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## **Fluorescent Nanobeads: a First Step Toward Intelligent Water Tracers**

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### **Abstract**

Reservoir monitoring is an essential tool to optimize oil production. Among other techniques, water tracers are very useful to understand flow patterns between wells (i) during regular waterflood operations, (ii) for EOR pilot or (iii) field development. This paper focuses on the elaboration of a new family of tracers based on fluorescent silica colloids for in situ real-time optical detection. Indeed, these architectures of nanometric size (nanoparticle diameter controllable between 30–100 nm) permit (i) the encapsulation of fluorescent dyes (the intrinsic signal of tracers) and (ii) a tailored interface with the environment (by specific surface functionalization). Dyes, such as organic molecules and/or rare-earth complexes could be quantified by conventional fluorescence apparatus. The smart incorporation of specific fluorophores of different nature within nanobeads allows multi-coding signal of tracers and therefore the possibility to supervise the properties of reservoir. We demonstrate that silica nanobeads could act as sensitive probes of physicochemical conditions of reservoir (volume, pH, temperature, oil ratio, salt content...), because of (i) their specific fluorescence coding, (ii) the long-term colloidal stability in seawater conditions, and (ii) the adaptable real-time monitoring detection setup. Actually, by the procedure described in this work, we are able to produce theoretically dozens of fluorescence tagging combinations based nanoparticles with suitable surface properties. The possible future utilization of fluorescent nanobeads as traces in well exploitation is also demonstrated by core-flood experiments.

### **Introduction**

Beyond the limits of conventional techniques for oil reservoir diagnosis, silica nanoscale tracers appear as new powerful tools for detection. During the past years, the volume and the flow distribution within the reservoir were estimated by conventional methods (volumetric, materials balance and production performance) but with limited results. These are due to (i) the complexity of reservoir and (ii) its modelisation (too many approximations). The reservoir is intrinsically complex as a result of all natural mechanisms at play during its formation at geological times. The modelisation of volumes of fluids to be produced requires a lot of information (such as the shape, size, thickness, porosity, relative saturations of oil, gas and water and even the historical production, reservoir pressures, etc...). For these reasons, nanotracers could overcome the limits of conventional methods of reservoir characterization hence ensuring the reliability of oil estimation by providing useful information gathered directly into the reservoir. Currently, (i) chemical (isotopic or ionic composition footprints) or (ii) radioactive tagging of the injected water is a direct method for reservoir characterisation. For example, InterWell Tracer Tests (IWTT) have been routinely used in the petroleum industry, showing cheering perspectives. (Du and Guan 2005). Briefly, this technique allows gathering informations on well-to-well connections and subsurface flow paths. Assessing oil saturation can be done using Partitioning Interwell Tracer Test (PITT) the information of reservoir fluids saturation is elaborated by the analysis of two families of aqueous tracers: (i) passive tracers (which travel at the same velocity as the injected water) and (ii) partitioning tracers (which are partially soluble in oil). Combined with passive tracers, partitioning tracers permit to evaluate the remaining oil saturation in the contacted zone (Tang 1991, Tang, 1992, Tang 1995, Wood 1990, Deeds 2000, Dwarakanath 1999, Jin 1995, Jin 1997, Mariner 1999). The use of reacting partitioning tracer is also illustrated in Single Well Tracer Test (SWTT, Deans 1971, Deans 1980). However, the advantages for a wide application of these tracers in oil exploitation are limited by some requirements. At present, each family of tracers (chemical or radioactive) possesses advantages and shows limitations: e.g. restricting regulation on radioactive tracer can make them difficult to implement on field in some areas. Chemical tracers such as fluorobenzoic acids (FBAs) have been routinely used for field tracer campaigns because of their low quantification limit but (i) they require fine analyses which cannot be performed on-line or in standard labs and (ii) their limited number

precludes repeated tracer campaigns over time or when produced water reinjection occurs. Needless to say that the global market opts for tracers that are sustainable for the environment, silica based nanoprobe constitute a preferable example of tracers compared to radioactive elements.

In this perspective, nanotechnologies have been increasingly used in tracing applications, and fluorescent silica nanoparticles seem to be a powerful tool for detection, monitoring and quantification of physicochemical properties in complex systems (Perriat 2005). Nowadays silica nanoparticles continue to revolutionize the diagnostic context because of (i) the intrinsic size (- nano concept) and (ii) the unique optical features (- smart concept). In this scenario, we underline the advantages of this technology for IWTT and we optimize the ideal architecture of nanotracer. We describe the design and characterization of fluorescent silica nano-objects, focusing on (i) the choice of fluorescent dyes and (ii) the assessment of their propagation in the porous media.

By experimental results we demonstrated that the unique association in fluorescent silica nanobeads combines the transport behavior in porous media with the specific fluorescence properties of dyes to open new *smart tracing* possibilities.

## Silica nanobeads preparation and optical characterization

### *The position of silica nanotracer in the nanotechnology framework*

A growing numbers of academics and oil companies get involved in nanotechnologies (Pourafshary 2009). Nanoparticles are developed for various applications in reservoir engineering and EOR fields: foam stabilization (Zhang 2011), fluid interface imaging (Prodanovic 2010), and oil/water emulsions stabilization (Zhang 2010). We positioned our scope of research in nanotechnologies on the development of fluorescent silica based nanotracer that minimize the interaction with the porous media (toward the ideal tracer) (Caldelas 2011, Agenet 2011). As depicted in Figure 1, the architecture of nanotracer is constituted by a gold core (5 nm) coated by polysiloxane matrix (30–100 nm), which contains fluorophores. Entrapped dyes will be chosen between organic molecules (Fluorescein, Rhodamine, Cyanine) and rare-earth ( $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Gd}^{3+}$ ) complexes (DOTA: 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid, DTPA: diethylenetriaminepentaacetic acid, TTHA: triethylenetetraminehexaacetic acid). The combination of dyes (number and nature) in each nanoparticle will be the coding character of tracer (-*smart* concept). The surface of beads is stabilized by specific silane molecules such as gluconamide – or PEG polyethylene glycol – types that provides the transport properties in porous media (-*nano* concept).

