The Use of the Fluorescence to the Study of the Water Quality

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Abstract. *We present a work proposal now in course that is based on the study of the fluorescence in cyanobacteria and toxicity, and the possibility of detecting their presence in freshwater environment, with a direct application in water assessment. The proposal is a consequence of a previous study about the fluorescence generated by hydrocarbon residue on the sea surface.*

In the first part of this work we present a review of results obtained from the analysis of hydrocarbon samples from the "prestige" oil spill accident and other referential hydrocarbons. In the second part we show the capability of this technique for the development of probes to explore the water quality.

Keywords

Fluorosensing, fluorometry, detection of contaminant substances.

1. Introduction

The ecological disaster of "Prestige", derived from the sinking of the tanker ship of this name at the Galician coast in the North-West of Spain, suggested the idea of the development of a method or instrument to detect the presence of small quantities of hydrocarbon residues on the sea surface or on the coasts, as it is done in other countries

A working group headed by the Polytechnic University of Madrid, and through the University of Santiago de Compostela, presented a proposal to study the viability of an airborne instrument based on the identification of the fluorescence signature of oils and fuel substances, using optical instrumentation off the shell. This work has been just finished and the obtained results suggest new applications of this technology to the assessment of the water quality.

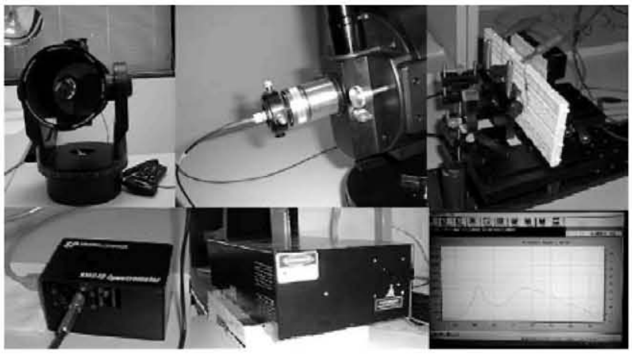

Fig. 1. Elements of our laboratory instrument.

2. The hydrocarbon signature

As it is known, the spectral response of fluorescence is extended to wavelength greater than the incident signal, and it can be detected at distance, through a zoom lens

The spectral signal can be analysed by software which was developed with the objective of discriminating the fluorescence signature of samples, by means of a comparison with a data base.

Figure 1 shows the laboratory components of an experimental instrument designed to obtain the fluorescence signature at a distance of several meters (i.e. 5 to 20). This prototype allows the acquisition of the required database for the identification of the samples.

The essentials of this experimental instrument consist of a nitrogen laser generator that works in the ultraviolet part of the spectrum, used to induce fluorescence on the target.

The instrument is completed with a conventional portable astronomical telescope coupled to a collector of optical radiation, both designated to capture the fluorescence emission. A diffraction-type spectrometer covering the visible part of the spectrum, where the hydrocarbons response is located, provides the spectro-fluorometry. Finally, a personal computer supports the software for spectra graphic representation and recording, as well as the discriminator and spectra identifier.

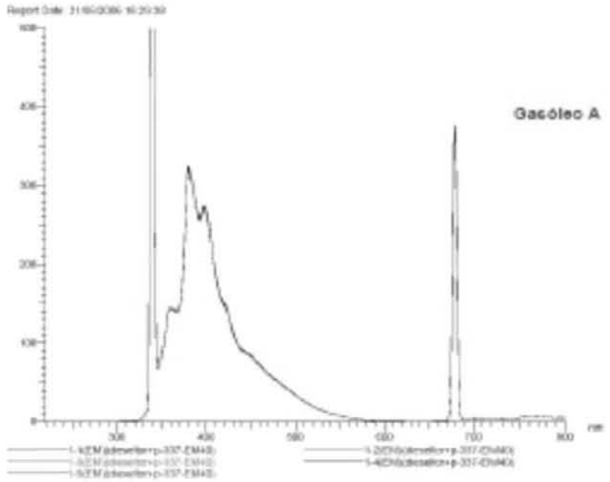

Fig. 2. Fluorescence of Diesel A.

