

SPE-173768-MS

How to Monitor Scale Inhibitor Squeeze Using Simple TRF Tracers

Matteo Martini, Thomas Brichart, Arthur Marais, Albert Moussaron, and Olivier Tillement, Universite Lyon 1
Christian Hurtevent; Salima Baraka-Lokmane, Total S.A.

Copyright 2015, Society of Petroleum Engineers

This paper was prepared for presentation at the SPE International Symposium on Oilfield Chemistry held in The Woodlands, Texas, USA, 13–15 April 2015.

This paper was selected for presentation by an SPE program committee following review of information contained in an abstract submitted by the author(s). Contents of the paper have not been reviewed by the Society of Petroleum Engineers and are subject to correction by the author(s). The material does not necessarily reflect any position of the Society of Petroleum Engineers, its officers, or members. Electronic reproduction, distribution, or storage of any part of this paper without the written consent of the Society of Petroleum Engineers is prohibited. Permission to reproduce in print is restricted to an abstract of not more than 300 words; illustrations may not be copied. The abstract must contain conspicuous acknowledgment of SPE copyright.

Abstract

Mineral scale deposition in oilfield reservoirs has caused millions of dollars in damage every year. The most common remedy to the build-up of scale inside well bores and the surrounding reservoir is the periodical “squeeze” treatment by inhibitor additives. The real-time and on-site control of inhibitor concentration during production remains one of the big challenges. Indeed, current techniques of inhibitor monitoring that use elemental analysis appear too complex for an efficient long-term industrial solution. With this in mind, we have developed a simple and accurate method for scale inhibitor quantification in production waters based on the use of time-resolved fluorescence (TRF) tracers. The characteristic luminescence signature (lifetime value, emission and excitation spectra) of TRF tracers allows the reliable tracking of inhibitors additives. Moreover, their long-lifetime luminescence signal can significantly increase the signal to noise ratio thanks to the suppression of organic oil residual background emission. Our experimental tests on produced water collected from different sites confirm the detection of a larger variety of inhibitors i.e. for carboxylates, phosphonates and sulphonates by simple post-chelation with TRF tracers at low concentration. Indeed, the non-fluorescent inhibitor species have been switched to fluorescent compound by the addition of few amounts of tracer in order to be detectable and quantified at sub-ppm concentrations. The coupling between TRF tracers and specific TRF spectrofluorometer apparatus then open new and accurate ways for the online and/or on-site monitoring of scale inhibitors for better risk management of flow assurance during production.

Introduction

A regular squeeze treatment with inhibitor chemicals is a well-established procedure in oil and gas production facilities that help to maintain production by preventing near wellbore and production tubing scaling. The real-time and on-site monitoring of inhibitor concentration is an essential requirement for minimizing chemical additives consumption (Graham, G. *et al.* 1995; Boak, L.S. and Sorbie, K., 2010). After 20 years of research and publications, scale inhibitor R&D has focused on the efficiency of scale treatments: (i) minimal sample preparation and detection, (ii) differentiation of multiple scale inhibitor compounds, (iii) high accuracy in the ppm range, (iv) reduction of total treatment costs.

Several analytical procedures and standard methods for inhibitor analysis have already been developed (e.g. Johnstone, *et al.* 2014); these methods include the colorimetric analysis, inductively coupled plasma

(ICP) spectroscopy, U.V. spectrophotometry, hyamine methods and ion chromatography HPLC. Nevertheless, some techniques require laborious pre-treatment/purification stages for the separation of inhibitor chemical from the interfering brine salts (Chilcott *et al.*, 2000). Moreover, as in the case of Hyamine 1622 assays, the quantification is time consuming, labour intensive and difficult operation (Graham *et al.*, 2010). Calibrations and repeats for sulphonated copolymers required extensive dialysis and sample preparation. HPLC and ICP detection techniques – that achieved accurate measurements within a 5-10% error bar – require P-tagged co-polymer type SI that it is not classified as environmental-friendly additive.

