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ON-LINE HYDROCARBONS DETECTION IN WASTEWATER TREATMENT PLANT

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Abstract − Monitoring of hydrocarbon pollutants at the entrance of wastewater treatment plants is imperative for keeping them in good working order. The systems of detection existing on the market place are firstly analysed in order to understand why they are not an effective solution to the problem. The needed characteristics of an acceptable system follows from this analysis. A study of the different methods applicable to the distinction hydrocarbon/water allowed to highlight the attractive method of fluorescence. The main originality of our paper is the transposition of this method to the problem of concern. We conclude by the validation of our method through an in-situ preliminary test.

Keywords: water quality monitoring; hydrocarbons detection; fluorescence.

1. INTRODUCTION

Nowadays, the quality of the water is a major concern of our society. Unfortunately, its intensive use makes its level of pollution too important to be purified in a natural way by the environment. That is why the use of wastewater treatment plants does not cease growing. However, a weakness of these facilities resides in their low capacity to fight pollution by hydrocarbons. The principal sources of this type of pollution are the leakage in heating oil tanks (or their overflow during a filling inlet), illicit discharges of oils and weak losses in service stations. The consequences of an hydrocarbon pollution in a treatment plant are an emergency stop of the station (which implies a quantity of untreated polluted water), the cleaning of the various stages polluted, the degradation of the biology and thus of the efficiency of the station, as well as the destruction of the sludge unusable in farming.

A solution would consist in detecting these products upstream and preventing their passage in the vital stages of the station by means of a derivation system and an emergency basin. This procedure is used in wastewater treatment plants but the detection system is often completely human-dependent as it consists of the human eyes or nose. This procedure is difficult to practice in a systematic way especially because an important percentage of (illicit) pollution is performed during the night. That is why a high need for a reliable online automatic detection system exists.

The different systems available on the market are not effective solutions to the problem either due to technical reasons (lack of reliability, inability to measure the quantity of pollutants entering the station) or economic reasons (cost of the equipment or of the consumables). Our study consists thus to elaborate a system coping with these two requirements of technical adequacy and cheapness.

2. METHODS OF DETECTION

The first step of our study consisted of searching and analysing all the methods applicable to the problem of concern [1]. Those were divided into two classes: detection of the level of gas freed by the hydrocarbon at the water surface and detection of the level of hydrocarbon liquid. For each class, the choice of the most suitable detection method was carried out. The following methods are identified and analysed in more details. For gas level: the solid-state gas-detector; for liquid level: the fluorescence method [2].

2.a. Gas level

Concerning the detection of the gas level by solid-state gas-detector technology, an experience was done on a diesel oil sample. The poor selectivity of that kind of sensors implies to use a variety of them with different characteristics (doping). The sensors used were the gas sensors models TGS 800, 812, 813, 816 and 821 from FIGARO's company. These sensors were placed in crown on top of a closed box containing the oil sample. Figure 1 represents the electrical resistance (kΩ) evolution of the sensor vs. time when exposed to 1 ml oil sample. This search confirms the possibility to detect hydrocarbons by means of this technology.

Unfortunately this experience reveals also a number of inherent drawbacks: high temperature required, humidity sensitiveness, poisoning, high response time,… This result claims, in the present state of the art of solid-state gas sensors, the impossibility for this detection method to fulfil the criteria given in the specifications.

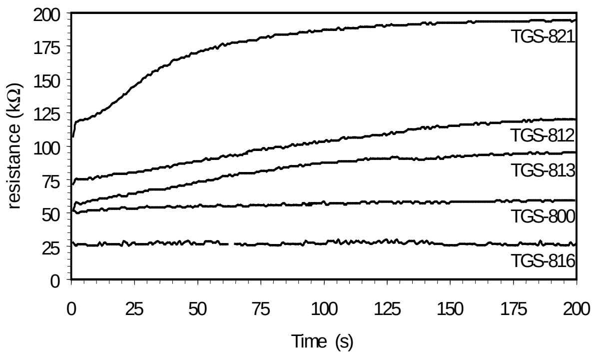

Fig. 1. Time evolution of Figaro TGS sensors'electrical resistance when exposed to a 1ml oil sample

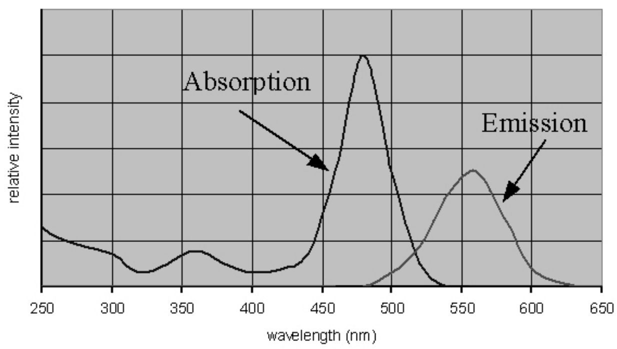

Fig. 2. Emission and absorption (excitation) spectra of a typical fluorochrome

2.b. Liquid level

The search of all applicable detection techniques for detection of hydrocarbons at the liquid level leads to the fluorescence method. We will firstly describe the fluorescence principle to permit its optimal use for hydrocarbons detection in wastewater treatment plant.

