

P334

Field Fluorometer for Simultaneous Detection of 3 Colourless Tracers

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SUMMARY

Field hydrogeologists employ groundwater tracer tests with artificial tracers to demonstrate the underground interconnection between sinkholes and springs. In surface waters however, and particularly near the injection site, the intense water coloration can arouse legitimate surprise or even fear among the population. There is an increasing demand for "blind" tracer tests. Since the recent offer of LEDs that can radiate UV light at shorter wavelengths (316 nm, and down to 240 nm), field fluorometers can be upgraded to detect a new range of colourless tracers. We describe the characteristics of a flow-through fluorometer equipped with three optical channels. This field instrument detects and measures the individual concentration of as many as three colourless tracers found in a cocktail at concentrations near 1 ppb.

Introduction

We have designed flow-through field fluorometers for simultaneous detection of two or three invisible, colourless tracers, because there is an increasing demand for “blind” tracer tests.

Although most dye tracers used in hydrogeology are harmless to the environment (Behrens et al. 2001, FOEN Report 2002) their visible and indiscreet impact on the population remains a source of annoyance for the field hydrogeologist.

The recent appearance of small, inexpensive LEDs radiating UV light made it possible the excitation of colourless tracers of the naphthalene family.

A few years ago, companies could not always afford multi-tracer tests because laboratory expenses increase with the number of tracers. Today, thanks to the field fluorometer, multi-tracing is the rule (Schnegg and Doerfliger 1997). However, a successful separation of tracers by the field fluorometer presupposes dissimilar spectral characteristics of each tracer (Schnegg 2003). Careful selection of the set of tracers remains mandatory.

In this work, we describe the choice of colourless tracers and their associated optical components, as well as the achievable detection limit of the upgraded field fluorometer.

The methodology

The field fluorometer conveniently replaces the water sampler. With this instrument there is no need for frequent sample collection and subsequent laboratory analysis of the samples. Very high time resolution is also of great interest. However, the separation of two or three different dye tracers cannot be performed at the resolution achievable in the laboratory with a spectro-fluorometer. The optics of the field fluorometer is characterized by pass-band filters. To separate 2 or 3 dyes in a multi-tracer test, the fluorometer requires as many light sources (usually LEDs) as tracers, and detectors. Each optical channel is equipped with adequate optical filters. The unknown concentrations of each tracer are obtained by resolving a system of 2 or 3 linear equations (Schnegg 2003).

For optimal tracer separation, the determinant of the system of equations must be as large as possible. Low values of the determinant indicate inadequate association of tracers of similar excitation/emission spectra. For example, there is no chance to separate a cocktail of rhodamine B, G or WT. Even the sophisticated laboratory instrument will have trouble performing the separation.



Figure 1 Visible impact of usual dye tracers (concentration: 1000 ppb). The impact is very high for uranine (green) and amidorhodamine G (red), but very weak for duasyne and nil for naphthionate and amino G acid.

Most frequently dye tracers used are: Uranine, eosine, naphthionate, sulforhodamine B, amidorhodamine G, rhodamine WT, duasyne, tinopal, amino G acid (Käss 1998). The problem with most of them is the visual impact in surface water or in drinking water, particularly near the point of injection (they disappear at concentrations below 10 µg/L) (Figure 1). Two of them, naphthionate and amino G acid are much more discreet in the environment. This is because their excitation band is located in the UV part of the spectrum, and their emission is close to the short wavelength limit of visible light.

Following details have been collected with a field fluorometer equipped with three LEDs illuminating in turn the water sample at 316, 365 and 425 nm. As can be seen in Figure 2, the 316 and 365 nm wavelengths are appropriate for excitation of naphthionate and amino G acid respectively. The longest one (425 nm) is suitable for excitation of duasyne (excitation/emission: 449/474 nm), a third, nearly colourless tracer that can be used jointly with the others.

