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Applications of Laser Spectroscopy

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Introduction

Laser radiation is finding many applications for analysis and diagnostics based on the wavelength dependent interaction between electromagnetic radiation and matter. The narrow bandwidth of modern tuneable lasers makes the interaction extremely selective in the interaction with free atoms and molecules, which have sharp spectral features. 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 many millions of photons per second leading to an extreme sensitivity. As a matter of fact, single-atom or molecule detection is widely used representing the ultimate sensitivity in analytical chemistry. In a further developmental trend, ultrafast lasers have allowed detailed studies of chemical reaction dynamics (femtochemistry). In this way much insight into the basic steps in chemical processes has been gained.

During recent years, laser sources have become more rugged, easy-to-use and cheaper to allow real world applications of laser spectroscopy. Semiconductor diode lasers have become very reliable and easily accessible, and their wavelength range is extended higher and higher up into the visible region. We can mention the emerging blue diode lasers based on gallium nitride, and frequency conversion of the output of reliable, high-power diode lasers into new wavelength regions using quasi-phase-matching in periodically-poled non-linear crystals. New laser materials, such as titanium-doped sapphire, allow all-solid-state tuneable systems with considerable power to be constructed. Diode-laser pumping of solid-state materials is making flash-lamp pumping gradually obsolete and enable compact, reliable and energy-efficient laser sources.

Laser-based analysis and diganostics can readily be performed *in situ*. Then the laser radiation is locally brought into contact with the sample either directly or after sample preparation. A special feature enabled by the unique properties of laser radiation in terms of coherence, intensity and directionality is the possibility to use it for remote chemical sensing, where the analytical equipment and the sample are separated by large distances, which can be a kilometre or more. 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 transported in optical fibres to remotely located measurement sites. Various properties of the fibre itself influence the laser light propagating through the fibre, thus forming a basis for fibre-optical sensors.

Applications of laser spectroscopy constitute a vast field, which is difficult to cover comprehensively in a review. Rather than attempting such a review, examples from a variety of fields are chosen to illustrate the power of applied laser spectroscopy.

Applications in Analytical Chemistry

Laser spectroscopy is making a major impact in many traditional fields of analytical spectroscopy. 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.

Tiny 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 employs 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 utilised 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, to provide simultaneous detection of all species undergoing separation. Differences in fluorescence spectra can also be utilised for further discrimination. Fluorescence labelling can be used, detecting simultaneously chromophores with different fluorescence characteristics and binding to different positions in the DNA strand. These developments are very important, e.g. for the Human Genome Project.

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

Conclusions

Laser spectroscopy is finding many real-world applications. The many powerful methods allow advanced sensing, both locally and remotely. Of great importance in the process of taking the technology into everyday applications is the fast development of cheap and reliable laser sources, fibre-optical components and computers.

Acknowledgements

The author would like to thank a large number of colleagues and graduate students for a most fruitful collaboration through the years, and many Research Councils and Foundations for generous support.

Further reading

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S. Svanberg, New Developments in Laser Medicine, Phys. Scr. T72, 69 (1997).

Figure Captions

Figure 1. Concentration map of atomic mercury close to one of the cooling towers at the largest geothermal plant in Europe (Larderello, Tuscany). Point monitor data obtained using gold amalgamation followed by atomic absorption measurement are included in the figure. (H. Edner et al., J. Geophys. Res. **97**, 3779 (1992))

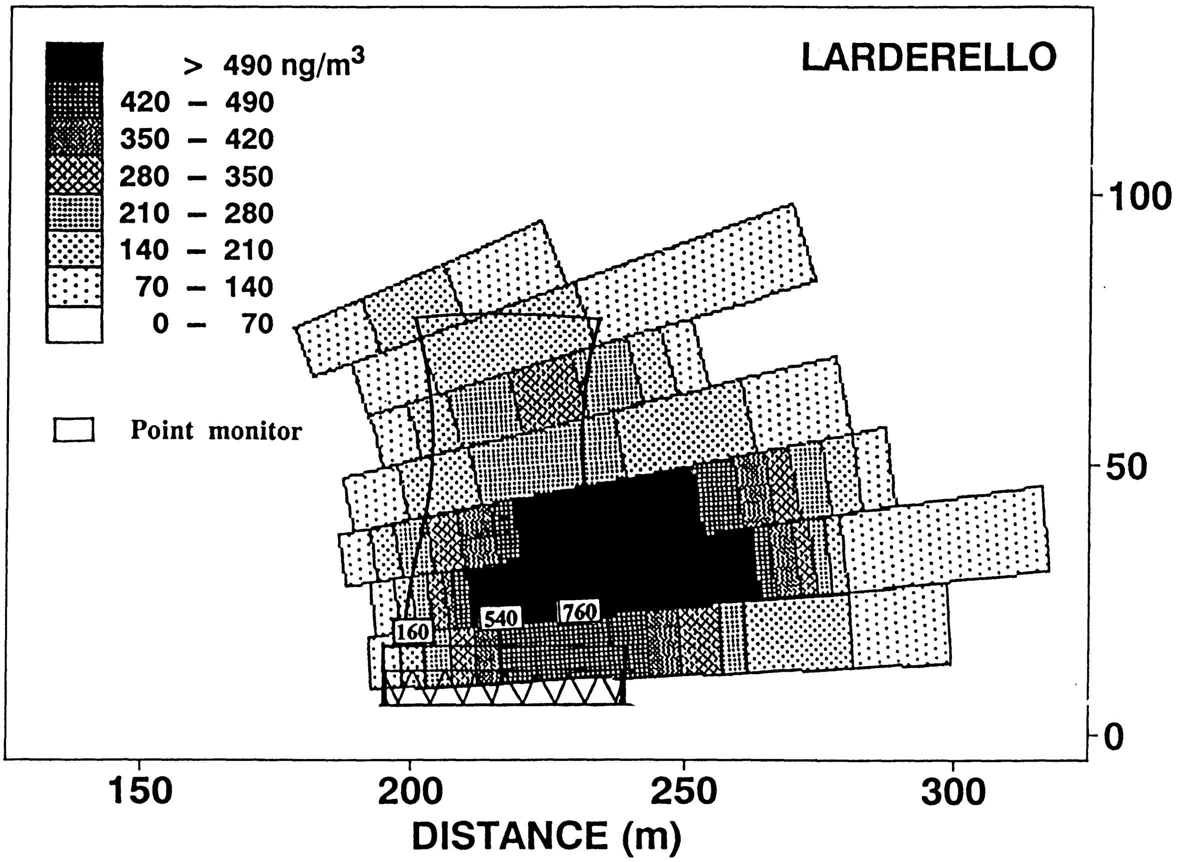
Figure 2. The volcanic plume of Mt Etna recorded by laser radar techniques in an August 1997 ship-borne traverse under the plume. Integrated vertical and horisontal profiles of sulphur dioxide are also shown. The total flux was about 44 tonnes/hour (P. Weibring et al., Appl. Phys. B, in press)