### *Synthesis of nanobeads*

Silica nanoparticles are prepared in a microemulsion system (Martini 2009, Martini 2010, Figure 2). We observed that the microemulsion method opens new ways for the hybrid structure synthesis since it permits the easier control of particle growth from the seed to the final architecture. Indeed, each nanoparticle of colloid grows within a micellar compartment and coalescence between beads is forbidden. Microemulsion is a thermodynamically stable dispersion of oil and water stabilized by a surfactant and a co-surfactant. In particular, we will use a reverse microemulsion where spherical water droplets are dispersed in a continuous medium of oil (W/O water-in-oil microemulsion). Currently, for tracer synthesis we will choose a quaternary W/O microemulsion, constituted by the mixture of Triton X-100 (surfactant), *n*-hexanol (co-surfactant) and cyclohexane (oil), following by addition of aqueous solution. The proportion of the water amount in microemulsion, usually expressed in term of water to surfactant ratio *R*, controls (i) the dynamics of W/O microemulsion droplets, (ii) the number of seeds and (iii) the final size of particles. By such description, it is clear that we will control the morphology and functionality of particles by (i) the water to surfactant ratio *R* and (ii) the sequence of addition of reactants. In the aforesaid microemulsion system, we will form firstly the metallic core by the direct reduction of Au salt in the presence of a specific ligand (MES: sodium 2-mercaptoethanesulfonate) by  $\text{NaBH}_4$ . The synthesis continues by successive additions of silane precursors that contain the specific dyes. The addition of TEOS (tetraethoxysilane) and APTES (3-aminopropyl)triethoxysilane precursors will be followed by ammonia, and hydrolysis and condensation process will start. In this mixture of polysiloxane precursors, the fluorescent dyes are covalently bound to the APTES form. The sol-gel reaction continues at the room temperature for 24 hours. The core-shell architecture of tracers would be modified as needed by the sequence of addition of reactants, their amount and their nature. Entrapped dyes will be chosen between organic molecules and rare-earth complexes according to the application. Reaction will end with the addition of specific surface functionalization to ensure the colloidal stability, constituted of silane mixture precursors such as gluconamide – or PEG polyethylene glycol – types. The microemulsion will be broken by the addition of an excess of alcoholic solution (ethanol/isopropanol) and/or water, followed by the purification steps.

### *Physical characterization*

Before coreflood tests, colloids are characterized in order to collect information about (i) the morphology (size, polydispersity, stability) and (ii) the functionality (optical properties). (i) TEM (JEOL 2010F) and ESEM (FEI XL 30) apparatus for structural and morphological information (Figure 3); (ii) Dynamic Light Scattering (Zetasizer NanoS) for the hydrodynamic size (Figure 4), Z-potential, stability; (iii) UV-Vis Spectrometer (Varian Cary 50) for the dye – plasmon quantification; steady-state fluorescence spectrometer (Hitachi F-2500) and time-resolved fluorescence portable spectrometer (Axint) for quantum yield analysis; Inductively Coupled Plasma-Optical emission spectrometer (ICP-ES Varian 720-ES) for silica and gold quantification.

### Fluorescence characterization

Microemulsion system permits to encapsulate fluorophores of different nature within nanobeads, controlling their concentration and position. Dyes are chosen among organic species and organometallic complexes such as rare-earth complexes. We oriented the work on two main directions: (i) the reduction of signal over noise ratio and (ii) the codification of optical signal for intelligent tracers. To reduce the signal over noise ratio inorganic rare-earth complexes are preferably chosen for encapsulation, because of their longer fluorescence lifetime (typically in the microseconds range) compared to the nanoseconds range due to organic compounds. In this case, the “phosphorescence” behavior of rare-earth allows the detection via time-resolved fluorescence spectroscopy. The time-resolved fluorimetric detection has been widely used in the bioanalysis (Gudgin Dickson 1995). Figure 5 illustrates the measurement principle: the sample is illuminated by a fixed wavelength during a short period (light pulse). A delay time after pulse is set before the collection of the fluorescence signals (gate time). This remarkable feature helps to suppress the background fluorescence of organic residues contained in crude oil and therefore decreasing the quantification limit of tracer (towards ppt level). Oil contaminants fluorescence signals are preponderant in the short period and their signal decays quickly. On the contrary, rare-earth complexes display a longer lifetime signal and they could be detected in the gate time window. In figure 6 is reported the emission spectrum of a colloidal solution of nanoparticles containing Terbium complexes and fluorescein molecules dispersed (concentration of 200 ppm) in synthetic seawater containing 5% crude oil. In the case of standard fluorescence measurements (absence of delay time), the fluorescence coming from the crude oil compounds completely masks the signal from the rare-earth complex or the organic dye; whereas in time-resolved mode (delay 0.1 ms), the classic emission spectrum of Terbium is shown. By this fluorescence technique, we are able to detect Europium-DOTA complexes with concentrations as low as 50 ppt (figure 7). Specific coding signal is possible by the addition of different dyes within each nanobead.

