

PAPER • OPEN ACCESS

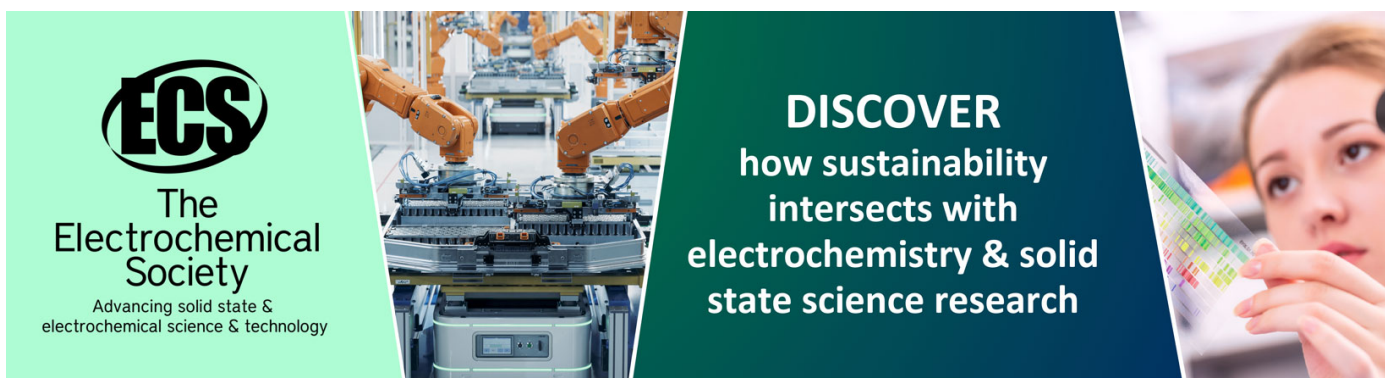
Characteristics Evaluation of Fluorescein Sodium as Fluorescent Tracer for Petroleum Wells

To cite this article: Harid Pataveepaisit and Falan Srisuriyachai 2020 *IOP Conf. Ser.: Earth Environ. Sci.* **609** 012102

View the [article online](#) for updates and enhancements.

You may also like

- [Method for determining microbial activity \(hydrolysis of fluorescein diacetate \(FDA\), 490 nm\)](#)
O A Frlolov, A V Terekhin, A V Yakushev et al.
- [Non-invasive assessment of intestinal permeability in healthy volunteers using transcutaneous fluorescence spectroscopy](#)
Jonathan Gan, Elena Monfort Sánchez, James Avery et al.
- [Synthesis of praseodymium-and molybdenum- sulfide nanoparticles for dye-photodegradation and near-infrared deep-tissue imaging](#)
Ye Wu, Pengfei Ou, Jun Song et al.



ECS
The
Electrochemical
Society
Advancing solid state &
electrochemical science & technology

DISCOVER
how sustainability
intersects with
electrochemistry & solid
state science research

Characteristics Evaluation of Fluorescein Sodium as Fluorescent Tracer for Petroleum Wells

Harid Pataveepaisit ¹, Falan Srisuriyachai ¹

¹Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University, Phaya Thai Road, Wang Mai, Pathum Wan, Bangkok 10330, Thailand

6171206421@student.chula.ac.th

Abstract. Fluorescein sodium (FluNa) is an organic xanthene-derivative fluorochrome appearing as crimson powder. In the form of solution, fluorescein absorbs blue light and emits green-to-yellow fluorescence under the incidence of visible or ultra-violet light. In petroleum industry, it is normally used as fluorescent tracer to determine reservoir connectivity between injection and production wells. In this study, fluorescein concentration at 10 ppm was critical concentration that reversed relationship between fluorescence intensity and fluorescence concentration. Emission wavelength at maximum fluorescence intensity became a function of fluorescein concentration until 512 nm at 1 ppm and there was no longer reduction of emission wavelength beyond this value at lower concentration. Fluorescence of fluorescein could not be observed by naked eyes at concentrations below 100 ppb, whereas its detection limit by fluorescence spectrophotometer could be lowered to 1 ppb. Fluorescence spectra of fluorescein concentrations at 10 ppt and 100 ppt were similar to those of tap water, formation water, and deionized water. Therefore, detection limit of fluorescein was determined to be at 1 ppb. Fluorescence of fluorescein was photodegraded by light up to 30% when stored inside transparent glass bottles and being exposed to light for 7 days and fluorescence of the solution became darker with time. On the other hand, fluorescence intensities of FluNa solution stored inside amber-coloured glass bottles in both all-time concealment and normal room conditions were almost identical. Fluorescence spectra of the solution at pH of 3 had lower fluorescence intensity and shorter emission wavelength at maximum fluorescence intensity than the solutions at pH of 7 and 11 that were mostly identical. Fluorescence of fluorescein was not affected by temperature in the range of 30-70°C for 12 days. Hence, the storage conditions for fluorescein solution were recommended to be stored inside amber-coloured glass bottle to prevent photodegradation with pH 7 or above.