Figure 3. The Italian research vessel *Urania* and the Swedish lidar system just hoisted off its rear deck in the port of Bari (Italy).

Figure 4. Fluorescence imaging of the Northern Gate of the Lund Cathedral. Images (8x8 m2) were recorded through passbands centred at 438 and 682 nm using a scanning laser radar system positioned about 50 meters from the gate. A normal colour photograph of the gate is also included.

Figure 5. Imaging fluorescence tumour diagnostics. Pixels, fulfilling a "cancer criterion" in fluorescence are shown in false colour superimposed on a normal colour video representation of the area. Left: basal cell carcinoma (note the non-cancerous brown spot, which is a benign naevus) Right: Tumour on the vocal cord. ALA had been administered to the patients a few hours before the investigation (K. Svanberg et al., Acta Radiologica **39**, 2 (1998))

Figure 6. Difference in backscattering signals from sarcoma and normal breast tissue. A pulsed diode laser operating around 800 nm was used in conjunction with a time-resolving photon counting system. (Courtesy: C. af Klinteberg and O. Jarlman).


LARDERELLO
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420 – 490
350 – 420
280 – 350
210 – 280
140 – 210
70 – 140
0 – 70
Point monitor
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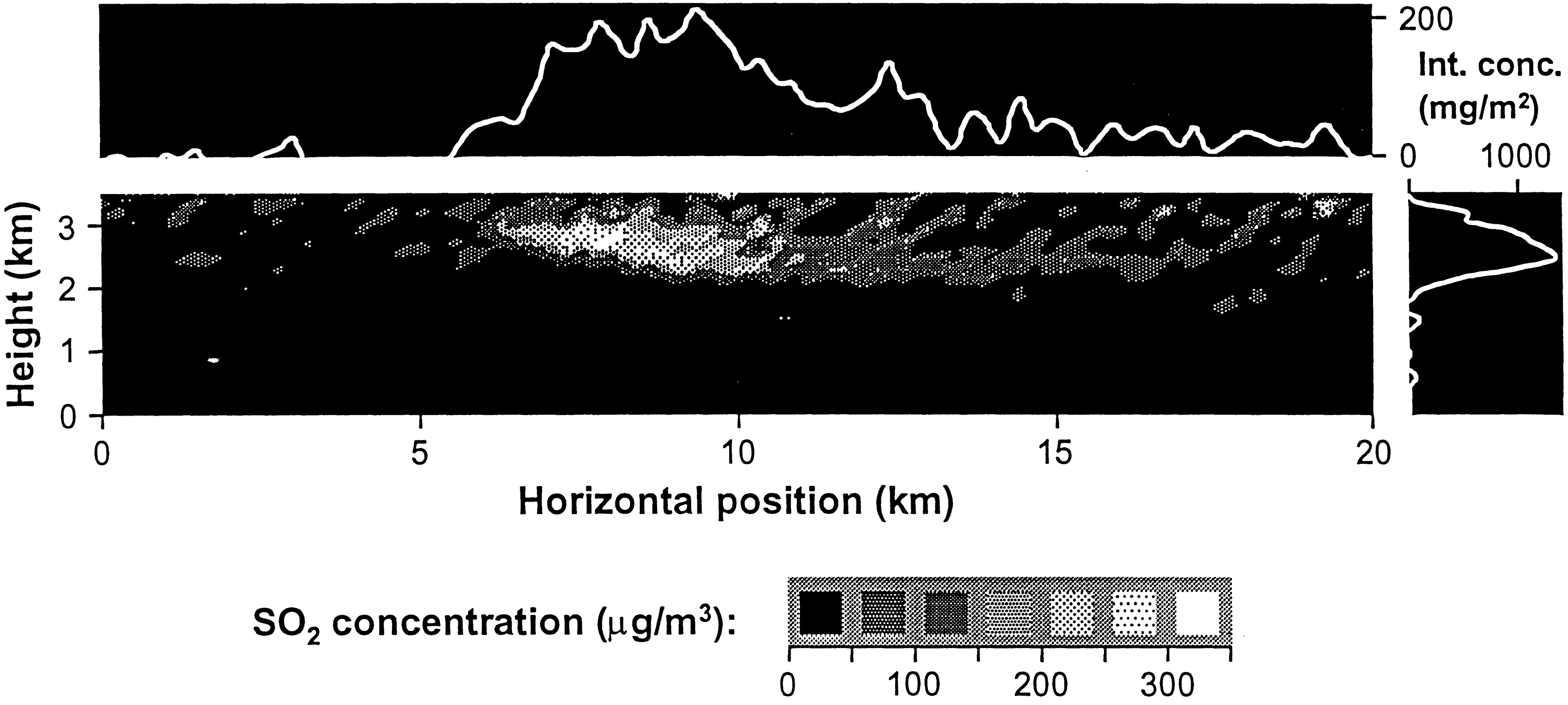
540
760
100
50
0
HEIGHT (m)
150
200
250
300
DISTANCE (m)