We also demonstrated that the close combination (inter-dye distance < 5 nm) of organic molecules and inorganic complexes leads to smart optical signal of particles (-*smart* concept). By the fact that only the fluorescence of organic dyes is sensitive to pH, temperature or residual oil/water ratio, we combined within nanobeads (i) a stable lanthanide complex acting as a reference (no environmental influence of fluorescence) and (ii) the organic dye. This association of fluorescent entities (memory effect) could be analyzed for the understanding of physicochemical properties of reservoir. Several tests on nanobeads containing both fluorescein and Europium-DTPA complexes were conducted to show the dependence of tracer fluorescence on physicochemical conditions of environment.

#### Experiment 1

A solution containing 5 ppm nanoparticles was aged for 72 hours at 80°C. Fluorescence spectra are collected and summarized in Figure 8. For excitation wavelength of 395 nm (absorption of Europium ions) we do not observe any modification in the emission intensity whereas for 330 nm the signal is dependent to the heat time. The decrease in emission intensity is due to the degradation of fluorescein molecule under heating. The signal of this family of tracers is useful to collect information about the maximum temperature encountered by the nanoparticle within high temperature medium.

#### Experiment 2

The fluorescence signals of 5 ppm nanoparticles solutions were studied at different pH. Excitation spectra with an emission at 615 nm are reported in Figure 9. The spectra show a dramatic evolution of the signal attributed to the FITC signal (485 nm), whereas the  $\text{Eu}^{3+}$  component (395 nm) does not display variation between pH 12 to 5 and a slight variation from pH 5 to 1. The signal of this family of tracers is useful to collect information about the pH encountered by the nanoparticle within porous medium.

#### Experiment 3

Fluorescence spectra of 5 ppm nanoparticles solutions was taken in an organic solvent (100% DEG: diethylene glycol) or water-DEG (1:2) solvent mixture. The excitation spectra with an emission at 615 nm are summarized in Figure 10. The spectra show an important variation of the particles signals with respect to the water content.

### Coreflood tests

#### Experimental setup

Experimental procedure for the synthesis of nanobeads used for corefloods can be found in Appendix A. Colloidal tracer solutions are dispersed into synthetic sea water (composition in Table 1) by the desired concentration. Potassium iodide (KI, ideal tracer) is added to brine. Core material is a Bentheimer sandstone outcrop. Cores used are typically 2"-diameter and 5"-long. The permeability of the Bentheimer sandstone is 800 mD and 20% porosity. X-ray fluorescence and to X-ray diffraction on powder provided the mineralogical analysis (Table 2). The rock contains 4.5% clays as kaolinite and illite. The core was encapsulated in epoxy resin before use. The experimental setup consists of a dual-piston syringe pump (Labotron) used to inject the fluid. Effluents are collected via an automatic sampler. Differential pressure is measured over the core length to check for plugging. Prior to the experiment, the core is thoroughly vacuumed, and saturated with synthetic seawater (without KI). Samples are analyzed using a UV-spectrophotometer to determine iodide concentrations. A continuous and a time-resolved spectrofluorimeter are used to measure respectively the fluorescein and the Eu-DOTA concentration.

## Results

We present here a set of preliminary corefloods that were conducted at room temperature, in the absence of crude oil. The main goal of these is to study the interaction of the nanobeads with the rock to validate the concept of the nanobeads and to illustrate their propagation capabilities. The nanoparticles solution was injected at 60 ml/h flowrate (1.2 PV/h).

### Experiment A

A solution containing 5 ppm nanoparticles was injected in a Bentheimer sandstone core. After 3.8 PV, injection was switched to synthetic seawater (without KI). Analyses of the effluents are summarized in Figure 11. The small shift in nanoparticles breakthrough combined to the skewness of the elution curve denotes small interactions with the rock. Unfortunately, erratic parts of the signals prevent any reliable quantitative interpretation in terms of nanoparticles retention. Although qualitatively more than 95% of the nanoparticles are recovered in the process. In order to better quantify the retention of the nanoparticles, the same experiment was conducted using a lower concentration of nanoparticles to give a better sensitivity.

### Experiment B

A solution containing 0.5 ppm nanoparticles was injected in a Bentheimer sandstone core. After 4.3 PV, injection was switched to synthetic seawater. Analyses of the effluents are summarized in Figure 12. The shift in breakthrough time and the skewness of the elution curve denotes some interactions with the rock. Integration of the signal according to the following equation gives access to the mass of nanoparticles irreversibly retained on the rock.

$$m_{\text{retained}} = C_{\text{inj}} \times PV \times \int (S_{\text{KI}} - S_{\text{fluor}})$$

This gives a value of 2 µg of nanoparticles retained in this experiment which corresponds to 4 ng retained/g of rock. These are very low value of retention; the nanobeads recovery factor is 98%.

## Conclusions

Silica-based nanoparticles including both rare-earth element complexes and organic dyes were successfully synthesized as oil field tracers. The longer lifetime fluorescence of rare-earth complexes is suitable for quantification thanks to time-resolved fluorimetric detection. The fluorescence background noise caused by organic contaminants from crude oil could be eliminated. By combining rare-earths, ligands and organic dyes within silica nanobeads, we are able to prepare a wide library of orthogonal fluorophores that could be use as smart tracers. Furthermore, the versatility of sol-gel chemistry and the flexibility of the microemulsion synthesis permit to finely tune the surface properties of the nanobeads. The gluconamide surface coating of the nanobeads proved efficient to minimize rock-nanoparticles interactions leading to 98% recovery factor upon injection of a 0.5 ppm solution of nanobeads in outcrop sandstone. We also demonstrated that the addition of organic dyes within nanoparticles could be used as outer-environmental-sensing agents. The careful fluorescence study of these tracers allows information recovery about conditions to which the nanoparticles were exposed (-*smart* concept).

