APPLICATION NOTE

WATER QUALITY BY MONITORING THE NATURAL ORGANIC MATTER OF ACQUATIC SYSTEMS

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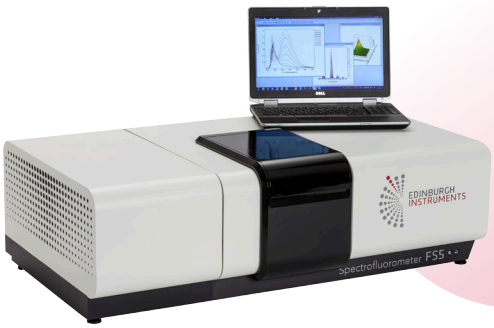
EDINBURGH INSTRUMENTS

INTRODUCTION

Water in aquatic environments may consist of a complex mixture of organic compounds. This involves a continuum of natural organic matter of variable size, particulate or colloidal nature[1,2]. The Natural Organic Matter (NOM) has been widely used to characterise water. Its measurement involves the Total



Organic Content (TOC), the sum of particulate and Dissolved Organic Carbon (DOC)[3,4], also known as humic substances or refractory organic substances.

Humic substances in aquatic systems originate from degradation of plant and animal tissue[5] with a precursor being lignin6 which fluoresces at 360 nm upon excitation between 240 nm and 320 nm[7]. Processes operative during the degradation are complex, with poly-condensation and formation of polyphenols being a possible candidate. The fluorescence can be related to substituted benzoic moieties with the start material being coniferyl alcohol, a basic unit of lignin[6]. Model compounds and component analysis also associated this fluorescence to coniferyl alcohol, stilbene and phenyl-coumarone structures[7–10]. On the other hand, protein fluorescence centres, especially observed in marine and pond water, are at the same wavelengths as those of tryptophan and tyrosine; although it is not known how these fluorescence centres relate to the structure of DOC[11,12]. Fluorescence centres ascribed to humic-like and fulvic-like material occur at higher emission wavelengths[3,13].

The complexity of the absorption and emission spectra makes it impossible to clearly assign individual peaks occurring from independent chromophores. Different techniques are used to characterise NOM[4]. A variety of analytical techniques such as fluorescence spectroscopy, Fourier Transform Infrared Spectroscopy, nuclear magnetic resonance, high pressure size exclusion chromatography, mass spectrometry have been widely employed[4], and even a combination of the techniques is used, especially when water components need to be quantified. In this application note, we present measurements of water obtained from river aquatic systems and show how fluorescence spectroscopy can easily provide initial results on the organic fingerprint of water.

METHODS AND MATERIALS

Excitation and emission maps (EEM) were measured using a standard configuration FS5 Spectrofluorometer equipped with a 150 W standard xenon lamp and a PMT detector (Hamamatsu, R928P). Higher diffraction orders were filtered by the integrated long wave-pass filters in the FS5. Excitation and emission bandwidth of 4 nm was used, while the integration time of 0.1 s and step of 2 nm enabled the acquisition of a complete EEM in 60 min.

Acquisition times as low as 15 min were also obtained for the same parameters and an integration time of 1 ms.

Water samples were acquired from two locations upstream and downstream of river Almond in Livingston, UK. A water sample from the tap was used as a reference. All three samples were filtered for particulates[14] in a syringe filter of 0.20 μm pore size (Sartorius, Minisart 17597) which resulted in OD=0.3 at 250 nm. The samples were measured in quartz cuvettes of 10 mm path-length in right angle geometry.

RESULTS - DISCUSSION

The EEM displayed in Figures 1, 2 and 3, correspond to a downstream, an upstream river sample and a water sample from the tap, respectively. The EEM have been scaled to the peak of visible DOC of the downstream river sample. All maps show the band of Raman scattering proportional to the excitation wavelength which can be further normalised[15] and corrected for inner-filter [16,17] to acquire pure DOC maps[6,17].

The assignment of EEM peaks is found in literature as the traditionally defined humic-like regions[4,11,19]. These are labelled as A with $\lambda_{exc}/\lambda_{em}$=260 nm/400–460 nm, and as C with $\lambda_{exc}/\lambda_{em}$=320–360 nm/420–460 nm. Soil fulvic acid (D and E) with $\lambda_{exc}/\lambda_{em}$=390 nm/509 nm and $\lambda_{exc}/\lambda_{em}$=455 nm/521 nm, phytoplankton (N) with $\lambda_{exc}/\lambda_{em}$=280 nm/370 nm and tryptophan/protein-like (T) with $\lambda_{exc}/\lambda_{em}$=275 nm/340 nm were not observed in these water samples.