Figure 1.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0
1000
Height (km)
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2
1
0
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Horizontal position (km)
SO₂ concentration (µg/m³):
0
100
200
300

Figure 2.

Figure 3.

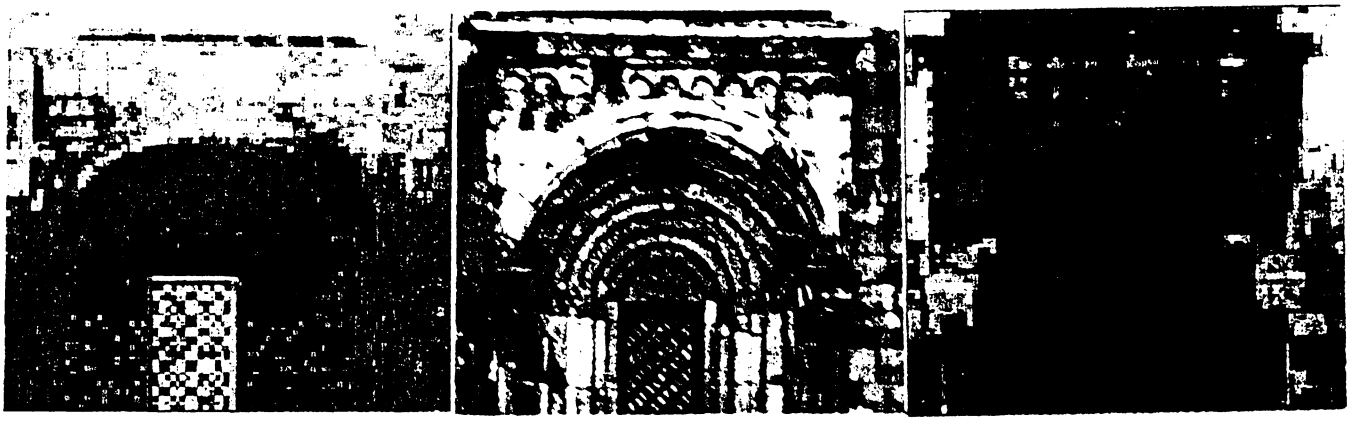
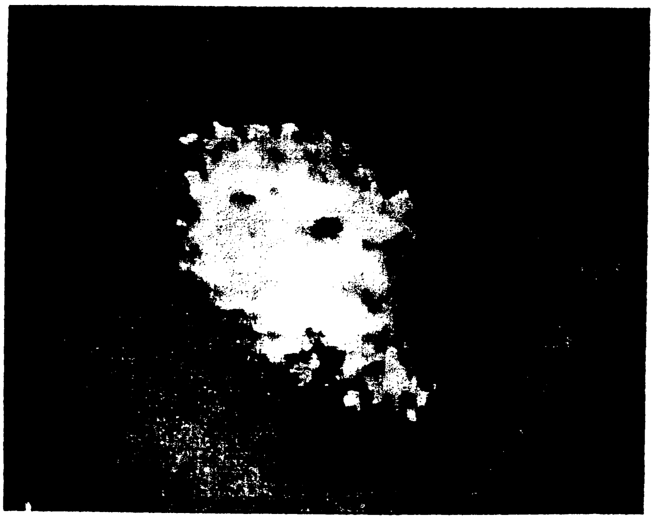


Figure 4.

