

Spectral Fingerprints of Weathered Crude Oils

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ABSTRACT. A newly patented method for spectral characterization of petroleum oils has been applied in fingerprinting crude oils under different weathering conditions. The method is based on measuring the time-resolved fluorescence (TRF) spectra at narrow temporal gate-widths within the time span of the excitation laser pulse. The fingerprints are constructed in terms of contour diagrams relating the intensities of the measured TRF spectra of each crude oil to the fluorescence emission wavelength and the position of the narrow time-gate at which the spectra were measured, simultaneously. The five marketed crude oils of Saudi Arabia; namely, Super Light, Extra Light, Light, Medium, and Heavy, were used in the study. For each oil grade, five fingerprints were constructed which corresponded to five different moderate weathering conditions: 1) neat, 2) weathering due to seawater, 3) weathering due to wind vaporization, 4) weathering due to wind vaporization and sunlight, and 5) weathering due to seawater, wind vaporization and sunlight combined. The fingerprints show the presence of a pattern which changes systematically with the oil grade even in the case of the weathered oils. This systematic change provides a powerful tool in identifying the weathered spilled crude oils and, consequently, connecting them to the original non-weathered oil shipment. The paper describes the procedure used to measure the TRF spectra and shows the unique fingerprint of each oil case. It also presents a quantitative method that relates the area-under-the-curves of the TRF spectra to the grade of the weathered oils.

Introduction

Oil identification using fluorescence methods is an approved technique by the American Society of Testing and Materials; method D3650-78 (ASTM, 1978), and by the U.S. Coast Guard (USCG, 1977). The main advantages of the fluorescence methods are their high sensitivity to the aromatic components of petroleum, their capability to be applied remotely, and the fact that they do not require elaborate sample preparation. All such properties enable them to be utilized in identifying oil spills in water directly.

There are several fluorescence methods that have been used in oil identification, the most common of which are (a) Excitation and Emission Spectroscopy (without time gating) (Parker, 1968; Eastwood *et al.*, 1978; Bentz, 1976), (b) Synchronous and Variable Synchronous Spectroscopy (Lloyd, 1971, 1974; Shen 1984), (c) Difference and Derivative Spectroscopy (Poro & Terhark 1976; Cook *et al.*, 1977), (d) Contour (Total Luminescence) Spectroscopy (Warner *et al.*, 1977; Giering & Horing 1977), and (e) Lifetime

Measurement and other remote methods. The latter technique is of special interest because it can be used in remote sensing.

As early as 1971, (Fantasia *et al.* 1971, 1974) suggested that lifetime measurements might add another tool for crude oil characterization. This was taken a step further by (Measures *et al.* 1974, 1975), who conducted experiments to study the variation of the fluorescence decay time as a function of wavelength across the emission profile for a variety of materials. They concluded that, in the case of a complex mixture of molecules, this variation could be used to discriminate between very similar substances, i.e., it could be used as a tool for true fingerprinting. The same method was also applied remotely by (Camagni *et al.* 1988, 1991), who employed a pulsed laser of 4-ns pulse width as an exciting source. Because direct deconvolution of the time response was not practical in their case, instead, they used a power-regression scheme and fitted their data to simple decay curves, which were then analyzed for several commercial crude oils. In another investigation, (Quinn *et al.* 1994) used a sophisticated detection system, including a streak camera, to obtain selected spectral and temporal characteristics of the fluorescence spectra of 400 crude oils. They subjected their data to linear discriminant analysis to obtain a scheme by which oils can be identified remotely.

In the present paper, we employed the temporal behavior of the fluorescence spectra as a tool to characterize crude oil also, except that we used a slightly different approach (Hegazi *et al.*, 2001, 2003). We used a finite laser pulse also, but instead of measuring lifetimes at particular wavelengths, we monitored the variation in the spectral profile of the emitted fluorescence bands as a function of time. Because crude oils constitute different complex mixtures of molecules with a medley of lifetime decay curves, the wavelength-resolved spectrum of each crude oil is expected to vary when measured at different times, just as the lifetime decay curves vary when measured at different wavelengths. This variation in the wavelength-resolved spectra is different for different crude oils, and therefore could be thought of as another possible tool for oil discrimination if an adequate and standard time sampling procedure is employed. We concentrated on determining the fingerprints of weathered crude oils of the five grades of crude oil that Saudi Arabia markets, namely, Super Light, Extra Light, Light, Medium, and Heavy were used. We subjected each one of these grades to five different weathering conditions and produced their fingerprints for each case. We also measured certain areas under the TRF spectra and related them to the oil grade in each weathering case. The five weathering conditions were 1) neat, 2) weathering due to seawater, 3) weathering due to wind vaporization, 4) weathering due to wind vaporization and sunlight, 5) weathering due to seawater, wind vaporization, and sunlight.

