

## FEASIBILITY EXPERIMENTS ON TIME-RESOLVED FLUOROSENSING APPLIED TO OIL SLICKS

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The introduction of time-resolved observations can provide a very penetrating tool in the practice of laser fluorosensing (1). A general advantage is the possibility of isolating the signal from definite volumes within an extended fluorescing target, which may help to resolve between time-distributed and range-distributed contributions (surface vs. volume effects) (2). A specific advantage consists in giving access to the measurement of decay times, thus adding a further bonus to the spectral fingerprinting of complex fluorophores.

An experimental exploitation of these concepts was undertaken by us some time ago (3) in order to test possible applications to the case of oil polluted waters. Fluorescence studies and simulation experiments were devoted, in this phase, to assess the specific information content which can be gained from combined measurements of spectral and temporal response, as well as the technological limits to be encountered in the field practice.

Concerning the first point, our investigations have demonstrated a relevance of multi-spectral, time resolved analysis for oil fingerprinting. By comparative studies on a variety of crude oils and their most significant fractions, it was found that the process of time decay in a composite oil is characterized by a few steps, which are associated with specific components in the medium-light range (e.g., kerosene and gasoil). The average decay times of these "pure" fractions are markedly differentiated as to absolute values and spectral spread; as a consequence, the corresponding parameters in the resultant crude are quite sensitive to the particular mixture of these components. Measurements of the time response give then a finer discrimination between oil classes, depending on the relative content of certain fractions (see Fig. 1).

Experiments have been pursued with an improved fluorosensor facility, in order to test the application of time-resolved fluorosensing to remote samples on water. The apparatus is now based on excitation by the 3rd harmonic line of a Nd:YAG Laser, with pulse width of about 4 nanoseconds. Fast spectral analysis of the fluorescent return is carried out as before (see Ref. 2) by an OMA-2 multichannel analyzer with a gatable acquisition window of less than 5 nanoseconds. By accumulation of repetitive shots at

increasing delay, observation of spectral emission decay is obtained.

Figs. 2 and 3 show the results acquired from two representative crude oils. In each case, the semilog plots reproduce the time response of emission, as measured in fixed contiguous regions covering the entire emission spectrum from u.v. to the red. The visible differentiation between the two oils is well backed by the numerical inserts, showing systematic differences of  $\tau(\lambda)$  and  $\Delta\tau/\Delta\lambda$  for the two cases, which are in fair agreement with previous data obtained from laboratory measurements (compare with the results in Fig. 1 for the same samples). This is achieved at comfortable levels of detection ranging from  $\sim 10^4$  to  $\sim 10^3$  photon counts/shot/nanosecond, which should ensure good statistics over at least 3 lifetimes of any particular decay compatible with our resolution, even in view of finer wavelength subdivision.

Systematic collection of time-resolved signatures has been started on a variety of commercial oils. Results from a group of four typical crudes have been subjected to preliminary elaboration, in order to assess the elements for new time/spectral fingerprinting criteria. The use of regression and correlation techniques seems particularly appropriate to a multispectral analysis of time-decay, for in this case one expects that only a few parameters will enter the picture, namely weight and decay-time (at given  $\lambda$ ) of one or two dominating components. The situation is quite different from that encountered in correlating full emission spectra, where the large number of emission and absorption unknowns, as well as the influence of the matrix, tend to obscure the role of deterministic correlations.

The successful performance of time-resolved fluorosensing, as obtained here, convinced us that this technique can be up-graded and fully exploited with technologically available means. These are: i) use of laser excitation in the range of 50  $\sim$  100 m J, with pulse-width of a few nanoseconds; ii) adoption of integrated multispectral detectors, providing a sensitive and truly simultaneous scanning of whole spectra over the time axis, at nanoseconds speeds. Recent development of streak-camera systems has led us to study the specifications for a compact field fluorosensor based on the above solutions. Construction of this apparatus is presently under way by terms of an external contract.

