EVALUATION OF WATER POLLUTION BY LIF LIDAR

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ABSTRACT

Within the framework of ERA-AMPERA Program (Project DEOSOM), INOV is developing a modular sensor for short and intermediate range remote oil spill detection and evaluation. The sensor is based on laser induced fluorescence light detection and ranging (LIF LIDAR), an innovative, efficient and fast water inspection method, capable of providing quantitative data for chemical pollution and biomass distribution studies over large water bodies with high spatiotemporal resolution. The sensor can be installed aboard watercraft and used for intensive surveillance of harbours, rivers, channels, and coastal waters. The paper presents experimental evidence of the applicability of a LIF LIDAR sensor based on a solid-state Q-switched Nd:YAG laser and a CCD spectrometer for oil spill surveillance. The detection was laboratory tested with typical crude brands transported in the Mediterranean region and the dynamics of oil film on the water surface investigated. Good sensitivity of the sensor in the UV range of 400-500 nm enables the LIF spectra to be calibrated using water Raman scattering peak and the LIF emission of very heavy oils and dissolved organic matter to be reliably detected. The feasibility of the method was demonstrated by successful detecting and analysing the spreading of an experimental spill of rhodamine in the Atlantic Ocean coastal waters near Vigo (Spain).

INTRODUCTION

Due to the increasing traffic of cargo ships in European navigable rivers, channels and coastal waters, the risk of water pollution by accidental or criminal oil spillage is increasingly high. The same situation occurs in more than 1100 ports in the EU. Protection against oil spillage includes three levels: 1) the satellite-borne surveillance (range about 50 to 200 km), 2) the airborne inspection by visual analysis and IR/UV sensors (range about 100 to 500 m) and 3) the in situ watercraft borne monitoring.

The article presents preliminary experimental results of development of a low cost, efficient sensor for the third level of surveillance, which may be installed on watercraft or small aircraft and used for intensive surveillance of harbours, rivers, channels, and coastal waters. The sensor is based on LIF LIDAR technique [1] and uses pulsed radiation from a Q-switched solid state laser for fluorescence excitation.

First the study of the dependence of oil-film LIF emission on the oil type and film thickness is presented, providing crucial information on the stability of the detected LIF signature of the spill with respect to variation of the spill thickness in real detection conditions. Then the influence of another essential factor, the oil weathering (natural transformation of oil due to oxidation, biodegradation, dissolution, emulsification, etc.) is investigated, followed by results of watercraft borne detection of an experimental spill, in which less polluting agent, rhodamine, was used instead of oil.

Revealed limited performance of the sensor in detection of heavy oils, water Raman scattering peak and LIF emission from dissolved organic matter (DOM) is significantly improved by introduction of a new spectrometer based on an intensified CCD camera.

Concluding results related to the performance of the upgraded sensor include reliable detection of LIF from an extra-heavy oil sample (Marlin) and DOM, as well as measurements of the water Ra-
man scattering peak and presentation of the oil-film spectra in the Raman-calibrated, laser-fluence independent form.

METHODS

Background

Fluorescence is the process whereby a molecule in a lower electronic state is excited to a higher electronic state by radiation, followed by the light emission, as the system returns back to the original state. Fluorescence is generally observed for many organic molecules, in particular, aromatic ones that absorb in the visible and near ultraviolet regions. LIF offers the advantage of more efficient generating upper-state populations, potentially increasing the sensor sensitivity. In addition, the narrow frequency band of the laser source provides better energy selectivity of the upper state that is being populated.

The use of fluorescence for the analysis of crudes dates back to early 1940s, being initially focused on detection of the presence of oil in the drilling mud and sands [i] and further developed into a more universal LIF LIDAR technique [ii, iii, iv]. The hydrocarbon fluorescence mostly derives from its aromatic fraction and thus is strongly influenced by the chemical composition (especially fluorophore and quencher concentrations) and physical characteristics (e.g., viscosity and radiation extinction coefficient) of the oil [v].

For the application in question, the detected laser induced spectrum of oil films on the see- or river-water surface contains, apart from the oil LIF, several other components. The most significant of them are the water Raman scattering (for 355 nm excitation, the O-H stretch Raman peak of liquid water occurs at 404 nm [vi, vii]) and LIF emission from DOM.