1. Introduction

Tracer is described as any compound added to injected fluids and can be easily detected even in a trace amount. Tracer is normally used in applications of petroleum industry to determine reservoir connectivity between injection and production wells. Tracer selection is based on following characteristics including (1) being non-existent substance in the reservoir, (2) having low detection limit level, (3) having simple and easy quantitative analysis, (4) being thermally, biologically, and chemically stable in atmospheric and reservoir conditions, (5) following the phase being injected with the same flood front velocity and having minimal influence to other phases, (6) having no adsorption



and reaction to the formation, surface and subsurface equipment, (7) having minimal environmental consequence, and (8) being inexpensive [1]-[3].

Fluorescent tracer is a tracer that can illuminate itself upon receiving specific wavelength of light. It is considered to be inexpensive, safe, and simple to analyse, and can also be detected visually without conducting laboratory analysis. Fluorescein sodium (FluNa), one of the most referenced fluorescent tracer due to its fluorescence and the absence of toxicity and biodegradability, is an organic xanthene-derivative fluorochrome appearing as crimson powder. It is made from two petroleum products called resorcinol and phthalic anhydride [4]. It has very low detection limit and absorbs light from blue spectrum and emits light in green spectrum under the incidence of visible or ultra-violet light. Since it is widely used in many medical and pharmaceutical applications such as antibody-labelling agents and ophthalmic armamentarium, it can be obviously verified that it is absolutely harmless to the environment and human being. Furthermore, FluNa is usually used in other petroleum applications to determine fluid residence time distribution within the reservoir, dispersive characteristics, preferential flow channels, and fracture volume. However, the main drawbacks of FluNa are that it is highly pH-dependent, and can be photodegraded. Therefore, in this study, detection limit of FluNa would be determined and both drawbacks of FluNa would be evaluated. Chemical structure of FluNa is shown in figure 1, and physical and chemical properties are shown in table 1.

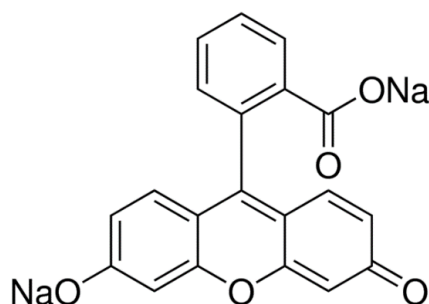


Figure 1. Chemical structure of fluorescein sodium.

Table 1. Physical and chemical properties of fluorescein sodium.

Properties	Value
Molecular formula	$C_{20}H_{10}Na_2O_5$
Molecular weight	376.3
Melting point	315°C
Decomposition temperature	395°C
Solubility in water	100 mg/mL at 20°C
Excitation wavelength	480 nm
Emission wavelength	520 nm

2. Theory

Fluorescence is one of photoluminescence which is related to a photonic emission process by fluorochromes during the molecular relaxation from electronic excited states to electronic ground state after being excited by electromagnetic radiations. The transition of excited electrons involves with two states: electronic and vibrational states. Electronic states are separated by energies of the order of $10,000\text{ cm}^{-1}$. Each electronic state is divided into multiple sublevels so-called vibrational states which are separated by energies of the order of 100 cm^{-1} . The electromagnetic radiations in the ultraviolet are required to trigger an electronic transition.

Originally, electrons remain as electron pairs on the lowest vibrational state of the electronic ground state and rotate on their own orbitals around the nucleus. Each electron pair stays in the form of antisymmetric electronic wave function so-called singlet state or single electronic state in which each electron has opposite electron spin. After electron pairs are impacted by electromagnetic radiations, an absorption occurs which excites electrons. After that, one electron from each electron pair leaves its own orbital on the lowest vibrational state of the electronic ground state and goes to the higher orbital on the accessible vibrational state of the accessible electronic excited state. This makes the singlet state of electron pair to be excited singlet state in which one electron on the electronic excited state still has the opposite electron spin from another electron that remains on the electronic ground state. The higher the energy impact from electromagnetic radiation on electrons, the higher the accessible vibrational state of the accessible electronic excited state of the excited electrons.

Subsequently, the unstable excited electrons are quickly relaxed back to the lowest vibrational state of the electronic ground state. During the relaxation, the excited electrons lose their energies through three processes: vibrational relaxation, collisional quenching and internal conversion. Vibrational relaxation is a process that makes excited electrons lose their energies in the form of vibrational energy, whereas collisional quenching is a process that excited electrons lose their energy by colliding with quenchers which are substances that can absorb fluorescence such as oxygen, chloride ions, iodide ions and acrylamide. These two processes result in the excited electrons to relax from higher vibrational state to lower vibrational state of the same excited electronic state. Internal conversion is a process that makes excited electrons on the lowest vibrational state of the higher excited electronic state to lose their energies and goes to the highest vibrational state of the lower excited electronic state. These three processes continue until the excited electrons reach the lowest vibrational state of the lowest electronic excited state. Next, the last interval conversion from this state to the allowable vibrational state of the electronic ground state occurs in two ways: non-radiative and radiative processes. Non-radiative process is a process that the excited electrons lose their energies in the form of thermal energy, whereas radiative process is a process that the excited electrons lose their energies by emitting photon in the form of fluorescence. Fluorescence has wavelength longer than that of electromagnetic radiation due to the loss of energy through vibrational relaxation, collisional quenching and internal conversion. Eventually, vibrational relaxation and collisional quenching occur until the excited electrons reach the lowest vibrational state of the electronic ground state.