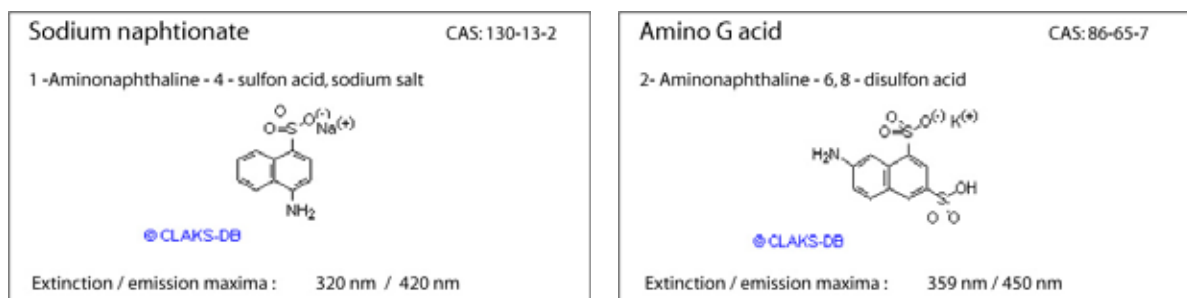


Figure 2 Formulas and spectral characteristics of two common colourless dye tracers.

The synchro-scans of Figure 3 show that the 365 nm LED will mostly excite amino G acid, whereas the 316 nm LED will excite both tracers equally. The large gap between the emission maxima (30 nm) allows separation of their fluorescence with colour filters such as Kodak Wratten Nr. 2A (naphthionate) and Nr. 44 (amino G acid).

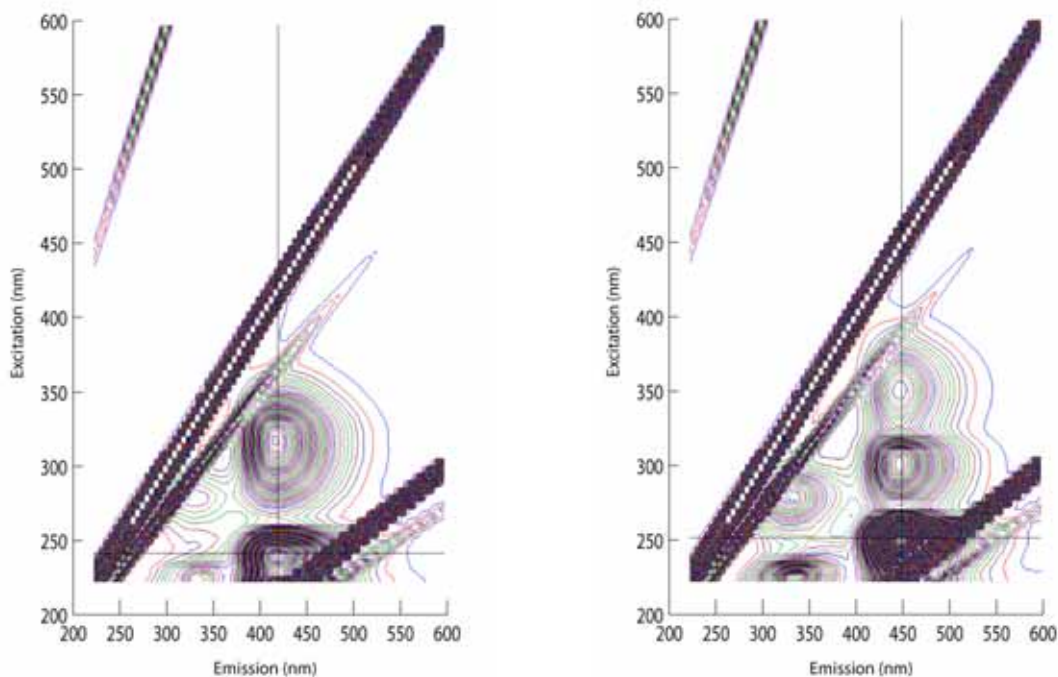


Figure 3 Synchro-scan spectra of naphthionate (left) and amino G acid (right) obtained with a laboratory spectro-fluorometer.

Figure 4 shows the fluorescence response to the excitation LEDs after removal of the zero signal of pure water. Since each tracer has its “favourite” LED (365 nm for amino G acid, and 316 nm for naphthionate) and detection system, the determinant in the separation equations is optimally high, and so is the separation power.