Materials and Methods

The technique used in this work relies on measuring the fluorescence spectra of the oils at consecutive narrow time gates within the time span of the laser pulse. Figure 1 shows the temporal profiles of the laser pulse at 280nm and the resulting crude oil fluorescence signal at 420nm. The time gates (TG) were mainly of 5-ns widths and were chosen in a specific manner such that the maximum of the laser intensity profile represented a reference by which the locations of the time gates are identified. The TGs are marked here as TG -5, TG 0, TG 5, TG 10, and TG 15 so that the left edge of each TG could be easily recognized. For example, TG 0 is a time gate of 5-ns width beginning

exactly at the peak of the laser pulse, TG 5 is a time gate of 5-ns width beginning 5 ns after the peak of the laser pulse, and so on. The whole concept behind measuring the TRF spectra at these narrow gate widths is to investigate how the nonlinear disturbance, presented here by the shape of the laser pulse, affects the collective temporal/spectral fluorescence emission of the crude oils. The interesting advantage of using the shape of the laser pulse as the nonlinear disturbance and measuring the TRF spectra within its time span is that the convolution of the resulting TRF spectra with the laser pulse will be dependent only on the shape of the laser pulse but not on its intensity. This is a desired property especially if the measurements are to be made remotely where it would not be practically possible to know the intensity of the laser radiation that is arriving at the location of the crude oil target.

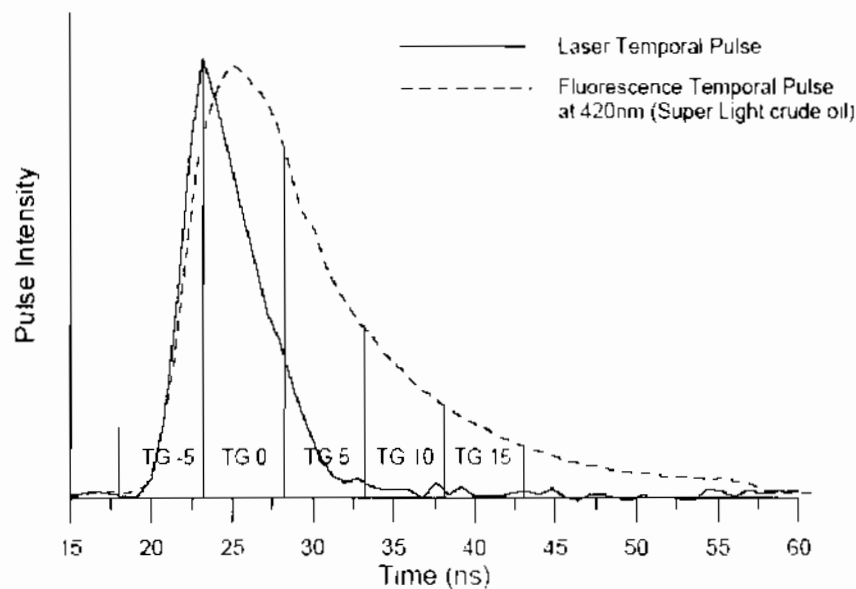


Fig. (1). The temporal profiles of the laser excitation pulse and the fluorescence signal of Super Light crude oil at 420nm. The vertical lines represent the beginnings and ends of the selected time-gates of 5 ns widths.

From the TRF spectra of each crude oil sample a fingerprint is constructed in the form of a contour diagram in which the intensities of the spectra are plotted as functions of time gate and wavelength simultaneously. Before doing so, however, the spectra must be normalized first in some manner. This is done here by either normalizing the intensities of the spectra so that they are all unity at a specific wavelength or by simply normalizing the areas under the curve to unity. In addition to the fingerprints, areas under the curves were also measured to provide quantitative rather than qualitative results.

A schematic sketch of the experimental setup (Hegazi *et al.* 2001, 2003) is shown in Fig. 2. The crude oil samples were placed in quartz cuvettes of 4-mm width and were excited by 280-nm pulsed laser radiation from a YAG-pumped dye-laser system (Spectra-Physics). The resulting fluorescence was dispersed by an $f/3.4$ monochromator (Applied Photophysics), and detected by a photomultiplier (Hamamatsu R1564U-07). An EG&E signal processor (Model 4402) coupled with a gated-integrator (Model 4422), and a PC computer were then used to sample and digitize the acquired fluorescence signal according to specific time sampling points (SP) and time gate-widths (GW), and finally to analyze the data numerically.