## Acknowledgement

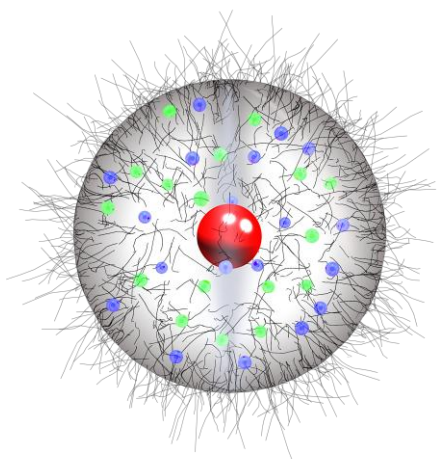
The authors would like to thank Total for funding.

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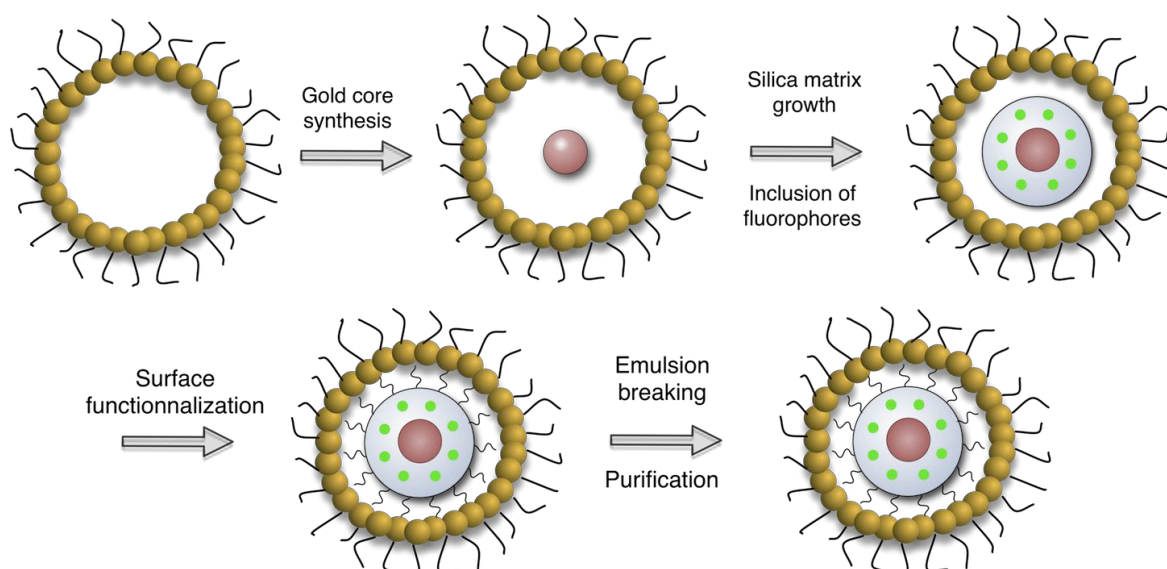
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## Figures



**Figure 1. Nanobeads schematization: red sphere: gold core, green and blue dots: fluorophores, light grey: silica matrix, black lines: surface functionalization**



**Figure 2. Nanobeads synthesis procedure.**



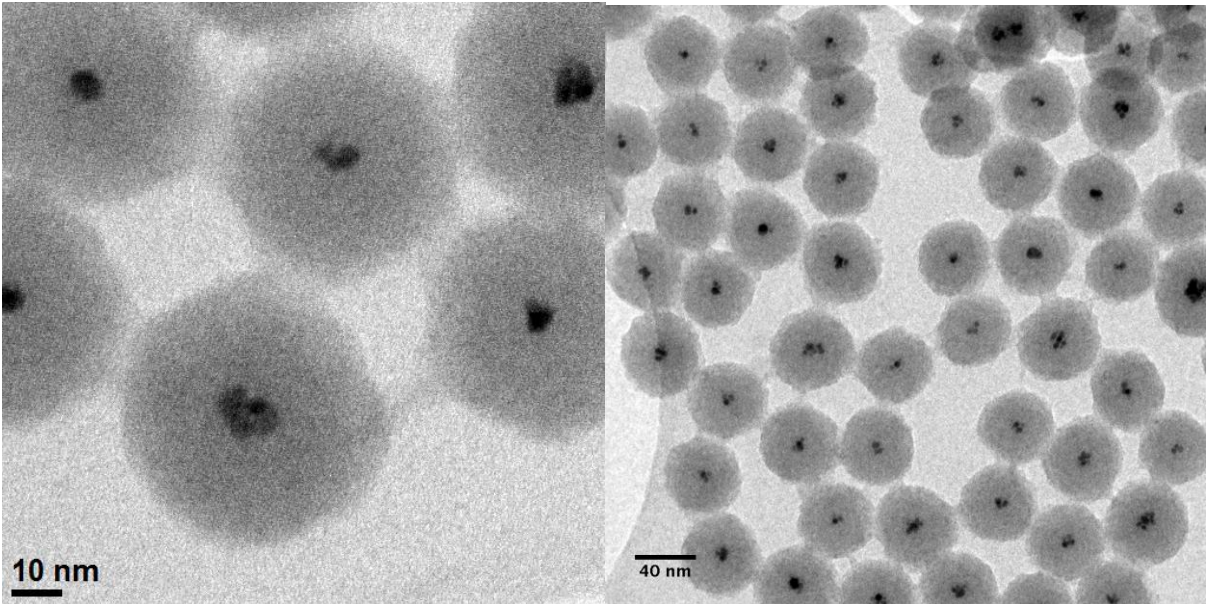


Figure 3. TEM images of nanobeads.