- 1) see for instance: R.M. MEASURES, W.R. HOUSTON, D.G. and STEPHENSON: Optical Eng., Vol. 13, 6, 494 (1974)  
R.M. MEASURES, J. GARLICK, W.R. HOUSTON and D.G. STEPHENSON: Canad. Journ. Rem. Sens., Vol. 1, 2, 95 (1975)

- 2) P. CAMAGNI, G. COLOMBO, C. KOECHLER, N. OMENETTO, A. PEDRINI, G. ROSSI: Procs. of "Telerilevamento dei Mari Italiani", I.R.O.E., Florence, Oct. 1985 (to be published).
- 3) P. CAMAGNI, C. KOECHLER, N. OMENETTO, A. PEDRINI, G. ROSSI and G. TASSONE: Procs. 1984 World Conference on Remote Sensing, Bayreuth-October 1984 (K.M. Morgan, Ed.; University of Bayreuth and Texas Christian University).

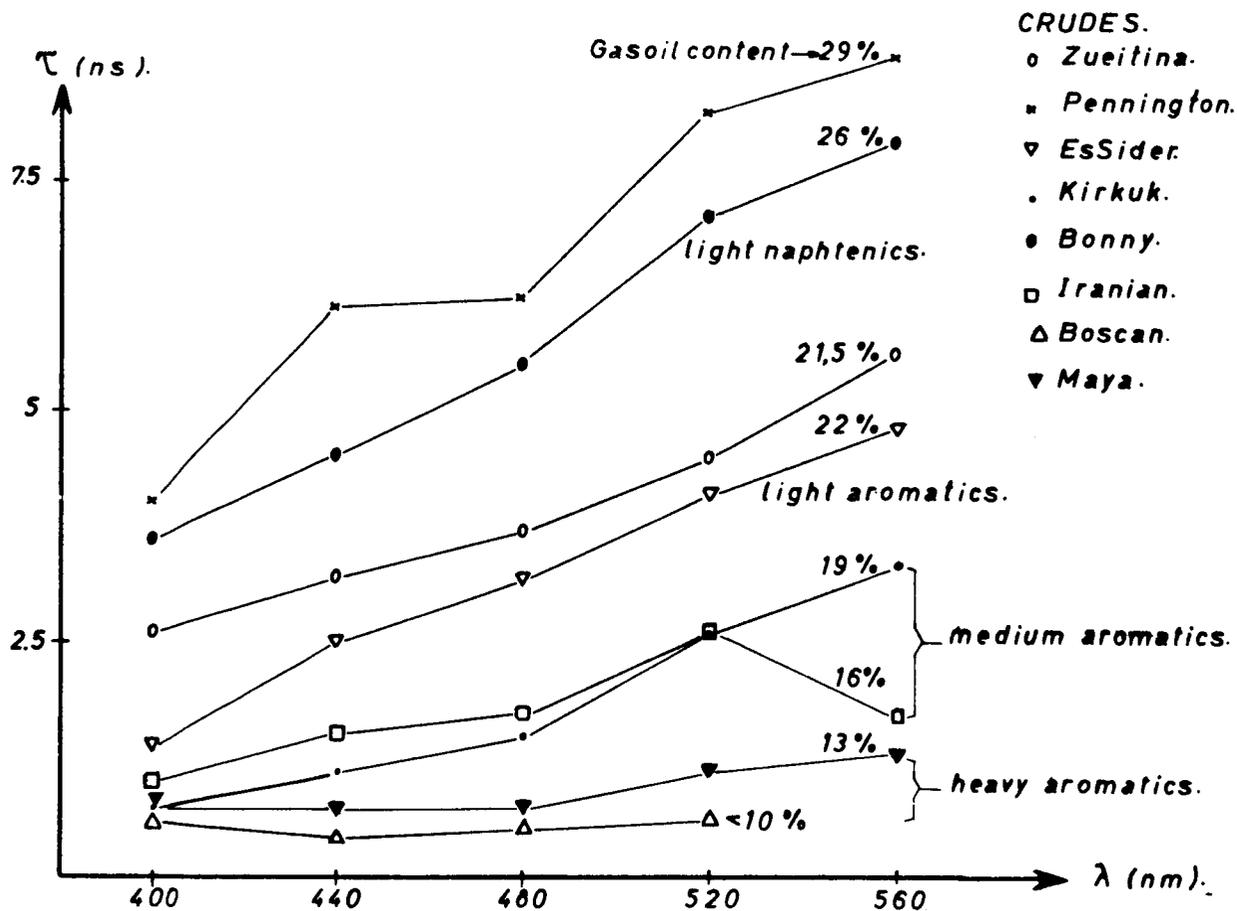


Figure 1): Distribution of fluorescent decay times vs. emission wavelength for various crude oils ( $\lambda_{exc} = 337 \text{ nm}$ ). Numerical inserts indicate weight percent of gasoil.