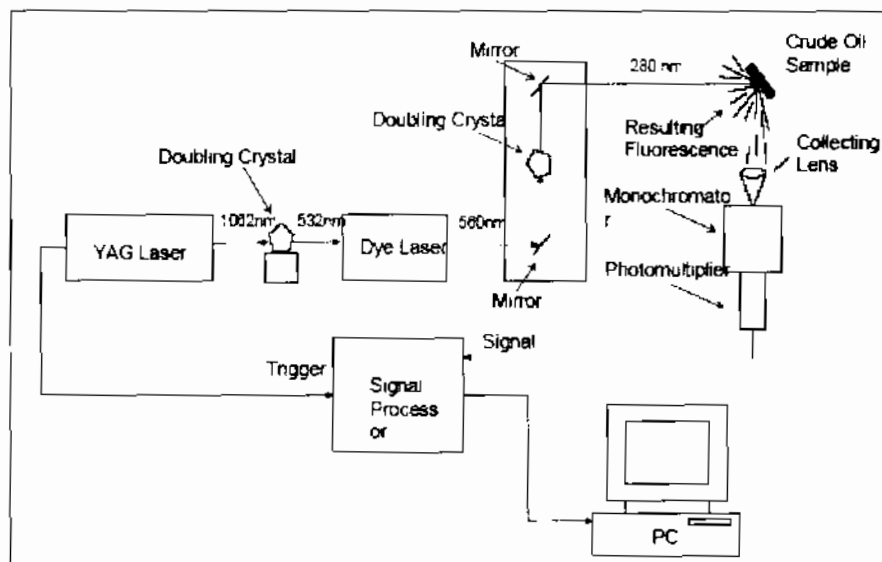


Fig. (2). Schematic setup of the experiment.

Five sets of the five marketed Arabian crude oils, i.e. Super Light (S), Extra Light (E), Light (L), Medium (M), and Heavy (H), were used at different weathering conditions. These five sets correspond to the following conditions.

- 1) Neat (fresh) condition, i.e. no weathering involved.
- 2) Exposure to wind and sunlight condition, in which the originally neat samples were placed in glass containers and placed on top of the roof of the building for 4 consecutive days. The average daylight temperature was 38°C while the humidity ranged between 40-60%.
- 3) Exposure to seawater, in which 20mL of the originally neat oil samples were poured on top of 500mL of seawater and were kept for 4 days in a dark and closed plastic containers. The temperature and humidity of the storage place were kept stable at 20°C and humidity of ~15% respectively.
- 4) Volatilization by wind condition, in which the originally neat crude oil samples were placed in open glass containers inside a fume-hood. The samples were removed after 2 days, after which the volume of the Super Light oil sample was found to be reduced by 50%. The temperature and humidity inside the fume hood were stabilized at 20°C and ~15%, respectively.
- 5) Exposure to wind, seawater, and sunlight condition, in which the originally neat crude oil samples were poured on top of seawater in open plastic glass containers and then placed on top of a building roof for 4 days. The average daylight temperature was 38°C while the humidity ranged between 40-60%.

Results and Discussion

Figure 3 shows the non-gated fluorescence spectra (time gate-width = 20ns) of the five grades of the marketed Saudi Arabian crude oils (in neat condition) when excited by the 280nm laser wavelength. It can be seen that, with the exception of a prominent shoulder at 370nm appearing in the case of the Super Light grade, the shapes of all the

spectra are basically identical, indicating that such spectra cannot serve as useful information from which crude oils could be distinguished from one another.

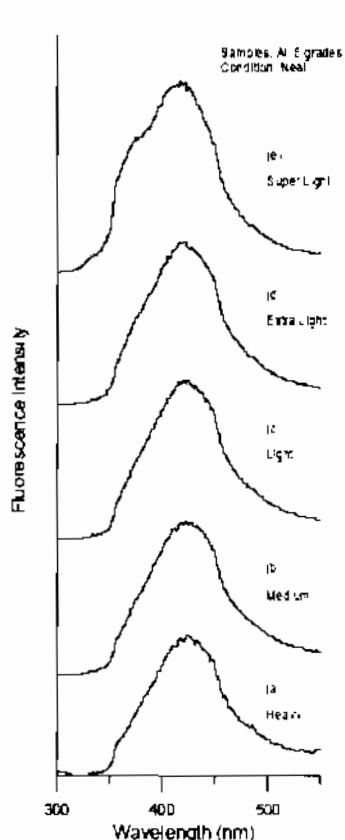


Fig. (3). Non-gated Fluorescence Spectra of all neat crude oils.

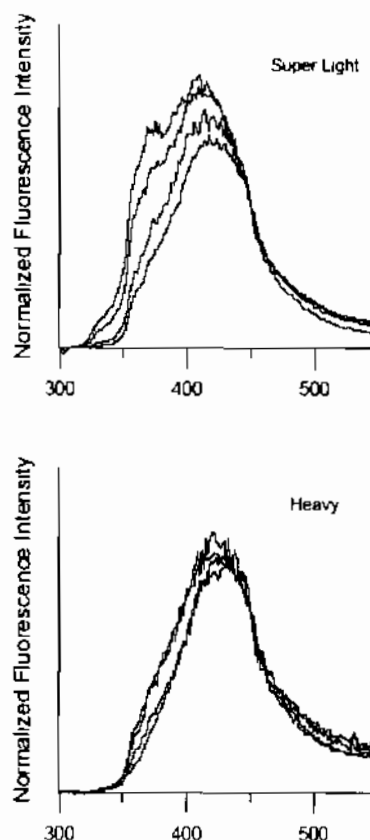


Fig. (4). Time-resolved Fluorescence Spectra of neat Super Light and Heavy crude oils.

