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Fluorescence Lifetime Investigation and Characterization of Dysprosium and Terbium Doped Taggants

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ABSTRACT

An investigation was made into the use of fluorescent materials called taggants that would give a better discrimination against the background interference arising from hydrocarbons and having a longer lifetime than other sources of interference. Borosilicate and tellurite glass host were doped with dysprosium and terbium rare earth elements. Their absorptions and fluorescence lifetime characterisation was used to determine their interaction and compatibility with cyclohexane and crude oil. The fluorescence lifetime test established Dysprosium doped glasses as the optimum taggants for cyclohexane and terbium doped tellurite glass as the ideal taggants in crude oil and both achieving better lifetime discriminations respectively.

1. Introduction

Unlike most organic fluorescence compounds having lifetime in 10^{-9} s to 10^{-6} s, the lifetime of lanthanide fluorescence are in milliseconds, thus interfering fluorescence emanating from other species may be allowed to fade away before lanthanide fluorescent measurement is taken. This forms the basis of lifetime measurement [1]. Fluorescence lifetime is defined by the average time the molecule spends in the excited state before it returns to the ground state. Fluorescence lifetime measurement system elucidates the study of energy transfer in molecules which fluoresces when they absorb UV/Vis wavelength by providing details of their spectra measurement and lifetime decays at same time. It uses a fast photodiode to provide a complete time resolved spectrum in a single measurement and the measurement is independent of signal intensity from external forces like absorption and scattering or even concentration [2]. Therefore the fluorescence decay times can be measured without the constraints imposed by fluorescence fluctuation measurements. Two main methods are generally applied: frequency-domain and time-domain data acquisition; however the time decay sequence was employed. The time domain measurement assumes that when photons are absorbed, the excited molecules move into a brief transition state and subsequent signal emitted are obtained as a measurement of pulse widths [3].

The fluorescence lifetime measurement takes into account the average time the molecule spends in the excited state before returning to the ground state usually through fluorescence emission [4]. Research has shown that the fluorescence taggant in a stable host that would fluoresce beyond sources of interference and having a longer fluorescence lifetime [5] would be advantageous to the identification of different sources of hydrocarbon. Similarly, studies on sol-gel derived luminescent thin films [6] doped with rare earth (RE) complexes ($Tb^{3+}$and Eu^{3+}) showed longer fluorescence lifetime in gel thin films and improved thermal stability. In contrast, Dyes transitions are symmetry allowed and in general in-homogenously broadened by the local environment and often give high oscillator strengths and short lifetimes. Furthermore an appropriate glass host of RE dopants offer an excellent potential method of molecular dispersal of rare earths as tags because materials can be designed to efficiently absorb light and certain elements, like Terbium (green) and Dysprosium (reddish-yellow) which fluoresces and emits a characteristic luminescence colour have been severally observed and reported [7, 8]. In addition with modern spectroscopic instrumentation, several analyst having nearly identical fluorescence spectra can often be determined simultaneously by taking advantage of differences in their fluorescent life times or differences between the phase angles in their excitation and emission spectra rather than between their fluorescence spectral band intensities. This work will therefore investigate the fluorescent lifetime characterization of borosilicate and telluride glass matrices doped with dysprosium and terbium rare earths which would achieve a longer fluorescence lifetime and their compatibility with cyclohexane and crude oil.

2. Material and Methods

2.1 Materials

All of the chemicals were obtained from Sigma Aldrich. Zinc oxide, silicon dioxide, terbium III chloride hexahydrate and dysprosium III chloride hexahydrate were all of 99.9% purity while boron oxide, tellurium dioxide, lithium carbonate and cyclohexane were 99% purity and Crude oil sample obtained from NALCO Britannia platform, Aberdeen, Scotland.

2.2 Synthesis of Zinc Borososilicate Glass

The chemical composition of zinc borosilicate glass used was $60ZnO + 20B_2O_3 + 20SiO_2$, (Mol%). The batches of the chemical mix weighed approximately 7g (ZnO = 4.5717g, B_20_3 = 1.3034 g, SiO_2 = 1.1253 g). The composition of the doped borosilicate glass was $(60\text{-}x)\ ZnO + 20B_2O_3 + 20SiO_2 + xLa^{3+}$ (where La^{3+} = Tb and Dy), and values of x corresponds to mol% increase from 0.5, 1.0, 1.5 and 2.0 and subsequent decrease of ZnO composition. The residue weight was subtracted from each glass batch, then batch mixture transferred to an agate ball mill and ball milled for 3 minutes obtaining a homogenous mixture. The mixture was then transferred to a platinum crucible whose initial weight had been noted and then introduced into the Carbolite 1600 high temperature chamber furnace at a controlled temperature program from 400 °C to 1300 °C. At 1300 °C the melt was poured into a heated brass mould at an annealing temperature of about 150 °C which reduces glass cracking [9].

