Real-World Applications of Laser Spectroscopy

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Abstract

Laser spectroscopic techniques constitute powerful tools for the monitoring of real-world phenomena, e.g. in the domains of energy conversion, environmental studies and medical diagnostics Atoms and molecules can be identified and quantified by their specific spectral signatures and the strength of the signals. A wide variety of methods for establishing spectroscopic contact with the species exist: absorption, emission, fluorescence, Raman scattering, acousto-optic, and opto-galvanic phenomena can be employed. Extreme sensitivity and specificity characterise the methods, which can be used for *in situ* monitoring and in some cases, for remote sensing. Combustion diagnostics and atmospheric pollution monitoring are examples on gas-phase applications, while vegetation studies and early cancer detection illustrate interactions with solids.

Introduction

Laser radiation can be used for chemical sensing based on the wavelength dependent interaction between electromagnetic radiation and matter. The narrow bandwidth of modern tuneable lasers makes the interaction extremely selective, based on the complex and sharp spectral features of free atoms and molecules. Further, the high spectral intensity available with pulsed as well as CW lasers makes saturation of the optical transition possible. Thus, individual atoms or molecules can absorb more than a million photons per second leading to an extreme sensitivity. As a matter of fact, single atom or molecule detection becomes a reality. In a further developmental trend, ultrafast lasers have allowed a detailed assessment of the dynamics of chemical reactions (femtochemistry). In this way much insight into the nature of many basic chemical processes has been gained.

During the last few years, laser sources have become more realistic for real-world applications. Semiconductor diode lasers have become very reliable and easily accessible, and their range is extended higher and higher up into the visible region. Tuneable crystal materials, such as titanium-doped sapphire, allow all-solid-state systems with considerable power to be constructed. Diode-laser pumping of solid-state materials is making flash-lamp pumping gradually obsolete and is resulting in compact and very reliable sources.

Practical sensing can readily be performed *in situ* with laser spectroscopic techniques. Then the laser radiation is locally brought into contact with the sample either directly or after sample preparation. A special feature of laser light, being coherent and basically only diffraction limited in terms of beam propagation, is the possibility to use it for remote sensing, where the measurement device and the sample, frequently distributed, are separated be distances of typically kilometre size. Absorption, and in particular differential absorption, can be utilised in long-path measurements, whereas elastic and inelastic backscattering as well as fluorescence can be used for range-resolved radar-like measurements (lidar). Laser light can also be efficiently focused into optical fibres and can in this way be transported over large distances to a number of remotely located measurement sites. Fibre optic techniques provide a link between truly local measurements and remote sensing. Various properties of the fibre itself influencing the laser light propagating through the fibre also form the base for fibre-optical sensors.

Applied laser spectroscopy is a vast field, which is difficult to cover comprehensively in a review. Rather than attempting such a review, examples from a variety of fields, where the author has own experience will be chosen to illustrate the power of applied laser spectroscopy. References to reviews are given to provide further entries to this rich field. General material pertaining to applied laser spectroscopy can be found in Refs. 1-5.

Analytical Chemistry

Laser spectroscopy has entered many traditional fields of analytical spectroscopy[5,6]. E.g., opto-galvanic spectroscopy on analytical flames increases the sensitivity of absorption and emission flame spectroscopy. Extremely sensitive direct absorption measurements with CW lasers can be performed using frequency-modulation spectroscopy with a $1:10^7$ absorption sensitivity. Small absorptions can also be detected in intra-cavity experiments.

Small amounts of material can be detected using the REMPI (Resonance Enhanced Multi-Photon Ionisation) or RIMS (Resonance Ionisation Mass Spectroscopy), both employing pulsed, tuneable lasers. In the first method, selectively produced ions of the element are detected through the ion current, whereas the second method uses a mass spectrometer for additional selectivity.