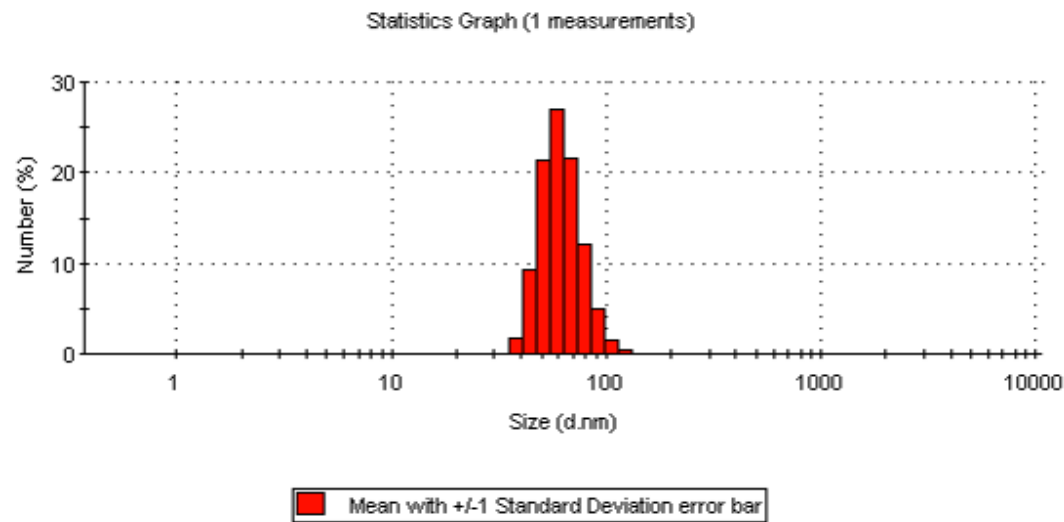
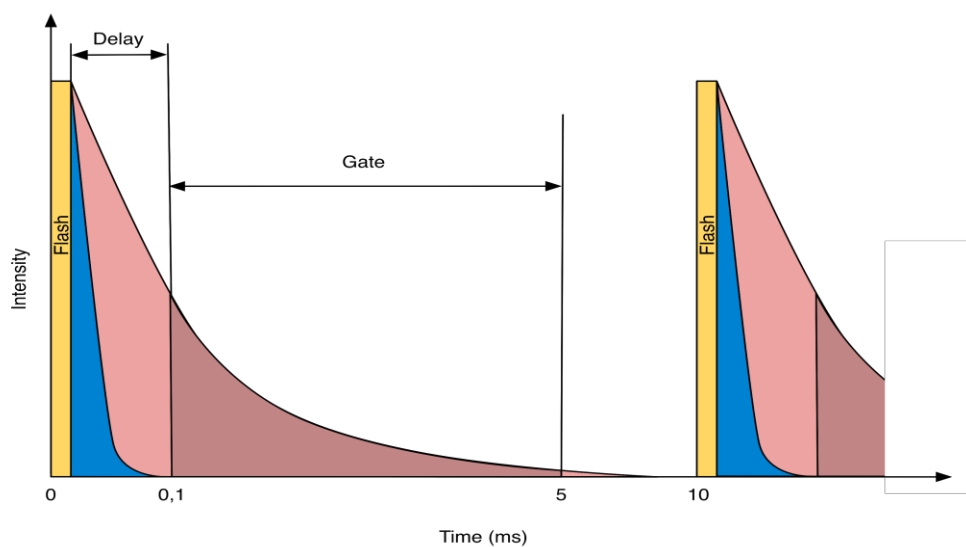
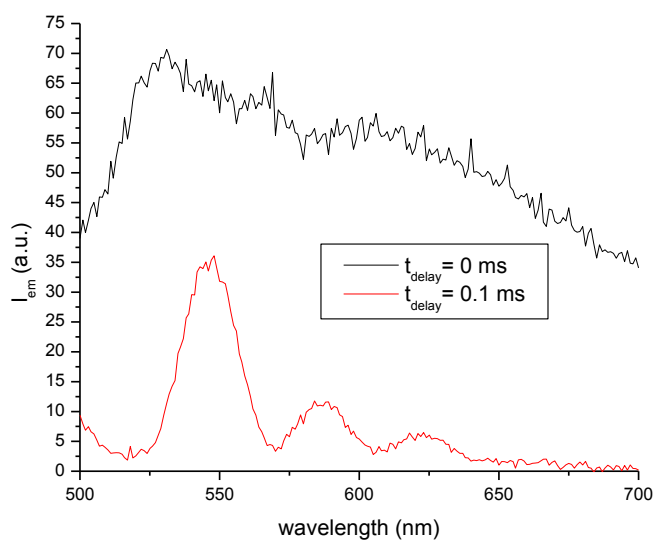


Figure 4. DLS distribution of nanoparticles diameter (in number), nanoparticles containing FITC and Eu-DOTA fluorophores, 50-nm-mean diameter, 0.091 polydispersity index



**Figure 5. Time-resolved fluorescence measurement principle.** At 0 s an excitation pulse irradiates the sample. Organic compounds fluorescence intensity is represented in blue, rare-earth element complexes fluorescence signal intensity is depicted in orange. Acquisition of the signal takes place during the gate time.