Detection of the Raman scattering peak of relatively clear water outside the spillage yields the reference intensity \( I_{\text{Raman}} \) that can be used for calibration of the spectra (detected for certain configuration and operation mode of the sensor). Moreover, as the Raman scattering peak of contaminated water is subjected to attenuation due to absorption of both the excitation and scattered radiation in by hydrocarbons, the attenuation factor can be used for estimation of the oil-film thickness.

The LIF from DOM complicates the laser-induced emission spectra of spills and additionally hampers the problem of oil recognition and identification. On the other hand, the DOM signal can carry important collaterall information about the organic contamination.

Equipment

Two LIF LIDAR sensor prototypes, Nd:YAG-CCD and Nd:YAG-ICCD, were designed around the solid-state Nd:YAG laser (Ekspla NL 303) generating up to \( \sim 100 \text{ mJ} \) pulses at the 2nd and 3rd harmonics at the wavelengths of 532 and 355 nm correspondingly. Mechanical design represents a rigid structure, sufficiently compact for installation on small ships. The pulsed 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 - the collimation package F810SMA-543 from Thorlabs Inc. installed in the downward-looking position on the same arm (for non-intensified CCD configuration) or a built-in Ø80-mm telescope installed directly on the receiver (intensified CCD configuration, here the LIF radiation is pointed to the receiver by a second mirror as illustrated in Fig. 1)\( \text{a)}\)\( (1)(b) \). In the former case the radiation is input into the spectrometer OceanOptics USB4000 via an optical fiber BFH22-365 (whose core plays a role of the input slit) while in the latter case the radiation is input into the Multichannel Optical Detector (MOD-2LC10212 by Laser Diagnostic Instruments with a gated ICCD camera) through the slit unit. The unit allows adjustment of the slit width, enabling one to establish an \textit{ad hoc} trade-off between the sensitivity and the spectral resolution.

The short-time detection of the emission is implemented via synchronization of the CCD gating with the laser pulse start (a BNC output socket of the Ekspla NL 303 laser provides a 50-ns-rise-time synchronization pulse, the jitter with respect to the optical pulse is not worse than 0.5 ns).
Figure (1): Principal sketch of the developed LIF LIDAR sensor prototypes with a low-noise CCD spectrometer (a) and an intensified CCD spectrometer (b).

In the first Nd:YAG-CCD sensor the single measurement time, 10 μs, corresponded to the minimum allowed by the control software and hardware of the OceanOptics USB4000 spectrometer. This time interval greatly exceeds the characteristic duration of the LIF signal (tens of nanoseconds). Although not causing significant solar-radiation component to appear even in the case of strong-daylight measurement conditions, such big measurement time introduces additional background-radiation and electronic noise. The upgraded sensor Nd:YAG-ICCD provides the possibility of measuring with nanosecond-scale gating, and the single measurement time is chosen to be about 52 ns, an experimentally obtained value corresponding to saturation of the signal growth with the augment of the measurement time. Apart from providing better sensitivity and lower noise, the ICCD spectrometer permits the detected spectra to be extended to the important region of 370-405 nm.

RESULTS
Nd:YAG-CCD: Preliminary tests of the solid-state-laser architecture

The Nd:YAG-CCD sensor prototype was tested with several samples of crude brands included in Table 1.

Table 1: Crudes used in the experiments.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Product name</th>
<th>Product origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Asgard</td>
<td>Al Yarmouk</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>
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First the variation of the LIF intensity with the oil film thickness was studied. Increasing of the oil film thickness \(d\) results in a 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 \([\lambda - \delta \lambda/2, \lambda + \delta \lambda/2]\).
\[ \delta S_\lambda (d) = C_0 \left( 1 - e^{-(\alpha_\lambda + \alpha_\alpha) d} \right) \delta \lambda \]  

Here \( \alpha_\alpha \) and \( \alpha_\lambda \) represent the radiation extinction coefficients of the oil at the excitation and emission wavelengths, respectively and

\[ C_0 = \frac{E_0 \sigma g_\lambda \tau}{\alpha_\alpha + \alpha_\lambda \tau^*}, \]

where \( E_0 \) is the total radiation 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 normalized line shape of the fluorescent emission over the spectral band, and \( \tau^* \) the effective-to-radiative lifetime ratio of the excited level [viii].