Beyond such analytical techniques, our long experience in luminescence detection has revealed that fluorescence techniques can be surprising suitable for a “smart” real-time scale monitoring (Agenet *et al.*, 2012; Brichart *et al.*, 2014). We found that the industrial expectations of detection thresholds, costs, and management on scale monitoring matched the time-resolved fluorescence (TRF) analysis. The perspectives of smart monitoring by TRF are focused on two main aspects. Firstly, time-resolved fluorescence spectroscopy differs from the classical steady-state fluorescence by the use of series of light-pulses (instead of a continuous irradiation of the sample); the light emitted by the tracer (lanthanide-based) is then collected after a micro- or milli- second delay and analyzed. The delay between excitation and detection allows a dramatic increase of the S/N (signal-to-noise) ratio because crude oil only emit during a short period whereas the lanthanide ions emit within a long millisecond range. Secondly, the inhibitor molecules and polymers are found to be excellent chelator species for ions (Collins, I.R. *et al.* 2001, Jordan, M. M. *et al.* 2000) and thus they can be used as probes.

In this paper we will prove that TRF detection of lanthanide-chelated inhibitors allows a quantitative monitoring of inhibitors with a user-friendly apparatus and a simple management of samples. Moreover, this technique allows accurate real-time squeeze supervision even in the case of simultaneous detection of two different inhibitors.

Materials and Methods

Solutions used

Synthetic Gabon seawater was used for all calibration and performance studies. The composition of synthetic brine is listed in Table 1. Chemical 1 (based on terpolymer of maleic anhydride, sodium allyl sulfonate and HEDP) and Chemical 2 (based on phosphonate) have been chosen as inhibitors because of their co-exploitation in Gabon sites. Both commercial solutions contained between 10 % and 30 % of inhibitor molecules; in this paper we have always considered the commercial concentration, and we will shift to the real inhibitor concentration during the conclusions. Two series of seawater solutions with an increasing amount of inhibitors have been prepared in order to obtain concentrations ranging from 0 to 100 ppm. A flask containing 100 ppm of Eu-light tracer (NanoH S.A.S.) diluted in 20 g/L NaCl 6.5 pH buffered aqueous solution was prepared for further calibration and performance studies. Typical oilfield synthetic brine for calibration steps has been composed by a mixture of 4.5 mL of Eu-light solution and 0.5 mL of specific inhibitor solution.

Table 1—Gabon synthetic seawater composition

Gabon seawater (mg/L)	
NaCl	1921
CaCl ₂	2693
MgCl ₂ .6H ₂ O	528
KCl	114
BaCl ₂ .2H ₂ O	11
SrCl ₂ .6H ₂ O	38

Calibration and Sample analysis

Standard samples used for calibration have been prepared in PMMA cells with 1 cm optical path. No heating steps were required and cells have been stocked at room temperature. The TRF luminescence signal was collected by using Cary Eclipse spectrophotometer (Agilent Technologies). In time-resolved configuration (75 kW Xenon flash lamp, Czerny-Turner monochromators, $\Delta_{\text{pulse}} = 2 \mu\text{s}$, 800 V PM detector), the excitation wavelength was adjusted to 395 nm, which corresponds to the absorption band of the Eu-light solution, and the emitted light was collected in a gate window of $0.7 \div 1.7 \text{ ms}$ (lamp pulse 50 Hz). The TRF configuration is reported in Figure 1. All of data have been treated by OriginLab software.