Fluorescence Imaging
Following ALA Administration

Basalioma + Naevus



Vocal Cords

Figure 5,

Time-resolved diffuse back-scattering

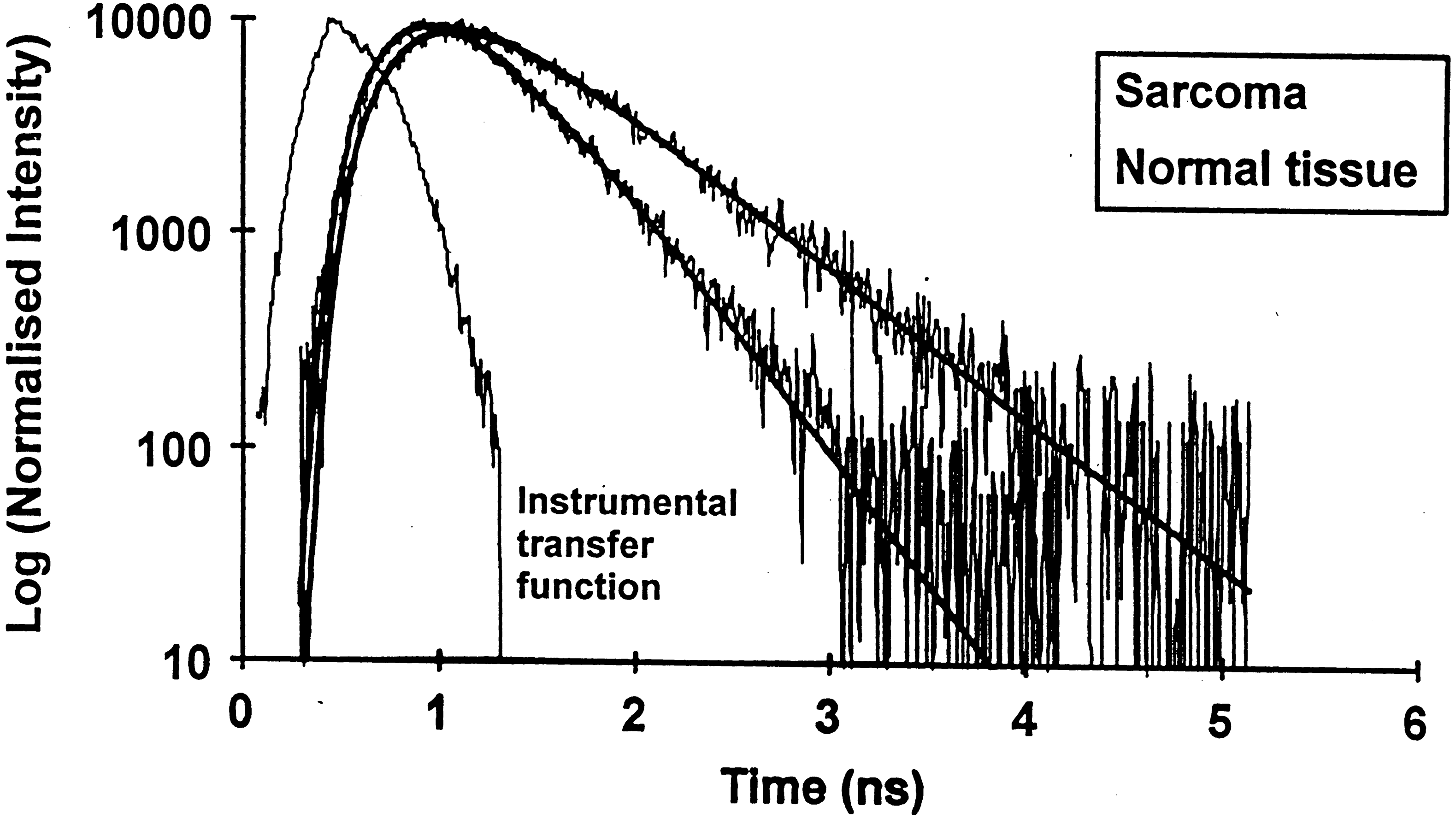


Figure 6

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Further reading

S. Svanberg, *Atomic and Molecular Spectroscopy - Basic Aspects and Practical Applications*, Springer Verlag, Heidelberg, 2nd edn., 1992.

A.C. Eckbreth, *Laser Diagnostics for Flame Temperature and Species,* Abacus Press, Turnbridge Wells, 1987.

M. Sigrist (ed.), *Air Monitoring by Spectroscopic Techniques*, Wiley, New York, 1994.

S. Svanberg, New Developments in Laser Medicine, Phys. Scr. T72, 69 (1997).

Figure Captions

Figure 1. Concentration map of atomic mercury close to one of the cooling towers at the largest geothermal plant in Europe (Larderello, Tuscany). Point monitor data obtained using gold amalgamation followed by atomic absorption measurement are included in the figure. (H. Edner et al., J. Geophys. Res. **97**, 3779 (1992))

Figure 2. The volcanic plume of Mt Etna recorded by laser radar techniques in an August 1997 ship-borne traverse under the plume. Integrated vertical and horisontal profiles of sulphur dioxide are also shown. The total flux was about 44 tonnes/hour (P. Weibring et al., Appl. Phys. B, in press)

Figure 3. The Italian research vessel *Urania* and the Swedish lidar system just hoisted off its rear deck in the port of Bari (Italy).

Figure 4. Fluorescence imaging of the Northern Gate of the Lund Cathedral. Images (8x8 m2) were recorded through passbands centred at 438 and 682 nm using a scanning laser radar system positioned about 50 meters from the gate. A normal colour photograph of the gate is also included.

Figure 5. Imaging fluorescence tumour diagnostics. Pixels, fulfilling a "cancer criterion" in fluorescence are shown in false colour superimposed on a normal colour video representation of the area. Left: basal cell carcinoma (note the non-cancerous brown spot, which is a benign naevus) Right: Tumour on the vocal cord. ALA had been administered to the patients a few hours before the investigation (K. Svanberg et al., Acta Radiologica **39**, 2 (1998))

Figure 6. Difference in backscattering signals from sarcoma and normal breast tissue. A pulsed diode laser operating around 800 nm was used in conjunction with a time-resolving photon counting system. (Courtesy: C. af Klinteberg and O. Jarlman).

