Online Field Fluorometers for Hydrogeological Tracer Tests

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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. The fluorometer has been successfully applied to monitor for multiple tracers in both fissured and unconsolidated environments.

Introduction

Tracer testing is an important and sometimes essential means of quantifying hydrological and hydrogeological parameters. Nonetheless, as an activity, this method is often expensive and time-consuming. The availability of inexpensive, yet reliable, means of automatic data collection provides a way to reducing necessary manpower and overheads. Many on-line methods meet these requirements and often provide data that is as good as, if not better, than those collected manually. Moreover immediate data availability permits sampling strategies for other tracers which may require laboratory analysis to be modified thus optimising analytical resources.

With the above issues in mind, the Geomagnetism Group of the University of Neuchatel (GGUN) recently developed a field flow-through fluorometer. Application of this instrument by collaborators at the Hydrogeology Centre of the University of Neuchatel (CHYN) has allowed the approach to tracer testing to be modified to optimise tracer test sampling strategies and methodology. This paper outlines the functioning of the GGUN field flow-through fluorometer and provides some case studies of its application under a variety of circumstances.

The flow-through fluorometer can advantageously replace mechanical samplers in tracer tests that use dyes. If sample archiving for future detailed laboratory analyses is not required, this instrument is the solution of choice, since it can work unattended for days or even weeks. Since the tracer concentration is directly measured in a flow stream, the fluorometer eliminates the risk of contamination or sample ageing. Furthermore, flow-through cells are insensitive to frost, unlike mechanical samplers

The Geomagnetism Group of the University of Neuchâtel (GGUN) has been actively involved in the development of robust and inexpensive fluorometers suited for fieldwork. It extended the optical capabilities of its recently developed instrument from two to four 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.

The flow-through fluorometer is watertight, lightweight (3.6 kg) and compact. A 12 V battery acts as the instruments power source, thus making it well suited to field activities where more bulky dedicated instrumentation is impractical.

The fluorometer is available as either a surface mounted (tambourine) form or as a cylindrical downhole form that may be used in wells as small as 55 mm in diameter. Despite differences in design the overall operation of both models is identical.

Operation of 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 (Fig.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).
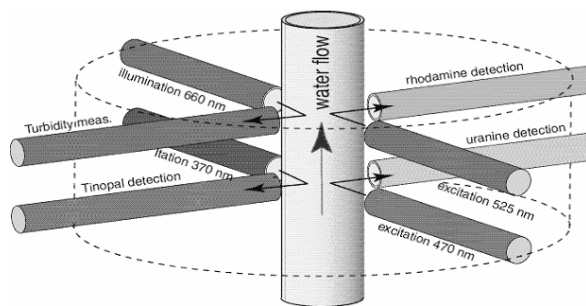

Fig. a: Optical cell (glass tube) and four sets of light sources and photo-detectors

Instrument sensitivity and linearity

The relative sensitivity of 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 linear equations of the concentration. Small absolute discrepancies appear at 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 (Fig. 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.
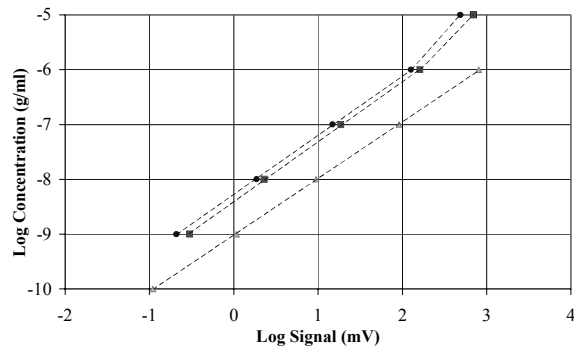

Fig. b: Calibration curves for uranine ($\triangle$), sulforhodamine B ($\boxtimes$) and Tinopal CBS-X ($\bullet$)

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 (Fig. 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.

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.
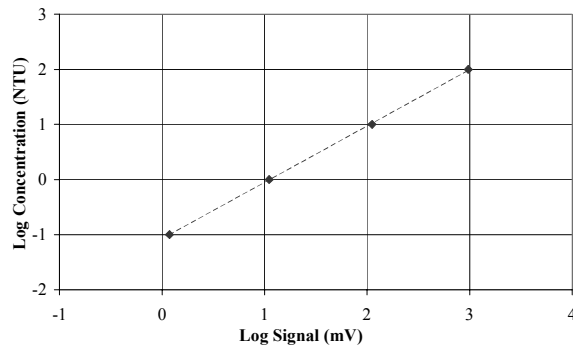
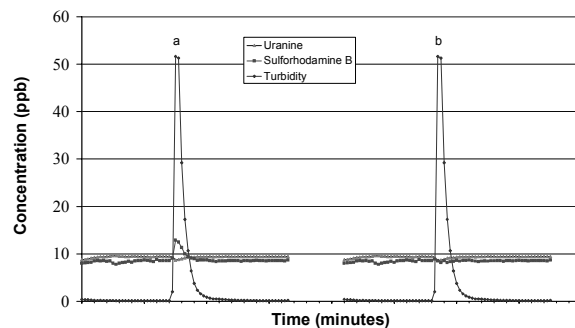