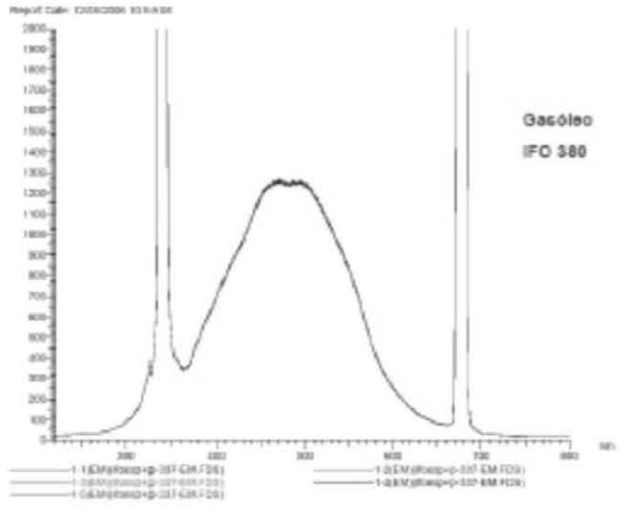

Fig. 3. Fluorescence of diesel IFO380.

3. Results of the instrument prototype

Figures 2, 3, 4, 5 and 6 show the fluorescence signature of several hydrocarbon samples; some of them are different diesel oils (figures 2, 3 and 4), and the other ones (figures 5 and 6), are different residues from "Prestige". As it can be seen in this figure, each sample presents a different response, and the fluorescence trace can be used to identify the kind of substance to be tested.

The "Prestige" hydrocarbon type was IFO380, used as a fuel. In figure 5 is represented the fluorescence trace of the "Prestige" residue acquired from a container in Galicia two years after the ecological disaster.

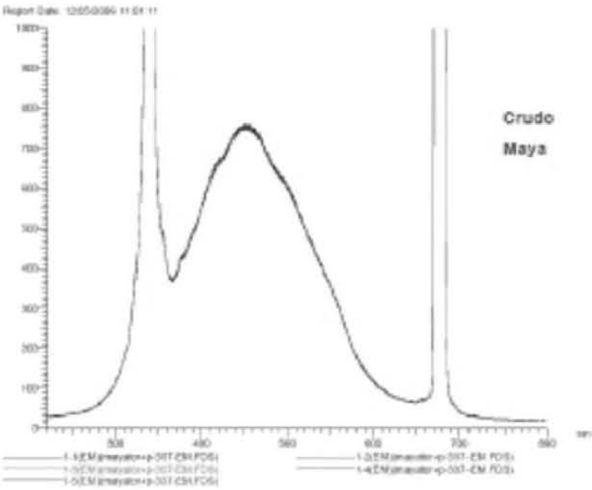

Fig. 4. Fluorescence of "maya crude-oil"

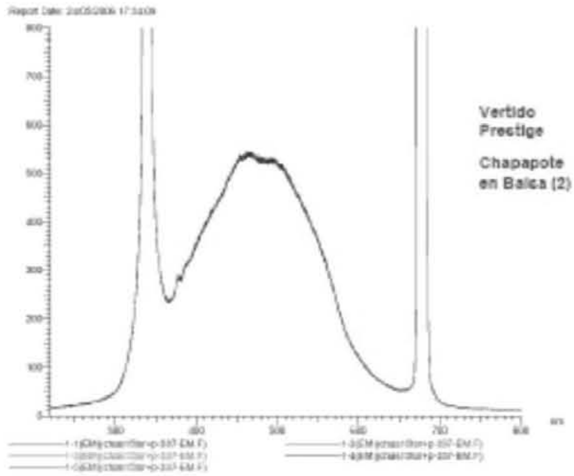

Fig. 5. Fluorescence of "Prestige" residue sample 1.

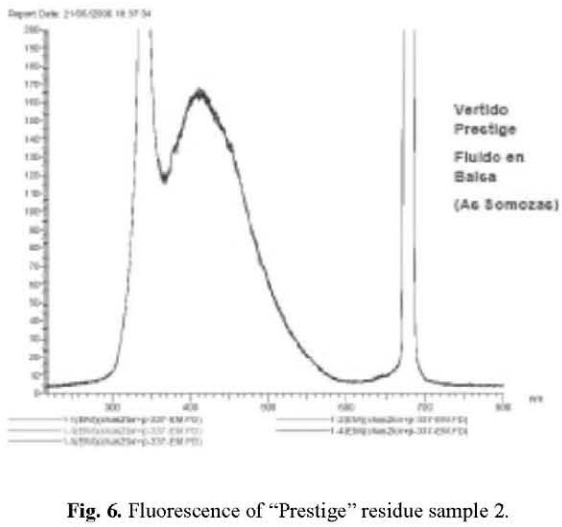

Fig. 6. Fluorescence of "Prestige" residue sample 2.