Moreover, during the relaxation of the excited electrons on the excited singlet state, intersystem crossing can occur instead of internal conversion which is caused by spin orbit coupling that reverses the electron spin of electron pairs from antisymmetric (opposite electron spin; singlet) to symmetric (same electron spin; triplet) electronic wave function; that is, the relaxation of excited electrons from higher energy of excited singlet state to lower energy of excited triplet state occurs. The following processes occur in the same manners as described in the previous paragraph. When excited triplet electrons reach the lowest vibrational state of the lowest electronic excited state, intersystem crossing occurs again which makes excited triplet electrons to lose energies and change back to grounded singlet electrons upon reaching the electronic ground state. The energies are also lost in two ways: non-radiative and radiative processes. Non-radiative process also causes the energy lost in the form of thermal energy, whereas radiative process causes the excited triplet electrons to lose energies by emitting photon in the form of phosphorescence. Unfortunately, phosphorescence can occur only at least cryogenic temperature and is rarely detected in aqueous systems at average temperature. [5]-[8].

The electronic transition is illustrated by using Jablonski diagram shown in figure 2. It is noted that in figure 2, S_0 , S_1 , S_2 , and T_1 represent electronic ground state, lower electronic excited singlet state, higher electronic excited singlet state, and electronic excited triplet state, respectively. The singlet and triplet states of electron spin are shown in figure 3.

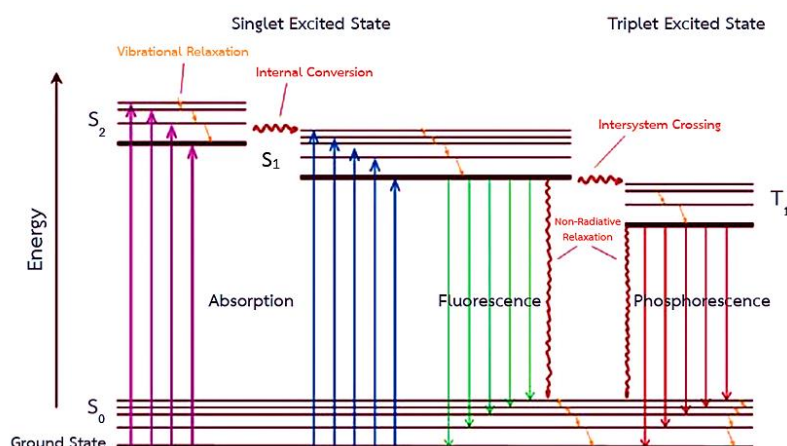


Figure 2. Jablonski diagram. [7]

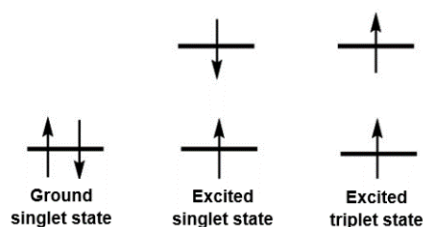


Figure 3. Singlet and triplet states of electron spin.

3. Materials and Methods

3.1. Materials

Fluorescein sodium salt was used to represent fluorescent tracer in this study. Deionized water was used as a solvent. Sodium carbonate and 5% acetic acid were used in potential of hydrogen (pH) sensitivity evaluation of FluNa. Acetone was utilized to clean all laboratory equipment before and after performing the tests. Formation water used in detection limit determination of FluNa was based on chemical composition of formulation taken from Sirikit Oilfield (S1) operated by PTT Exploration and Production Public Company Limited. Total dissolved solid (TDS) of formation water was 14,098 ppm and it was artificially prepared by using NaCl, KCl, NaHCO₃, MgCl₂, CaCl₂, and Na₂SO₄.

3.2. Characterization of Fluorescein Sodium

FluNa was characterized by using Cary Eclipse fluorescence spectrophotometer available at the Department of Chemistry, Faculty of Science, Chulalongkorn University. Photomultipliers (PMT) voltage was ranged between 400-800 V and slit sizes for both excitation and emission filters were 5 and 10 nm. Standard rectangular fluorimeter quartz cuvette with dimensions of 12.5 mm × 12.5 mm × 45 mm, path length and internal width of 10 mm, and nominal volume of 3.5 ml was used to contain sample inside fluorescence spectrophotometer. The cuvette had four windows and base-polished, and a polyethylene vanned lid was used to provide a liquid-tight seal.

3.3. Detection Limit Determination of Fluorescein Sodium

FluNa solution with concentration of 1,000 ppm was prepared and diluted to 500 ppm, 200 ppm, 100 ppm, 50 ppm, 10 ppm, 1 ppm, 500 ppb, 200 ppb, 100 ppb, 50 ppb, 10 ppb, 1 ppb, 100 ppt, and 10 ppt. Suitable PMT voltages and slit sizes were selected to match with the detectable limit of each concentration. Deionized water, saline water, and tap water were used to compare the results with FluNa solution at very low concentrations.

3.4. Photosensitivity Evaluation of Fluorescein Sodium

FluNa solution with concentration of 100 ppm was prepared and poured into transparent and amber-coloured glass bottles. Three sets of the experiment were designed including (1) all-time exposure to light using transparent glass bottles, (2) all-time concealment using amber-coloured glass bottles, and (3) normal room conditions (approximately 30°C) using amber-coloured glass bottles. Each sample in each set was collected within 1, 2, and 7 days.

