



Short Communication

Development of online automatic detector of hydrocarbons and suspended organic matter by simultaneously acquisition of fluorescence and scattering



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ABSTRACT

Permanent online monitoring of water supply pollution by hydrocarbons is needed for various industrial plants, to serve as an alert when thresholds are exceeded. Fluorescence spectroscopy is a suitable technique for this purpose due to its sensitivity and moderate cost. However, fluorescence measurements can be disturbed by the presence of suspended organic matter, which induces beam scattering and absorption, leading to an underestimation of hydrocarbon content. To overcome this problem, we propose an original technique of fluorescence spectra correction, based on a measure of the excitation beam scattering caused by suspended organic matter on the left side of the Rayleigh scattering spectral line. This correction allowed us to obtain a statistically validated estimate of the naphthalene content (used as representative of the polyaromatic hydrocarbon contamination), regardless of the amount of suspended organic matter in the sample. Moreover, it thus becomes possible, based on this correction, to estimate the amount of suspended organic matter. By this approach, the online warning system remains operational even when suspended organic matter is present in the water supply.

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1. Introduction

Surface water pollution by hydrocarbons is a matter of concern [1,2] not only for environmental quality but for drinking water quality. Drinking water production plants use groundwater from drilling or raw river water. These plants must be continuously protected from accidental hydrocarbon pollution that could contaminate the entire facility and be difficult to remove from tap water. It is therefore necessary to analyse the hydrocarbon content of the water supply in real time to detect any concentration over an alert threshold determined by the plant's processing capabilities.

Our present paper addresses this objective by presenting an automatic online detector, namely AQUAPOD®, whose primary function is to quantify hydrocarbon content by fluorescence spectroscopy, which is a suitable technique due to its sensitivity and moderate cost [3,4,5,6].

A complicating factor in such measurements arises due to waterborne organic matter. Surface or ground waters contain varying amounts of particulate or suspended organic matter [7,8] (SOM) with

a diameter superior to 0.45 μm . The quantity of SOM may be high in ground waters, up to 1.000 mg L^{-1} , especially in rainy periods or following thunderstorms.

SOM disturbs fluorescence measurements by causing Mie scattering [9] and by absorbing the excitation beam [10], which will decrease the irradiance of the sample; thus leading to an underestimation of the amount of hydrocarbons present. To correct this artefact, we present a specifically developed spectral correction technique that can instantly determine the true hydrocarbon content by taking into account the amount of SOM.

Moreover, quantities of SOM are also a matter of concern for water treatment plants. The second function of the online detector presented here is therefore to simultaneously estimate the amount of SOM contained in raw waters, through measurements excitation beam scattering.

The originality of the detector is its use of a single source of UV excitation by LED to simultaneously record beam scattering and sample fluorescence. This design has a reasonable cost for the construction and operation of the detector whose function is to automatically detect a warning threshold (over than 0.5 mg L^{-1} in non-turbid water) of total hydrocarbon content. As contamination could come from different sources (fuel, gasoline, kerosene, aviation fuel, oils) we chose to work

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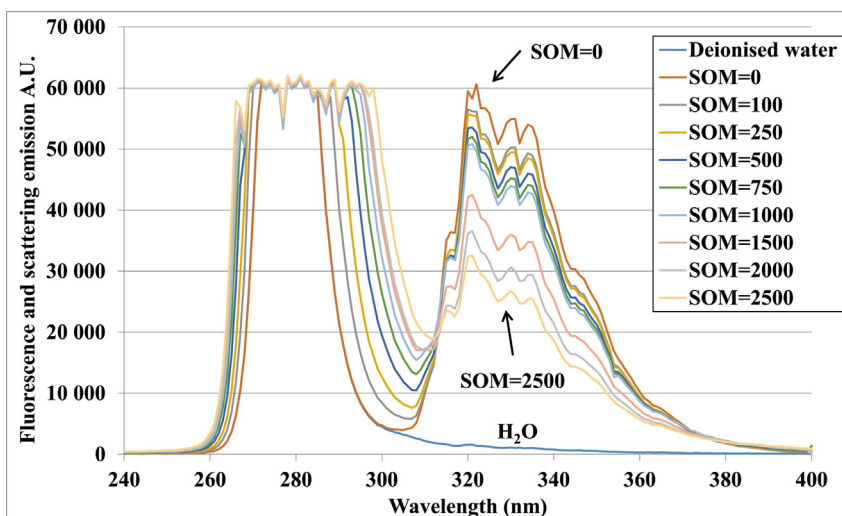


Fig. 1. Naphthalene fluorescence spectra (0.75 mg L^{-1}) for different amounts of suspended organic matter (0, 100, 250, 500, 750, 1000, 1500, 2000 and 2500 mg L^{-1}).

on naphthalene as a representative of polyaromatic hydrocarbon (PAH) contamination.