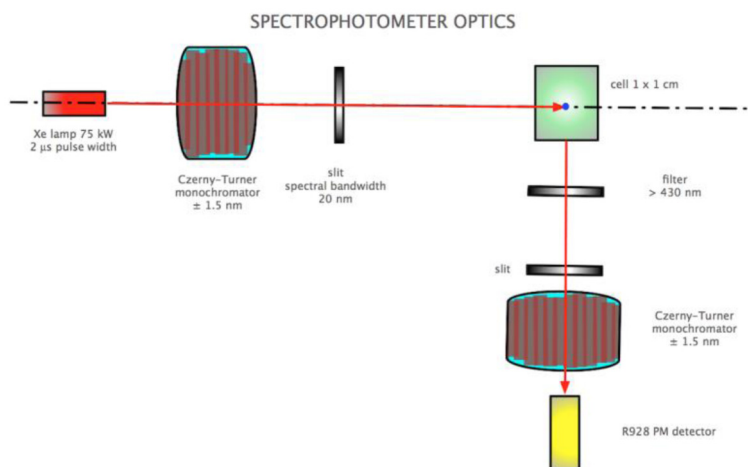


Figure 1—Cary Eclipse TRF spectrophotometer scheme from Agilent Technologies

Presentation of Data and Results

Optical signature of Eu-light chelated inhibitors

The TRF detection applied to the smart real-time scale monitoring appears as a fast, reproducible, and easy procedure that does not require any time-consuming pre-treatments nor complex calculations. The calibration series of samples were easily obtained from 100 ppm - standard solution by serial dilutions. Neither gel-filtering nor other purification steps have been required before the optical analysis; all samples have been stocked at room temperature. The Eu-light tracer solution has been directly mixed with the inhibitor samples without pre-treatments. All ready-to-use measurement samples were prepared by dispensing 2 mL of fluorescent mixture into PMMA standard fluorescence cells.

The signal obtained by TRF fluorescence is typical of chelated europium ions and really easy to treat. Terbium tracer solution has also been used with excellent results (Brichart et al., 2014). The reasons for using Eu-light above other lanthanide-based solutions are manifold. Firstly, under UV light irradiation the europium element (+3 oxidation state and $4f^6$ electronic configuration) displays monochromatic phosphorescence emission in the visible range, with two main emission transitions at 595 nm and 615 nm (Figure 2 right) (Liu, 2005; Lakowicz, 2008). The millisecond timescale emission of europium is excellent for monitoring phenomena in oil waste. Indeed, the collection of luminescence signal by TRF apparatus (e.g. 0.7 ms delay time) allows the separation of the tracers' signal (long-life emission) from the crude oil background (that emits in a short temporal range till the microseconds). As a consequence, the increasing S/N ratio (i) directly limits the amount of tracers necessary for analyses and (ii) enhances the threshold of inhibitor quantification. Furthermore, the fact that Eu^{3+} ions display excitation transition peak centred at 395 nm (i) facilitates the measurements using low-cost disposable plastic cells instead of quartz cells (Figure 2 left) and (ii) reduces the influence of signal coming from organic compounds of oil waste. The

two main emission peaks in the red region of visible spectra correspond to the magnetic dipole (595 nm) and electronic dipole (615 nm). Their ratio gives information about the close environment of europium ions: the chelations of europium tracer by inhibitors modify the ratio of peaks and then give the signature of inhibitor species. The presence of chelators also increases the quantum yield and the lifetime of europium ion by displacing water molecules away from the emitter center. The Eu^{3+} complexes formed remain stable at room temperature during the measurement session and no photobleaching was observed. The following experimental analyses will prove that Eu-light tracers seem to be good candidates for the real-time monitoring of scale inhibitors.

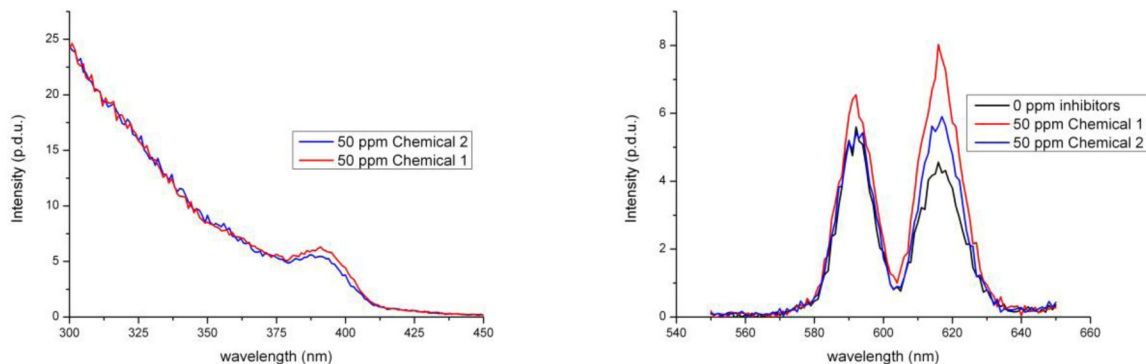


Figure 2—(left): excitation spectra of Chemical 1 and Chemical 2. The emission wavelength was fixed to 615 nm, delay 0.2 ms, gate time 1 ms. The peak at 395 nm is specific of europium ions. (right): emission spectra of inhibitors under 395 nm excitation (delay 0.2 ms). The signal of Eu-light in presence of Chemical 1 is more intense than the one of Chemical 2 at the same concentration. The ratio between the 595 nm and 615 nm peak depends on the nature of inhibitor and the parameters used (delay, gate, and excitation wavelength).