3.5. Potential of Hydrogen (pH) Sensitivity Evaluation of Fluorescein Sodium

FluNa solution with concentration of 100 ppm was prepared and equally divided into three beakers. Acetic acid (CH_3COOH) and sodium carbonate (Na_2CO_3) were added into two beakers to make the solution acidic and basic, respectively. The last beaker was left without adding anything to make it neutral. The pH universal indicator papers were used to measure pH of each solution. Each sample was poured into borosilicate glass measuring cylinders for better qualitative comparison.

3.6. Thermal Stability Evaluation of Fluorescein Sodium

FluNa solution with concentration of 100 ppm was prepared and poured into amber-coloured glass bottles. The bottles were soaked in water bath at temperatures of 30°C, 50°C, and 70°C. Each sample of each temperature was collected within time period of 1, 2, 5, and 12 days.

4. Results and Discussion

4.1. Detection Limit Determination of Fluorescein Sodium

The results showed that fluorescence intensity of 1,000-ppm FluNa solution had lower maximum fluorescence intensity than that of 500-ppm solution as shown in figure 4a. In addition, 1,000-ppm solution had emission wavelength at maximum fluorescence intensity of 545 nm, whereas 500-ppm solution had slightly shorter emission wavelength of 541 nm. The physical appearance of 1,000-ppm solution (figure 5a) was darker in fluorescence compared to 500-ppm solution (figure 5b).

Likewise, fluorescence intensity of 200-ppm solution still had lower maximum fluorescence intensity than that of 100-ppm solution as shown in Fig. 4a. Also, 200-ppm solution had slightly longer emission wavelength at maximum fluorescence intensity of 532 nm than that of 100-ppm solution which had emission wavelength of 528 nm. Both 100- (figure 5c) and 200-ppm (figure 5d) solution showed brighter fluorescence than 500- ppm solution and 100-ppm solution emitted brighter fluorescence than 200-ppm solution.

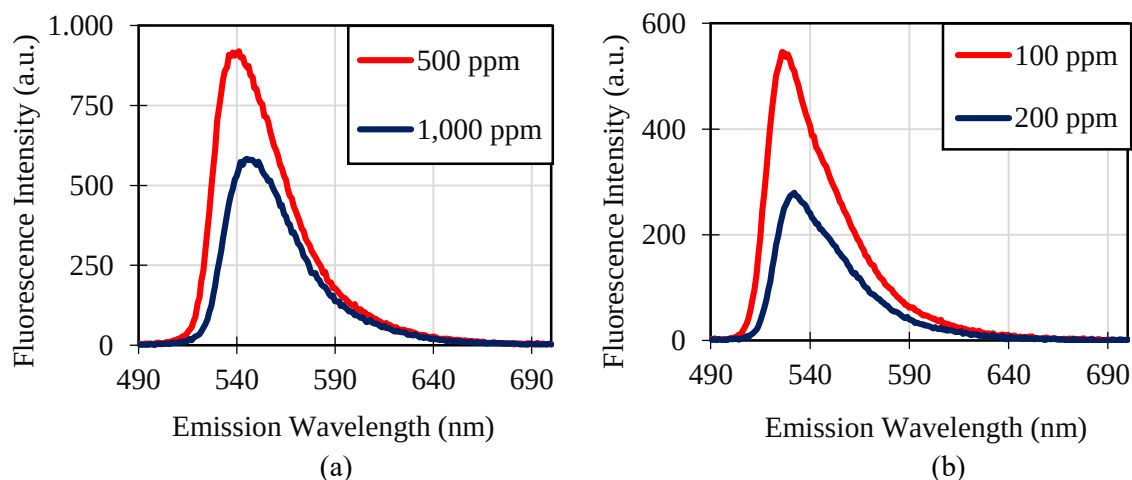


Figure 4. Fluorescence emission spectra of FluNa solution with (a) PMT voltage of 600 V and slit size of 5 nm, and (b) PMT voltage of 500 V and slit size of 5 nm.

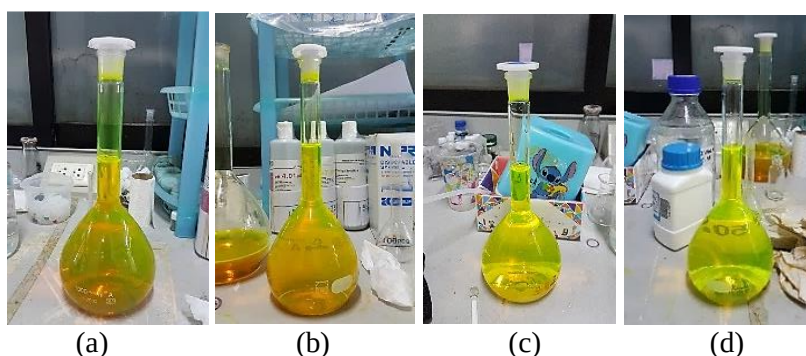


Figure 5. FluNa solution with concentrations of (a) 1,000 ppm, (b) 500 ppm, (c) 200 ppm and (d) 100 ppm.