**Figure 6. Emission spectrum of a 200 ppm solution of nanoparticles in synthetic seawater with 5% crude oil.** Black curve: no delay (excitation wavelength 480nm, regular fluorescence measurement). Red curve: Time resolved (excitation wavelength 280 nm, 0.1 ms delay, time-resolved mode).



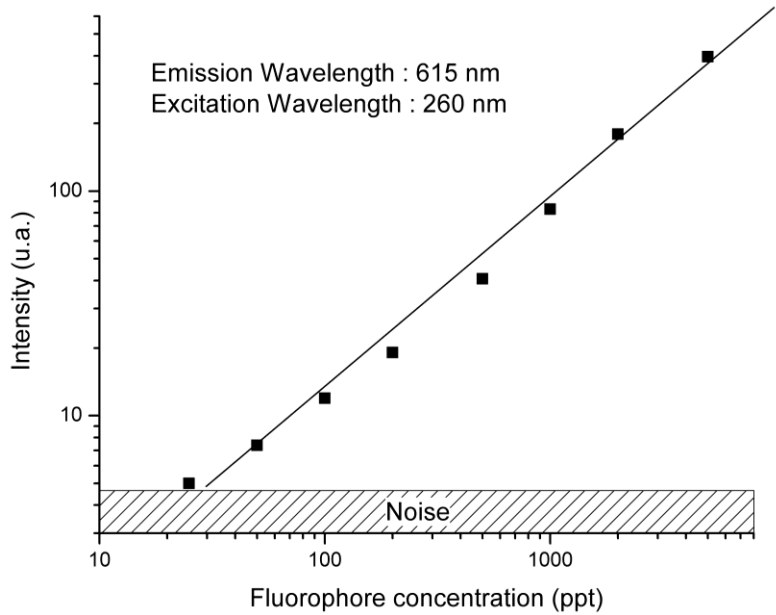


Figure 7. Detection limit of a DOTA derivative in water (Axint SAS, excitation wavelength 260 nm, emission wavelength 615 nm, 0.1 ms delay, time-resolved mode).

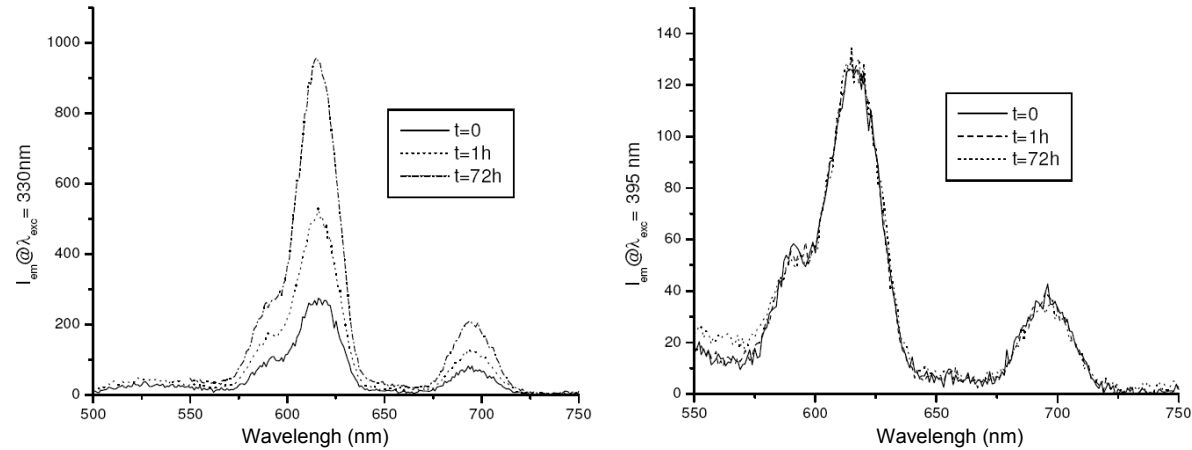


Figure 8. Effect of temperature on the optical signals of multimodal fluorescent particles (fluorophores : FITC + Eu-DTPA)

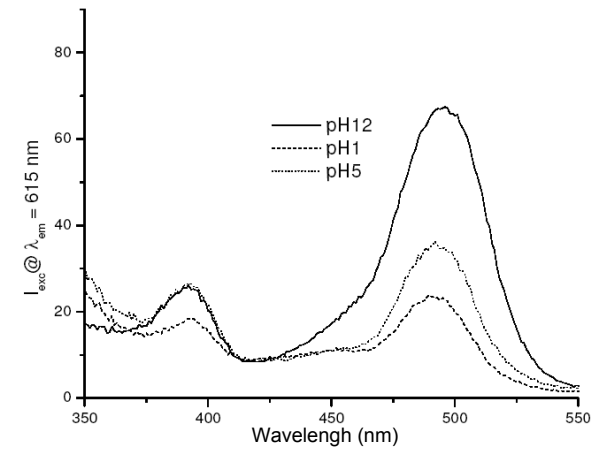


Figure 9. Effect of environmental pH on the optical signals of multimodal fluorescent particles (fluorophores : FITC + Eu-DTPA)