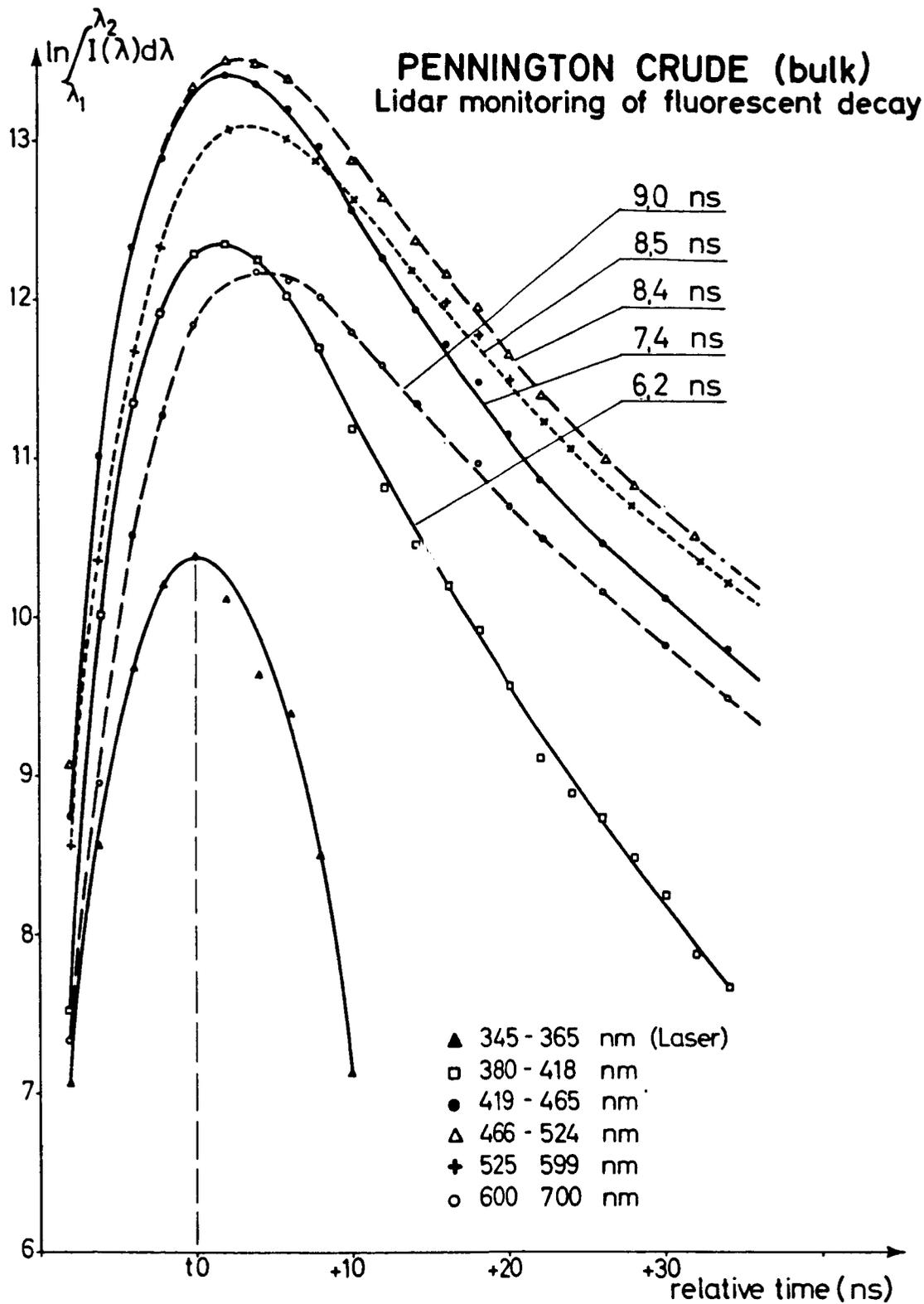


Figure 2): Decay of fluorescent emission (photon counts) in different spectral bands of a PENNINGTON light crude (200  $\mu$  oil film on water; monitoring distance  $\sim$ 100 m;  $\lambda_{exc.} = 355$  nm; 10 laser shots per point).