Next, figure 6 showed that 10-ppm solution had the highest maximum fluorescence intensity. FluNa solution with concentrations higher than 10 ppm showed lower fluorescence intensity with higher concentration, whereas concentrations lower than 10 ppm also showed lower fluorescence intensity with lower concentration, meaning that self-quenching effect had stopped. Similarly, higher fluorescein concentration still had slightly longer emission wavelength at maximum fluorescence intensity than the lower one where the wavelengths were 528, 523, 516, 512, and 512 nm for the concentrations of 100, 50, 10, 1, and 0.5 ppm (500 ppb), respectively. Besides, 50-ppm solution had brighter fluorescence than 100-ppm solution (figure 5d) and below 10 ppm, the fluorescence became fader as shown in figure 7.

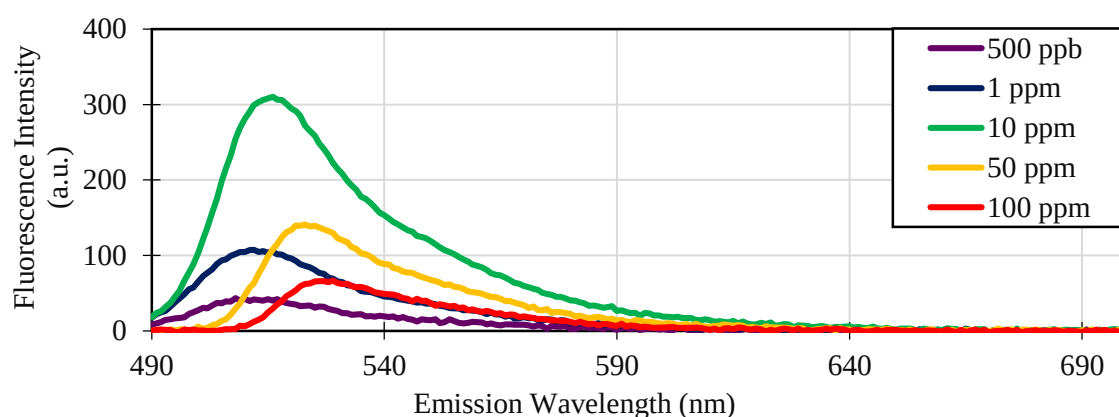


Figure 6. Fluorescence emission spectra of FluNa solution with PMT voltage of 400 V and slit size of 5 nm.

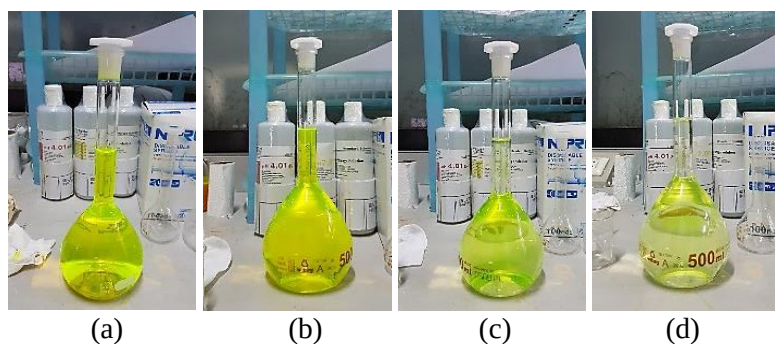


Figure 7. FluNa solution with concentrations of (a) 50 ppm, (b) 10 ppm, (c) 1 ppm, and (d) 500 ppb (0.5 ppm).

Later, as fluorescein concentration was diluted, maximum fluorescence intensity had decreased as shown in figure 8. Emission wavelength at maximum fluorescence intensity of each concentration stopped to decline at 512 nm when the concentration fell below 1 ppm. As shown in figure 9, fluorescence of FluNa solution became fader as the concentration decreased and eventually fluorescence could not be observed by naked eyes when the concentration falls below 100 ppb.

