Evaluation of oil spills by laser induced fluorescence spectra

Andrei B. Utkin*ª, Alexander Lavrovª, Rui Vilarb

ªINOV - INESC Inovação, Rua Alves Redol 9, 1000-029 Lisbon, Portugal
ª Instituto Superior Técnico, Universidade Técnica de Lisboa,
Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal

ABSTRACT

A low cost modular system for automatic oil spill detection, based on laser induced fluorescence light detection and ranging (LIF LIDAR) technology, which may be installed aboard watercraft and used for intensive surveillance of harbors, rivers, channels, and coastal waters, is described. First experimental results obtained with the developed LIF LIDAR detector prototype in the laboratory conditions are reported.

Keywords: oil spill, laser induced fluorescence, LIDAR

1. INTRODUCTION

Protection against oil spillage includes three levels of surveillance: the first level is satellite-borne (range about 50 to 200 km); the second level consists of airborne inspection by visual analysis and IR/UV sensors (range about 100 to 500 m); the third level of surveillance is waterborne.

During the last 25 years, the attention of scientists and engineers concentrated mainly on the development of detection methods and equipment for the first and second levels of surveillance. A number of active and passive optical methods were developed, mainly sophisticated and costly long range instruments. As a result, almost no techniques suitable for the 3rd level of surveillance (one of the most important, due to its flexibility and lower cost) are available in this moment. In particular, the need for lightweight, low-cost detectors that can be widely used for watercraft borne as well as airborne coastal inspection remains unmet.

The authors aim at developing an innovative water inspection method based on laser remote sensing, namely, on laser-induced fluorescence light detection and ranging (LIF LIDAR). Laser remote sensing is an efficient, proven tool capable of providing quantitative, spatially-resolved, real-time data for chemical pollution, eutrophication, biomass, and hydrographical processes over large water surface areas with high spatial resolution; and is often the only solution for many environmental marine applications. Various types of LIDAR systems utilize laser induced fluorescence and light backscattering to analyse bodies of water remotely. LIDAR systems are installed as a payload on airborne, shipboard or stationary platforms for operational purposes and scientific research.

The article reports first experimental results obtained with the developed LIF LIDAR detector prototype. They include investigation of dynamics of oil film on the water surface in the laboratory conditions and study of variation of LIF spectra of spills depending on the oil type and film thickness.

2. EQUIPMENT

The LIF LIDAR sensor was designed around the solid-state Nd:YAG laser NL303 manufactured by Ekspla (Vilnus, Lithuania), generating up to ~100 mJ pulses at the 3rd harmonic 355 nm. The main characteristics of the sensor are given in Table 1. Mechanical design represents a rigid structure, sufficiently compact for installation on small ships. The laser radiation is sent downwards by a mirror mounted in an outrigger arm as shown in Fig. 1 and is collected by a light-gathering telescope installed in the downward-looking position on the same arm.

Table 1. Main characteristics of the developed LIF LIDAR sensor

* andrei.utkin@inov.pt; phone 351 213100426; fax 351 213100445; www.inov.pt
### Transmitter

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser type</td>
<td>solid-state, Nd:YAG</td>
</tr>
<tr>
<td>Regime</td>
<td>pulsed</td>
</tr>
<tr>
<td>Operating wavelength</td>
<td>355 nm (3rd harmonic)</td>
</tr>
<tr>
<td>Pulse power</td>
<td>10–40 mJ</td>
</tr>
<tr>
<td>Pulse duration</td>
<td>3 ns</td>
</tr>
<tr>
<td>Light gathering optics</td>
<td></td>
</tr>
<tr>
<td>Entrance aperture diameter</td>
<td>22 mm</td>
</tr>
<tr>
<td>Detector</td>
<td>linear CCD-array spectrometer, intensified or non-intensified with low noise</td>
</tr>
</tbody>
</table>

**Fig. 1. Mechanical scheme of the LIF LIDAR sensor.**

Collected light is transmitted to the spectrometer (both intensified and low-noise CCD spectrometers were used in preliminary tests) by an optical fiber. The software for operation of the developed LIF/LIDAR sensors controls the data acquisition process. The package controlling the LIF LIDAR sensor is based on the utility supplied by the manufacturer of the low-noise CCD spectrometer, which provides external and internal triggering modes.