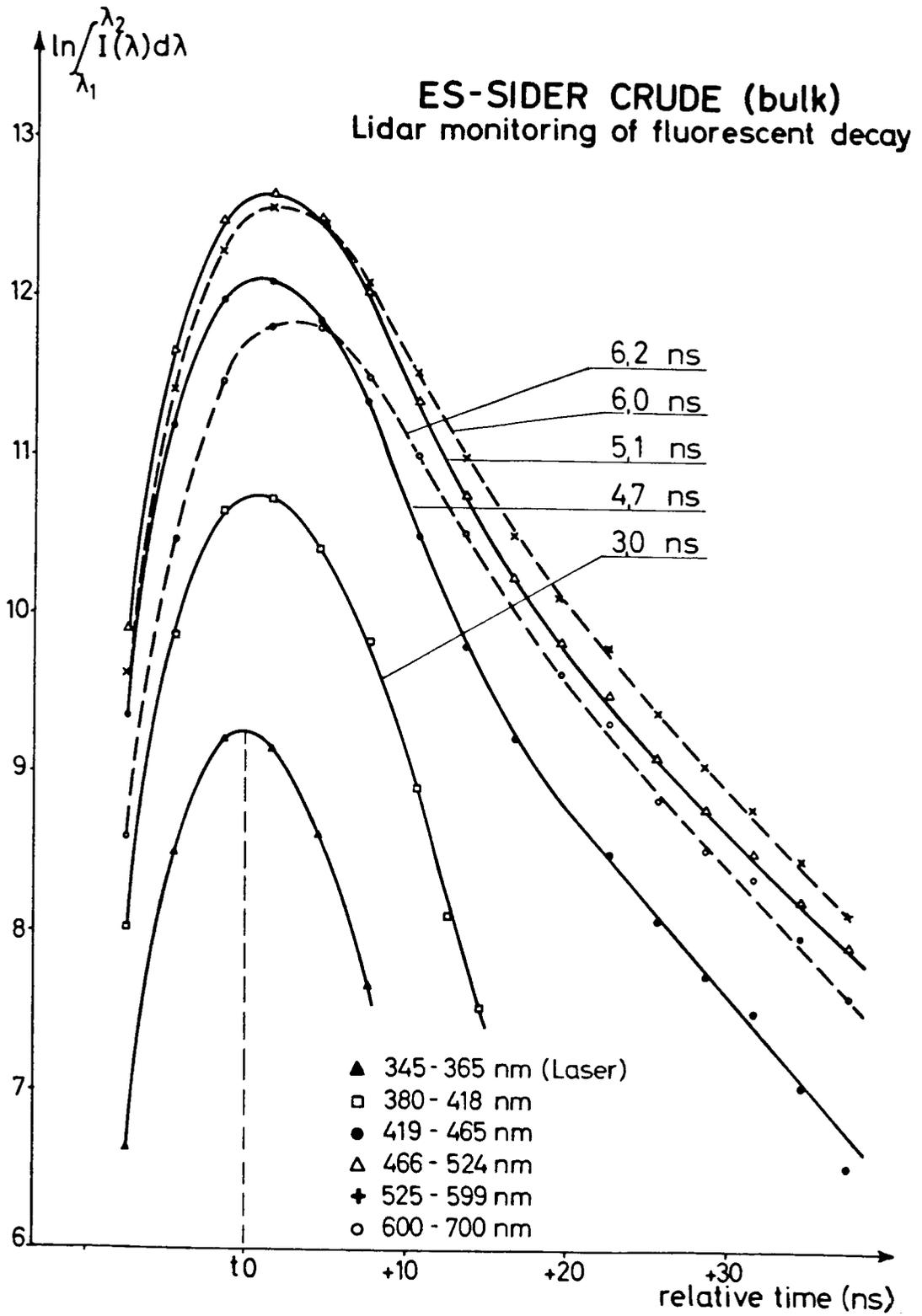


Figure 3): Same as 2 for an ES-SIDER medium-heavy crude.