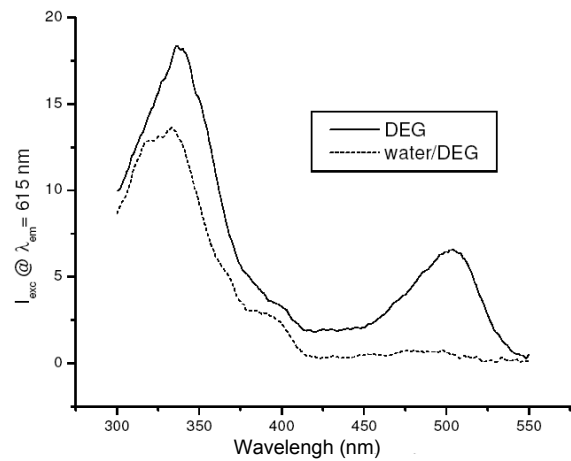


Figure 10. Effect of environmental water/organics ratio on the optical signals of multimodal particles (fluorophores : FITC + Eu-DTPA)

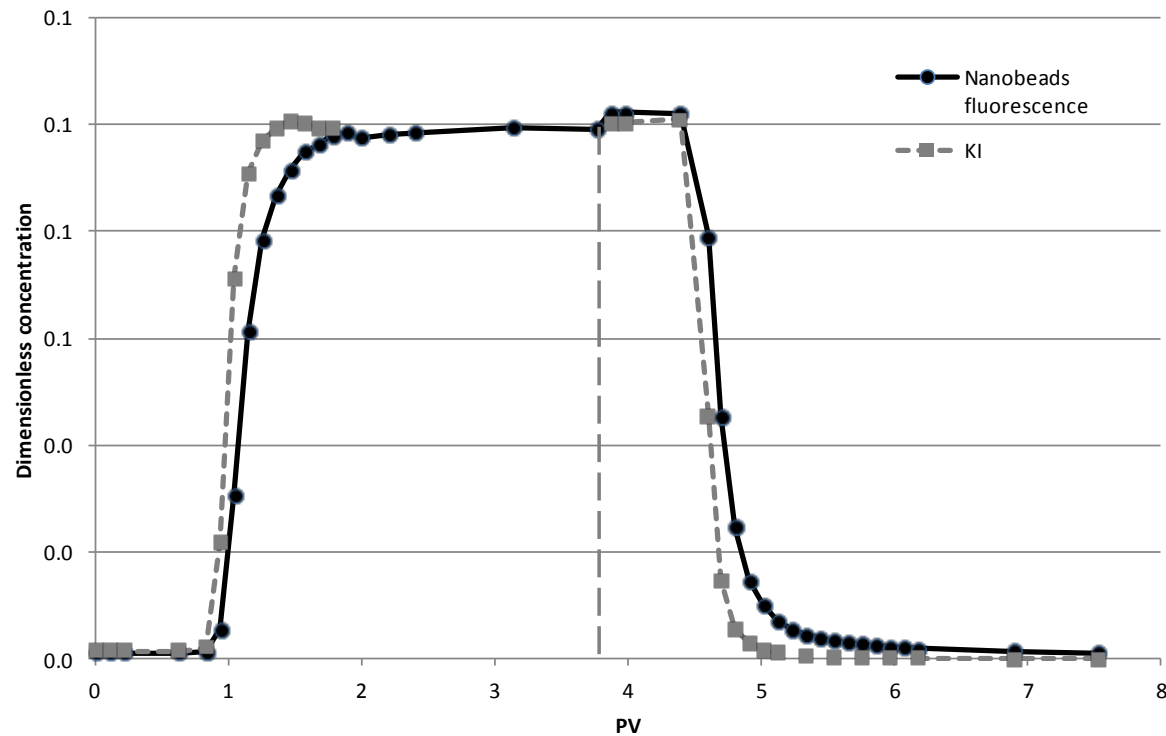


Figure 11. Nanobeads and conservative tracer concentration in experiment A effluents