### 3. OIL SAMPLES

The laboratory experiments were carried out with the crude oil samples listed in Table 2 provided by GALP Energia Group, which are specific for oil transportation/processing in the Mediterranean and Western European regions.

**Table 2. Oil samples used in the laboratory experiments**

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Product name</th>
<th>Product origin (tanker)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Asgard</td>
<td>Alyarmouk</td>
</tr>
<tr>
<td>2</td>
<td>Azeri Light</td>
<td>Jag Lata</td>
</tr>
<tr>
<td>3</td>
<td>Agbami</td>
<td>Maersk Producer</td>
</tr>
<tr>
<td>4</td>
<td>Sahara Blend</td>
<td>Dalmacija</td>
</tr>
<tr>
<td>5</td>
<td>Mellitah</td>
<td>Phoenix Beta</td>
</tr>
<tr>
<td>6</td>
<td>Brega</td>
<td>Brega</td>
</tr>
<tr>
<td>7</td>
<td>Zafiro Blend</td>
<td>Da Yuan Hu</td>
</tr>
<tr>
<td>8</td>
<td>Marlin</td>
<td>Finesse</td>
</tr>
</tbody>
</table>
4. MIDDLE-TERM DYNAMICS OF LIF SPECTRUM OF OIL SPILL

4.1 Preliminary considerations

Complex processes of oil transformation start developing from the first seconds of oil contact with water. The progression, duration, and result of these transformations depend on the properties and composition of the oil itself, parameters of the actual oil spill and environmental conditions. Preliminary laboratory tests with samples 1-8 (several-millimetre oil film over ~36 l of riverine water, covering about 0.15 m² of the experimental reservoir surface) conducted by the team reveal two characteristic periods of the oil-spill dynamics. The first period lasts from several seconds to one minute and is connected with very fast processes of physical transport and dissolution of highly volatile and water-soluble hydrocarbons. The fluorescence spectra rapidly degrade to about 60-80% of its initial intensity. After this very short stage the oil slick enters into a more stable state, in which characteristic changes occur in hours-to-weeks time scale. It is this period that corresponds to the time scale of proactive decisions on the oil detection and evaluation related to the Project and is worthy to be investigated in the laboratory conditions. From here on we will refer to related processes as the “middle-term dynamics” in order to distinguish them from the truly long-term, months-to-years time scale epoch during which a marine ecosystem destroys, metabolizes, and deposits the excessive amounts of hydrocarbons, transforming them into more common and safer substances.

According to the literature, the oil spill dynamics is determined by the following factors:

**Physical transport.** The distribution of oil spilled on the sea surface occurs under the influence of gravitation forces. It is controlled by oil viscosity and the surface tension of water. During the first several days after the spill, a considerable part of oil transforms into the gaseous phase. Besides volatile components, the slick rapidly loses water-soluble hydrocarbons. The rest - the more viscous fractions - slow down the oil transport.

**Dissolution.** Most oil components are water-soluble to a certain degree, especially low-molecular-weight aliphatic and aromatic hydrocarbons.

**Emulsification.** Oil emulsification in the marine environment depends, first of all, on oil composition and the turbulent regime of the water mass. The most stable emulsions such as water-in-oil contain from 30% to 80% water. They usually appear after strong storms in the zones of spills of heavy oils with an increased content of nonvolatile fractions (especially asphaltenes). They can exist in the marine environment for over 100 days in the form of peculiar "chocolate mousses".

**Oxidation and destruction.** Chemical transformations of oil on the water surface and in the water column start to reveal themselves no earlier than a day after the oil enters the marine environment. They mainly have an oxidative nature and often involve photochemical reactions under the influence of ultraviolet waves of the solar spectrum.

**Sedimentation.** Some of the oil (up to 10-30%) is adsorbed on the suspended material and deposited to the bottom. This mainly happens in the narrow coastal zone and shallow waters where particulates are abundant and water is subjected to intense mixing.

**Microbial degradation.** The fate of most petroleum substances in the marine environment is ultimately defined by their transformation and degradation due to microbial activity. About a hundred known species of bacteria and fungi are able to use oil components to sustain their growth and metabolism. In pristine areas, their proportions usually do not exceed 0.1-1.0% of the total abundance of heterotrophic bacterial communities. In areas polluted by oil, however, this portion increases to 1-10%, see Ref. 3.