Instead of measuring the dc-convolved lifetimes of the fluorescence signal as functions of emission wavelength, our approach is based on measuring the shapes of the fluorescence spectra as functions of time gate when the fluorescence emission spectra are detected at small consecutive time gates. Figure 4 shows the TRF spectra of the neat Super Light and Heavy when measured at TG 0, 5, 10, and 15 as examples to show how the TRF spectra are different in each case. The intensities of all of these spectra were normalized to unity at 450nm. Contour diagrams constructed from each set of the oils' TRF spectra are shown in Fig. 5. It can be seen in Fig. 5 that the contour diagrams show an unmistakable trend with respect to the oil grade, not only in pattern but also in intensity level. The higher the crude oil grade the higher the intensity levels appear in the contour diagram toward later times. For example, the intensity levels above 1.6 appear only in the Super Light grade and the 1.3 and 1.4 levels recede towards shorter time in a gradual manner as the oil quality degrades. It should be emphasized here that the intensity levels in all of the contour diagrams are indeed relative to each other since all of the TRF spectra have been normalized in the same way.

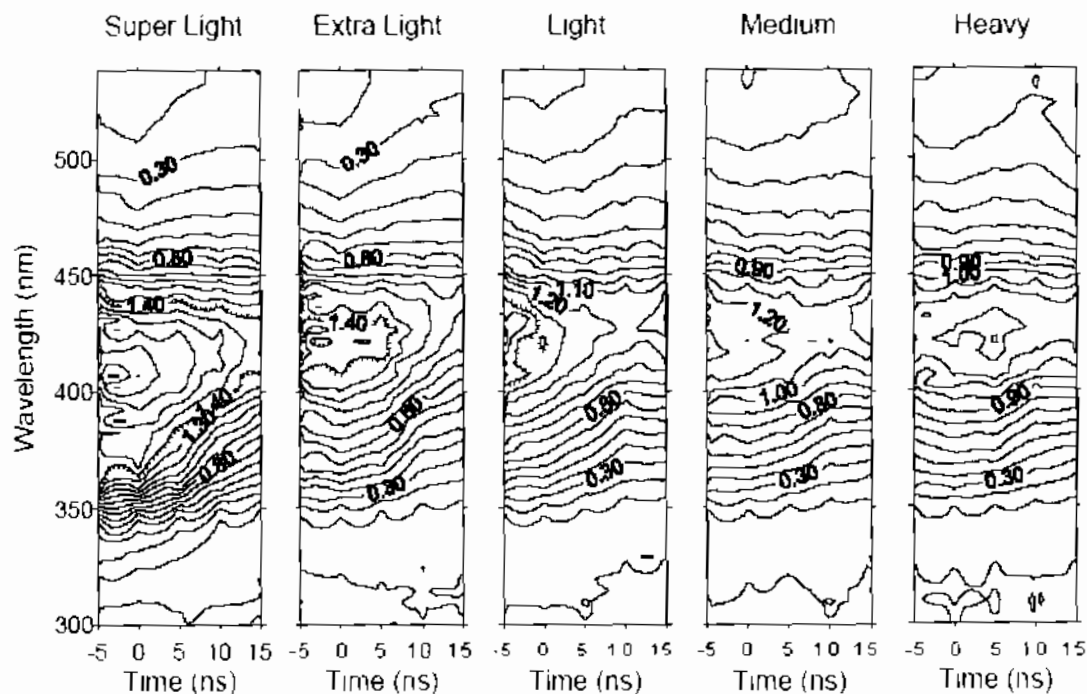


Fig. (5). Contours of equal fluorescence intensities of the TRF spectra of the 5 neat crude oils drawn as functions of wavelength and TG simultaneously. The contour lines of 1.4 intensity level are hatched (they cease to appear in the medium and heavy grades).

The fingerprints of the rest of weathered crude oils are shown in Figures 6, 7, 8, and 9, for the "wind and sunlight", seawater, wind, and "wind, seawater, and sunlight" weathering conditions, respectively. The construction of these fingerprints was done in the manner the fingerprints of the neat oils was done.