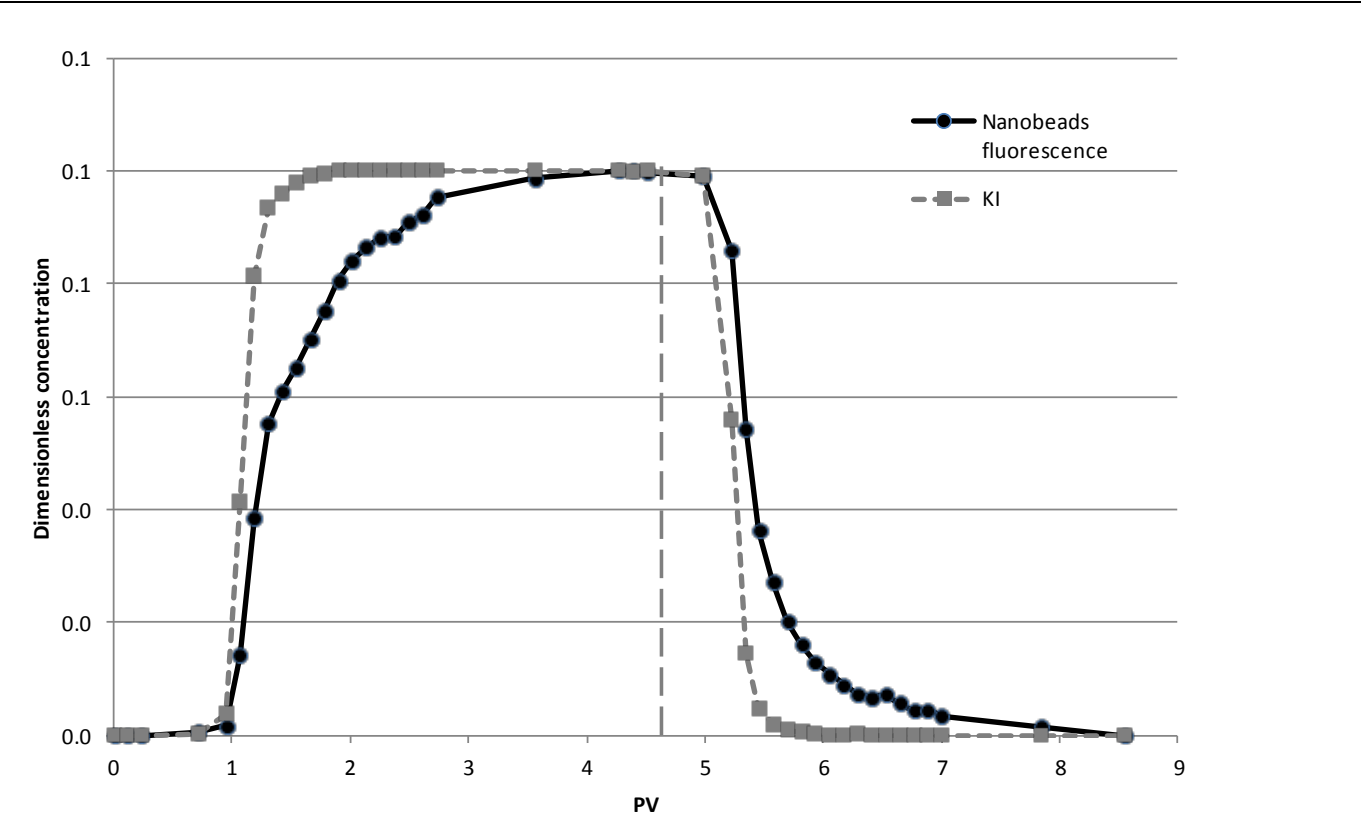


Figure 12. Nanobeads and conservative tracer concentration in experiment B effluents

**Tables**

<b>Salt</b>	<b>Concentration (g/L)</b>
NaCl	24.80
KCl	0.79
MgCl <sub>2</sub> ·2 H <sub>2</sub> O	5.25
CaCl <sub>2</sub> ·2 H <sub>2</sub> O	1.19
NaHCO <sub>3</sub>	0.20
Na <sub>2</sub> SO <sub>4</sub>	4.16
KI	1.00

**Table 1. Composition of the synthetic seawater including potassium iodide (KI) as conservative tracer.**

<b>Mineral</b>	<b>Content (%w)</b>
Albite	2,2
Microcline	4,0
Quartz	86,6
Dolomite	1,0
Siderite	0,8
Apatite	0,1
Pyrite	0,1
Barytine	0,0
Anatase	0,4
Kaolinite	2,5
Illite	2,0
Chlorite C	0,3

**Table 2. Mineralogical composition of Bentheimer sandstone.**

**Appendix A****Experimental procedure for the preparation of a solution of gold core/silica matrix containing fluorescein and Eu-DOTA fluorophores.**

In a 2.5 mL flask, 20 mg of FITC (fluorescein isothiocyanate) were introduced with 0.5 mL of APTES ((3-aminopropyl)triethoxysilane) under vigorous stirring. The solution was homogenized during 30 min at room temperature. In a 2.5 mL flask, 20  $\mu$ mol of lyophilized SRP-europium nanoparticles (5-nm-diameter, SRP polysiloxane-DOTA-Eu from Nano-H SAS, France) were dispersed in 1.5 mL of distilled water. In a 500 mL flask, 36 mL of Triton X-100, 36 mL of *n*-hexanol, 150 mL of cyclohexane, and 21 mL of an aqueous solution made from 9 mL of 16.7 mM aqueous solution of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , 9 mL of a 32.8 mM aqueous solution of MES (sodium 2- mercaptoethanesulfonate), and 3 mL of a 412 mM aqueous solution of  $\text{NaBH}_4$  were introduced under vigorous stirring. After 5 min, 0.400 mL of the previously prepared fluorescein solution was added to the microemulsion together with 1.5 mL of europium solution. Afterward, 0.200 mL of APTES and 1.5 mL of TEOS (tetraorthosilicate) were added to the reaction medium. After 10 min, the silica polymerization reaction was completed by the addition of 0.800 mL of  $\text{NH}_4\text{OH}$ . The microemulsion is kept under stirring at room temperature for 24 h. Then 190  $\mu$ L of a 50% solution in ethanol of silane-gluconamide (N-(3-triethoxysilylpropyl)gluconamide) was added to the microemulsion. After 24 h, another 190  $\mu$ L of the silane-gluconamide solution was added. The microemulsion was broken 24 h after this last addition by adding 250 mL of distilled water and 250 mL isopropanol to the reaction medium in a separatory funnel. The lower phase, containing the nanoparticles, was recovered and purified by tangential filtration (VIVASPIN©, 300 kDa, 4000 rpm) until a 500 purification ratio. The solution was filtered at 0.2  $\mu$ m and diluted 5 times in DEG (diethyleneglycol). This nanoparticles DEG solution was then directly used for the preparation of aqueous solutions.