2.3 Synthesis of Tellurite Glass

The chemical composition of tellurite glass was $80TeO_2 + 20LiCO_3$, (Mol%). The batch of the chemical mix measured approximately about 7 g (TeO_2 = 6.2741 g, $LiCO_3$ = 0.1037 g). The composition of doped tellurite glass composition was $(80\text{-}x)\ TeO_2 + 20LiCO_3 + xLa^{3+}$ (where La^{3+} = Tb and Dy) and values of x corresponding to an increase in mol% from 0.5, 1.0, 1.5

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and 2.0 with equivalent decrease in of TeO_2 composition. Each glass batch was weighed into agate ball mills. The mixture was then ball milled for 3 minutes and transferred to a platinum crucible whose initial weight had been already weighed. The platinum crucible was introduced into 1600 Carbolite high temperature furnace at a controlled temperature program from 400 °C. At 800 °C the melt was poured into the hot plate brass mould at annealing temperature of 1500 °C which reduce cracking of the glass [9].

2.4 Preparation of Stock Solution

A stock solution of 100 ppm of crude was prepared by pipetting 0.5 mL of the crude oil into 50 mL cyclohexane. 10 ppm were then prepared by a 10 x dilution in cyclohexane and wavelength determined Using the UV/Vis absorption spectrometer, the absorption maxima of cyclohexane was 261 nm and crude oil at 219 nm while fluorescence spectrometer determined the emission wavelength of cyclohexane to be 523 nm and crude oil at 350 nm.

2.5 Characterization of Taggants

Using Perkin Elmer Lambda 900 UV/Vis and the Perkin Elmer LS50B fluorescence spectrometer, Terbium doped borosilicate glass had absorption maxima at 350 nm and 483 nm while the terbium doped tellurite glass had absorption maxima at only 484 nm. The dysprosium doped borosilicate glass had absorption maxima at 349 nm and 452 nm while the dysprosium doped tellurite glass was observed to be 453 nm and 481 nm respectively.

2.6 Fluorescence Lifetime Characterization

Using FLS 900 Edinburgh fluorescence lifetime spectrometer, characterization of each glass batch was carried out using the manual lifetime scan process then performing an exponential frit to determine their exponential curve which gives the fluorescence decay time. This involved the use of each respective glass excitation wavelengths and emission wavelengths obtained from UV/Vis absorption and fluorescence spectrometer. However some parameters were kept constant.

2.7 Theory of Fluorescence Lifetime Characterization

The sample was placed in the sample compartment and excited with the micro flash lamp. This causes a histogram to build up in correlation to the pulse from the excitation (START) and the first observation of the fluorescence photon (STOP). It is the histogram that forms a typical spectrum. Individual photons emitted are detected by a photomultiplier tube forming the pulse height. The constant fraction discriminator (CPD) retrieves the timing information from the detector output while the voltage output is defined by the time to amplitude converter (TAC), then the analogue to digital converter (ADC) interprets the defined voltage and the result is stored in the memory (MEM). Also using the exponential frit, the exponential curve is interpreted and decay time obtained and recorded as growth and decay of the fluorescence of the sample [4].

3. Results and Discussion

The lifetime characterization of doped glasses were analyzed using their respective excitation and emission wavelengths as observed and keeping other parameters Constant.

From the Fig. 1 the average decay time decreases as the concentration increased in dysprosium borosilicate glass and only a small variation in decay time of between 349 nm and 425 nm while terbium borosilicate glass in contrast had decay time increasing as concentration increased. The results of 1.5 mol% of terbium borosilicate glass showed inverse variation in values and it got saturated at 3 mol% concentration. The standard deviation indicated a gradual decrease of deviation from 0.5-2.0 mol% at 483 nm excitation and could be as a result of increase in concentration causing equivalent increase in decay time with higher sensitivity and less deviation.

Dysprosium tellurite glass lifetime decreases as the concentration increased showing that the dysprosium molecule in both cases have experienced shorter fluorescence growth and decay sequence as concentration increased. Moreover there were close values of decay time at 453 nm and 481 nm as shown in Fig. 2 below showing statistically, high reproducibility of result. Also in contrast, terbium tellurite glass appeared to be parallel. Furthermore the Table 1 of six mean replicates of decay time at various concentrations shows that fluorescence lifetime decay sequence of terbium tellurite glass almost remained constant even as concentration increased.