For thin oil spills \( (\alpha_\alpha + \alpha_\lambda) d \ll 1 \), and the exponential term in Eq. (2) can be approximated by

\[ e^{-(\alpha_\alpha + \alpha_\lambda) d} = 1 - (\alpha_\alpha + \alpha_\lambda) d, \]

predicting a linear intensity growth with the layer thickness \( d \):

\[ \delta S_\lambda (d) \approx C_0 (\alpha_\alpha + \alpha_\lambda) d, \quad (\alpha_\alpha + \alpha_\lambda) d \ll 1. \]

In the opposite situation, \( (\alpha_\alpha + \alpha_\lambda) d \gg 1 \), the exponential term is negligible with respect to unity, predicting the emission saturation

\[ \delta S_\lambda \approx C_0 \delta \lambda = \text{const}, \quad (\alpha_\alpha + \alpha_\lambda) d \gg 1. \]

This saturation must be observed for oil film thicknesses of the order

\[ d_o \sim 3(\alpha_\alpha + \alpha_\lambda)^{-1}. \]

The LIF variation with the oil film thickness, experimentally studied for the case of Sahara Blend oil, is illustrated in Fig. 2. The LIF-spectrum maximum increases with the thickness in accordance with relation (2), first growing nearly linearly and then tending to saturate.

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**Figure (8): Variation of maxima of the fluorescence spectra with the oil film thickness for Sahara Blend oil, sample #4.**
The analysis of the LIF spectrum maxima obtained for all oil samples (typical changes in the entire LIF spectrum with the oil-film thickness for light (Asgard) and heavy (Brega) crudes are presented in Fig. 3), reported in details in [ix], indicates that the transition to saturation takes place for the oil film thickness $d_f$ of about 30 µm, yielding an estimation $\alpha + \alpha_x \sim 0.1$, which is in a good agreement with the literature data [x].

**Figure (9)**: Typical growth of the LIF spectrum intensity with the oil-film thickness for samples #1 (Asgard) and #6 (Brega). Small peaks in the vicinity of 532 nm are due to residual radiation of the 2nd Nd:YAG laser harmonic reflected from the water surface.

The time evolution of the LIF spectra of 300-µm-thick film of Asgard crude on water was monitored during 16 days. Series of 24 spectra were recorded daily, each resulting from averaging the fluorescence emission from 100 laser pulses. The evolution of the fluorescence spectra is represented in Fig. 4a. As seen from the figure, the fluorescence intensity decreases with time. Simultaneously, change in the spectral shape in the short-wavelength range is observed. One can notice nearly linear degradation of the spectrum maximum in the logarithmic scale, which corresponds to an exponential decay with signal decrease by one order of magnitude during about 10 days, as illustrated in Fig. 4b.

**Figure (10)**: LIF spectra recorded during 15-day monitoring (a) and dynamics of the decay of its maximum (b).
The preliminary tests involving the Nd:YAG-CCD sensor prototype were finalized by field experiments carried out jointly with the Universidade de Vigo (Spain) and Laser Diagnostic Instruments, Lda. (Estonia) in the delta of Ria of Vigo.

Figure (11) : Field tests in Vigo: Nd:YAG-CCD sensor prototype installed onboard of a small ship.

Less polluting agent, rhodamine, was used instead of oil for spill simulation, and LIF from contaminated water surface was induced by the second laser harmonic. The LIF spectrum of the spill was reliably detected, as illustrated in Fig. 6.

Figure (12) : Field tests in Vigo: Signal from the rhodamine spill (1) and rhodamine-free seawater (2). Curve (3) represents the fluorescence spectra of a 0.16 mM ethanol solution of Rhodamine 6G measured by Hung et al. [xi] in similar conditions: excitation by a 532 nm laser radiation with the fluence of 3.5 mJ/cm².