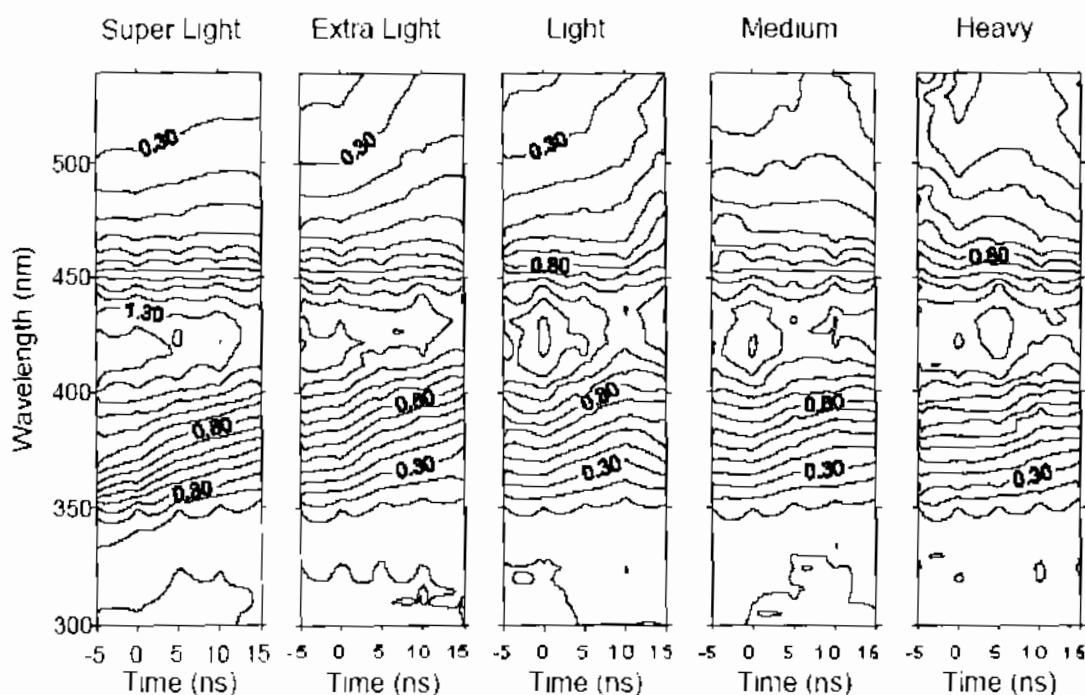


Fig. (6). Contours of equal fluorescence intensities of the TRF spectra of the 5 crude oils exposed to wind and sunlight drawn as functions of wavelength and TG simultaneously.

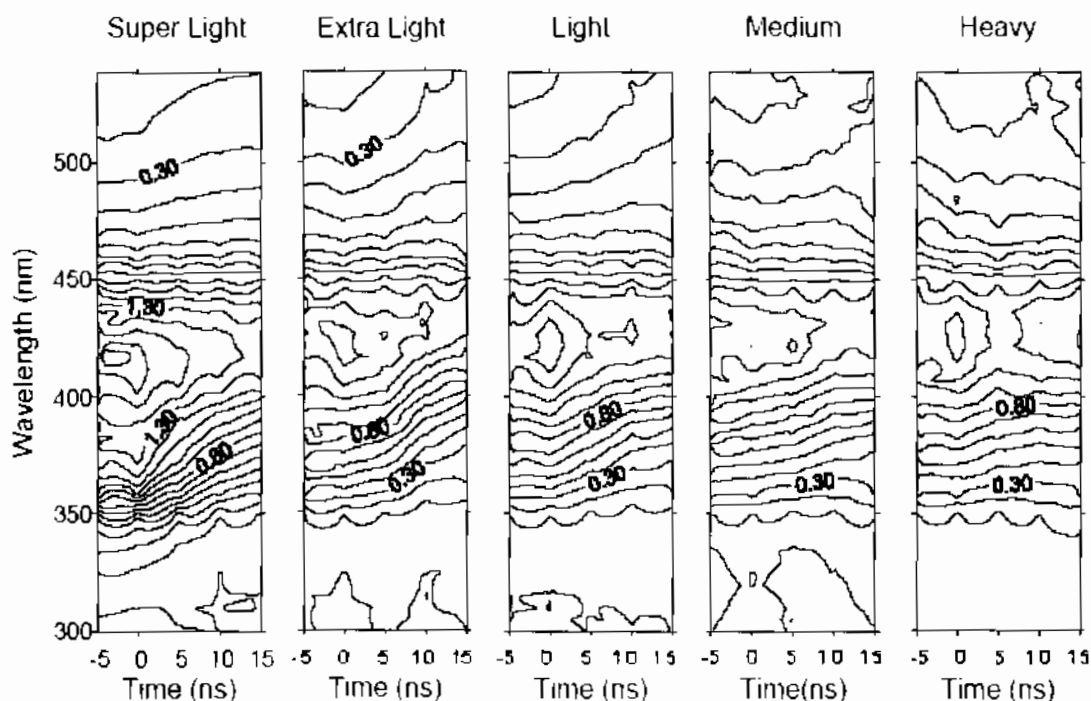


Fig. (7). Contours of equal fluorescence intensities of the TRF spectra of the 5 crude oils exposed to seawater drawn as functions of wavelength and TG simultaneously.