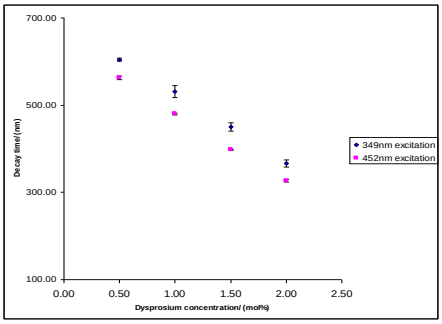

Fig. 1 Graph of decay time against 1% mol concentration of dysprosium borosilicate glass at 349 nm and 452 nm

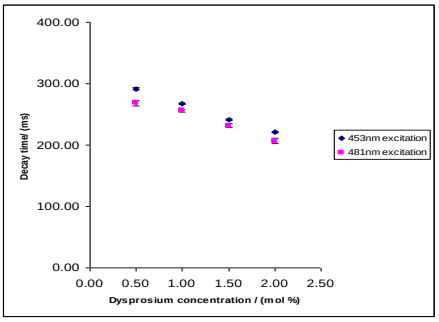

Fig. 2 Graph of decay time against 1% mol concentration of dysprosium tellurite glass at 453 nm and 481 nm

Table 1 TBTEG fluorescence lifetime mean decay count and concentration

Decay count (μs)	883.90	882.09	880.59	876.84
Concentration/ mol %	0.5	1.0	1.5	2.0

The fluorescence growth and decay sequence of terbium borosilicate glass was the highest around 2,000,000 microseconds followed by terbium tellurite glass at 1,500,000 microseconds. The least decay sequence was recorded with dysprosium tellurite glass 700,000 microseconds while dysprosium borosilicate glass had lifetime value of around 100,000 microseconds as shown in Fig. 3 below.

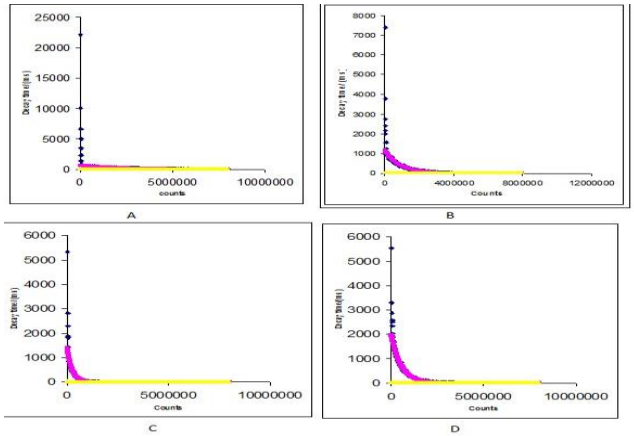

Fig. 3 Fluorescence growth and decay sequence of terbium borosilicate glass (A), terbium tellurite glass (B), dysprosium borosilicate glass (C) and dysprosium tellurite glass

Additionally dysprosium tellurite glass and dysprosium borosilicate glass demonstrated similar relationship of decrease in decay count as the concentration increases which means that at higher concentration it experiences a shorter decay sequence. However non conformity of terbium borosilicate characterisation in cyclohexane using lifetime characterization and was investigated with two factor ANOVA with replication.

Table 2 ANOVA results for terbium borosilicate glass characterisation in cyclohexane

Source of Variation	SS	Df	MS	F	P-Value	F Crit
Sample	7594.044	3	2531.348	0.976067	0.436214	3.4903
Columns	90.67343	2	45.33672	0.017481	0.982695	3.88529
Interaction	1747.138	6	291.1896	0.11228	0.993129	2.996117
Within	31120.99	12	2593.415			
TOTAL	40552.84	23				

Thus since the value of Fcrit in the Table 2 is greater than Fexp at 0.976 the results shows no significant difference between the samples and also Fcrit for column interaction was less the corresponding Fexp at 0.017 indicating that there was no significant difference. Therefore the variation not induced by random error. It can also be confirmed that the different days (row) of experiments caused no interaction while they had a significant interaction due to concentration (column).

In terbium tellurite glass characterisation in cyclohexane, at 0.50 and 1.0 mol% the mean values increased while at 1.5 and 2.0 mol% concentration subsequently decreased and beyond the scope of the project but could be further investigation. However investigation with ANOVA single factor at 95% confidence limit to determine if the different days of the experiment induced variations in the result from the analyses was carried out.