Fig. c: Calibration curves for turbidity

Fig. d: Influence of turbidity on tracer concentration measurement, without (a) and with (b) correction.

The same data set is shown on Figs. 4a and 4b, but the turbidity correction has only been applied only 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.

Similarly, data collected by the fluorometer may be treated and the relative contributions of up to three different tracers to the fluorometer signal can be ascertained. Details of this separation process are provided in the Appendix at the end of this article.

Case Studies

The following examples serve to illustrate a variety of applications in which both models of the GGUN fluorometer have assisted in tracer test data acquisition and analysis. All hydrogeological data are derived from tests in porous media. Nonetheless, many of these applications have been shown to be equally valid in karstified/fissured media.

River Water/Groundwater Interactions:

A multiple tracer test competed in the Aare River in January 2002 aimed to assess the vulnerability of water supply wells situated close to the Aare River to a contamination event emanating from the river. A contamination event was simulated by injecting a tracer cocktail consisting of 160 litres of 10 (w/v) uranine and $6 \cdot 10^{15}$ pfu of the H40/1 bacteriophage into the river and monitoring for the tracer concentrations further downstream in the river and in adjacent wells.

A tambourine-model GGUN fluorometer, set on the bed of the river in the vicinity of the supply wells approximately five km downstream of the injection point, monitored uranine concentrations for two hours prior to injection and for 8 hours thereafter at 4-minute intervals. The resulting data could be obtained on-site and thus allow an optimal sampling program for the particulate tracer to be modified. Figure 5 presents the resulting breakthrough curve for both the bacteriophage and solute in the Aare River.
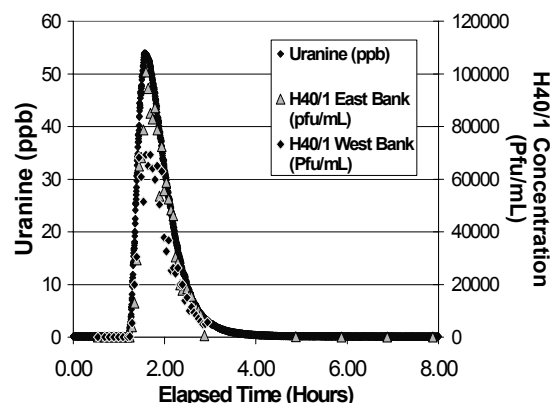

Fig. e: Uranine and bacteriophage breakthrough curves, Aare River at Muri, 24 –25 January 2002.

Additional on-line fluorometers were installed in the two water-supply wells exploiting the associated alluvial gravels 50 metres from the eastern bank of the river. A tambourine model monitored uranine concentrations at 4-minute intervals in the discharge water pumped from one well. A stainless steel downhole fluorometer monitored tracer concentrations in the second well. Measurements from these instruments allowed high-resolution breakthrough curves to be reliably and inexpensively generated despite the low concentrations observed. Figure 6 presents the curve for one of these wells.

Based on the measurements made in the Aare and in the wells, the capacity of the river / aquifer to attenuate solute and particulate contaminants emanating from further upstream can be assessed. In this case the uranine dilution factor observed between the river and the wells is approximately 0.001. In contrast the trace concentrations of the H40/1 bacteriophage observed in the same well reflect the strong microbial attenuation capacity of the aquifer. Such data can form an important basis for verifying riparian groundwater protection strategies.
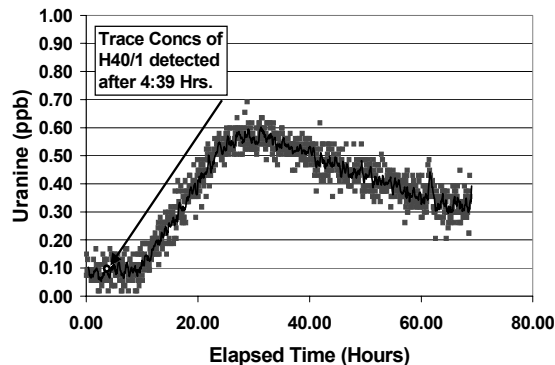

Fig. f: Uranine /H40/1 Breakthrough Curve for Well W2, Muri, Berne.