In Figure 6, which shows the contour diagrams of the crude oils that were exposed to wind and sunlight, the major factors affecting the fluorescence spectra of the crude oils, and hence their contour diagrams, are the change of the concentration distribution of the compounds due to evaporation of the volatile compounds, oxidation, and photodegradation. The scope of this study does not include an investigation on how these changes in the concentration relate to the changes in the spectral profiles, it only assesses if the resulting contour diagrams of the oils could still be distinguishable from each other. It is interesting to notice that the same trend in the contour patterns still appears in this weathered case as well, but at different intensity levels. In fact, when Figure 6 is compared with Figure 5 one can immediately see that the patterns of the oils' contour diagrams have been more or less preserved in shape relative to each other, with the exception of the intensity levels (i.e., colors).

In Fig. 7, which shows the contour diagrams of the seawater weathering cases, the major factor affecting the fluorescence spectra of these weathered crude oils, and their contour diagrams, is the change of the concentration distribution of the compounds due to the dissolving of the water-soluble compounds into water. The trend in the contour patterns in this seawater weathering case is the same as the neat case also but with less distinctive differences in the intensity levels between the Extra Light, Light and Medium grades. The feature that helps in distinguishing between these three grades is actually the way the contours below 400nm appear. They become gradually parallel to the x-axis as the grade of the oil becomes lower.

The weathering due to wind evaporation also gives rise to the same intensity pattern but with much less distinctive difference between the Light and Medium grades as Figure 8 shows. The contours below 400nm are also the feature to use in distinguishing between, for example, the Extra Light and the Heavy grade.

Finally, in the contour diagrams of the oils under all of the previous weathering elements, i.e., "wind evaporation, seawater and sunlight", which are shown in Figure 9, the same pattern still persists with reasonably distinguishable differences. The contour diagram of the Super Light seems to be quite different from all of the previous cases of Super Light, which may suggest some impulsive deviation in the sample handling routine. But in any case, the intensity level distribution is still stands as the main distinctive feature in the diagram.

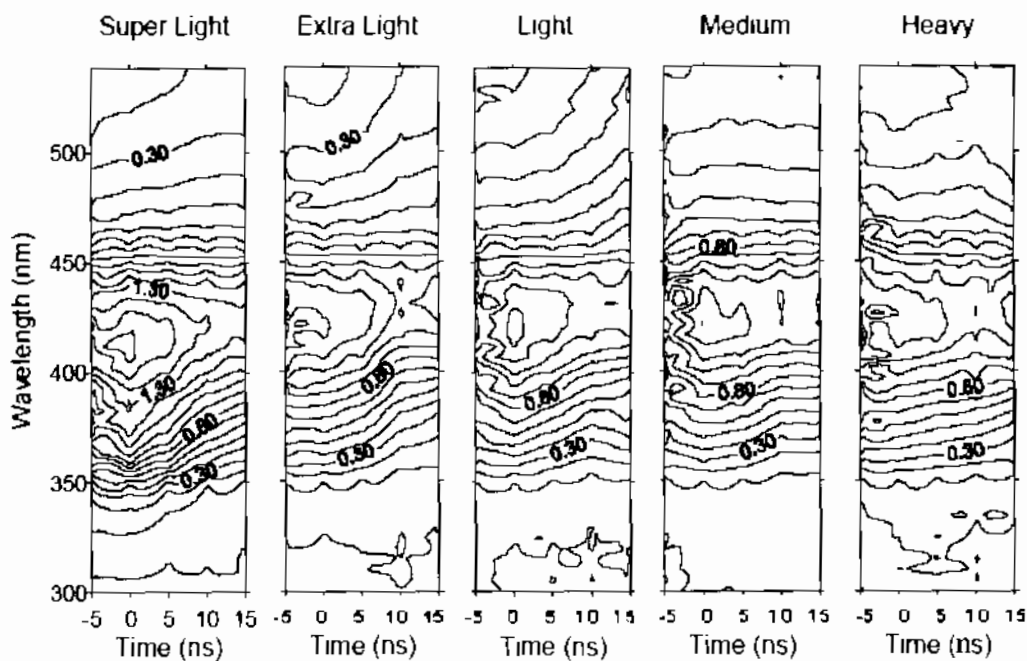


Fig. (8). Contours of equal fluorescence intensities of the TRF spectra of the 5 crude oils exposed to wind drawn as functions of wavelength and TG simultaneously.