The power of standard analytical-chemistry techniques can be further improved through laser spectroscopy, employed for enhanced detection sensitivity and multiplexing. Thus, laser-induced fluorescence (LIF) can be employed for detecting the separated peaks passing the detector position in HPLC (High Performance Liquid Chromatography) and Capillary Electrophoresis. Further, a whole section of the column can be illuminated and the fluorescence along the column can be imaged on a linear array or CCD detector, providing simultaneous multi-species detection. Differences in fluorescence spectra can also be employed for further discrimination. Fluorescence labelling can be used, detecting simultaneously four chromophores with different fluorescence characteristics and binding to different positions in the DNA strand. An illustration of fluorescence monitoring along a capillary is given in Fig, 1., where the separation of an oligonuclotide mixture is demonstrated[7].

Combustion Diagnostics

Laser spectroscopy provides non-intrusive measurement capability in reactive and aggressive media, such as burning or exploding combustion gases. A host of techniques has provided new possibilities to measure the concentration of species including short-lived radicals, and also the capability to measure temperature and flow[8]. The measurements have allowed an interplay with the advanced kinetic computer codes that are used for modelling combustion.

LIF has been extensively used, also in imaging configurations, to monitor the distribution of molecules such as OH, C_2, CH and CN. Using a gated and image-intensitied CCD detector the full distribution can be captured using a single laser shot ($\approx 10^{-8}$ s). In a similar way, temperature distributions can be obtained by recordings using transitions starting in states with a temperature-dependent population. Flow velocities are evaluated using Doppler shifts in the recorded signals.

CARS (Coherent Anti-Stokes Raman Scattering) is a powerful technique, especially for temperature measurements in realistic, strongly luminous media. A coherent, laser-like beam is obtained carrying the signal making it largely immune to the background light. By single-shot CARS recordings PDF:s (Probability Density Functions) for temperature can be determined yielding important information on statistical fluctuations in turbulent combustion. Polarisation spectroscopy and DFWM (Degenerate Four-Wave Mixing) spectroscopy are further powerful techniques in combustion diagnostics, which aim at an improved understanding of pollution and soot formation as well as engine ignition and knock.

The methods developed for combustion diagnostics are also applicable for the monitoring of other reactive media such as in plasma etching or MOCVD (Metal Organic Chemical Vapour Deposition) for semiconductor processing[9].

Atmospheric Remote Sensing

The atmosphere can be monitored by laser techniques employing absorption and laser-induced fluorescence[10]. The LIDAR (LIght Detection And Ranging) technique using a pulsed laser as a transmitter and an optical telescope as a receiver in a radar-like manner allows a three-dimensional mapping of pollution concentrations and also meteorological parameters, such as temperature, humidity and wind velocity.

At atmospheric pressures LIF cannot be used for species monitoring because of a strong quenching (Combustion diagnostics with LIF is still feasible because of the possibility to saturate the optical transitions even in the presence of collisional transitions). Mesospheric monitoring of meteorite-derived Li, Na, K and Ca layers using LIF lidar is still possible because of the low pressures, and powerful applications related to the use of laser guide-stars have emerged. Tropospheric pollution monitoring is most frequently performed using DIAL (Differential Absorption Lidar)[11]. Range-resolved optical transients due to elastic backscattering from aerosol particles are recorded for a laser wavelength set on a characteristic absorption line and just off it for reference, in alternating laser shots. By dividing the resulting curves, unknown atmospheric parameters are eliminated and the concentration of the particular specie can be evaluated. Typical ranges for SO_2, O_3, NO_2, NO and Hg monitoring are 0.5-5 km. The techniques are particularly valuable for urban and industrial monitoring. Total fluxes from an industrial complex can be evaluated in near real time. Lidar techniques have also been used for monitoring of gases of geophysical origin. Examples are emissions from geothermal fields and active volcanoes. As an illustration the SO_2 plume from the Italian volcano Etna is shown in Fig. 2[12].

Hydrosphric and Vegetation Remote Monitoring

If an ultra-violet pulsed laser beam from a lidar system is directed onto a water surface or vegetation, laser-induced fluorescence is induced, and can be collected and analysed at the site of the lidar system[10,13]. Fluorescence data from the earth surface can complement reflectance data widely collected by multi-spectral sensors installed in satellites such as LANDSAT or SPOT. LIF lidar is under development and can presently only be used in test experiments at km ranges (truck, helicopter or aeroplane installations). Water LIF signals include a sharp OH-stretch Raman signal for water that is valuable for referencing, a broad blueish fluorescence light distribution due to distributed organic matter (DOM), and rather sharp peaks in the near IR region (685 and 740 nm) due to chlorophyll. The technique is particularly valuable for monitoring of oil spills and algal blooms.