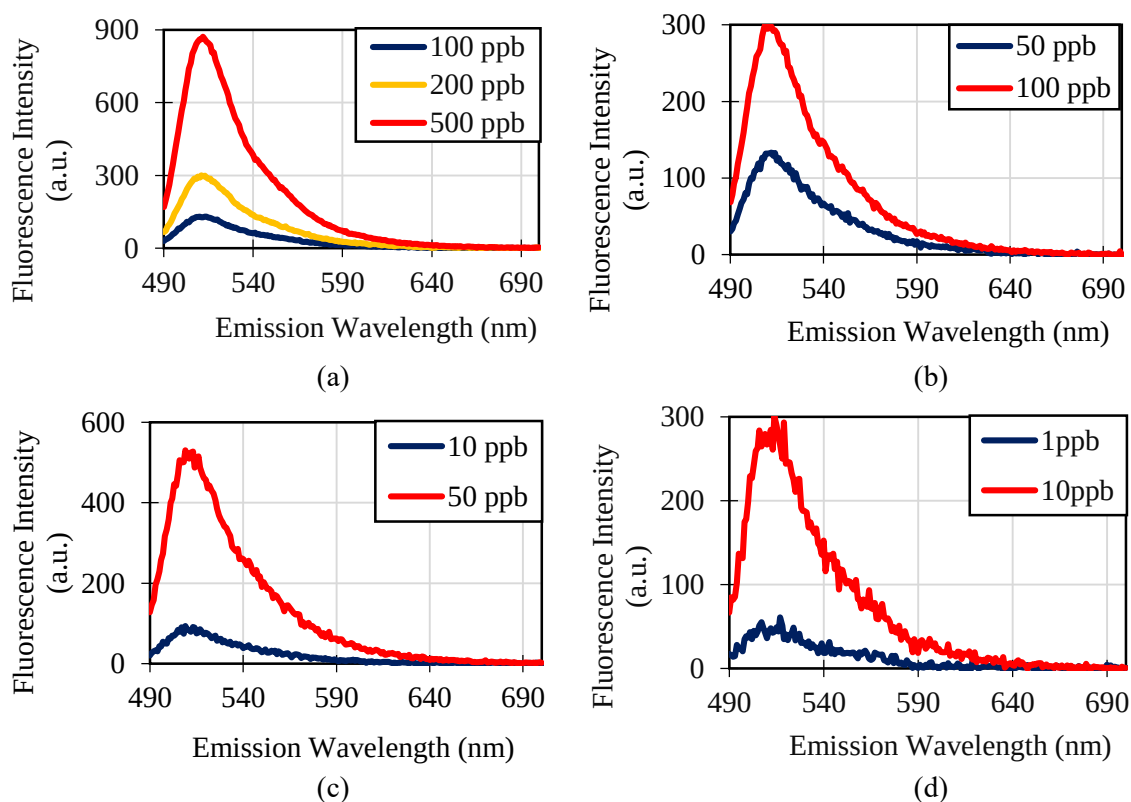


Figure 8. Fluorescence emission spectra of FluNa solution with (a) PMT voltage of 550 V and slit size of 5 nm, and (b) PMT voltage of 600 V and slit size of 5 nm, (c) PMT voltage of 700 V and slit size of 5 nm, and (d) PMT voltage of 800 V and slit size of 5 nm.

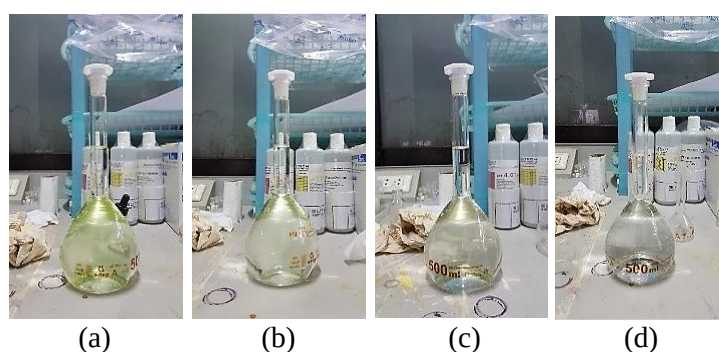


Figure 9. FluNa solution with concentrations of (a) 200 ppb, (b) 100 ppb, (c) 50 ppb, and (d) 10 ppb.

As shown in figure 10, at concentrations of 100 ppt and 10 ppt with slit size of 10 nm, fluorescence intensity peak could not be observed in the spectra, meaning that fluorescein could not be detected. Moreover, fluorescence emission spectra of deionized water, formation water, and tap water also

showed no peak similar to that of 10- and 100-ppt FluNa solution. Therefore, the detection limit of FluNa was determined to be at the concentration of 1 ppb.

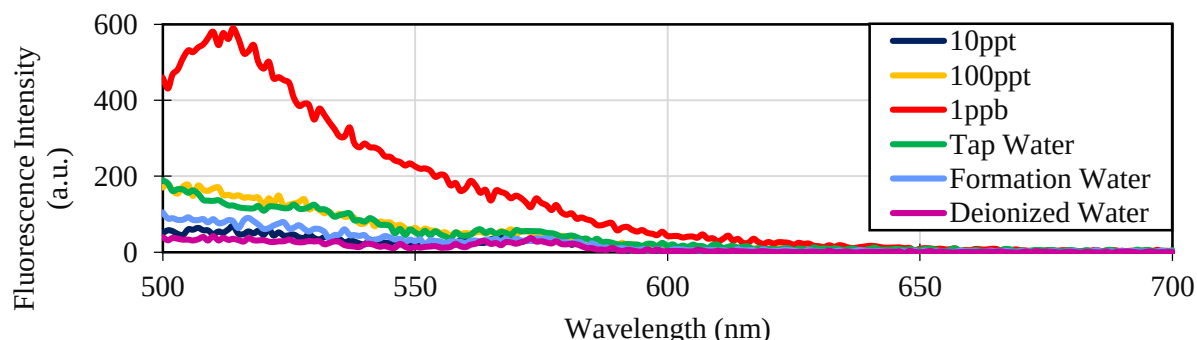


Figure 10. Fluorescence emission spectra of FluNa solution and various types of water with PMT voltage of 800 V and slit size of 10 nm.

4.2. Photosensitivity Evaluation of Fluorescein Sodium

The results showed that FluNa was photodegraded by light. As shown in figure 11, for all-time exposure to light, fluorescence intensity had lost its intensity up to 30% compared to maximum fluorescence intensity of 545 a.u. for 7 days, respectively and fluorescence spectra were slightly shifted to left. Fluorescence of FluNa solution also became darker as time passed as shown in figure 12. On the other hand, both all-time concealment and normal room conditions showed almost no difference in fluorescence spectra for all days. Therefore, amber-coloured glass bottle was considered as an appropriate storage for FluNa solution.