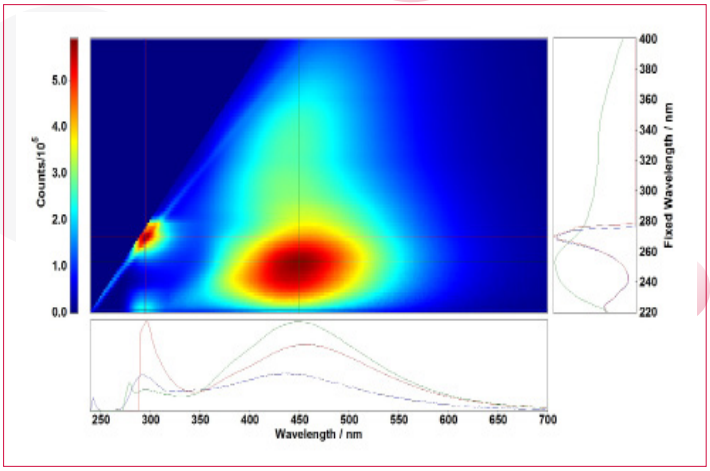


Figure 1: Exictation-map of water downstream of the river. The blue cross is at $\lambda_{exc}\lambda_{em}$=222 nm/292 nm, the red at $\lambda_{exc}\lambda_{em}$ =270 nm/296 nm and the green at $\lambda_{exc}\lambda_{em}$ =254 nm/450 nm

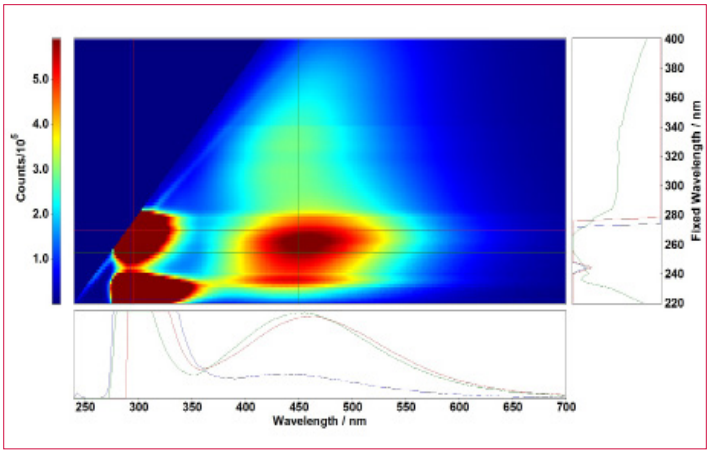


Figure 2: Excitation-emission map of water upstream of the river. Crossings are the same as shown in Figure 1.

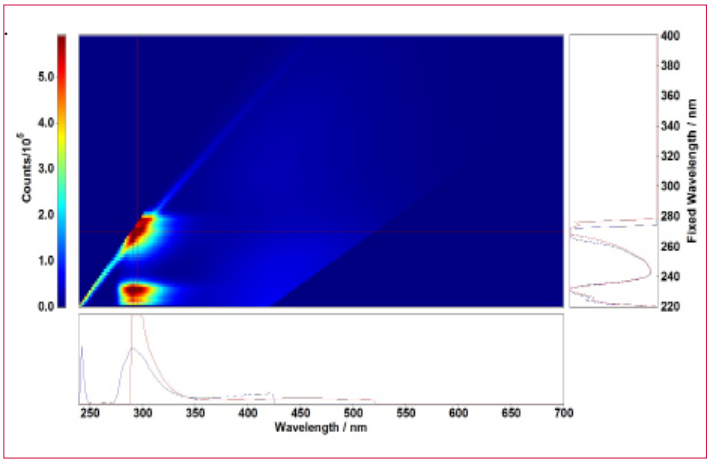


Figure 3: Excitation-emission map of tap water. The blue cross is at $\lambda_{exc}\lambda_{em}$= 230 nm/290 nm, while the red at $\lambda_{exc}\lambda_{em}$=270 nm/300 nm

It can be seen that the DOC of water is centred at $\lambda_{exc}/\lambda_{em}$=250 nm/450 nm, see green cross in Figures 1 and 2.

This is in agreement with running river waters[6] compared to the red-shifted EEM at $\lambda_{exc}/\lambda_{em}$=250 nm/470 nm from channels and wetlands.

In addition to the humic-like peak, two additional peaks are present in all samples at $\lambda_{exc}/\lambda_{em}$=230 nm/ 290 nm and $\lambda_{exc}/\lambda_{em}$=270 nm/300 nm, marked as blue and red in the Figures, respectively. The peak with $\lambda_{exc}/\lambda_{em}$=230 nm/290 nm is associated with the superposition of electron-transfer and benzenoid bands in NOM molecules[20].

The UV humic-like peak with $\lambda_{exc}/\lambda_{em}$=270 nm/300 nm agrees very well with lignin units. In fact, lignin model compounds based on styrene derivatives with excitation 31847-36496 cm-1 274-314 nm and emission 28818-34246±200 cm-1 292-347 nm[21] agree very well with the peaks in the presented maps.

The broad peak at $\lambda_{exc}/\lambda_{em}$=320 nm/440 nm can also be associated to lignin. This agrees with the results of Radotic et al. on dehydrogenative polymers in water as another lignin model compound[10], with excitation at 360 nm-465 nm and fluorescence at 360 nm-600 nm.

The water supplied to domestic or industrial premises follows several treatment processes to make it usable or potable13. Although the treatment process of the tap water is unknown to the authors, it can be seen that the humic-like peaks are absent in the EEM of tap water, indicating that certain DOM was removed. Similar fluorescence fingerprints have been reported for raw and treated water samples in reference[13].

CONCLUSION

It can be concluded from the presented excitation-emission maps that the content of aquatic systems is a complex mixture of degradation products of lignin containing aromatic, primarily benzene units. Moreover, it has been shown that the high sensitivity of an FS5 Spectrofluorometer enabled the resolution of both lignin, UV humic-like in addition to humic-like substances. The technique can also be used for rapid routine measurement of maps permitted by the high scanning speed of the instrument, as well as monitor the quality of water in treatment facilities.

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