Table 3 ANOVA results for terbium tellurite glass characterisation in cyclohexane

Source of Variation	SS	Df	MS	F	P-Value	Fcrit
Between Groups	712.0047	3	237.3349	8.863544	0.006355	4.06618
Within Groups	214.2122	8	26.77652			
TOTAL	926.2169	11				

From the result above in Table 3, Fcrit value is 4.066 at 95% confidence limit and less than Fexp value which is 8.863, then statistically, the fluorescence was affected by the different days of the analyses and further investigation can be made with new repeats at different days.

The fluorescence lifetime characterization of dysprosium tellurite and dysprosium borosilicate glass in crude oil showed that the decay counts decreased as the concentration increases as seen in Fig. 4 and 5 proving the compatibility of dysprosium borosilicate and tellurite glass with crude oil and detected as a taggant in the sample.

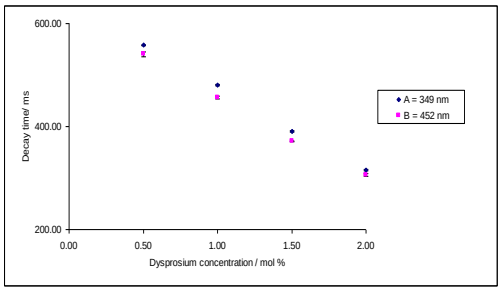

Fig. 4 Lifetime characterisation of DYTEG in crude oil at 453 nm and 481 nm excitation wavelengths using 574 nm emission wavelength

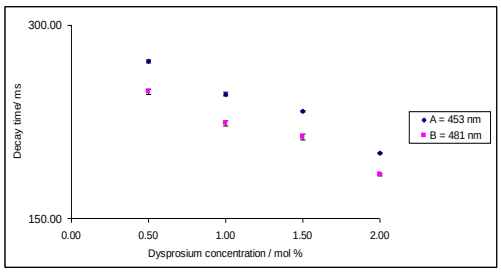

Fig. 5 Fluorescence lifetime characterisation of DYBSG in crude oil at (A) 349 nm and (B) 452 nm excitation wavelengths using 574 nm emission wavelength

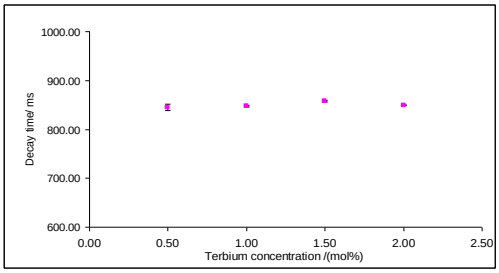

Fig. 6 Lifetime characterisation of TBTEG in crude oil at 484 nm excitation wavelength and 545 nm emission wavelength

Also a comparison of terbium tellurite glass and terbium borosilicate glass showed that terbium tellurite glass values increased slightly in decay count as the concentration increases as shown in Fig. 6.

However terbium borosilicate glass showed unusual characterization in both crude oil and cyclohexane and a two way ANOVA without replication was performed for each excitation wavelength to determine the sample concentration interaction with the mean value of different days of the analysis.

Table 4 Terbium borosilicate ANOVA result at 350 nm excitation wavelength

Source of Variation	SS	Df	MS	F	P-Value	F Crit
Rows	6899.13996	3	2299.713319	8.511887	0.0139465	4.75705519
Columns	200.7362	2	100.3681	0.371491	0.7045274	5.14324938
Error	1621.06007	6	270.1766778			
TOTAL	8720.93623	11				

The Table 4 above shows the Fexp for rows was greater than Fcrit and it indicates that there was significant difference between the samples concentrations. Also, the Fcrit for column was greater than Fexp and it shows that there was no significant difference between the different days of the measurement, thus no sample concentration interaction with the different days of the analysis.

4. Conclusion

The characterization of glass taggants with the fluorescence lifetime spectrometer showed that terbium borosilicate glass had the highest of decay count and the least was dysprosium tellurite glass. Also dysprosium borosilicate glass was around 300-650 µs while terbium tellurite glass was within 875-885 µs and achieved an enhanced lifetime characterization than all taggants. The lifetime determination of compatibility of the taggants showed that both terbium tellurite and terbium borosilicate glass could not discriminate against cyclohexane while dysprosium tellurite and dysprosium borosilicate glass had similar lifetime characterization and remained compatible as they were detected in the solvent. Finally, the determination of their compatibility with the crude oil sample identified only terbium borosilicate glass as not been compatible, while the other taggants had good compatibility and discrimination as over their fluorescence lifetime characterization.

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