Land vegetation signals feature clear chlorophyll signals (the ratio between the two peaks allows an evaluation of the chlorophyll concentration) as well as blue fluorescence due to a variety of molecules present in the leaves[13]. Recently, a considerable effort has been devoted to assessing the possibilities of early detection of forest decline in the fluorescence signals (i.e. the European LASFLEUR project). By expanding the laser beam, a certain area can be illuminated, and by a fluorescence imaging system the whole scene can be captured in properly selected wavelength bands. An example of fluorescence imaging of a spruce tree in 60 m distance is shown in Fig. 3[14].

Medical Fluorescence Diagnostics

Laser spectroscopy has an impact on medical research through its use in various analytical-chemistry techniques. However, much more direct applications in medical diagnostics have emerged during the last few year. Thus, tissue LIF has been extensively studied and applied for early detection of malignant tumours and for studies of atherosclerotic plaque[15,16].

Tissue exhibits a natural fluorescence when excited by UV or violet light. Important natural chromophores emitting fluorescence are elastin, collagen, NADH and NAD^+. They all yield broad, but somewhat different distributions in the blue-green spectral region. However, exogenously administered agents such as porphyrins or phtalocyanines, which are selectively retained in tumor cells, yield sharp and characteristic peaks in the dark red wavelength region, signalling the presence of cancer. An increase in the red fluorescence is frequently accompanied by a decrease in the blue-green fluorescence, and thus by a ratio formation an enhanced tumour demarcation from normal tissue can be achieved at the same time as the monitoring of a dimensionless quantity makes the data immune to changes in geometry, illumination, detection efficiency etc. Fibre-optical probes through which both excitation light and induced fluorescence are conducted have been developed and utilised for the building up of a spectral library for tumors in different organ systems. Multi-colour imaging devices have also been constructed, making the presentation of an image processed for cancer detection possible, video mixed with the normal white-light reflectance image obtained through an endoscope. Tumours detected can be treated by photo-dynamic therapy (PDT) using red laser light, which exites the administered sensitiser molecules with subsequent transfer of ground-state triplet oxygen to the toxic singlet state. A selective necrosis of tumour cells will result.

Atherosclerotic plaque can be fibre-optically detected in *in vivo* transluminal monitoring in vessels. Atherosclerotic plaque is characterised by a change in the elastin/collagen balance and can be observed in time integrated or time-resolved measurements of LIF. The construction of a guidance device for the safe use of a fibre-optical laser coronary angioplasty system would be of considerable interest.

Raman spectroscopy is also being tested for tissue diagnostics. Much sharper but weak signal features are obtained. In order to suppress competing fluorescence the laser irradition wavelength is chosen in the near IR region.

Scattering Spectroscopy in Turbid Media

Red light penetrates tissue particularly well due to the reduced haemoglobin absorption. This is utilised to achieve PDT over tissue thicknesses of few millimetres. The weak penetration of red light also through thicker tissue layers would suggest optical mammography without using ionising radiation. However, the heavy multiple scattering in tissue leads to image blurring reducing the value strongly. By transmitting picosecond laser pulses through tissue and electronically detecting only the first emerging photons it is possible to reject the scattered light and retain an image with good contrast. Many different techniques working on this general principle are now being developed with the main aim of breast cancer detection[17]. Prototype systems for optical mammography are being constructed. Similar technology can also be used for oxygenation measurements in the brain, and also possibly for localising haematoma following trauma to the skull. An example of gated viewing detection of a breast cancer tumor (in vitro) is shown in Fig. 4, where pulsed a near-IR diode laser and time-correlated single-photon counting were employed[18].

Spectroscopy in strongly scattering media can also be used in other applications, such as studies of light propagation in green leaves (photosynthesis) or sheets of paper (quality assessment through information of fibres etc).

Conclusions

Applied laser spectroscopy is a rapidly evolving field, where new applications appear all the time. The methods can be expected to make their way into everyday applications at an increased rate with the fast development of cheap and reliable laser sources, fibre-optical components and computers.