2.b.1. Fluorescence principle

Absorption of light by a molecule causes the excitation of electrons which move from a ground state to an excited state. After an electron has been excited, it rapidly decays to the ground state by a number of mechanisms: internal conversion (heat), quenching (external conversion) emission of a photon (fluorescence), or by intersystem crossing (phosphorescence).

Most compounds decay by non-radiative processes (such as heat) and are therefore not fluorescent. Fluorescent compounds, on the other hand, decay to the ground state by the emission of light.

Note that there can be, for a given atom, many types of transitions from higher to lower energies, and thus different energies of emitted photons and, subsequently, many different wavelengths of light waves, each of them being necessarily higher than the exciting one.

This phenomenon is described by excitation (or absorption) spectrum and emission spectrum. These spectra for a typical fluorochrome are illustrated in Figure 2 where the relative intensity is plotted against wavelength.

The relative fluorescence emission spectrum is reasonably independent of the excitation wavelength, particularly, the wavelength of the maximum of the curve. On the other hand, the amplitude of this maximum is dependent on the excitation wavelength, which is represented by the excitation (or absorption) spectrum the interpretation of which is as follows : this latter curve represents, for each wavelength, the (relative) amplitude of the emission curve peak for an excitation at this wavelength. The wavelength difference between the light captured (absorbance/excitation) and released (emission) is called the Stokes shift.

To achieve maximum fluorescence intensity, the fluorochrome is usually excited at the wavelength corresponding to the peak of the excitation curve, and the emission is selected at the peak wavelength of the emission curve. The selections of excitation and emission wavelengths are controlled by appropriate filters.

2.b.2. Fluorescence for hydrocarbons detection

As the fluorescence process is described both by the excitation and the emission spectrum of the substance studied, the first step consists in determining the optimal excitation wavelength for making hydrocarbons fluoresce and the emission spectrum for this excitation. This will help us to select the right source and the right detector.

It is known that hydrocarbons fluoresce under near UV light. [3] shows that the emission spectrum covers a waveband roughly between 400 and 600 nm, with a peak between 450 and 520 nm depending on the excitation wavelength, and that the intensity of this fluorescence emission increases with the excitation wavelength, at least until 420 nm of this latter, which is the practical limit for avoiding overlapping onto the emission spectrum. We confirmed these results for the concerned products by various tests carried out with a fluorometer.

To avoid overlapping between the source spectrum and the detector bandwith (in order for this latter to selectively discriminate the fluorescence phenomenon), we conclude to recommend a source rich in near UV and/or deep blue light limited to 420 nm ; and a detector with a spectral sensitivity typically between 460 and 530 nm.

2.b.3. The light source

The production of light can be obtained by different methods: incandescence, gas discharge (at low or high pressure, with or without additional fluorescent powder), laser (gas or diode), Led,… The poor spectrum of the incandescent light in the desired range makes it unsuitable for the application. The Laser, Led and Laser diode sources offer possibilities in the deep blue but with currently very low economical attraction. On the other hand, the line spectrum of the mercury gas (figure 3) has specific rays (366, 405, 408, 436 nm) well placed with absence of rays in the interval 436-546 nm which is precisely the band of interest for hydrocarbon fluorescence.

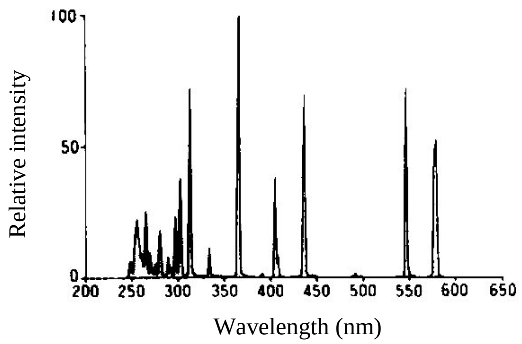

Fig. 3. High pressure mercury spectrum

2.b.4. Light source test

A spectrofluorometer was organised as on figure 4 around a spectrophotometer type ZEISS PMQII, completed by an integrating sphere placed at the entrance slit to enhance the light capture. This set-up was used to measure the emission spectrum of various products (heating oil, gasoline, diesel benzine, wastewater). The light source was a Philips mercury HP 125 W lamp.