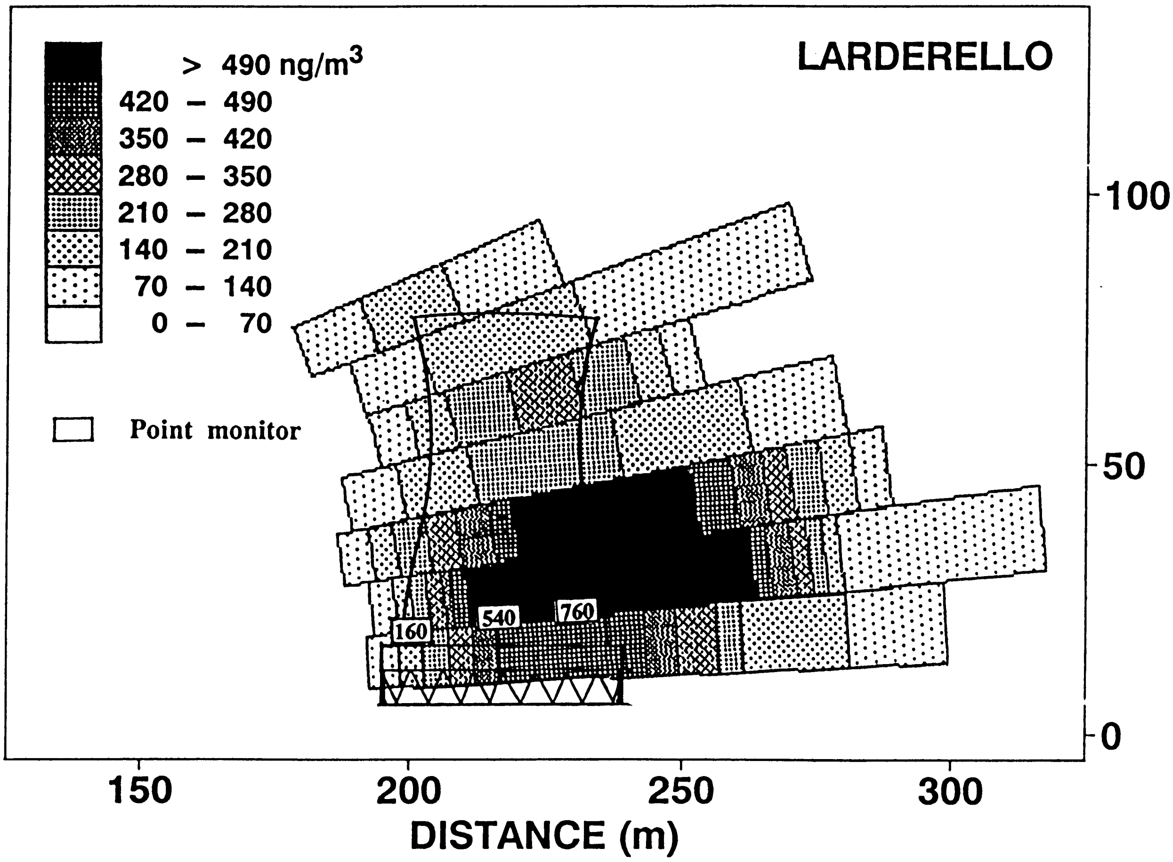

LARDERELLO
> 490 ng/m3
420 – 490
350 – 420
280 – 350
210 – 280
140 – 210
70 – 140
0 – 70
Point monitor
160
540
760
100
50
0
HEIGHT (m)
150
200
250
300
DISTANCE (m)

Figure 1.