In view of the current application context, the most important phenomena that influence the shape of the detected LIF spectra are those that significantly change the oil chemical composition within day-to-week time scale: evaporation of volatile components and dissolution of water-soluble hydrocarbons. The aim of study is to investigate how significant may these processes distort the initial signature of the oil film on the water surface.

4.2 Choice of the experimental parameters

The experiments were carried out with Sample 1 (Asgard crude oil, Alyarmouk), which provided, among all the samples, the sufficiently high level of the fluorescence signal coupled with medium density, viscosity and volatility.
The initial oil film thickness was chosen to be 300 µm. From one hand, it yields sufficiently small quantity of oil (44.7 ml) with respect to that of water (36 l) to provide good similarity to the natural oil-spill ambience, especially from viewpoint of hydrocarbon dissolution. From the other hand, the film is thick enough to provide very homogeneous initial distribution of the oil film over the experimental reservoir’s surface and certain stability of the measured parameters. Asgard crude oil films of ~200 µm or thinner tend to split into several spots of different thickness and consistency. The fluorescence-excitation laser pulse energy of about 14.5 mJ was chosen as a trade-off between the opposite requirements of method sensitivity and non-invasiveness. At this energy the laser beam has a quasi-circular 1.77 cm² footprint on the oil film, maintaining the per pulse laser energy density \( \varepsilon_p \) at the level of 8.2 mJ/cm². For \( \varepsilon_p \sim 15 \) mJ/cm² and higher, preliminary experiments demonstrated noticeable LIF spectra degradation during measurements, caused by oil deterioration resulted from interaction with intense laser radiation.

### 4.3 Results and discussion

The middle-term dynamics of the LIF spectra originated from 300-µm Asgard crude oil film on the riverine water surface was monitored during 16 days. A series of \( N_{di} \sim 24 \) signals were recorded once a day, each signal

\[
S_i = \frac{1}{N_p} \sum_{p=1}^{N_p} s_{ip} \quad i = 1, 2, \ldots, N_{di},
\]

resulted from averaging the fluorescence returns from \( N_p = 100 \) laser excitation pulses. Each partial LIF spectrum

\[
s_{ip} = \{s_{ip1}, s_{ip2}, \ldots, s_{ipj}, \ldots, s_{ipN_j}\},
\]

was recorded by the low-noise CCD spectrometer in \( J = 3646 \) wavelengths in the range from \( \lambda_i = 346.24 \) nm to \( \lambda_j = 1040.94 \) nm.

The total set of the recorded spectra is represented in Fig. 2(a). As seen from the figure, both the decrease of the spectrum amplitude and changes of the spectrum shape are observed. The decrease of the spectrum intensity is represented in a more illustrative form in Fig. 2(b), where the same curves are plotted in the logarithmic scale. One can notice nearly linear degradation of the spectrum maximum, which corresponds to an exponential decay.

The quantitative characterisation of this phenomenon is given in Fig. 3, which show the 16-day evolution of the maximum signal amplitude in linear and logarithmic scales. The plot points represent the averaged signal in its maximum

\[
S_{\text{ave} \max} = \max_j S_{ij} = \frac{1}{N_p} \sum_{p=1}^{N_p} s_{ip} \bigg|_{j=\text{max}}, \quad (3)
\]

and the error bars the corresponding error estimation

\[
\sigma_{\text{ave} \max} = \frac{1}{N_p (N_p - 1)} \sum_{p=1}^{N_p} (s_{ip \text{ave} \max} - S_{\text{ave} \max})^2. \quad (4)
\]

This dynamics can be well described by an exponential low, with signal decrease by one order of magnitude during about 10 days.

Fig. 4, in which the LIF spectra are plotted in a scale-independent normalised form (unit maximum), illustrates evolution of the spectrum shape. Gradual loss of lighter, more volatile and water-soluble hydrocarbons, characterised by shorter-wavelength fluorescence, results in significant changes of the spectrum shape, especially in the range of 400-460 nm. Light hydrocarbons, which in the fresh oil provided very noticeable input in the separate band of 440-450 nm, vanish nearly completely within the first five days. As a result, the spectral intensity tends to take a more symmetric bell-shape form. The spectral maximum shifts toward longer wavelengths, in the case in question, from 495.3 to 503.19 nm.
Fig. 2. LIF spectra recorded during the 16-day monitoring represented in linear (a) and logarithmic (b) scales.
Fig. 3. Maximum-signal amplitude decay: linear (a) and logarithmic (b) scales.