Calibration curves

Standard curves have been acquired for the estimation of inhibitors concentrations in Gabon brine. For that purpose, a fixed amount of Eu-light solution has been added to incremental doses of inhibitors. The detection parameters such as PM voltage, slits and integration time have been fixed for all measurements. Under a 395 nm monochromatic irradiation, we collected the emission signal in a 10 nm - window centered at 595 nm and at 615 nm. The delay time has been varied from 0.3 ms to 0.7 ms while the gate time was fixed at 1 ms. A dozen of independent repeats have been performed during a 7 days time period; two samples of each concentration were measured daily and no significant difference of signal has been observed. [Figure 3](#) summarizes the optical response of Chemical 1 and Chemical 2 inhibitors coupled with Eu-light tracer.

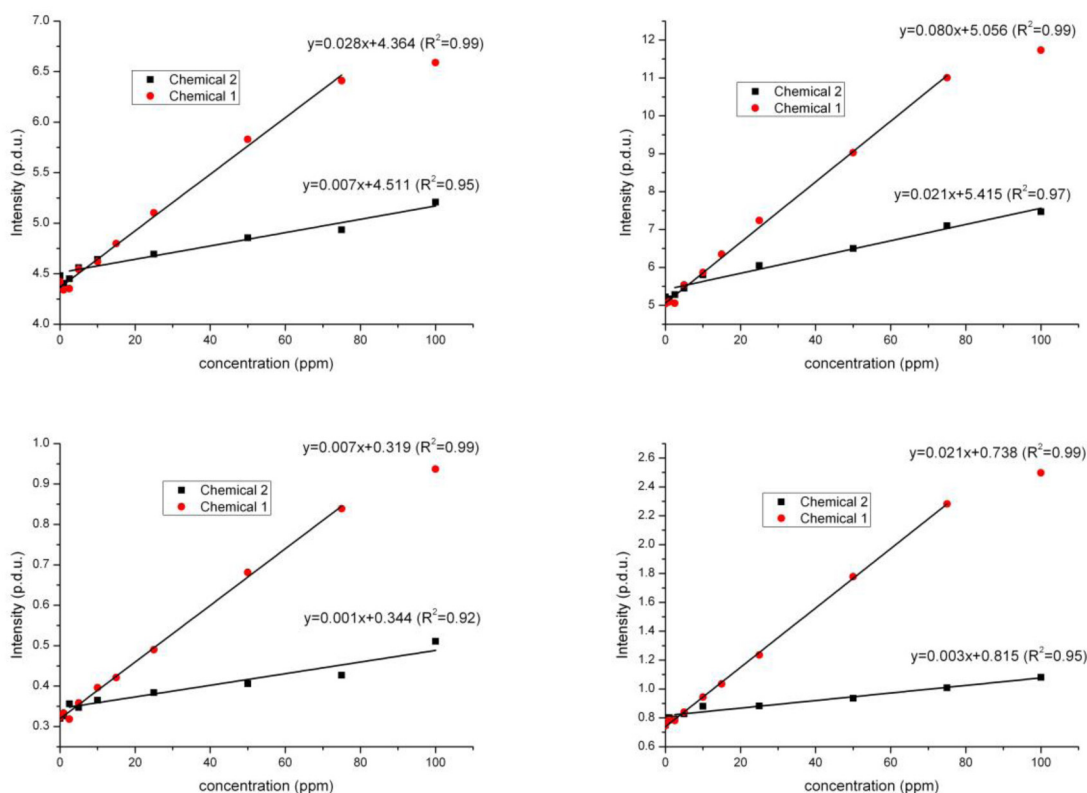


Figure 3—Calibration curves of Chemical 1 and Chemical 2 in the range 0 - 100 ppm diluted in Gabon water. Four different detection conditions have been considered (395 nm excitation, gate 1 ms). A: delay 0.3 ms, peak 595 nm; B: delay 0.3 ms, peak 615 nm; C: delay 0.7 ms, peak 595 nm; D: delay 0.7 ms, peak 615 nm. The fitting of experimental points considers the sub-range 2.5 ppm – 100 ppm for Chemical 2 and 2.5 ppm – 75 ppm for Chemical 1. R^2 values prove the application of TRF method for Gabon tests.