2. Material and Methods

2.1. Detector System

Fluorescence spectra were recorded by an AQUAPOD UV/Fluo detector (HOCER, France) equipped with a 5 mm pathlength flow cell, a 280 nm emitting LED and a CCD spectrometer. Water samples (10 mL) were taken by a peristaltic pump, and the raw spectrum then measured in stop flow status for 10 s; 100 mL of deionised water were then pumped through to clean the system and a reference spectrum recorded. The system was controlled by a dedicated program via a touch-sensitive screen.

2.2. Chemicals and Samples

SOM was obtained from a river sludge sample; dissolved organic matter was eliminated by filtration at $0.45 \mu\text{m}$.

3. Experimental Results

3.1. Spectrum Analysis

We analysed different concentrations of naphthalene (0.1, 0.25, 0.325, 0.5, 0.625 and 0.75 mg L^{-1}), with different amounts of SOM (0, 100, 250, 500, 750, 1000, 1500, 2000 and 2500 mg L^{-1}). Fig. 1 shows the results obtained for a naphthalene concentration of 0.75 mg L^{-1} with the different amounts of SOM.

The spectral line around 280 nm corresponds to the Rayleigh scattering of the excitation beam. In the presence of SOM, a particulate scattering effect (Mie scattering) also appears, inducing a spectral line broadening (together with a saturation of the detected signal), which increases with the SOM content. This effect can be mainly seen to the right of the 280 nm spectral line, but also to a lesser extent to the left.

The band between 310 and 380 nm corresponds to the characteristic shape of naphthalene fluorescence. Without SOM, the signal reaches 60,000 arbitrary units (A.U.). With increasing SOM, we observe a gradual decrease of the naphthalene fluorescence caused by the particulate scattering of the excitation beam, and by its partial absorption by the SOM, both of which reduced the naphthalene excitation. Scattering effects of the remaining fluorescence of the naphthalene can also occur.

As a consequence, presence of SOM in the sample will lead to an underestimation of the naphthalene concentration and consequently give

inaccurate measurements. To overcome this effect, we set up a spectrum correction that takes into account SOM scattering.

3.2. Scattering Correction

To measure the scattering effect, we can plot the signal recorded with SOM (at wavelengths corresponding to the broadening of the excitation spectral line) as a function of the signal without SOM. However, in the case of our study, the signal measured to the right side of the scattering spectral line is also dependent on the naphthalene fluorescence.

Consequently, we worked on the left side of the excitation scattering line, which is not modified by the naphthalene fluorescence, even though the broadening effect is smaller. Thus, the signal was recorded from 258 nm to 270 nm (or inferior to 270 nm to keep a signal below 45,000 A.U., corresponding to the upper limit of the linear response of the detection) and plotted as a function of a reference signal measured on deionised water without SOM 1 min earlier.

We obtained a straight line whose slope is equal to one without SOM, and which increases with the amount of SOM present (Fig. 2 and Table 1).

The corrected spectra, calculated from measurements that included scattering by SOM, were then obtained by dividing the raw spectra by

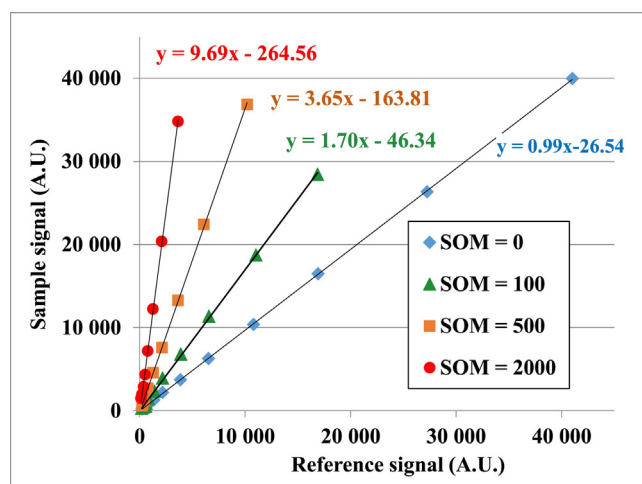


Fig. 2. Sample signal (from 258 nm to 270 nm, with one point per nanometre) without SOM, and with increasing amounts of SOM (100, 500 and 2000 mg L^{-1} , the other levels i.e.: 250, 750, 1000, 1500 and 2500 mg L^{-1} , have been omitted from this figure for clarity); as a function of the deionised water signal (without SOM, recorded 1 min earlier).

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