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References

1. W. Demtröder, *Laser Spectroscopy*, 2nd ed. (Springer Verlag, Heidelberg, 1995)
2. S. Svanberg, *Atomic and Molecular Spectroscopy - Basic Aspects and Practical Applications*, 2nd Ed. (Springer Verlag, Heidelberg, 1992).
3. L.J Radziemski, R.W Solarz, and J.A. Paisner, *Laser Spectroscopy and its Applications* (Dekker, New York, 1987).
4. S. Svanberg, "Laser spectroscopy applied to energy, environmental and medical research", Phys. Scr. **T21**, 281-87 (1988); Appl. Phys. **B46**, 271-82 (1988).
5. H. Medin, and S. Svanberg, *Laser Technology in Chemistry,* Special Issue, Appl. Phys. **B46**, No. 3 (1988).
6. V.S. Letokhov, *Laser Analytical Spectrochemistry* (Hilger, Bristol, 1986).
7. S. Nilsson, J. Johansson, M. Mecklenburg, S. Birnbaum, S. Svanberg, K.-G. Wahlund, K. Mosbach, A. Miyabayashi, and P.-O. Larsson, "Real-time fluorescence imaging of capillary electrophoresis", J. Capillary Electrophoresis **2**, 46-52 (1995).
8. A.C. Eckbreth, Laser *Diagnostics for Flame Temperature and Species* (Abacus Press, Turnbridge Wells, 1987).
9. D. Bäuerle, *Chemical Processing with Lasers* (Springer, Heidelberg, 1986).
10. R.M. Measures, *Laser Remote Sensing: Fundamentals and Applications* (Wiley, New York, 1984).
11. S. Svanberg, "Differential absorption lidar (DIAL)", Chap. 3 in *Air Monitoring by Spectroscopic Techniques*, Ed. Sigrist, M. (Wiley, New York, 1994).
12. H. Edner, P. Ragnarson, S. Svanberg, E. Wallinder, R. Ferrara, R. Cioni, B. Raco and G. Taddeucci, Total fluxes of sulfur dioxide from the Italian volcanoes Etna, Stromboli and Vulcano measured by differential absorption lidar and passive differential optical absorption spectroscopy, J. Geophys. Res. **99** (1994) 18827-38.
13. S. Svanberg, "Fluorescence lidar monitoring of vegetation status", Phys. Scripta T58, 79-85 (1995)
14. J. Johansson, M. Andersson, H. Edner, J. Mattsson, and S. Svanberg, "Remote fluorescence measurements of vegetation spectrally resolved and by multi-colour fluorescence imaging", J. Plant Physiology, in press.
15. S. Svanberg, "Medical applications of laser spectroscopy", Phys. Scripta **T26**, 90-98 (1989).
16. S. Svanberg, "Tissue diagnostics using lasers", in *Lasers in Medicine*, Eds G. Pettit, and R.W. Waynant (Wiley, New York, in press).
17. G. Müller *et al.* (eds), *Optical Tomography* (SPIE, Bellingham, 1994).
18. R. Berg, O. Jarlman, and S. Svanberg, "Medical transillumination imaging using short pulse diode lasers", Appl. Opt. **32** 574-579(1993).

