AN INEXPENSIVE FIELD FLUOROMETER FOR HYDROGEOLOGICAL TRACER TESTS WITH THREE TRACERS AND TURBIDITY MEASUREMENT

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Abstract. The Geomagnetism Group of the University of Neuchâtel has recently designed a flow-through field fluorometer with added spectral capabilities for hydrological tracer tests. This instrument is equipped with four optical axes allowing water sample illumination with four independent light sources at different wavelengths covering the full spectrum from UV to red. As many as three conveniently selected (dye) tracers can be simultaneously measured and separated from a cocktail. Careful turbidity measurement allows for correction of the fluorescence signals.

Keywords: Fluorometer, tracer, hydrogeology, uranine, rhodamine, Tinopal

INTRODUCTION

Flow-through fluorometers can advantageously replace mechanical samplers in tracer tests that use dyes. If sample archiving for future detailed laboratory analyses is not required, field fluorometers are the solution of choice, since they can work unattended for days or even weeks. Because the tracer concentration is directly measured in a flow stream, there is no contamination or sample ageing. Moreover unlike mechanical samplers, flow-through cells are insensitive to frost. Furthermore, tracing data are immediately available during a test as well as at the end, thereby eliminating the cost of laboratory analyses.

The Geomagnetism Group of the University of Neuchâtel (GGUN) has been actively involved in the development of robust and inexpensive fluorometers suited for field work. It extended the optical capabilities of its recently developed instrument from 2 to 4 light sources. Simultaneously, it has improved the measurement of water turbidity and applied a corrective term to the signals from the dye fluorescence prior to mathematical separation of the concentrations. Earlier designs can be found in Schnegg and Doerfliger (1997), Schnegg and Kennedy (1998). Field work in porous media is reported by Kennedy et al. (2001a,b). Experiments using a downhole version of the fluorometer are described in Schnegg and Bossy (2001).

THE FLOW-THROUGH FIELD FLUOROMETER

An optical cell made of a simple glass tube placed along the geometrical axis of a metal cylindrical waterproof casing measures the tracer concentration in the water flowing through the flow cell. The optical components used for the measurement of dye concentration are installed along the orthogonal axes of two square crosses in two separate planes (Figure 1). The measurement system consists of

- an excitation section, comprising a quasi-monochromatic light source, a filter and a condenser lens, and
- a detection section, orientated 90° to the excitation beam, with a lens, a filter and a photo-detector.

The light sources and the filters are selected according to the absorption-emission spectra of the dyes. Such a geometry allows for installation of up to four measuring systems. One of the sets is dedicated to the measurement of the water turbidity while the three others are used to measure the dye concentrations. Light sources with spectral maxima at 370, 470 and 525 nm are ideally suited for excitation of dyes such as Tinopal CBS-X, uranine (Na-fluorescein) and any molecule in the rhodamine family (amidorhodamine G, sulforhodamine B, rhodamine WT).
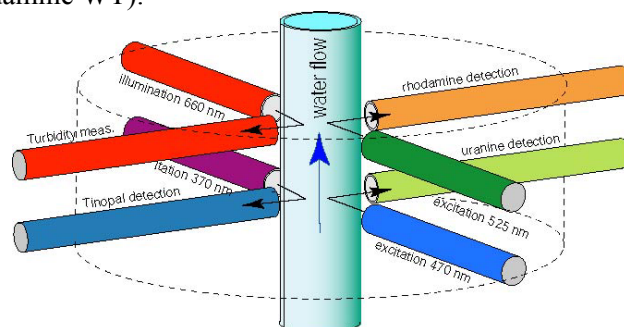

Figure 1: Optical cell (glass tube) and four sets of light sources and photo-detectors

Instrument sensitivity and linearity

The relative sensitivity to different dyes (smallest detectable concentration) is similar to that of laboratory spectrophotometers. Uranine is by far the most sensitive molecule (detected at concentrations approximately 8 times less than other dyes). The smallest detectable concentration variation (in clear water) is 0.02 ppb for uranine and 0.14 to 0.2 ppb for the other tracers.

Perfect linearity of the relationship between the concentration and the fluorescence signal cannot be achieved due to geometrical effects on the excitation light within the optical cell. This effect is wavelength-dependent. For the three available sources at 370, 470 and 525 nm we observed non-linearities of 8%, 3% and 11%. This is of concern when dye separation is performed, since the calculation assumes a set of three linear equations of the concentration. Small absolute discrepancies appear at the low-concentration end.