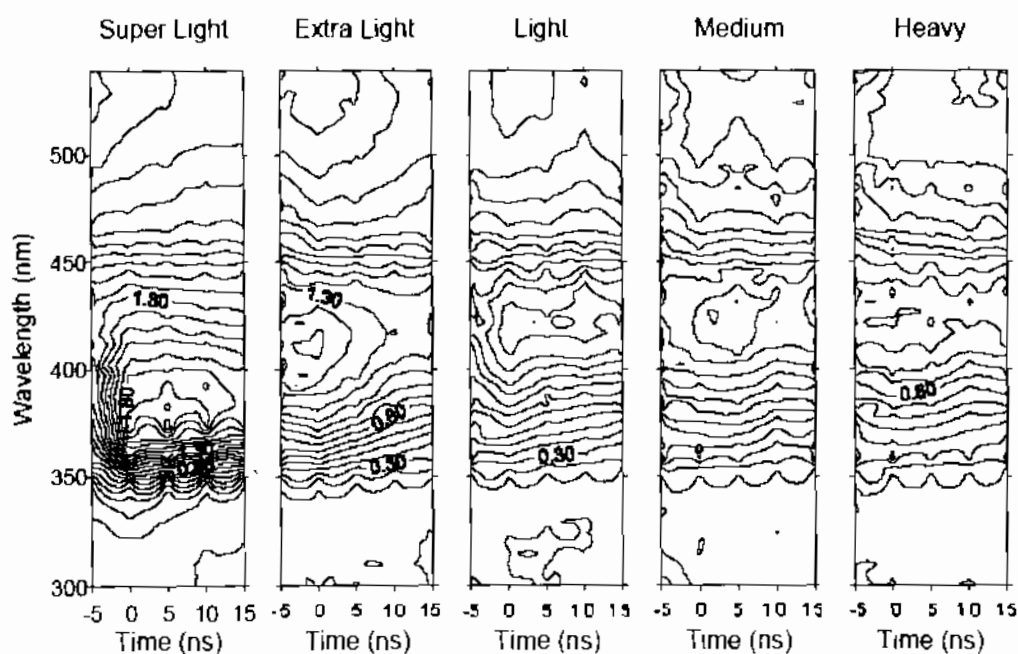


Fig. (9). Contours of equal fluorescence intensities of the TRF spectra of the 5 crude oils exposed to wind drawn as functions of wavelength and TG simultaneously.

A qualitative, rather than quantitative, way of analyzing the TRF spectra can be made by looking at the areas under certain segments of the spectral curves. It was found that the areas under two specific segments were the most useful in distinguishing between the tested crude oils. The first, which is designated as A1, was the area under the wavelength range between 314.4 and 452.0nm and the second, designated as A2, was the area under the wavelength range between 314.4 and 391.2nm. Similarly, it was also found that the TRF spectra of the TG -5 and TG 0 were the ones that gave the most useful distinguishing information. The calculated areas of these curves are all shown in Figures 10 and 11 in the form of regular bar charts. These bar charts help in figuring out at a glance which is the best area and the best TG to use for a specific weathering element. For example, for the fresh (neat) crude oils the A1 area at TG-5 provides the best separation possible between the bars, indicating that it is the optimum area-under-the-curve to focus on when distinguishing between the fresh oils quantitatively, while for the crude oils that were exposed to all the weathering elements (wind, seawater, and sunlight) the A2 area at TG0 seems more appropriate. The reason for this has to do with the fact that the different weathering elements will affect the concentration of different oil compounds within the crude oils' constituents. This in turn will deform the shapes of the TRF spectra in different manners depending on the spectral/temporal characteristics of the affected compounds. The exact assignment of these compounds and the exact description of the effect of their concentration variation on the TRF spectra are not simple to determine and go beyond the scope of this work as already mentioned. However, considering the bar charts of Figures 10 and 11 it can be at least figured out which areas under the spectral curves and which time gate produce the most distinguishable features between the different marketed Saudi Arabian crude oils. Table 1 summarizes the distinguishing ability of the contour diagrams (qualitative means) and the areas-under-the-curves (quantitative means) to distinguish between the crude oils at hand.