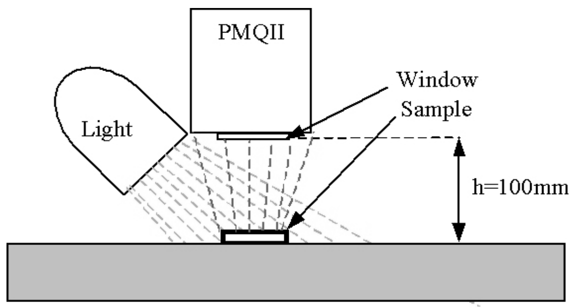

Fig. 4. Configuration of the spectrofluorometer

The results are represented in figure 5. The contrast between the absence of signal for water and the presence of a significant signal for the different types of oils in the intervals between the mercury rays, confirms the possibility to detect hydrocarbons with this method. The difference in relative intensity of the measured signals around the mercury rays is highlighting an other property which permits the hydrocarbons detection on water: the reflection coefficient. Figure 5 shows the evolution of this property with wavelength. However this high intensity difference (at 366 nm for example) is based on a specular reflection of the excitation light source. As the water flow in a treatment plant can be turbulent, this detection method is not suitable and justifies why the fluorescence (which diffuses in all directions) was preferred. The discrimination between the oil types is also possible when we consider the whole spectrum.

2.b.5. Detection sensor

Now the fluorescence is excited, we have to detect it. There are different ways to use the fluorescence as detection method. A contrast between fluorescent and non-fluorescent material can be obtained by time-domain measurements (Time-Resolved Fluorescence), by polarisation (excitation by a polarised light) or by spectral considerations (Stokes shift). The environment imposed by the wastewater treatment plant makes the polarisation method unsuitable for the detection system while economical considerations eliminate the time-domain approach (fluorescence lifetime: order of ns). The contrast by the Stokes shift phenomenon was chosen.

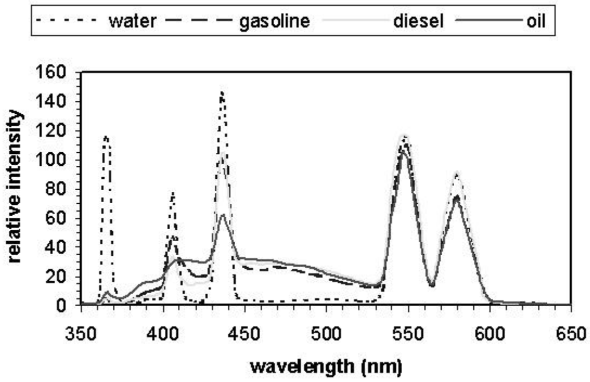

Fig. 5. Fluorescence spectrum measured with the PMQII on various pollutants and wastewater

The richness of information contained in a fluorescence spectrum allows not only the distinction between the different hydrocarbons but also the determination (between certain limits) of the thickness of the pollutant present at the water surface. In this preliminary study and to propose a reasonably prized solution, we limited our investigations in an unique wavelength band, with the aim to propose a binary information on the presence or not of the pollutant.

As already said, the sensor used for our system has to have a good spectral sensitivity limited in the range 460-530 nm. An additional filter is required for this purpose. Every photosensor based on the very popular silicon material is of course a good candidate as such a sensor covers the visible range (excepted the deep blue limit, note that they are also “blue enhanced” variants). Here we can choose between a single sensor, as a photodiode, or a sensor with multiple cells arranged in an array or in a matrix. For this latter, we of course think to a CCD camera for its high informative content – price ratio. Another acceptable candidate for a single sensor is the CdS resistor.

For our study, we opted for a camera to keep the 2D distribution of the hydrocarbon pollution at the water surface. This solution is attractive for its high spatial resolution, its integrated optic and low cost (as it is a “grand public” component). A single photodiode is of course a still simpler solution but we loose sensitivity if the aim is to observe (without spatial discrimination) the same water area as with the camera. Concretely, if the pollution concerns a small part of the scene, with the camera, it will be detected by the concerned pixels. With the single photodiode, the polluted zone, because it is a small part of the whole scene, will produce a weak signal, eventually not detectable.

The optical sensor we used for our experiments was a CCD monochrome camera (Philips LTC350) with an interferential optical filter (500nm central wavelength – 40nm half power bandwidth).