As it can be seen in figures 3 and 5, both traces have similar shape, with a maximum emission at the same wavelength. The trace of figure 3 was obtained from a sample provided by Repsol YPF, and the trace of figure 5 from the "Prestige" tanks.

The sample of figure 6 is also related with the "Prestige" disaster, but it is from a remaining fluid collected in a retaining pond in Galicia, used as a dump of the oil spill of "Prestige". The fluorescence trace changes and the emission intensity goes down.

This result shows that it has been got an effective experimental instrument demonstrating the viability of a sensor for the detection and identification of hydrocarbon residues on the water surface.

Depending on the characteristics of the equipment, available distance between sample and laser transmitter for an airborne instrument can be found. In this experimental model the sample is placed at 12 m from the laser transmitter.

The experience shows also that small sensors can be designed for the vigilance of any water store or conduction. In this case, a full time vigilance of water quality can be achieved.

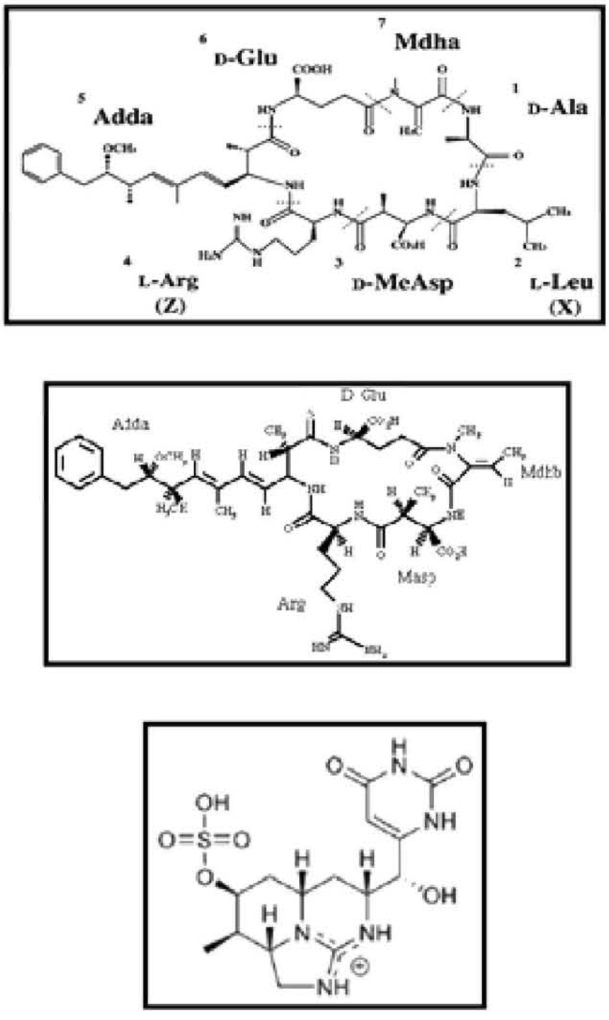

Fig. 7. Structures of some toxins in cyanobacteria.

4. The technique referred to cyano-bacteria signature

This fluorescence technique may be also used for other objectives. For example, we are now involved on the study of its viability for the detection of cyanobacteria, and their associated toxicity in freshwater environments . This could have a deep impact in public health policies through the improvement of the assessment of drinking water quality, recreational water pools, etc.

This study is based on the possibility to obtain a signature of the molecular structure of biomarkers of this and other algal groups . We are undertaking a direct research line, targeting the photosynthetic pigments and different toxins of cyanobacteria. Figures 7 and 8 show the structural composition of some cyanobacterial toxic substances The objective of our proposal is to demonstrate that the presence of conjugated double bond systems and relative motion restriction cyclic group in the molecular structure of these substances could produce a specific fluorescence signature

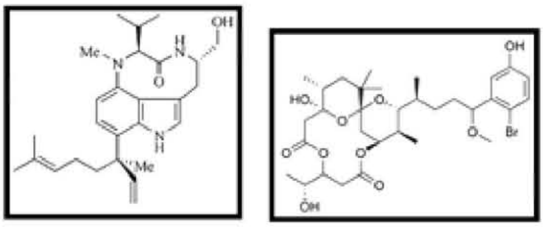

Fig. 8. Structures of some toxins in cyanobacteria.