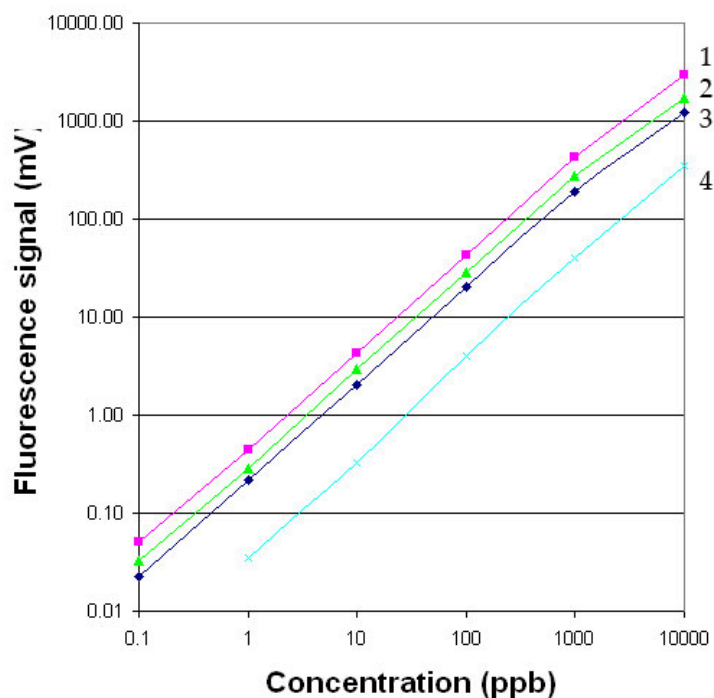


Figure 4 Fluorescence signal response of naphthionate (NAP) and amino G acid (AGA) to excitation by different LEDs: 1. AGA-365nm 2. AGA-316nm 3. NAP-316nm 4. NAP-365 nm. The offset signal of pure water (0.2 mV) has been subtracted. Note the slight saturation occurring above 1000 ppb.

Example

A field test was carried out in a surface stream (100 L/s) over a distance of 300 metres. Duasyne, a third tracer, was used jointly with the two other tracers. Quantities of 1 and 10 mg of each tracer were injected in turn at 2 minutes interval, so that the breakthrough curves would overlap, allowing thus for testing the separation method. Figure 5 shows the three breakthrough curves after mathematical separation. As expected, they display the same shape and height. Careful calibration of the fluorometer (Figure 4) is important for achieving perfect separation.

Conclusions

Ten years after the launch of bright blue or green LEDs, the electro-optical industry offers now UV-emitting LEDs that can be successfully employed in flow-through field fluorometers. This advent opens the way to inexpensive, invisible tracer tests that can use tracers with excellent sorption properties. No doubt that these UV LEDs will improve in brightness with time. In addition, a fluorometer equipped with a 280 nm LED can be used for detection of oil spill by measuring concentrations of polycyclic aromatic hydrocarbons (PAH) in real time. Detection limit of gasoil in water in the order of magnitude of ppb (expressed as C10-C40 integration of GC signal) is achievable.

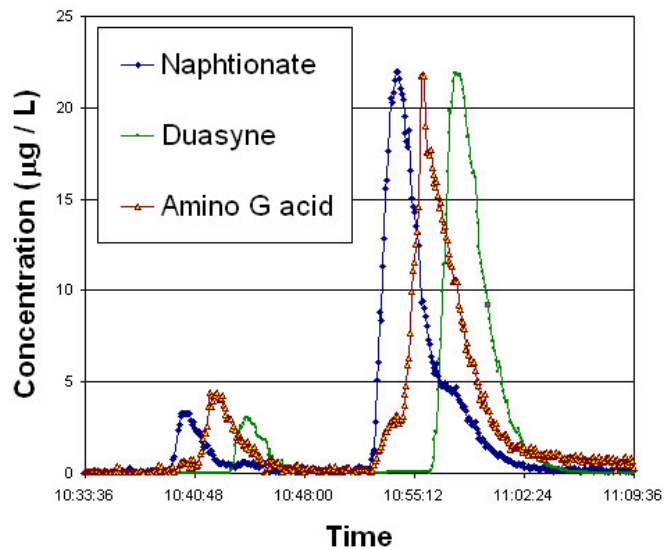


Figure 5 Breakthrough curves in a 100 L/s stream after mathematical separation of the three components. Tracers injected in 2 groups 300 m upstream at 2 minutes interval
 Injected mass of each tracer: First group: 1 mg Second group: 10 mg.

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