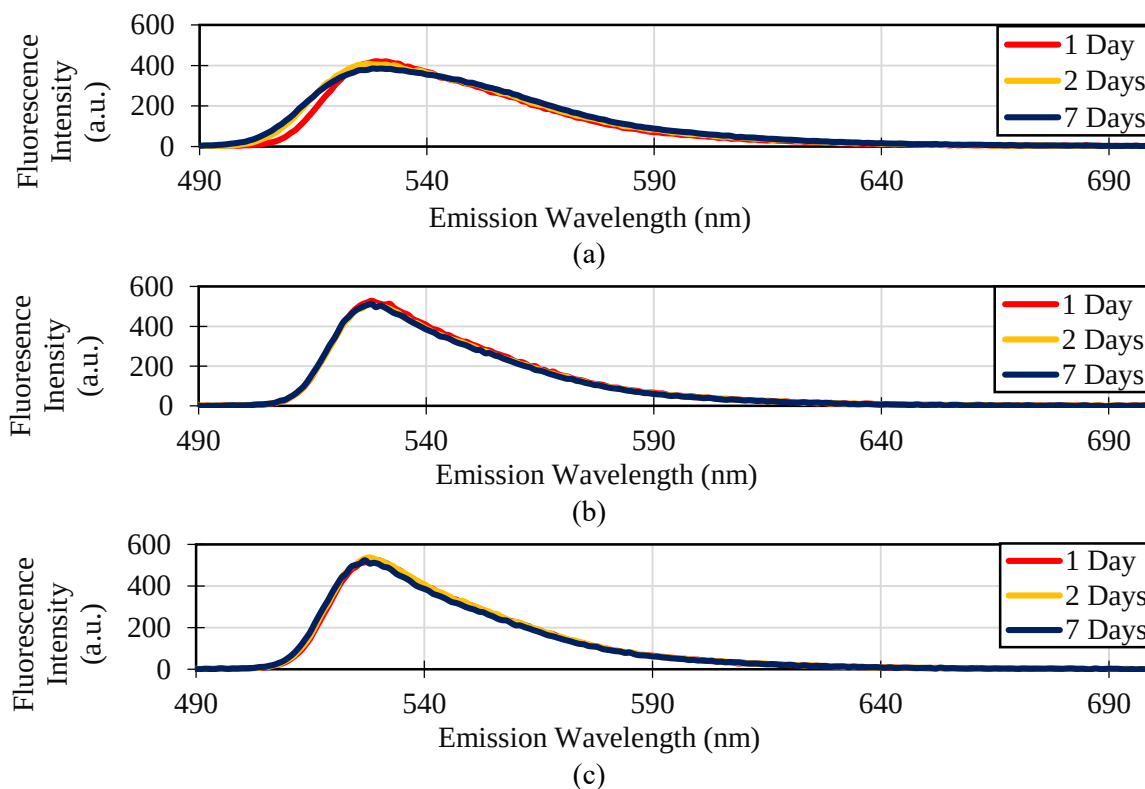


Figure 11. Fluorescence emission spectra of FluNa solution with PMT voltage of 500 V and slit size of 5 nm for (a) all-time exposure to light, (b) all-time concealment, and (c) normal room conditions.



Figure 12. Fluorescence of FluNa solution in all-time exposure to light including 1 day (left), 2 days (middle), and 7 days (right).

4.3. Evaluation of pH Sensitivity of Fluorescein Sodium

FluNa solutions were prepared with pH of 3, 7, and 11 to represent acidic, neutral, and basic conditions, respectively. Figure 13 showed that acidic solution had lower fluorescence intensity and shorter emission wavelength at maximum fluorescence intensity than the others. Moreover, the cylinder containing acidic solution showed darker fluorescence compared to the rest that showed almost the same fluorescence as shown in figure 14. Therefore, fluorescence of FluNa was affected in acidic pH, but unaffected and remained stable in neutral and basic pH.

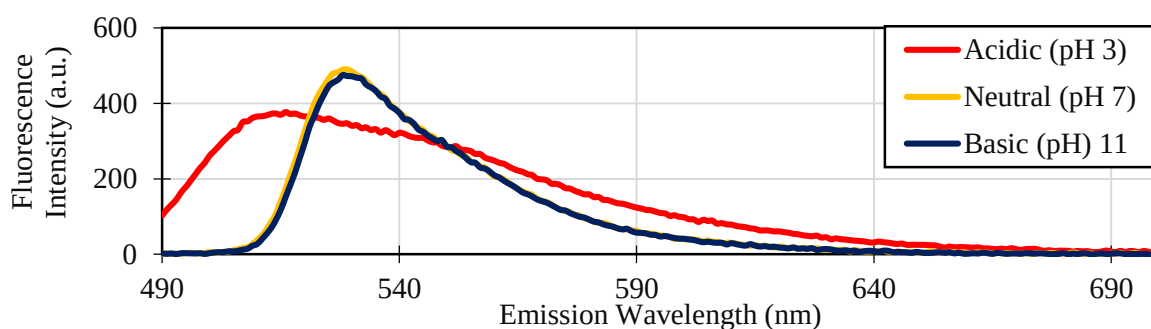


Figure 13. Fluorescence emission spectra of FluNa solution with different pH with PMT voltage of 500 V and slit size of 5 nm.