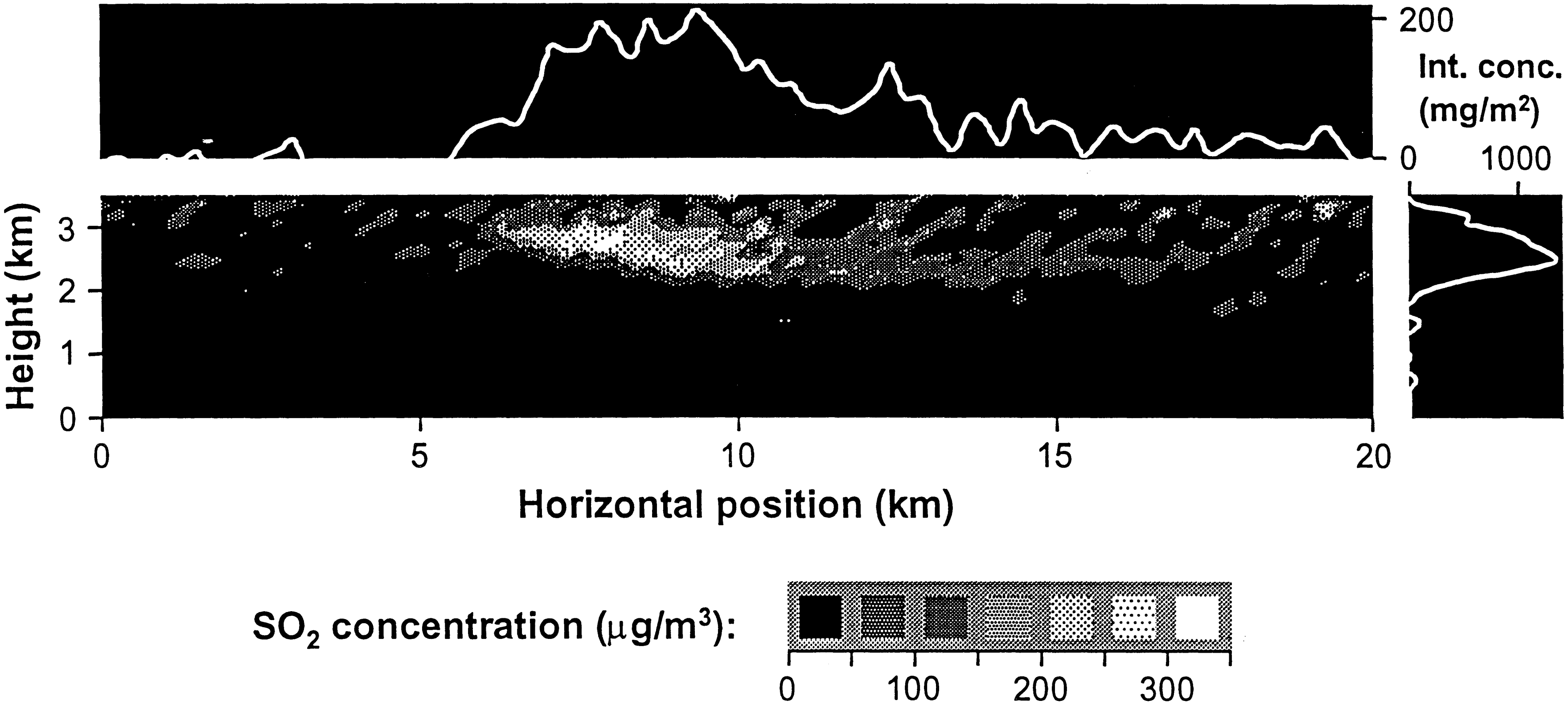

200
Int. conc. (mg/m^2)
0
0
1000
Height (km)
3
2
1
0
0
5
10
15
20
Horizontal position (km)
SO$_2$ concentration (μg/m^3):
0
100
200
300

Figure 2.

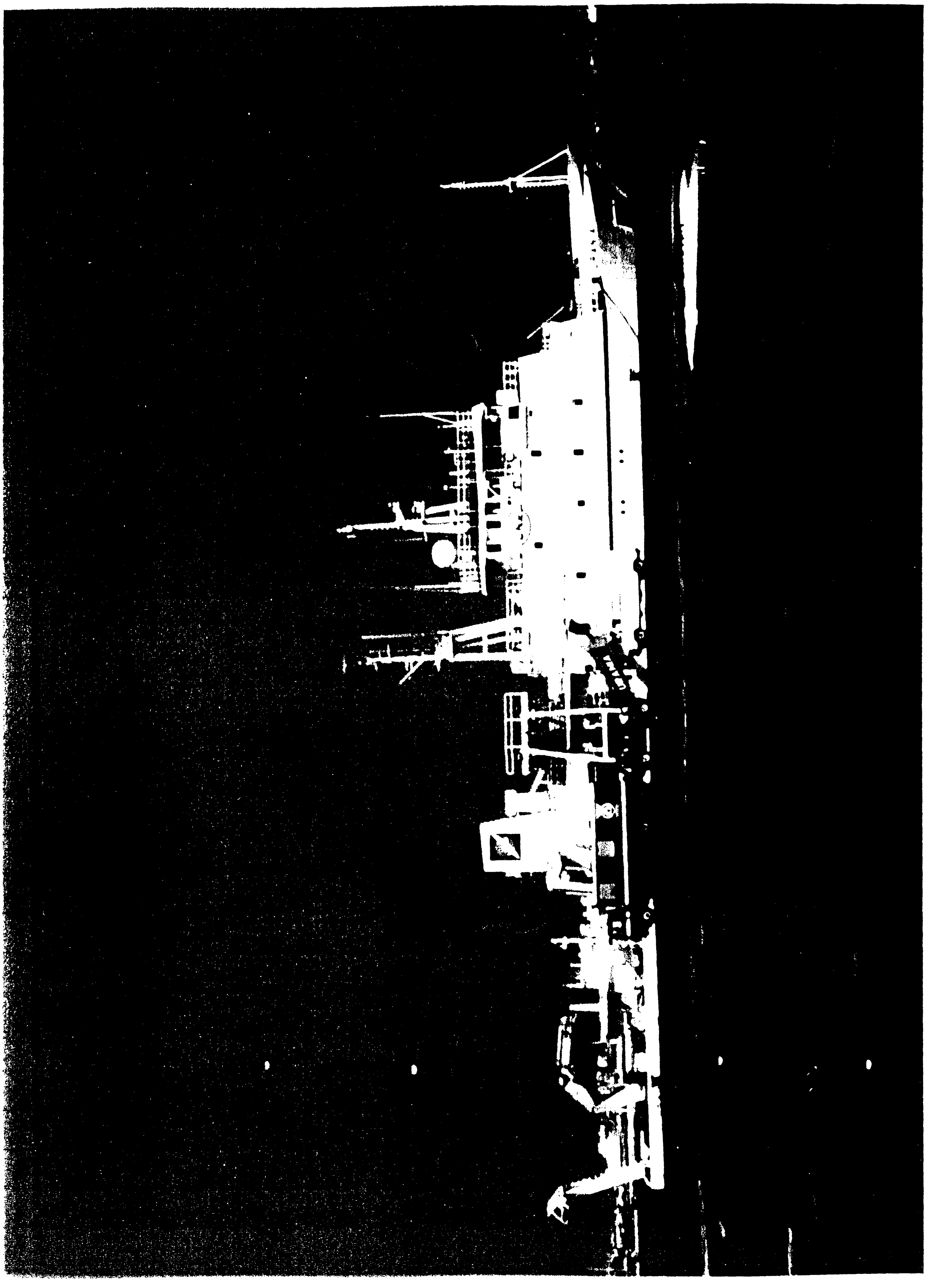


Figure 3.