This technique may be used also following an indirect approach, targeting the non-toxic photosynthetic pigments of the algal cells. This could lead to the identification of other dangerous algal groups, such as the highly toxic dinoflagellates, which are responsible of the "red tides", affecting with a deep impact mussel cultures.

Fig. 9. Sampling area: river source.

This viability study, now in progress, is included on a research project aiming at the characterization of the water quality of a mountain river in the North of Spain Figures 9 and 10 show some views of the sampling site.

The area of study in "Arroyo del Pozo Azul" and its vicinities, an outlet from the Burgos Karst System, in the Natural Reserve "Hoces del Alto Ebro y Rudrón", with several points of samples acquisition including different characteristics, clean water at the river source area (figures 9 and 10), and "non-clean" water at an area close to a fish farm outlet (figure 11). Some university students are also collaborating in the acquisition and identification of samples, as it can be seen in figure 10.

5. New probes to water study

A final part of the study consists in the design of a "multi-probe" to the whole parameterization of a river or a water store [6]. The idea is to have a central unit controlling several and different kind of probes. We have just a design of the control unit that would save periodically in a text file all data from connected probes. The file can be sent to the data processing centre, using different systems, depending of the distance between the unit and the processor centre.

Fig. 10. Sampling area: acquisition of samples at the river bottom.

Fig. 8. Sampling area: Close to a fish farm outlet.

Presently, we are testing a "multi-probe" with 3 commercial temperature probes. The prototype saves data on a small card, which can be periodically replaced by an empty card when its memory is full. The design allows saving data every 5 minutes, with a life time of 1 year without replacement of the card. All the parameters of control can be modified by specific software.

This has been the first step in the design of a "multi-probe". Of course, what we aim is to include fluorometry in the probe. As a matter of fact, remote sensing is a very flexible technique for global monitoring of an aquatic media or so, but in the referred case of cyanobacteria, the sensibility could be not enough, given that noticeable toxicity can be produced by a very low concentration of cyanobacteria, difficult to be detected.

In this case, the only possibility to detect toxicity is by means of underwater sensors of fluorescence of high sensitivity. We already have built a short-distance instrument which has provided some experimental conclusions. But our project contemplates a much advanced device, with a small submersible and water-resistant part easy to be maintained. Figure 12 shows a scheme of this device.

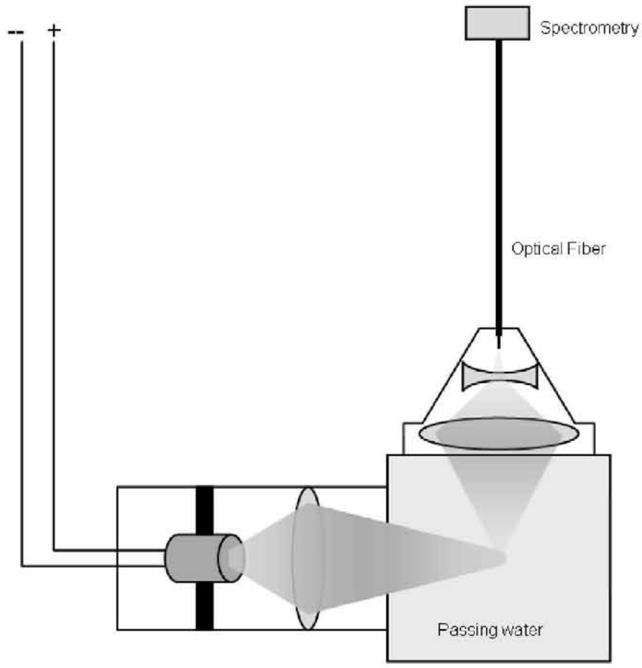

Fig. 12. Scheme of a fluorometric underwater probe.

In this case, the source of light is supposed to be continuous, and spectrometry, sequential, in order to be able to capture fluorescence with only one high-sensibility receiver. In this case, capture time is not a critical parameter.

On the other hand, data acquisition and collection system would be similar to that described for the current multi-probe.

6. Conclusions

We have presented in this paper some of the partial results of a study, which is now in progress, about the viability of fluorescence sensors for the detection and identification of hydrocarbon and cyanobacteria. This research line is currently focused in contributing to the assessment and control of the water quality.

Our previous results show that it is possible to identify petroleum-derived substances on the sea surface and coasts, by means of fluorescence detection.

The research aiming at the application of this technique to the identification of cyanobacteria and their associated toxicity is now in progress.

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