Both series of samples (the two test inhibitors with increasing concentration mixed with Eu-light solution) have been observed with TRF apparatus: in the graphs A and B we fixed a delay time of 0.3 ms whereas in the graph C and D the delay increases till 0.7 ms. Moreover, in graphs A and C we reported the intensity of 595 nm peak and in graphs B and D the intensity collected at 615 nm.

The experimental points reported in the graphs denote a linearity of luminescence signal with the inhibitor concentrations that is fundamental for the perspective of accurate inhibitor quantification: for n independent measurements, we associate n linear equations and the solving of such linear system gives the values of concentrations. Considering the problem of only two inhibitors additives (called 1 and 2), the system becomes:

$$\begin{cases} I_a = A_a + K_{1a} [1] + K_{2a} [2] \\ I_b = A_b + K_{1b} [1] + K_{2b} [2] \end{cases}$$

where I represents the intensity of luminescence and the subscript a and b indicate a specific measure. The values K are coefficients that indicate the proportionality with the corresponding inhibitor concentration. The amount of separate inhibitors can be calculated by:

$$[1] = \frac{(K_{2b}I_a - K_{2a}I_b) - (A_aK_{2b} - A_bK_{2a})}{(K_{1a}K_{2b} - K_{2a}K_{1b})}$$

$$[2] = \frac{(K_{1b}I_a - K_{1a}I_b) - (A_aK_{1b} - A_bK_{1a})}{(K_{2a}K_{1b} - K_{2b}K_{1a})}$$

In the range 2.5 – 50 ppm (the typical concentration used for real inhibitor monitoring), the response of tracer was linear with the inhibitor concentration for both series. The fitting of experimental points by a linear function gave R^2 values higher than 0.95 for Chemical 2 and even 0.99 for Chemical 1. In Chemical 2 samples, we clearly distinguished two behaviours with a break of the derivative curve at 2.5 ppm; the slope of tangential fit for small amounts of inhibitors (0 – 2.5 ppm) was higher than the one calculated in the range 2.5 ppm – 50 ppm. As expected, the signal collected after 0.7 ms delay was lower than the one collected after short delay (0.3 ms); beyond 0.7 ms delay, the signal collected reaches the same magnitude as the background noise and measurements have not been taken into consideration. Moreover, Chemical 1 samples exhibited more intense luminescence in all conditions; for example (Figure 3B), the slope for Chemical 1 series was equal to 0.080 whereas it decreased to 0.020 in Chemical 2 samples.

Supplementary calibration curves (e.g. emission peak at 595 nm) give additional information for the solving of system and can dramatically decrease the error bar on inhibitor quantification; in principle, we can choose two out of four courbes of Figure 3 (e.g. intensities at 595 and 615 nm with 0.7 ms delay) to solve the equations. For further analytical development we take into account the calibration curves where the difference of slope between inhibitors is maximal.

Performance curves

The calibration curves have been used for the estimation of both inhibitors amounts in some Gabon brine solutions containing different mixtures of Chemical 1 and Chemical 2 (5 – 50 ppm range); the final result will give us the efficiency of TRF method.

A first test has been made on samples that display an inhibitor ratio of 1:1 (Figure 4). Four separate measurements have been performed for each sample (delay 0.3 and 0.7 ms, emission collected at 595 and 615 nm). The fact that experimental points perfectly fit with a linear function (R^2 coefficients equal to 0.99) was not expected, but it boosted the performance of TRF technique. Indeed, we verified that the luminescence signal of one species (e.g. Chemical 2) is not dependent on the other one (e.g. Chemical 1), and their sum gives the total collected signal. We want to point out that even though Chemical 1 displays an intensity value 4 times greater than that of the Chemical 2, the total signal remains exactly the sum of them.

