribution of chlorophyll in water. The application of this technique to new roles will undoubtedly be stimulated by these results. The new applications will in turn encourage the further development of fluorosensors themselves.

In addition to the potential uses for fluorosensors referred to previously, applications can be seen in the mapping of surficial deposits of ores, such as uranium, and in the identification of the species of trees in forests and of agricultural crops.

The complexity of a general-purpose airborne laser fluorosensor system is unacceptable for routine operational monitoring of the environment; thus the new generation of systems will be optimized for the identification of a single group of targets. To assist in the detection and mapping, the fluorosensor data will be complemented by information from a variety of airborne sensing systems observing different properties of the same area.

Future developments in laser fluorosensing rest on advances in the laser science and technology. SN in existing systems will be increased by increasing the laser power and, in the case of oils and insecticide sprays, by making lower excitation wavelengths possible. Excimer lasers are promising in this regard.

The availability of higher-power lasers allows one to consider the possibility of satellite or space-lab operation of laser fluorosensors. Higher power also allows one to construct effective scanning or imaging fluorosensors that study a wide swath beneath the aircraft. Such a development would considerably increase the effectiveness of the technique in survey and mapping operations. Apart from the NASA prototype scanning system that uses a nitrogen laser, all existing fluorosensors are of the profiling type, viewing a narrow strip along the flight path. If sufficient power is available, an imaging system can be built by scanning the laser beam perpendicular to the flight path or by fanning out the beam and by incorporating a suitable receiver.

Another line of development was mentioned in the section on chlorophyll fluorosensing, in which a system that sequentially scanned four excitation wavelengths was described. The use of more than one laser or the rapid scanning of a dye laser gives added discrimination to a fluorosensor by taking advantage of the fluorescence-excitation spectral properties of the target.

The development of an airworthy fluorosensor system lags several years behind the development of the laser it uses. Lasers are now available that fulfill the requirements of the more advanced sensors discussed in this section. We can, therefore, look forward to the integration of these new lasers in the next generation of sensors, thus expanding the roles of fluorosensing in the remote monitoring of the environment.

(Report NRCC #17514.)

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