The measurement of single-tracer solutions can be carried out very accurately in a range of concentrations extending over 5 decades, from the detection limit to 1000 ppb (10^{-6} g/ml). Over this range, the calibration curve can be fitted with a 1st-degree polynomial in log-log space (Figure 2). Therefore, the fluorometer calibration requires only two solutions (usually 10 and 100 ppb). If higher concentrations are of interest, additional concentrations are used to fit higher-order polynomials.
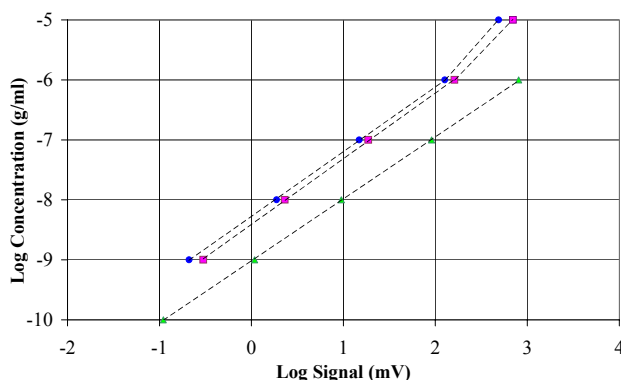
Figure 2: Calibration curves for uranine (Δ), sulforhodamine B (■) and Tinopal CBS-X (•)

Turbidity measurement and correction

Turbidity effects often occur in tracer tests. Suspended particles entering into the optical cell scatter the excitation light and produce a stray signal, simulating the presence of the tracer, since

excitation/detection filters partly overlap (a few $^0/_{00}$ of transmitted light). A dedicated optical system 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. To remove turbidity effects, the fluorometer must be calibrated with different turbid suspensions (we use typically 1, 10 and 100 NTU (nephelometric units, formazine standards). The measuring set (equipped with a red 660 nm light source) is calibrated (Figure 3) and the polynomial coefficients of the calibration curve obtained. Note that the relationship between the optical signal and the turbidity is linear in log-log space.
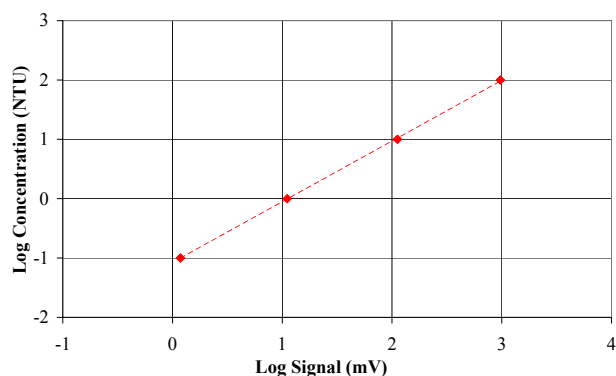
Figure 3: Calibration curves for turbidity

A second calibration is required to determine how much stray signal is produced by turbidity on each measuring set. Thus, a full measurement is done by collecting two signals, the tracer signal and the turbidity, measured both in mV. Inverting the latter yields the amount of stray signal that can then be removed from the tracer signal. Figure 4 shows the effect of a 40 NTU turbidity peak on a cocktail with constant (~ 8 ppb) concentration of uranine and sulforhodamine B.
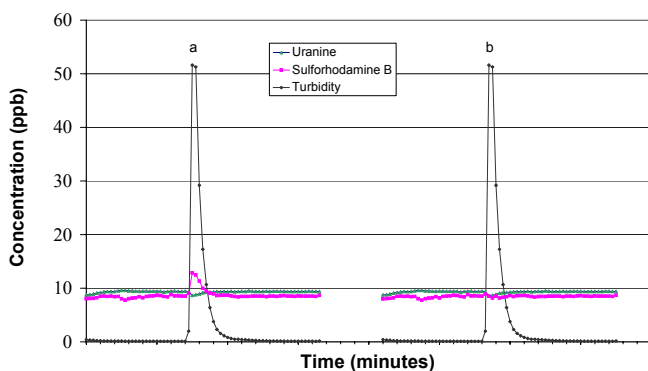
Figure 4: Influence of turbidity on tracer concentration measurement, without (a) and with (b) correction.

The same data set is shown on Figures 4a and 4b, but the turbidity correction has only been applied to Figure 4b. Obviously, the sulforhodamine measurement would be distorted at turbidity levels in excess of 20 NTU. The applied correction completely removes this distortion.