Fig. 4. LIF spectra normalized to unit maximum value.
The experimental study clearly showed that LIF spectra of oils containing significant percentage of volatile and/or water-soluble hydrocarbons are subjected to significant degradation that is characterized by a quasi-exponential decay with a one-order of magnitude per ten days scale, which agrees reasonably well with phenomenological observations of oil spills in natural conditions, indicating that 20% or even larger quantity of oil can evaporate in the first day or so after the spill. This decay not only diminishes the spectrum amplitude, but changes as well its shape, especially in the short-wavelength region. Light hydrocarbons provide very significant input in the LIF spectra of oils.

For this reason:

- Evaporation and dissolution of an oil spill influences the sensitivity of its detection by the LIF LIDAR method: detection of fresh oil spills can be done at significantly lower concentrations than in the case of several-day old spills.
- The training of artificial intelligence systems for automatic oil detection and recognition should be carried out taking into account possible modification of characteristic LIF-spectra signatures of the oil spill due to aging.

5. VARIATION OF LIF SPECTRA OF SPILLS DEPENDING ON THE OIL TYPE AND FILM THICKNESS

In evaluation and recognition of the oil spills one should take into account the possibility of wide variations in the spectrum intensity and shape due to different chemical composition and thickness of the oil films that can be encountered during monitoring. The activity described in this Section aimed at assessing possible spectrum variation for several oil types listed in Table 2, specific for oil transportation/processing in the Mediterranean and Western European regions. As in the previous experiments, the laser pulse energy was maintained about 14.5 mJ (laser energy density of 8.2 mJ/cm² at 1.77 cm² footprint) to provide sufficient sensitivity and in the same time not to provoke changes in the LIF spectra due to oil deterioration by too intense laser light.

5.1 Variation of the spectrum intensity

Study of the specific behavior of the LIF spectra corresponding to samples 1-8 demonstrate noticeable diversity of the LIF-spectrum signals, both in the amplitude and the shape. The detected intensity in the maximum varies from 15000-13000 counts (which corresponds to the spectral energy density of the collected radiation of about 2.7-2.2 pJ/nm per laser pulse) for Asgard and Azeri oils down to 2500 counts (0.45 pJ/nm) for Zafiro Blend (see Fig. 5). Moreover, it was found that sample 8 (oil type: Marlin, origin: Finesse) represents a class of oils that, due to peculiarity of their chemical composition, produce, at excitation by 355-nm wavelength, fluorescence signal at the noise level. Low-intensity fluorescence spectra of this oil at excitation by shorter-wavelength radiation of 310 nm were obtained in independent experiments in Universidade de Vigo. Spectral shape variation is especially manifested in the shorter-wavelength region: for Azer Light it the fluorescence starts from ~430 nm while for Zafiro Blend from ~460 nm.

Fig. 5. Variation of spill fluorescence with the oil film thickness.
As seen from Fig. 5, significant augment in the LIF spectra intensity was observed at increasing the oil film thicknesses up to about 20 - 40 μm. For thicker films, the fluorescence emission tends to saturate, yielding no noticeable changes in the spectrum intensity. This tendency is illustrated in the quantitative terms in Fig. 6, where the spectral intensity in maximum is plotted versus the oil film thickness.

![Graph showing variation of maxima of the fluorescence spectra with the oil film thickness.](image)

Fig. 6. Variation of maxima of the fluorescence spectra with the oil film thickness.

