A new field fluorometer for multi-tracer tests and turbidity measurement applied to hydrogeological problems

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Abstract

We have improved our flow-through field fluorometer, allowing for tracer tests with simultaneous injection of 3 tracers and enhancement of turbidity determination. This instrument (Fig. 1) is designed for measuring the concentration of dye tracers contained in the water flowing through it. No pump is required. A ray of monochromatic light excites the fluorescence of the dye. A detector yields an electric voltage of amplitude proportional to the fluorescence and therefore, to the tracer concentration. Carefully chosen filters prevent excitation light from entering into the fluorescent light detector. This scheme (light source and detector) is replicated three times in the probe, at wavelengths of 370, 470 and 550 nm, covering all the range of visible spectrum.

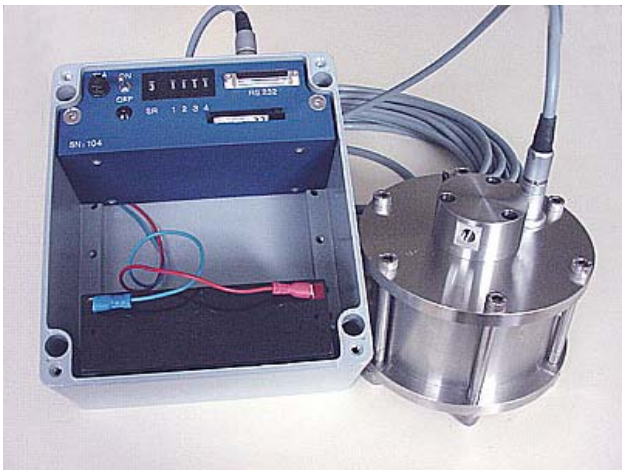

Figure 1 - Flow -through field fluorometer probe with datalogger. As many as four optics allow detection of any dye tracer with excitation band between 370 and 600 nm.

Introduction

The flow -through fluorometer has several advantages over the mechanical sampler: enhanced time resolution, reduced manpower requirements, no overhead costs (no subsequent lab analyses), immediate result availability, no contamination, no sample ageing and no sensitivity to frost.

Tracer separation

The separation of the three tracers is achieved by solving a set of 3 linear equations. Each equation gives the amount of fluorescence signal V_i on the photodetector P_i produced by each tracer under illumination by lamp L_i, *i=1,2,3*. For small tracer concentrations such as found in hydrogeological tests (< 1 PPM), tracer signals are additive. Suppose that the water contains 3 different tracers with concentrations α, β and γ. Previous calibration of the fluorometer yields the fixed coefficients C_j^i of 3 different sets *i* of lamps, filters and photodetectors for each tracer *j*. The set of equations

$$C_1^i\alpha + C_2^i\beta + C_3^i\gamma = V_i \quad , i=1,2,3$$

has following solution:

$$\alpha = \frac{\begin{vmatrix} V_1 & C_2^1 & C_3^1 \\ V_2 & C_2^2 & C_3^2 \\ V_3 & C_2^3 & C_3^3 \end{vmatrix}}{\begin{vmatrix} C_1^1 & C_2^1 & C_3^1 \\ C_1^2 & C_2^2 & C_3^2 \\ C_1^3 & C_2^3 & C_3^3 \end{vmatrix}}$$

$$\beta = \frac{\begin{vmatrix} C_1^1 & V_1 & C_3^1 \\ C_1^2 & V_2 & C_3^2 \\ C_1^3 & V_3 & C_3^3 \end{vmatrix}}{\begin{vmatrix} C_1^1 & C_2^1 & C_3^1 \\ C_1^2 & C_2^2 & C_3^2 \\ C_1^3 & C_2^3 & C_3^3 \end{vmatrix}} \qquad \gamma = \frac{\begin{vmatrix} C_1^1 & C_2^1 & V_1 \\ C_1^2 & C_2^2 & V_2 \\ C_1^3 & C_2^3 & V_3 \end{vmatrix}}{\begin{vmatrix} C_1^1 & C_2^1 & C_3^1 \\ C_1^2 & C_2^2 & C_3^2 \\ C_1^3 & C_2^3 & C_3^3 \end{vmatrix}} .$$

Stability of this solution largely depends on the choice of cut-off wavelengths for the various filters, on the central wavelength of the light sources and also, on the choice of tracers in the cocktail. Good tracer compatibility is achieved with dyes such as Tinopal (CBS-X, CBS-CL, ABP-Z, Uvitex), uranine and any variety of rhodamine. Cocktails of uranine and eosine (or pyranine) would not fulfil the compatibility conditions, because optical characteristics of these tracers are too similar to each other in terms of wavelengths. Same remark holds for cocktails with different rhodamines (amidorhodamine G, sulforhodamine B, rhodamine WT).