Separation of three tracers

There is a considerable interest in measuring tracer concentrations that were injected at different locations during a tracer test. The resulting tracer cocktail measurements can be separated to obtain the time curve for each tracer. This can be done with the GGUN fluorometer, provided the various tracers are properly selected, i.e. their excitation/emission spectra do not overlap excessively.

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 photodetector P_i produced by each tracer under excitation by lamp L_i with $i=1,2,3$. For small tracer concentrations such as found in many hydrogeological tests (< 1 ppm), tracer signals are additive. As an example we take the hypothetical case of a water containing three different tracers with concentrations α, β and γ. Previous calibration of the fluorometer yields the fixed coefficients C_j^i of three different sets i of lamps, filters and photodetectors for a fixed concentration (100 ppb) of each tracer j. The set of equations

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

yields following solution:

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

Stability of this solution 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, uranine and any type of rhodamine. Cocktails of uranine and eosine (or pyranine) do not fulfil the compatibility conditions, because optical characteristics of these tracers are too similar to each other in terms of wavelengths. The same remark holds for cocktails with different types of rhodamine (amidorhodamine G, sulforhodamine B, rhodamine WT).

To test the validity of the separation method, increasing quantities of tracer #1 solution (up to 107.5 ml @ 992 ppb) were added to a fixed volume (1 litre) of a solution containing tracer #2 and tracer #3 (100 ppb each), in which the sonde was immersed (Figure 5 a,b,c).
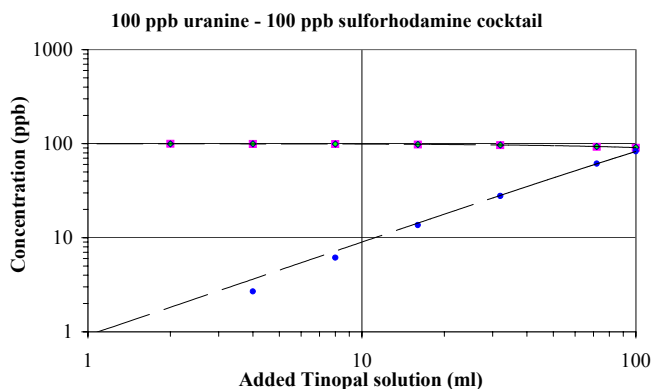

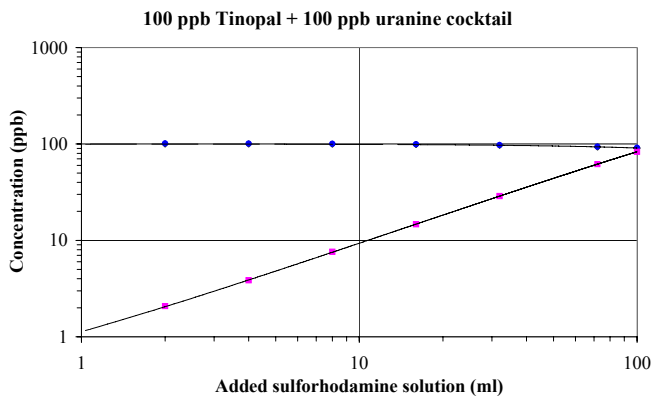**Figure 5a:** Tinopal CBS-X added to sulforhodamine B and uranine cocktail

100 ppb Tinopal + 100 ppb uranine cocktail

Figure 5b: Sulforhodamine B added to uranine and Tinopal CBS-X cocktail

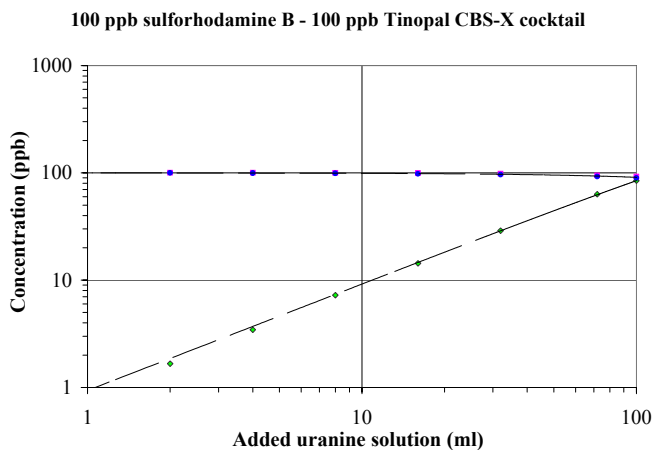**100 ppb sulforhodamine B - 100 ppb Tinopal CBS-X cocktail**