Figure Captions

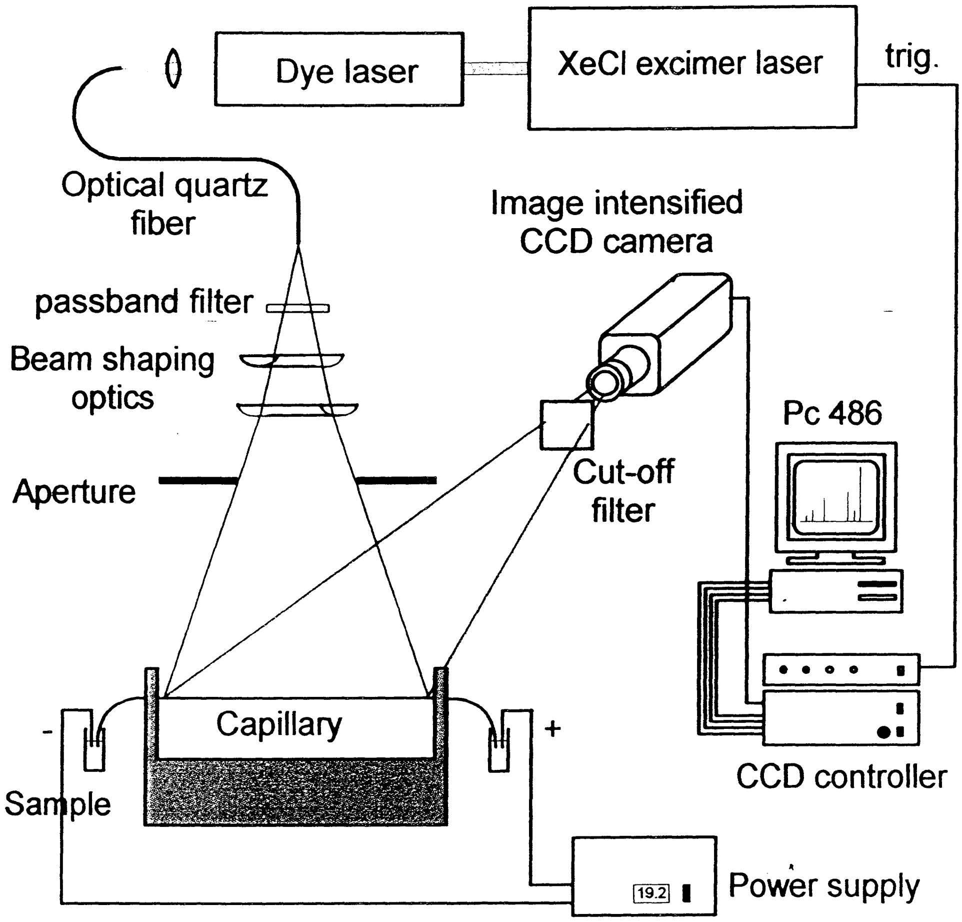
Figure 1. Experimental set-up and recorded signals in a capillary electrophoresis study of the separation of components in an oligonucleotide mixture. (From Ref. 7).

Figure 2. Lidar monitoring of the SO_2 plume from the Mt Etna volcanoe obtained in vertical soundings from a shipborne lidar system. The flux is about 60 tonnes/h. (From Ref. 12)

Figure 3. Simultaneous imaging of a spruce tree in three fluorescence bands using laser-induced fluorescence, where a horisontal streak of UV laser light was scanned over the tree from root to top. Selected fluorescence spectra are also included. (From Ref. 14)

Figure 4. Transillumination imaging of a ductal cancer in a mastectomy specimen. By gated viewing of the early arriving photons only the tumour emerges, while no contrast is obtained if all transmitted light is accepted. A pulsed near-IR diode laser and time-correlated single-photon counting were employed. (From Ref. 18)