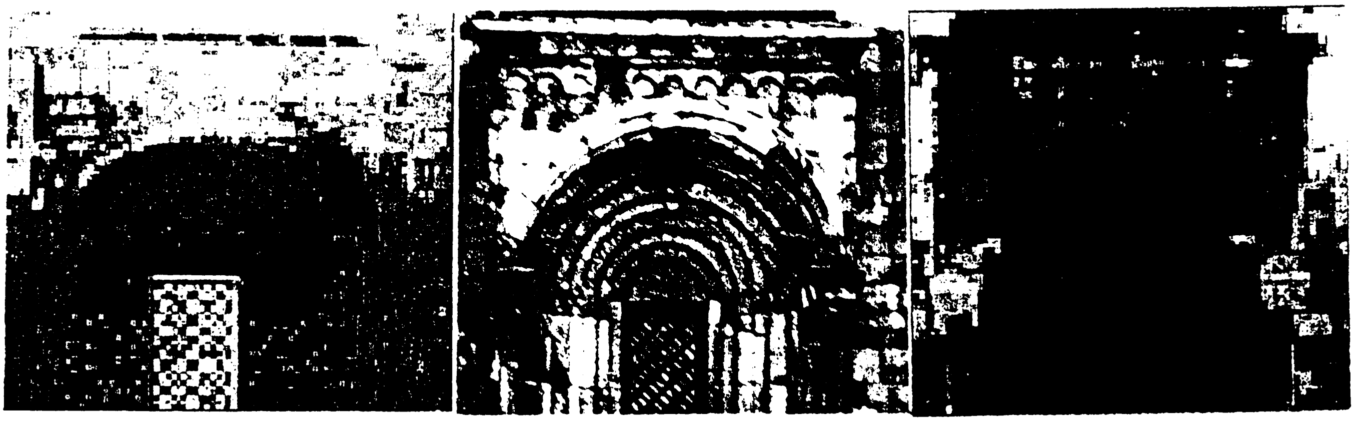
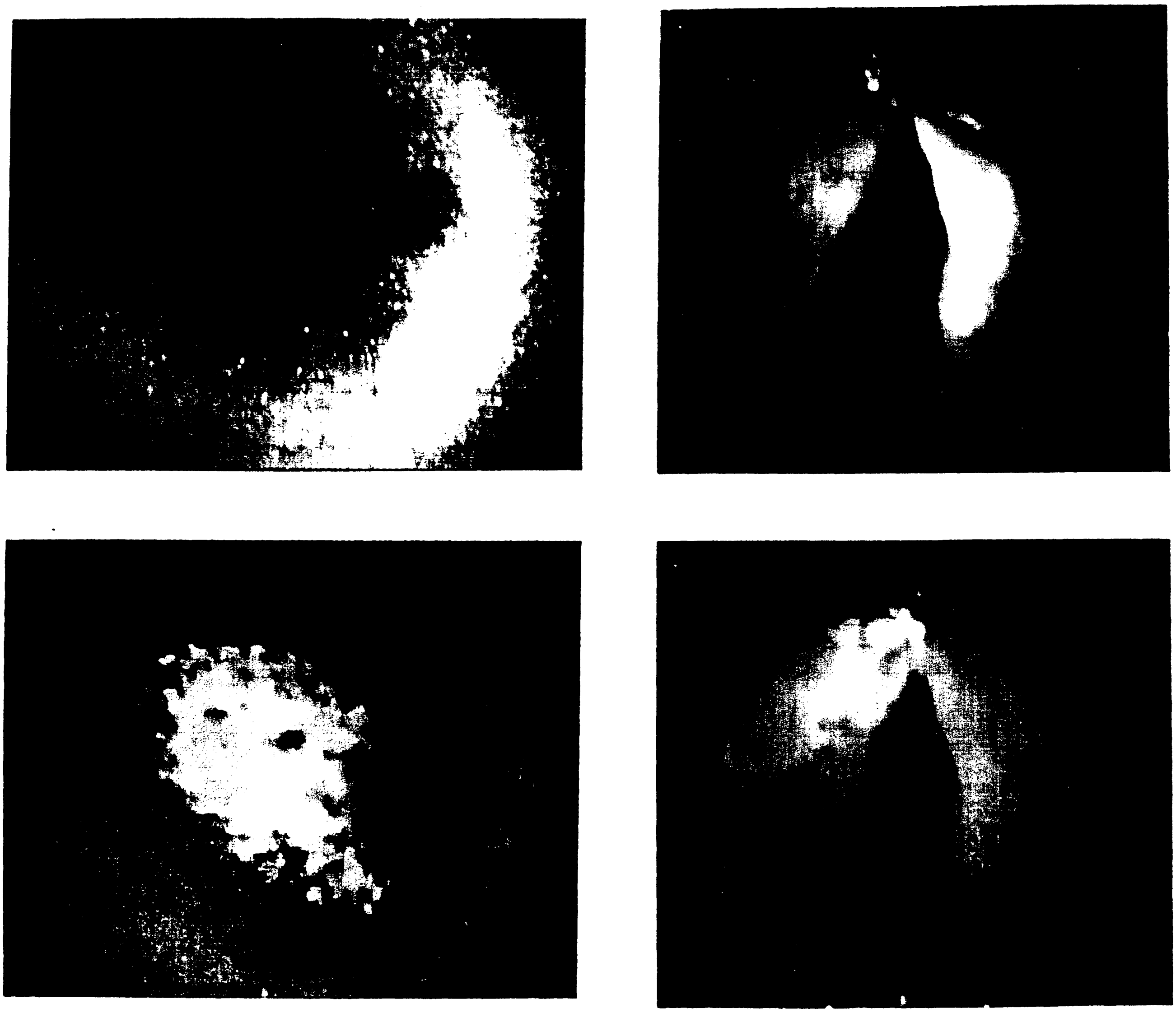