Continuous Circulation Testing

Continuous circulation tests involve pumping of groundwater from one end of a well screen through a flow cell to monitor tracer concentrations in groundwater before re-injecting the tracer at the other end of the well screen. The method has the advantage of allowing regular tracer measurements to be made while not altering the static water level in the well. The technique may be used to monitor for tracer concentrations in both injection wells and observation wells. Collaborators at the CHYN selected the GGUN fluorometer for these measurements due to its sensitivity and its ability to detect fluorescent tracers over a wide range of concentrations. Moreover its ability to detect different tracers simultaneously provided an opportunity to detect multiple tracers from different injection points in a single observation well. Figure 7 schematically illustrates this approach.

Measurements made in an injection well using this technique provides an indication of the rate of tracer disappearance from a well and consequently rates of groundwater flow. These data can be of importance when considering the input signals necessary to determine the transfer function relating between an injection well and monitoring point. An example of such a decline is provided in Figure 8.
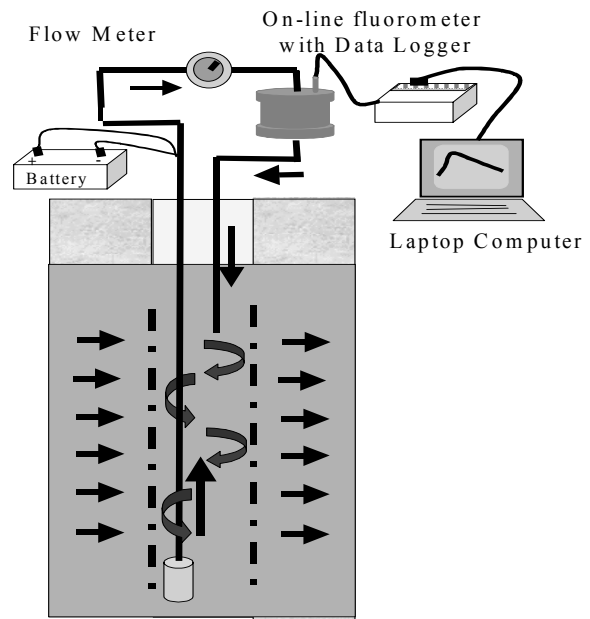

Fig. g: Schematic illustration of continuous circulation technique. Water is pumped from the base of the well across the flow-through fluorometer cell before being re-injected. Consequently no net drawdown results.

KENNEDY et al (2001) used the continuous circulation technique in observation wells to obtain detailed breakthrough curves at the Wilerwald Test Site in Canton Berne, Switzerland. The technique employed the tambourine model flow through fluorometer as illustrated in Figure 7, connected in series with an on-line flow cytometer. The approach allowed for simultaneous on-line measurements measure of uranine and fluorescent microsphere concentrations in three different observation wells at between 14 m and 64m from the injection well.

Downhole Methods

The use of the downhole fluorometer has already been mentioned in the section pertaining to river water / groundwater interactions, where a downhole meter was used to measure uranine concentrations at a fixed depth in a water supply well. The method can be particularly useful for monitoring at conditions at a particular depth over a prolonged period of time. This may be appropriate for tracer monitoring at a recognised zone of preferential groundwater flow.

Conversely the downhole fluorometer may also be used to detect zones of preferential flow in a well. The approach may prove particularly pertinent when considering in wells with long screened intervals that are set against units of
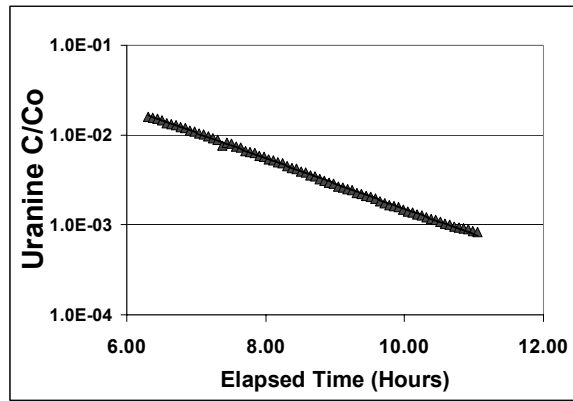
Fig. h: Plot of Relative Uranine Concentration with Time for K1-1 Injection Well, Kappelen Test Site. July 2001. Sampling Frequency: Every 4 minutes.

variable hydraulic conductivity. Under these circumstances single well methods provide bulked hydraulic parameters and mask much of the heterogeneity in groundwater flow velocity in a well. A method developed by CHYN and GGUN attempts to overcome this problem by moving a downhole fluorometer against the screened interval of a well and measuring the change of tracer concentration with time in a well. This technique thus allows zones of preferential flow and mass transport to be identified. GGUN researchers have developed a programmable automated pulley system to facilitate this activity that allows the measurement depth range and measurement frequency to be predefined prior to a test. In-hole fluorometer measurements are relayed to a data logger at the surface and sample signal and the time of the reading recorded on a laptop computer. This technique may be applied to both injection wells and observation wells.