Fluorescence imaging for capillary electrophoresis



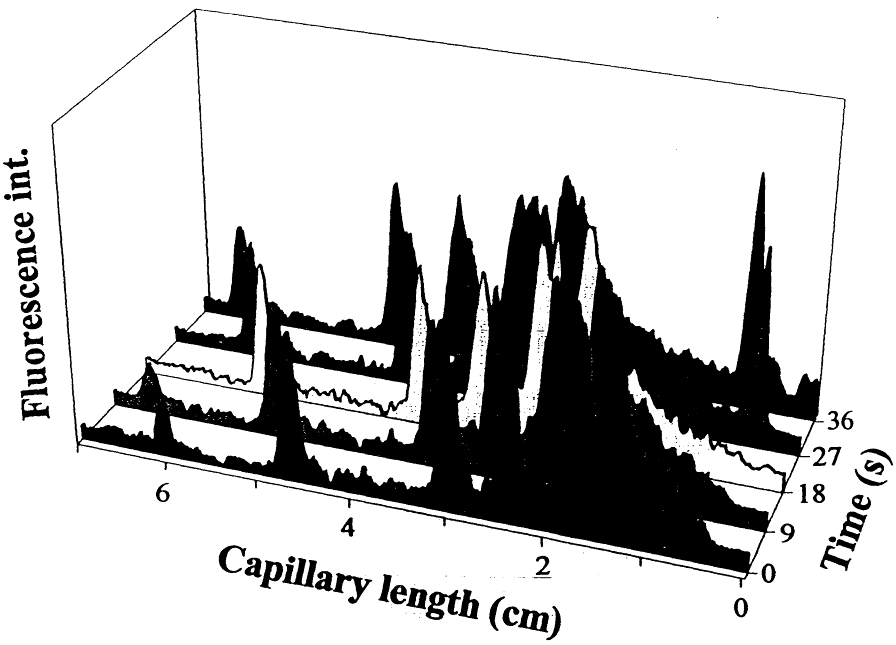


Figure 1

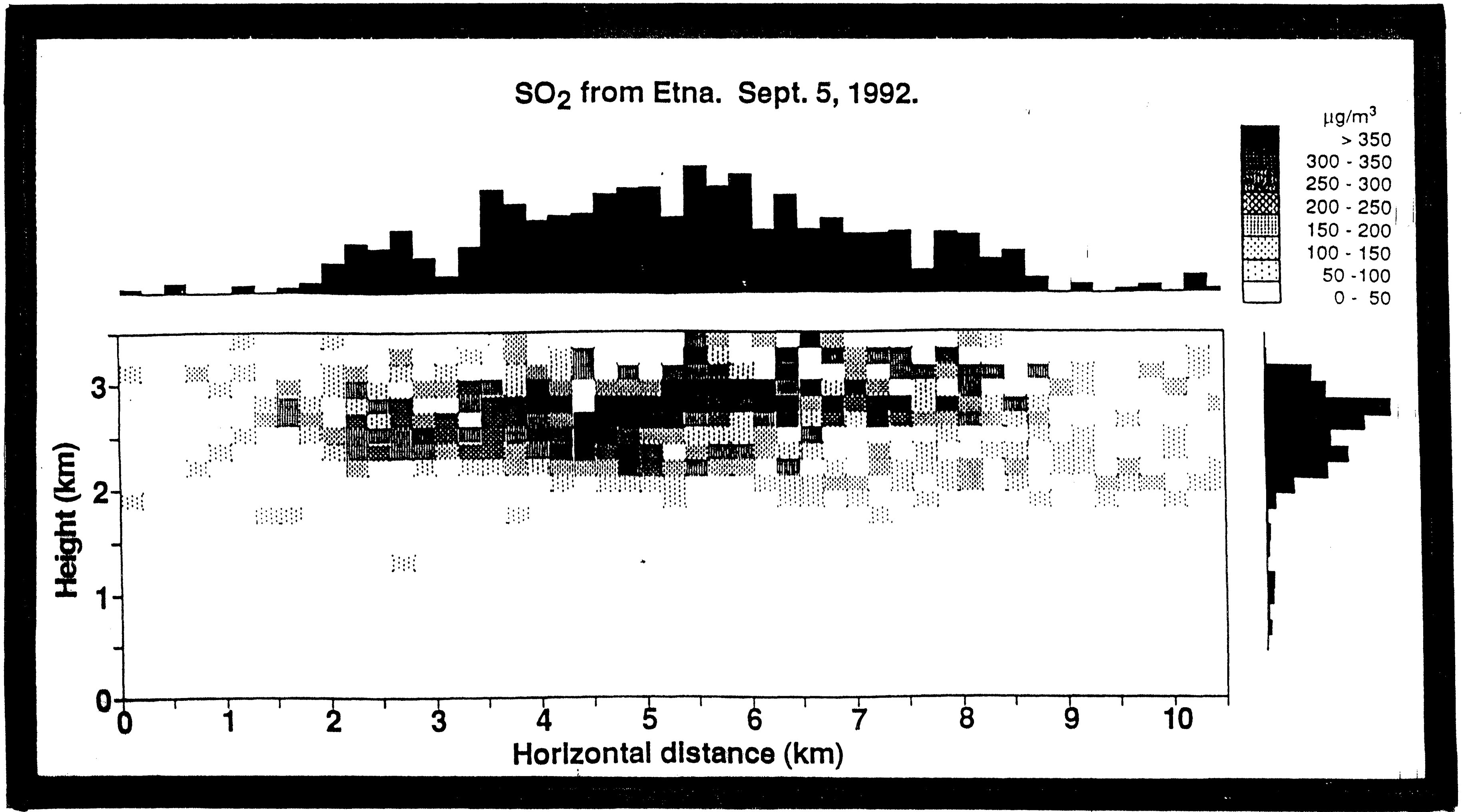

SO2 from Etna. Sept. 5, 1992.
µg/m3
> 350
300 - 350
250 - 300
200 - 250
150 - 200
100 - 150
50 -100
0 - 50
Height (km)
0
1
2
3
0 1 2 3 4 5 6 7 8 9 10
Horizontal distance (km)