2.b.6. First experiments

Preliminary experiments were performed in a black room with the HP mercury lamp and the CCD camera described above. The first one, realised in an ideal configuration, is shown in figure 6 where two side-by-side recipients (on the left containing diesel oil; on the right: water) were exposed to the light source. The visible dotted line represents the camera line, the electrical output of which is plotted versus time (and thus versus space) on the right figure. An usable contrast between oil and water is clearly observed.

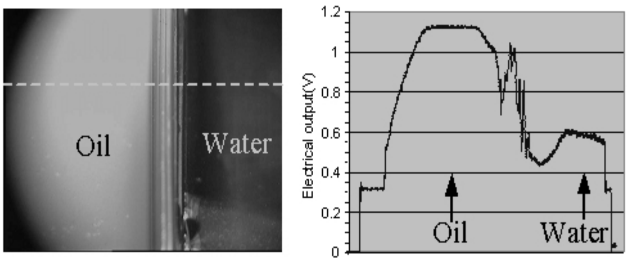

Fig. 6. Contrast obtained with the detection system between oil and water (CCD camera frame on the left ; electrical signal of one line - shown by a dotted line on the frame - on the right)

This idealised first test was followed by a set of experiments closer to the real environment. The contrast mentioned above was not more so effective. Indeed, in a wastewater treatment plant, various parameters will change and mainly two of them will degrade the detection performances. The turbidity of the water will increase the light source scattering. Hence, the CCD camera will receive a higher signal on water, because of the weak but not null spectrum of the HP lamp across the whole range of detection (this is probably due to a high pressure phenomenon). Moreover, the thickness of the pollutant can be very weak in the input of the station, producing therefore a weak signal.

The combination of these two effects makes the detection system until now elaborated, unusable in the real environment. The solution would consist in reducing the light source energy in the range of detection by appropriate filtering. Such a solution is used with a light source called "black light", very popular in disco clubs. It is a low pressure mercury lamp the bulb (or the tube) of which is made in "Wood glass" drastically blocking the visible part of the spectrum. The high UV energy at 366 nm of this lamp is sufficient to induce enough fluorescence to detect hydrocarbons even at very low thickness of pollutant (figure 7). An additional effect obtained with specific powdering of the glass is a secondary UV emission, which enlarges the 366 nm ray (blacklight-blue lamp). We used for our experiments a Sylvania 15W BLB tube.

The diesel oil detection is now obtained on wastewater with high turbidity or very low thickness of pollutant. The next experience consists in validating the same detection

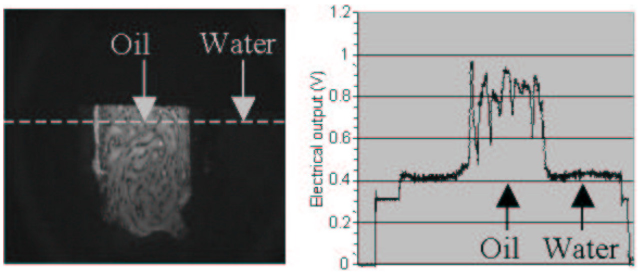

Fig. 7. Very low diesel oil thickness detection with "black light"

system on the other kinds of hydrocarbons potentially present in wastewater treatment plant. Figure 8 shows three drops of various hydrocarbons types exposed to UV and validates the detection system for all kinds of pollutants by way of a black light and a CCD camera.

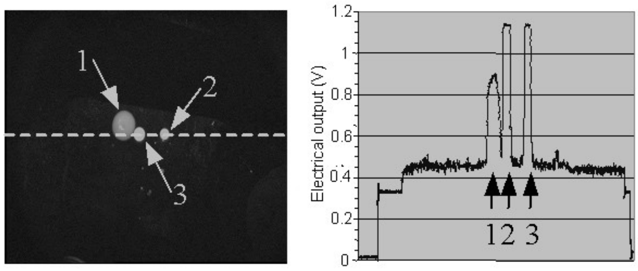

Fig. 8. Detection of various hydrocarbons with black light (1 : heating oil, 2 : oil type 2, 3 : gasoline)

2.b.7. Parasitic elements influence

The influence of parasitic elements was investigated in order to check the use of the system in the environment imposed by the treatment plant. The most important parasitic elements potentially present in a treatment plant and susceptible to fluoresce in the same wavelength range as hydrocarbons are: leaf of tree (or grass) as well as toilet paper.

We experimented that the first one has a very weak signal in comparison with hydrocarbons and does not represent a problem. The second has a signal more important than hydrocarbons but this problem can be moved away by considering the very different temporal and/or spatial signature by comparison to a high amount of hydrocarbons.