The injection well approach involves injecting a fluorescent tracer across the screened interval of the well. The fluorometer is subsequently lowered into the well using the automated pulley system. Given the known starting concentration Co, the decline in concentration in the well is attributed to groundwater flow. This may be related to groundwater velocity by the following expression:

$$Velocity = \frac{\pi r_o}{2\Delta t} \ln\left(\frac{C}{C_o}\right)$$

where r_o is the well radius
    Δt is the elapsed time since injection
    (C/Co) is the relative concentration.

Consequently, the resulting data allow approximate groundwater velocities in the well to be calculated and zones of preferential groundwater

flow to be identified. The approach is similar to the salt injection resistivity method used in geophysical logging (CHAPELLIER 1987) but does not have the problem of accounting for background concentrations. Moreover, the fluorometer is capable of detecting tracer at much lower concentrations than normal salt methods. It is however restricted to measuring the flow regime in the borehole. Figure 9 provides an example of the application of the method to a well with a three metre long screened interval at the Kappelen Test Site, Canton Berne Switzerland. The results show a clear difference in the flow velocity in the topmost metre of well screen compared to that of the lower two metres.
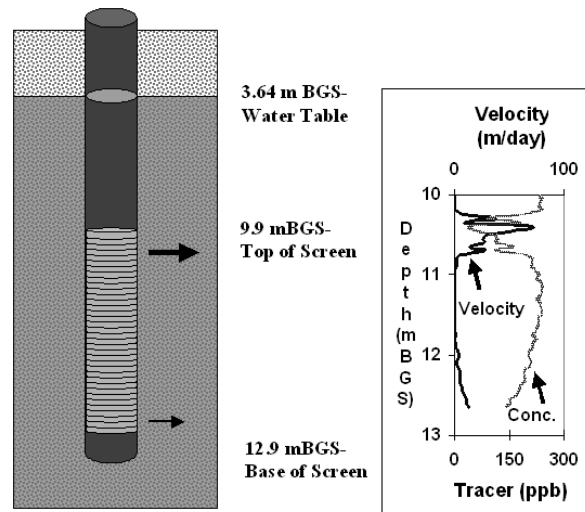

Fig. i: Example of identification of zones of preferential groundwater flow using a downhole fluorometer.

In a similar manner, the downhole fluorometer may also be used in mobile mode to detect zones of preferential connection between an injection well(s) and an observation well. This approach involves injecting tracer into one or more wells and observing tracer concentrations in an observation well down gradient by moving the fluorometer between predefined upper and lower depth limits at regular intervals.

Tests using wells set in the Munich Gravel Plain Fluvioglacial Aquifer at the Dornach Test Site, Dornach, Bavaria demonstrated the applicability of the method. Uranine concentrations in an observation well 10 metres down-gradient of an injection well monitored for the tracer at approximately 15-minute intervals. Figure 10 presents the concentration profile in the well at the time when maximum concentrations were observed. The results clearly illustrate that zones of preferential tracer hydraulic connection exist between the injection well and the observation

well. The use of such methods has provided a new means of investigating the hydraulic behaviour of aquifers, and particularly those deposits that show large-scale variations in hydraulic properties over short distances.
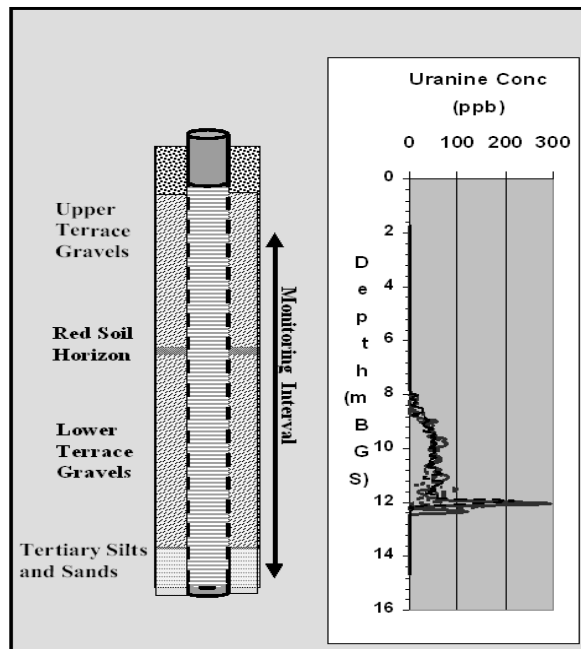

Fig. j: Maximum Tracer Concentrations observed in Well B8, Dornach Using a Mobile Downhole Fluorometer.