Figure 2

Picea abies
60 m distance

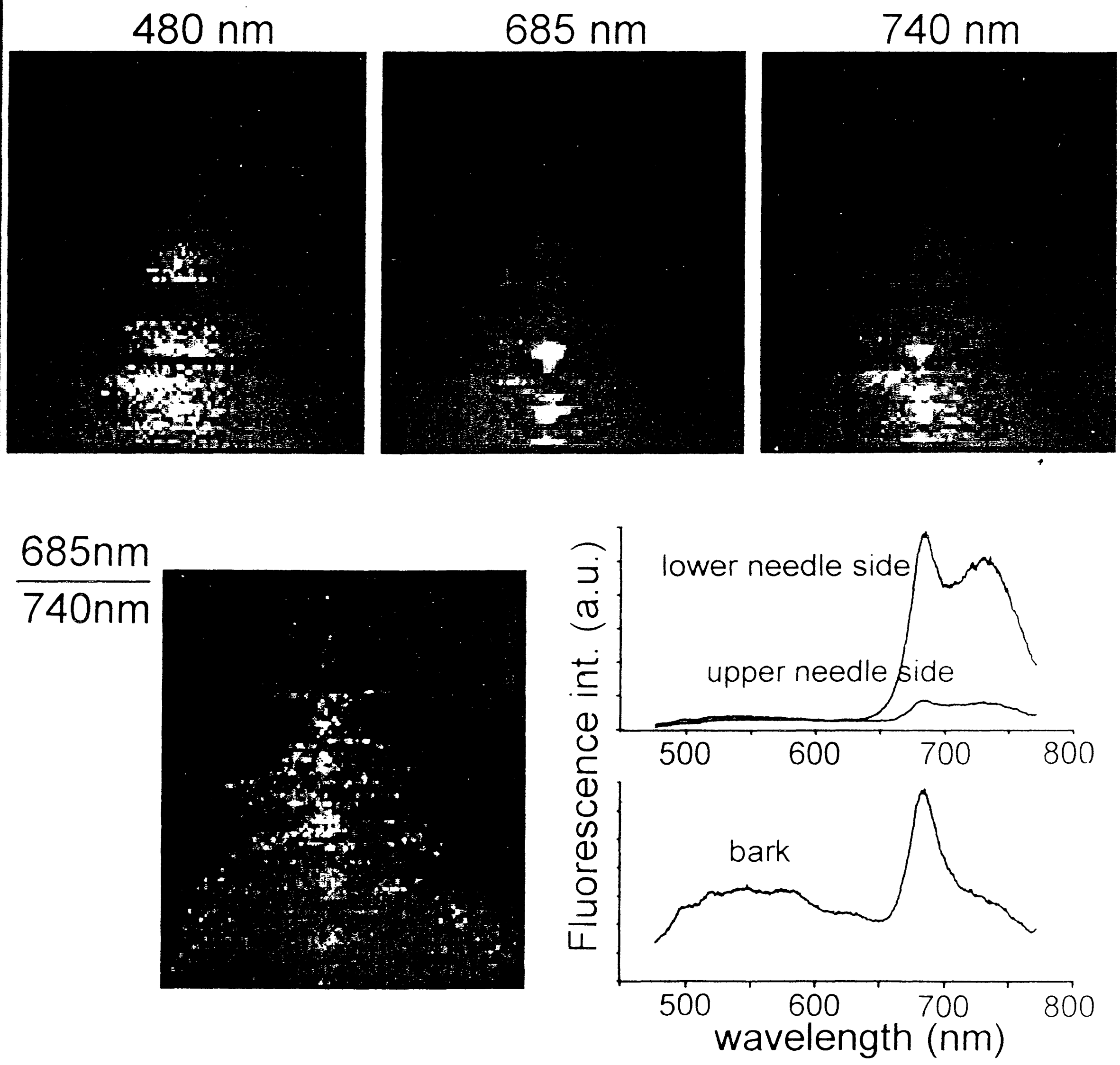


Figure 3

Picosecond Diode Laser