Figure 4.

Fluorescence Imaging
Following ALA Administration



Basalioma + Naevus

Vocal Cords

Figure 5,

Time-resolved diffuse back-scattering

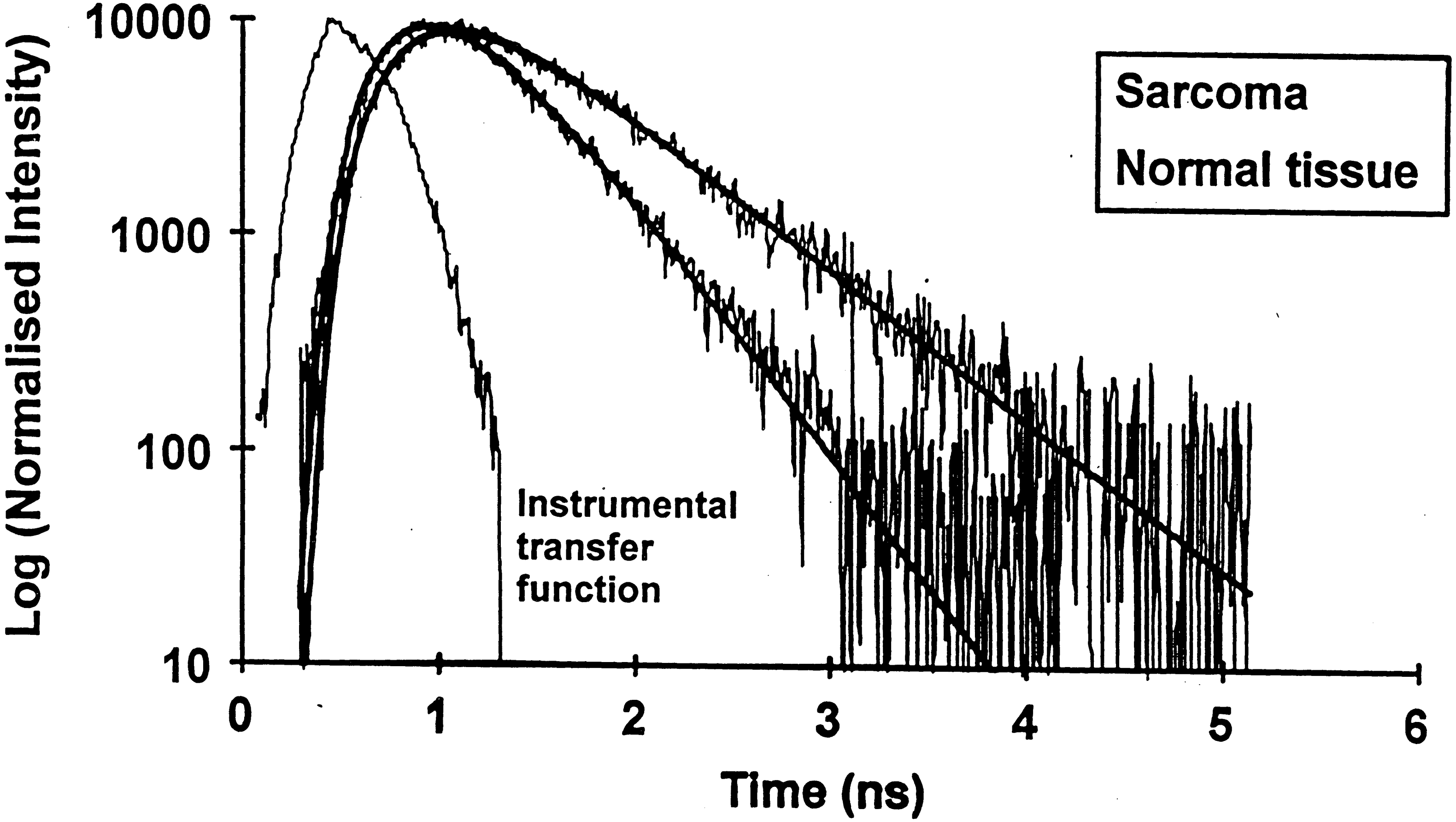


Figure 6