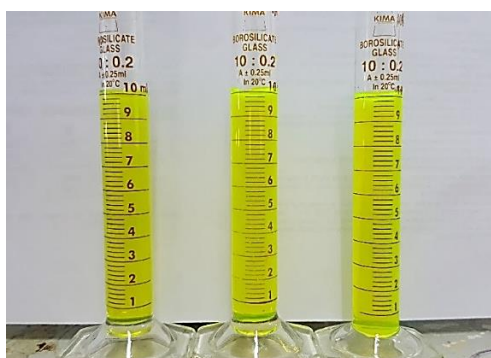


Figure 14. FluNa solution with different pH in borosilicate glass measuring cylinders including pH 3 (left), pH 7 (middle), and pH 11 (right).

4.4. Evaluation of Thermal Stability of Fluorescein Sodium

As shown in figure 15, fluorescence intensity of FluNa solution was not affected by temperature up to 70°C for 12 days, meaning that FluNa could be used in petroleum reservoir under these temperature ranges without substantial thermal degradation.

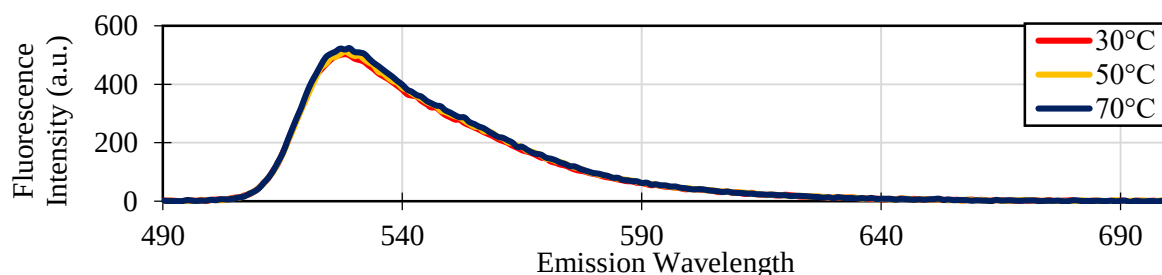


Figure 15. Fluorescence emission spectra of FluNa solutions at different temperatures for 12 days with PMT voltage of 500 V and slit size of 5 nm.

5. Conclusions

In this study, fluorescein concentration at 10 ppm was critical concentration that reversed relationship between fluorescence intensity and fluorescence concentration. Fluorescence of fluorescein could not be observed by naked eyes at concentrations below 100 ppb, whereas its detection limit by fluorescence spectrophotometer could be lowered to 1 ppb. Fluorescence of fluorescein was photodegraded by light up to 30% when stored inside transparent glass bottles and being exposed to light for 7 days and fluorescence of the solution became darker with time. On the other hand, fluorescence intensities of FluNa solution stored inside amber-coloured glass bottles in both all-time concealment and normal room conditions were almost identical. Fluorescence spectra of the solution at pH of 3 had lower fluorescence intensity and shorter emission wavelength at maximum fluorescence intensity than the solutions at pH of 7 and 11 that were mostly identical. Hence, the storage conditions for FluNa solution were recommended to be stored inside amber-coloured glass bottle to prevent photodegradation with pH 7 or above. Fluorescence of fluorescein was not affected by temperature in the range of 30-70°C for 12 days. This study was the first step of FluNa investigation in applications of petroleum industry. Further investigations shall focus on fluorescein adsorption on the rock matrix and appropriate fluorescein concentration used in the pilot project can be determined. Simultaneous use of FluNa with other fluorescent tracers shall also be evaluated.

Acknowledgment(s)

The authors would like to express our gratitude to PTT Exploration and Production PCL for supporting formulation of formation water, and The King Prajadhipok and Queen Rambhai Barni Memorial Foundation for providing research scholarship.

References

- [1] M. Aparecida de Melo, C. R. de Holleben, and A. R. Almeida, "Using Tracers to Characterize Petroleum Reservoirs: Application to Carmopolis Field, Brazil," *Soc. Pet. Eng.*, March 2001.
- [2] N. Gs and B. G. Desai, "Selection and Identification of Interwell Tracers for Reservoir Characterization of Clastic Rock: A Case Study from Cretaceous Himmatnagar Sandstones," *Pet. Petro. Eng. J.*, vol. 2, no. 7, 2018.
- [3] D. Tayyib, A. Al-Qasim, S. Kokal, and O. Huseby, "Overview of Tracer Applications in Oil and Gas Industry," *Soc. Pet. Eng.*, October, 2019.
- [4] J. Jacobs, "Fluorescein Sodium What is it?," *J. Oph. Photography.*, vol. 14, no. 2, pp. 62, December 1992.
- [5] P. Pramotethana, "Photoluminescence Extraction from Scales of Seabass Lates calcarifier Bloch, 1790", *Chulalongkorn University*, 2002.
- [6] P. T. So and C. Y. Dong, "Fluorescence Spectrophotometry," *Encyclopedia of Life Science*, 2002.
- [7] S. Sahasithiwat, "Emerging of Life! A Memo of Light Producer by Using Fluorescent Diode of Organic Substance," *J. Mat. Tech.*, vol. 79, pp. 33-40, September 2015.
- [8] C. Areejitranusorn, "Fluorometer," in *Scientific Instruments*, *Klunghana Witthaya Press*, 2001.