Transillumination Image of ductal cancer in female breast

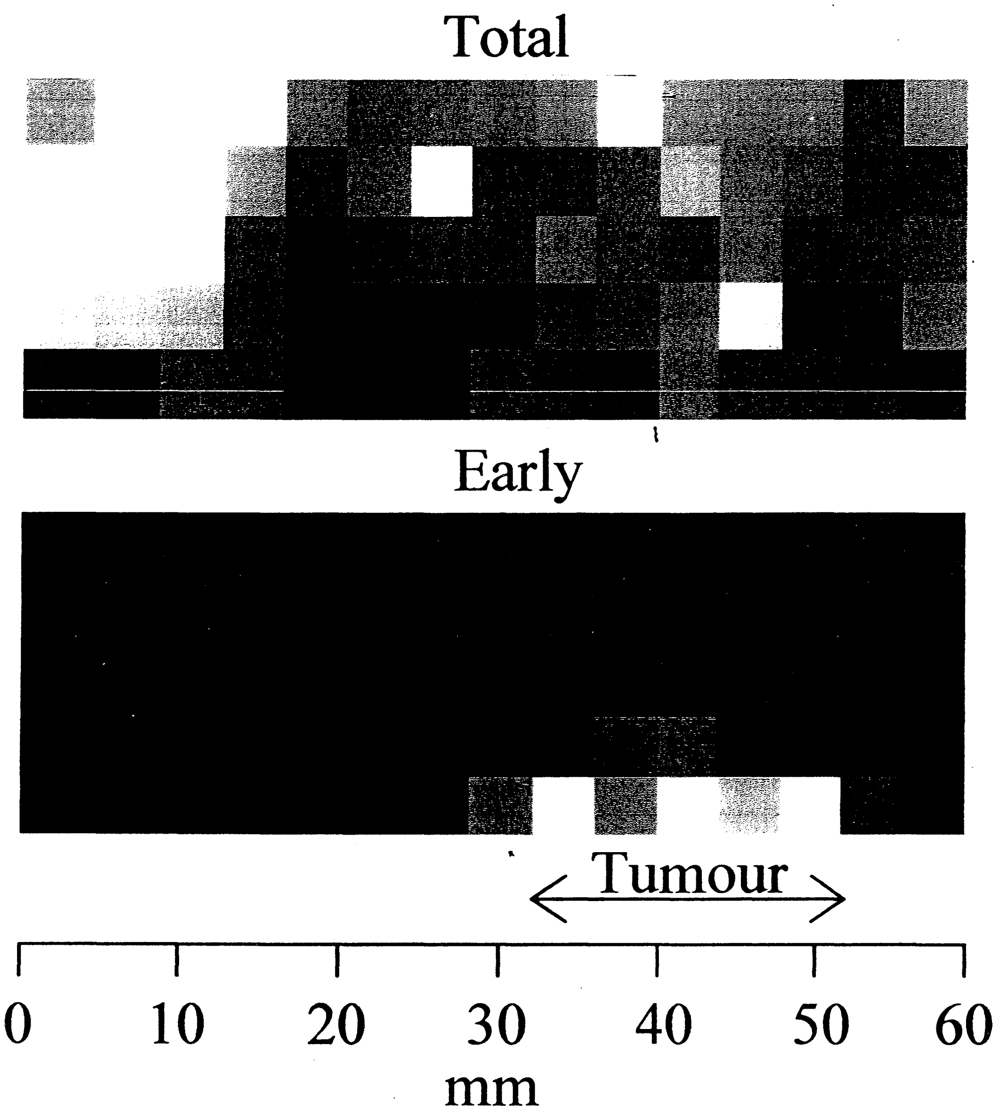


Figure 4.