Conclusion

The GGUN field fluorometer offers an accurate, inexpensive and non-destructive means of automatically monitoring for up to three different tracers while also removing the effects of turbidity. The apparatus has been shown to be well suited to field situations in which installation of permanent monitoring devices is either impractical or infeasible. The case studies cited above demonstrate its versatility and its potential for hydrogeological investigations under a wide range of circumstances.

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Appendix:

Separation Method for 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 need 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 that contains three different tracers with concentrations α, β and

γ. Previous calibration of the fluorometer yielded 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.
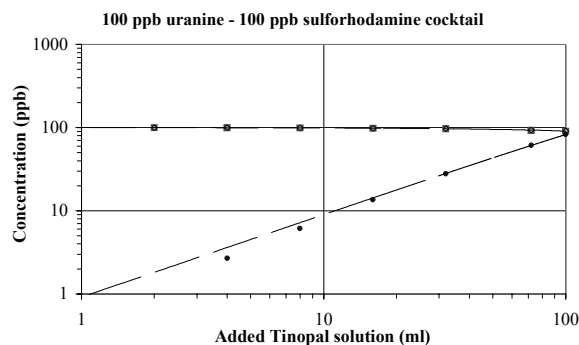

Fig. a: Tinopal CBS-X added to sulforhodamine B and uranine cocktail
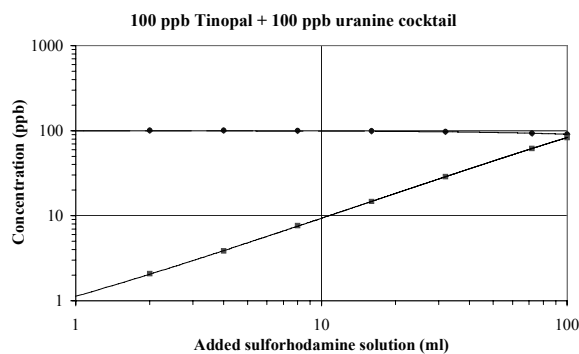

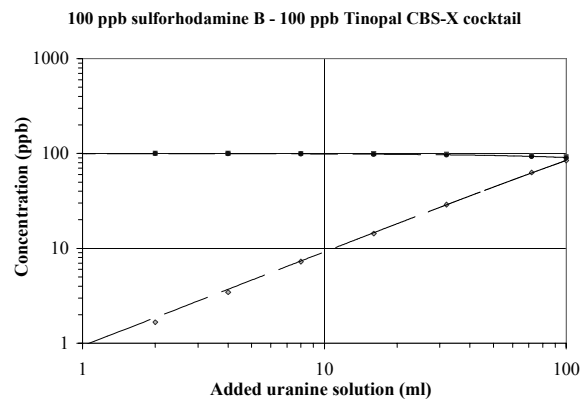Fig. b: Sulforhodamine B added to uranine and Tinopal CBS-X cocktail

Fig. c: Uranine added to sulforhodamine B and Tinopal CBS-X cocktail
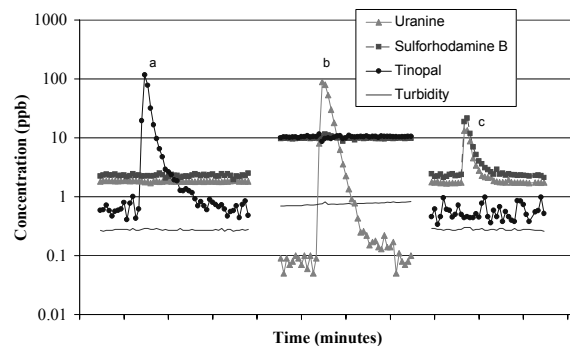

Fig. d: a,b: Dynamic behaviour of the separation scheme. c: Erroneous signal produced by uncalibrated tracer (eosine).

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 (Fig. a,b,c).

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 which has the smallest sensitivity 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 separating power for sudden concentration variations of tracer #1 in a cocktail of tracers #2 and #3 (Fig. d). No significant concentration variations are observed on 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 greater.