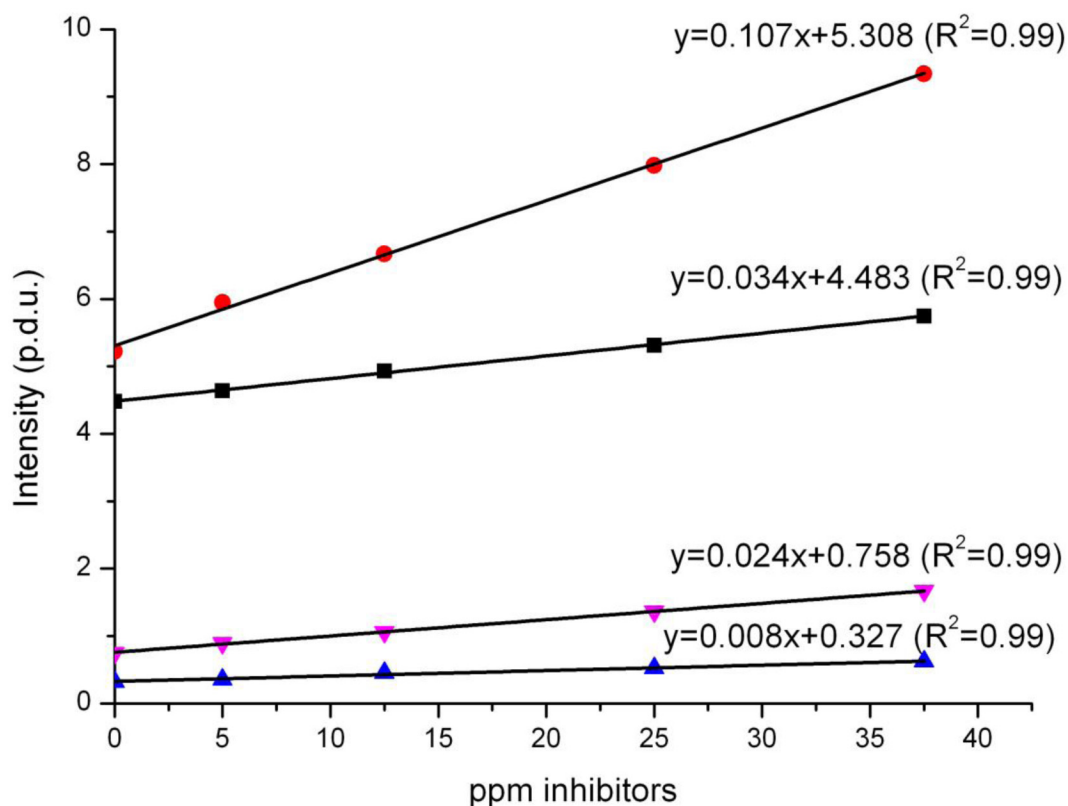


Figure 4—Performance courbes of 1:1 ratio Chemical 1 : Chemical 2 in Gabon water using Eu-light TRF detection (blue: delay 0.7 ms, peak 595 nm; violet: delay 0.7 ms, peak 615 nm; black: delay 0.3 ms, peak 595 nm; red: delay 0.3 ms, peak 615 nm). In all cases, the linearity of experimental points is proven by mathematical fit with $R^2 > 0.99$ and confirms the accuracy of TRF detection.

In a second test, we estimated the concentration of a single inhibitor species in a mixture by solving the equations. Beyond the 5 – 5 ppm, 12.5 – 12.5 ppm, 25 – 25 ppm and 37.5 – 37.5 ppm samples, solutions containing a ratio 5 ppm Chemical 1 – 25 ppm Chemical 2 and 25 ppm Chemical 1 – 5 ppm Chemical 2 have been prepared. The results were amazing since all of theoretical values were situated within the error bars (Table 2). Calculations for samples containing 1:1 of inhibitors give concentrations that differ from the nominal value of about 10%. The same margin of error was obtained for 1:5 and 5:1 ratios; for these two samples we chose as calibration curves the (i) Chemical 1 curve and (ii) the 1:1 mixture curve.

Table 2—Inhibitor quantification in sample containing both Chemical 1 and Chemical 2 compounds diluted in Gabon water. The experimental values closed to the nominal ones confirm the accuracy of TRF detection.