The obtained experimental data agree well with two fundamental facts concerning the fluorescence response of mineral oils:

1. Increasing of the oil film thickness $d$ results to the spectral intensity variation in accordance with the classical relationship for the total number of photons $\delta S_\lambda$ emitted during the laser pulse per unit area in the spectral range $[\lambda - \delta \lambda / 2, \lambda + \delta \lambda / 2]$

$$\delta S_\lambda (d) = C_0 \left(1 - e^{-(\alpha_e + \alpha_\lambda)}\right) \delta \lambda.$$  \hspace{1cm} (5)

Here $\alpha_e$ and $\alpha_\lambda$ represent the radiation extinction coefficients of the oil at the excitation and emission wavelengths correspondingly and

$$C_0 = \frac{E_0 \sigma n g_\lambda \tau}{\alpha_e + \alpha_\lambda \tau^*}.$$  \hspace{1cm} (6)

where $E_0$ is the total photon fluence of the laser pulse, $\sigma$ the optical absorption cross section for the excitation radiation, $n$ the mean molecular concentration of the fluorescent species, $g_\lambda$ the average of the normalised line shape of
the fluorescent emission over the spectral band, and $\tau / \tau^*$ is effective-to-radiative lifetime ratio of the excited level, see Camagni et al. \(^5\) for details.

For thin oil spills, $(\alpha_e + \alpha_\lambda) d \ll 1$, the exponential factor in (5) can be approximated as

$$e^{-(\alpha_e + \alpha_\lambda)d} \approx 1 - (\alpha_e + \alpha_\lambda)d \quad \text{(7)}$$

predicting a linear intensity growth with the layer thickness $d$

$$\delta S_\lambda(d) \approx C_0 \delta \lambda (\alpha_e + \alpha_\lambda)d, \quad (\alpha_e + \alpha_\lambda)d \ll 1. \quad \text{(8)}$$

In the opposite situation, $(\alpha_e + \alpha_\lambda)d \gg 1$, the exponential term is negligible with respect to unity, yielding the description of the saturation mode

$$\delta S_\lambda \approx C_0 \delta \lambda = \text{const}, \quad (\alpha_e + \alpha_\lambda)d \gg 1. \quad \text{(9)}$$

2. As follows from above, the transition to the saturation mode must be observe at the layer thicknesses of the order

$$d_\nu \sim 3(\alpha_e + \alpha_\lambda)^{-1}. \quad \text{(10)}$$

The experimentally observed transition thicknesses of $\sim 30 \mu m$ provide an order-of-magnitude estimation

$$\alpha_e + \alpha_\lambda \sim 0.1 \mu m^{-1}; \quad \text{(11)}$$

which is in a very good agreement with the literature data that typically assess $\alpha_e, \alpha_\lambda$ in the range of 1-0.01 $\mu m^{-1}$, depending on the oil type\(^6\).

### 6. CONCLUSION AND FUTURE WORK

Being a complicated mixture of different hydrocarbons, oil does not retain its chemical composition in the oil spill. As a consequence, the LIF spectra of oil vary with time. The variations manifest themselves not only as the fluorescence intensity degradation, but as changes in the spectrum shape as well. The temporal variance of the LIF spectra of oils is especially significant in high-fluorescence oils and in the spectral range of 400 - 470 nm, where the input of volatile hydrocarbons is the most considerable. Resulting variations of the spectrum shape should be taken into account at training of the automatic artificial-intelligence system of oil-spill detection and recognition.

Different oil components have different absorptivity of excitation and fluorescence light, which causes dependence of the LIF spectrum shape on the oil film thickness. As in the previous case, the differences in the spectrum shape are most noticeable for the high-fluorescence oils while those of low-fluorescence tend to hold the same spectrum shapes starting from the oil film thickness of about 20 $\mu m$.

Apart from the development of the artificial-intelligence algorithms for automatic oil recognition on the basis of LIF LIDAR spectra, the future work of the team is connected with improvement of the sensitivity of spectroscopic measurements, especially in the important range of 350-500 nm. Apart from obtaining valuable spectrum data that facilitate discrimination between different oil types, high-sensitivity spectrometer will allow to calibrate the LIF curves using the Raman signal from clear water. In addition, the measurements of attenuation of the Raman line due the presence of oil on the water surface enable the oil film thickness to be assessed in real time.
7. ACKNOWLEDGMENT

This research has been supported in part by Portuguese Fundação para a Ciência e Tecnologia (FCT) and the European Union within the framework of the European Coordination Action to Foster Prevention and Best Response to Accidental Marine Pollution, Program Accidental Marine Pollution ERA-NET (AMPERA), Project Detection and Evaluation of Oil Spills by Optical Methods (DEOSOM).

REFERENCES