Nd:YAG-ICCD: Extension of the detection capabilities

Although the laboratory and field tests clearly indicated that the developed LIF LIDAR sensor prototype is capable of detecting oil spills, they revealed its limited performance at detection of:
- water Raman scattering peak that, as discussed in the previous section, may serve for spectra calibration and for estimation of the oil-film thickness,
- dissolved organic matter emission,
- some types of heavy, low-fluorescence oils like Marlin crude (sample #8).

In order to understand whether the LIF LIDAR sensor capabilities can be improved for these important applications yet within the framework of the same solid-state laser design scheme - just due to improvement of the receiver -, another spectrometer was introduced into the setup, resulting in the new Nd:YAG-ICCD sensor prototype.

The comparative measurement results obtained with the upgraded sensor are given in Fig. 7. The instrument demonstrated good detection capability, being able to measure reliably the LIF emission from heavy oils.

The spectrum of a thin, less than 10 µm, Marlin oil film on the water surface is plotted in Fig. 8. LIF spectrum of water - predominantly composed by dissolved organic matter (DOM) - and spectrum of pure Marlin oil are shown on the same plot for comparison.

Figure (13) : Extension of the measuring capabilities of the solid-state-laser sensor architecture: spectrum of heavy, low-fluorescence oil (sample #8, Marlin) excited by 355-nm laser radiation measured by the initial sensor prototype Nd:YAG-CCD (laser pulse energy 60 mJ) and the upgraded prototype Nd:YAG-ICCD with an intensified CCD spectrometer (laser pulse energy 5.5 mJ).
Figure (14): LIF spectrum of a thin Marlin crude oil film on the water surface (black) plotted together with measured LIF spectra of water, predominantly composed by DOM (red) and pure Marlin oil (green). The oil film spectrum corresponds well to one artificially constructed by linear combination of the DOM and pure oil spectra (dotted blue).

As seen from the figure, the detected oil-film spectrum corresponds well to a linear combination of the spectra of its main components, oil and DOM fluorescence, measured separately. One can also note significant, about two times, diminution of the water Raman peak of the film with respect to the same peak of oil-free water due to strong absorption of both the excitation and Raman radiation in the oil layer.

Simultaneous measurements of the oil LIF spectra $\{I_{LIF}(\lambda)\}$ and the Raman scattering signal from non-contaminated water $I_{Raman}$ provide calibrated LIF signals $\{I_{LIF}(\lambda)/I_{Raman}\}$ that do not depend on the total photon fluence of the laser pulse $E_0$ in a wide range of its variation (as long as both $I_{LIF}(\lambda)$ and $I_{Raman}$ grow linearly with $E_0$). Such calibrated LIF spectra for the oil samples of Table 1 are shown in Fig. 9. They confirmed the fact (established earlier with the non-intensified linear CCD spectrometer) that for oil with higher fluorescence the spectral maximum is predominantly observed at a shorter wavelength.

**CONCLUSIONS**

Obtained results indicate applicability of the simple LIF LIDAR sensor based on a solid-state laser and a CCD spectrometer to detection of oil spills and marine pollution surveillance as well as to preliminary characterization of oils and estimation of some of their optical parameters, such as the radiation extinction coefficients.

Introduction of an intensified CCD spectrometer significantly improves the sensor sensitivity and extends the measurement capabilities of the solid-state-laser sensor architecture, making it suitable for investigation of dissolved organic matter and low-fluorescence oils and providing possibility of spectra calibration using the water Raman scattering peak.
Figure ii) : LIF spectra of the oil samples, calibrated with respect to the Raman scattering signal from non-contaminated water.

The LIF spectra of oil spills are subjected to changes due to weathering and the presence of DOM. However, the wavelength $\lambda_{\text{max}}$ corresponding to the fluorescence maximum remains practically unchanged, as well as the shape of the spectrum in the region $\lambda > \lambda_{\text{max}}$. As far as the dissolved organic matter inputs linearly to the resulting spectrum, its influence can be substantially reduced by recording LIF spectra of oil-free, but DOM-contaminated seawater in the vicinity of the spill.

Further research of the team is directed to establishing correlation between the LIF spectra of oils and other basic oil parameters, such as the aromatic composition and the API gravity.

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