Handling the turbidity

Special care was taken to minimise turbidity-induced errors. Suspended particles scatter the excitation light in all directions. Stray light reaches the photodetectors and adds undesirable contribution to the signal, because excitation/detection filters partly overlap (a few o/oo of transmitted light). A dedicated optics measures the amount of light scattered at 90° from the excitation beam. With clean water, this signal is close to zero (only Raman scattering), but increases with the number of suspended particles. The wavelength involved in this measurement must be selected in the red part of the spectrum, so that the light cannot generate fluorescence if a tracer is present in the water. Standard suspensions of formazine at 1, 10 and 100 NTU (nephelometric units) are used for calibration. The contribution of turbidity to the V_i signals from the 3 light sources is also calibrated. Thus, knowing the value of the turbidity, we can remove its effects from the V_i signals before solving the equation set.

Performance

Compared to laboratory analyses, the fluorometer shows similar sensitivity to uranine (clean water limit: 0.02 μg/l). The detection limit for other substances (rhodamine, Tinopal) is about 10 times higher. Organic matter can be a serious limiting factor (suspended particles in the ground water) because of its intrinsic fluorescence. The fluorometer does not have the full spectral resolution capability of laboratory spectro-photometers. In counterpart, tracers that decay quickly under the action of bacteria cannot be transported to the laboratory. In situ analysis by the field fluorometer removes this inconvenience. A downhole version of the probe can be employed in 2" boreholes (Fig. 2).

Figure 2 – Downhole fluorometer probe (max. diameter: 48 mm). This probe is equipped with two optics, one of which can be selected for turbidity measurements. The probe conveniently detects dye tracers in 2" boreholes to depths of 100 m.

Conclusions

Although not designed to replace completely the classical method of sampler-lab analysis, the fluorometer simplifies the work: After immersion of the probe into the water, data acquisition is started. One or two weeks later, data can be downloaded to a notebook PC (Fig. 3). No further visit is required, as well as sample analyses in the lab. The result of the test is directly available in the field, with equivalent sensitivity. Moreover, the capability of detecting 3 tracers at a time allows for sophisticated injection-detection strategies.

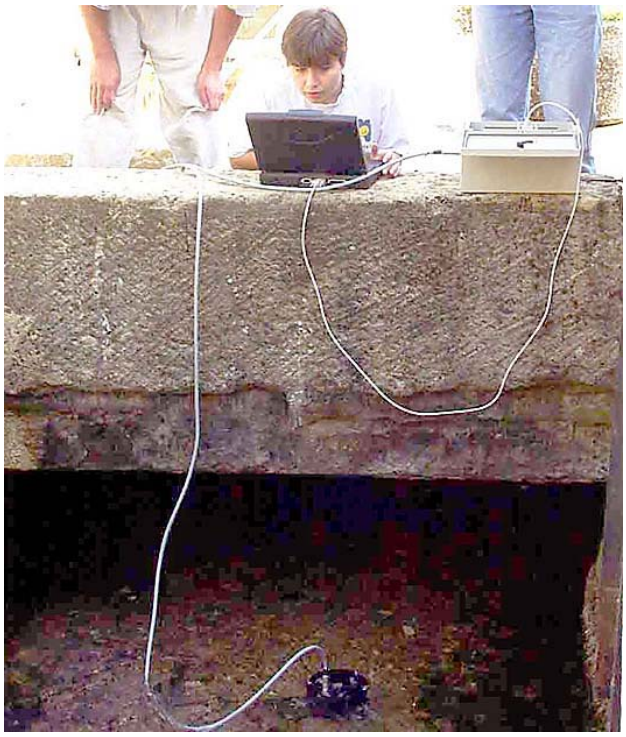

Figure 3 - Field fluorometer set-up in a stream

Fig. 4 shows the results of a simple tracer test in which three tracers were injected into a small stream with a lap-time of two minutes. The second injection used 9 times the mass of tracer of the first one. The method shows a good efficiency at separating the tracers in a real situation.

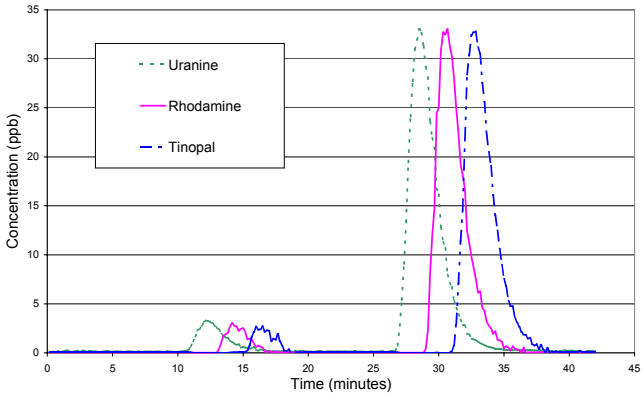

Figure 4: Tracer test made for testing the separation capability with three dye tracers.

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