Chemical 2 _{theoretical} (ppm)	Chemical 1 _{theoretical} (ppm)	Chemical 2 _{experimental} (ppm)	Chemical 1 _{experimental} (ppm)
5	5	6.3	5.7
12.5	12.5	13.2	12.9
25	25	28.3	25.8
37.5	37.5	40.3	38.2
5	25	6.4	22.7
25	5	22.2	5.5

Conclusions

The residual scale inhibitor detection of Chemical 1 and Chemical 2 compounds in Gabon waters has been successfully performed by time-resolved fluorescence (TRF) spectroscopy. A tracer solution of Eu-light

has been added to the Gabon water containing a single or multiple inhibitors and its luminescence signal monitored. The low amount of test water (9/10 are constituted of the Eu-light solution) necessary for the measurements gives an excellent sensitivity to the analysis set-up. The performances of TRF technique comes from the specific signature of the Eu-light tracer - that emits light over the crude oil signal – when it is chelated by inhibitors. Hence, a smart real-time scale monitoring is possible with a user-friendly analysis of fluorescence intensities of test waters. The linearity of calibration curves in the range 2.5 – 50 ppm is excellent for monitoring not only Chemical 1 or Chemical 2 compounds but also other kind of additives that present a strong interaction with luminescent tracers. The accuracy is even enhanced by the consideration that the real concentration of inhibitor detected is 10-30% of the commercial solutions used in this paper, which means an experimental quantification threshold below 1 ppm. Moreover, the fine assortment of time-resolved studies opens the ways for simultaneous multi-detection of scale inhibitors, without any interactions with residual oil or other chemical additives. The oil field industries have been warned.

References

- Agenet, N.; Brichart, T.; Martini, M.; Crowther, N.; Perriat, P.; Tillement, O. *Fluorescent Nanobeads: a First Step Toward Intelligent Water Tracers*; Society of Petroleum Engineers, 2012.
- Boak L. S. and Sorbie K., New Developments in the Analysis of Scale Inhibitors, *SPE Production & Operations* **25**, 533, 2010.
- Brichart T., Moussaron A., Marais A., Martini M., Tillement O., Hurtevent C., Baraka-Lokmane S. 2014. The Use of Fluorescent Tracers for Inhibitor Concentration Monitoring Useful for Scale Inhibitor Squeeze Evaluation. Presented at 8th International Petroleum Technology Conference, Kuala Lumpur 10-12 December 2014.
- Chilcott, N.P., Phillips, D.A., Sanders, M.G., Collins, I.R. and Gyani, A. 2000. The Development and Application of an Accurate Assay Technique for Sulphonated Polyacrylate Co-polymer Oilfield Scale Inhibitors. Presented at the International Symposium on Oilfield Scale, 26-27 January 2000. <http://dx.doi.org/10.2118/60194-MS>
- Collins, I. R.; Jordan, M. M. *Occurance Prediction And Prevention Of Zinc Sulfide Scale Within Gulf Coast And North Sea High Temperature/High Salinity Production Wells*; Society of Petroleum Engineers, 2001.
- Graham, G. M.; Sorbie, K. S.; Boak, L. S.; Taylor, K., Development and application of accurate detection and assay techniques for oilfield scale inhibitors in produced water samples, International Symposium on oilfield chemistry 1995, 543–557.
- Graham, G.M., Munro, I., Harvison, N., Marshall, K. and Kyle, M. 2010. Improved Scale Inhibitor Assay for Sulphonated Polymers in Oilfield Brines. Presented at the SPE International Conference on Oilfield Scale, 26-27 May 2010. <http://dx.doi.org/10.2118/131100-MS>
- Johnstone J.; Toivonen S., Griffin R., O'Brien A.; Mundill P., Siivonen J., Väisänen P., Tiittanen S., Lehmusto M., Härmä H., Hänninen P., Teimonen T., Novel Method for Real-Time Monitoring of Scale Control Products at the Site of Use, SPE International Oilfield Scale Conference and Exhibition held in Aberdeen, Scotland, UK, 14–15 May 2014.
- Jordan, M. M.; Sjursather, K.; Edgerton, M. C.; Bruce, R. *Inhibition of Lead and Zinc Sulphide Scale Deposits Formed during Production from High Temperature Oil and Condensate Reservoirs.*; Society of Petroleum Engineers, 2000.
- Lakowicz, J. R. *Principles of fluorescence spectroscopy*; Analytical and Bioanalytical Chemistry, 2008.
- Liu, G. and Jacquier, B., *Spectroscopic Properties of Rare Earths in Optical Materials*, 2005.