A supplementary parasitic element is the sunlight, which is rich in the waveband detected, and must therefore be cut off. A simple solution would consist in sealing the detection area, which implies no disadvantage in the final product. An alternative consists in filtration of the electric signal. As the light source is naturally pulsated at 100 Hz (the double of the electrical supply frequency), a distinction between the fluorescence signal and the sunlight can easily be done if the camera is replaced by a less sophisticated sensor as a simple photodiode (as already suggested above). The advantage of this alternative is that the photodiode output is read continuously. The steady-state sunlight can thus simply be eliminated by adding a high-pass filter keeping the 100 Hz fluorescence signal. Care must nevertheless be taken that the sun illumination does not saturate the sensor. In this feasibility study, a sealed system was kept.

2.b.8. Thickness measuring

As mentioned in the introduction, the measure of the pollutant quantity coming inside the treatment plant is important to avoid false alarms, under a definite pollution threshold. This is possible but implies to measure the fluorescence signal at different wavelengths and therefore a more expensive detection system. Indeed, the fluorescence emission depends on the thickness of the pollutant layer but also on the hydrocarbon type.

However this information of quantity does not have to be precise. We indeed observed, by analysing the situation in a treatment plant, that a two dimensional measure (a linear measure associated to a measurement of the temporal course of this pollution) combined with the hypothesis of a constant thickness, was sufficient to obtain a reliable alarm.

3. PRELIMINARY IN SITU TEST

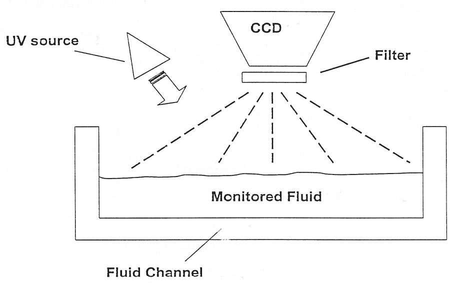

Fig. 9. Configuration of the in situ detection system

The results of these studies guided us in the choice of the most robust detection system. Finally, we suggest a relatively simple pack of technologies (UV source (black light) + filtered CCD camera), in the configuration shown on figure 9.

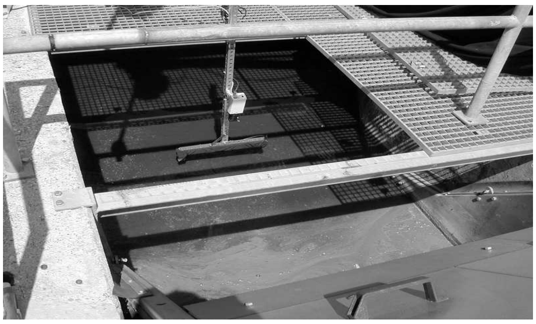

Fig. 10. Measuring system installed above the wastewater flow

We validated this system by placing a pre-prototype in a wastewater treatment plant in a localisation allowing the detection of hydrocarbons before their entrance in the vital stages of the station.

Figure 10 shows the chamber (cover removed) giving access to the wastewater collector where the system was placed: we see the tubular black light source topped by a reflector, and the camera above. The result obtained after the upstream pouring of a slight quantity of oil (diesel) is given in figure 11.

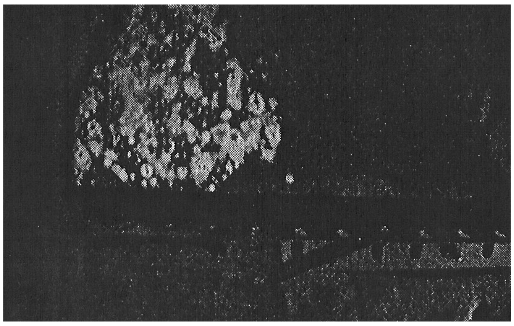

Fig. 11. Contrast obtained between wastewater and diesel oil during a pollution simulation in a wastewater treatment plant

This picture showing the contrast between the water and the pollutant proves the reliability of the chosen detection method.

4. CONCLUSION

It is known that a near-ultra-violet light causes oil to fluoresce, i.e. to reemit the excitation transposed into a higher (visible spectrum) waveband. The chosen method laying thus on a known principle but which, seemingly, has never been applied in the situation of concern, allowed us to elaborate a system of hydrocarbon pollutants monitoring, the performances of which suit the needs of wastewater treatment plants. This system is indeed a means of reliable and economic detection of the different hydrocarbons potentially present at the entrance of these plants. The way is now open for the industrialisation of this product.

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