Figure 5c: Uranine added to sulforhodamine B and Tinopal CBS-X cocktail

Indices 1, 2 and 3 refer to cyclical permutations of uranine, sulforhodamine B and Tinopal CBS-X. Generally, good tracer separation is achieved within 1% accuracy. Tinopal has the smallest sensitivity and shows slight departure from the theoretical curves (full lines) at lowest values. Note that the bending of tracer #2 and #3 curves results from dilution with tracer #1 solution (1 to 10 volume ratio).

A second experiment tested the separation power for sudden concentration variations of tracer #1 in a cocktail of tracers #2 and #3 (Figure 6). No significant concentration variations are observed in the cocktail. Similarly, the turbidity measurement is not influenced by the steep variation of tracer #1.

When tracer #1 level is low and close to the instrumental noise, accurate separation cannot be obtained if concentrations of tracers #2 and #3 are more that 10 times larger.
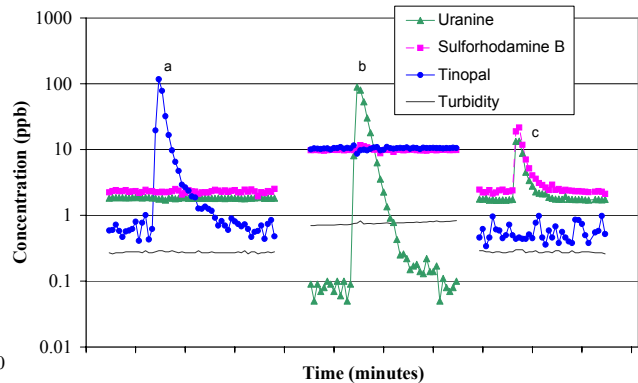

Figure 6: a,b: Dynamic behaviour of the separation scheme. c: Erroneous signal produced by uncalibrated tracer (eosine).

Careful calibration is mandatory for obtaining reliable tracer separation. Figure 6c shows what happens if an unexpected, uncalibrated molecule is detected (in this case, eosine). The equation set leads to a solution in terms of the tracers for which the instrument had been calibrated.

CONCLUSION

The GGUN field fluorometer equipped with three optical sets and an additional channel for turbidity can be successfully used for real-time separation of a cocktail of up to three tracers. After reduction of turbidity effects on each signal, the resolution of a set of linear equations leads to individual tracer concentrations. The success of the operation relies on accurate calibration of the instrument with the same chemicals as used during the tracer test. Finally, it is important to note that the concentration ratio should not exceed a factor of 10 for concentrations close to the detection limit.

References

Kennedy K, Müller I, Schnegg PA., Rossi P, Kozel R. 2001. Characterization of the Kappelen Groundwater Research Site (BE), Switzerland, and Preliminary Bacteriophage and Solute Tracer Component Responses. *Beiträge zur Hydrogeologie, 52,* 158-180.

Kennedy K, Niehren S, Rossi P, Schnegg PA, Müller I, Kinzelbach W. 2001. Results of Bacteriophage, Microsphere and Solute Tracer Migration. Comparison at Wilerwald Test Field, Switzerland. *Beiträge zur Hydrogeologie, 52,* 180-210.

Schnegg PA., and Doerfliger N. 1997. An inexpensive flow-through field fluorometer. **In:** Proc. 6th Conference on Limestone Hydrology and Fissured Media, la Chaux-de-Fonds, 10-17 August 1997, Vol. 2, 47-50.

Schnegg PA., and Kennedy K. 1998. A new borehole fluorometer for double tracer tests. **In:** Mass Transports in Fractured Aquifers and Aquitards, Geoscience Center, Copenhagen, 14-16 May 1998, 60-63.

Schnegg PA., and Bossy F. 2001. Sonde for downhole measurement of water turbidity and dye tracer concentration. **In:** New Approaches Characterizing Groundwater Flow, Munich 10-14 September 2001, 795-799.

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Test in a karst spring at St Blaise (NE) 5.04.2002

Demonstration of three dye tracer separation. Three cocktail solutions of 0.1 litre, then 1 litre @ 10,000 ppb have been injected 300 m upstream every two minutes. Stream flowrate: ~100 litre s^{-1}