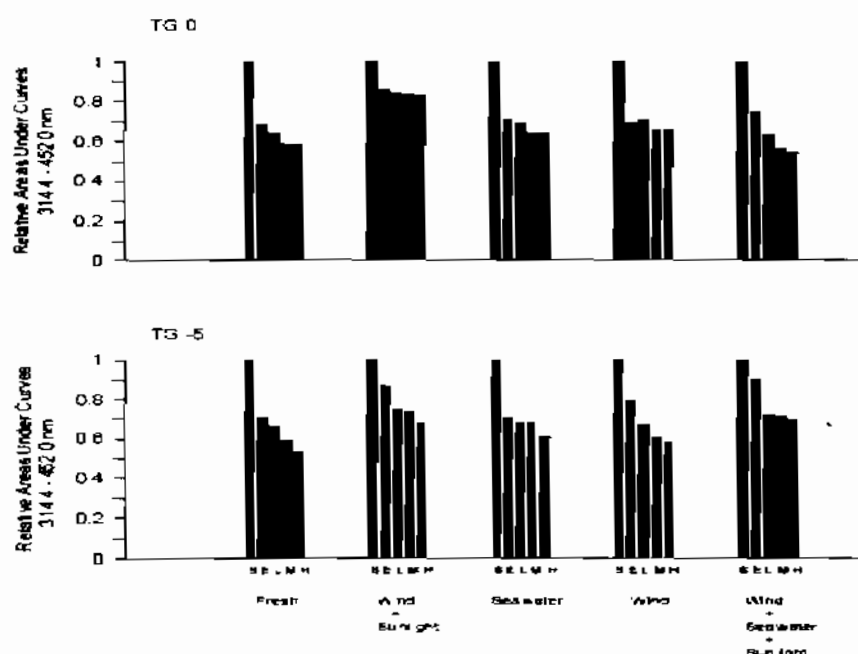


Fig. (10). Comparison between the relative areas under the TG -5 (bottom) and TG 0 (top) curves between 314.4 nm and 452 nm for all the samples. S = Super Light, E = Extra Light, L = light, M = Medium, and H = Heavy crude oils.

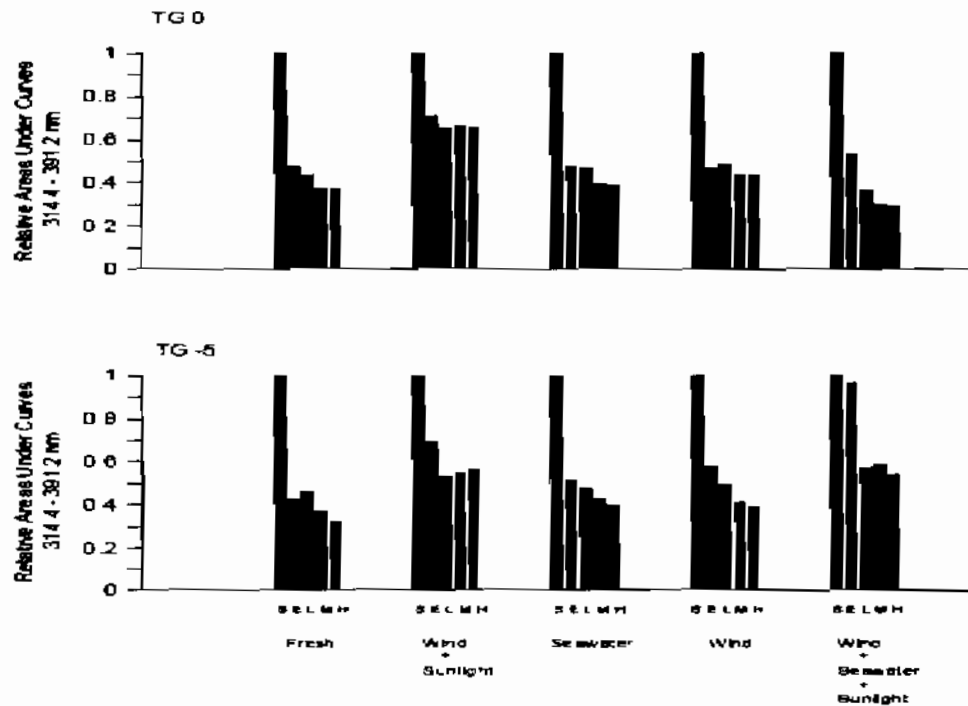


Fig. (11). Comparison between the relative areas under the TG -5 (bottom) and TG 0 (top) curves between 314.4 nm and 391.2 nm for all the samples. S = Super Light, E = Extra Light, L= light, M = Medium, and H = Heavy crude oils.

Table (1). Conclusions regarding the distinguishing ability using contour diagrams and areas under the curves for all neat and weathered cases of crude oils.

Condition	Using Visual Contour Diagrams	Using Areas Under The TRF Spectral Curves
Fresh	All oils are distinguishable from each other	All oils are distinguishable from each other. Best result is with A1/TG-5 and A2/TG0
Exposed to wind and sunlight	All oils are distinguishable from each other	Only Light and Medium are indistinguishable from each other. Best result is with A1/TG-5
Exposed to seawater	Only Extra Light and Light are indistinguishable from each other	All oils are distinguishable from each other. Best result is with A2/TG-5
Exposed to wind	Only Light and Medium are indistinguishable from each other	Only Medium and Heavy are indistinguishable from each other. Best result is with A1/TG-5 and A2/TG-5
Exposed to wind, seawater, and sunlight	All oils are distinguishable from each other	Only Medium and Heavy are indistinguishable from each other. Best result is with A1/TG0 and A2/TG0

Conclusion

The study shows that the established experimental approach of measuring the time-resolved fluorescence spectra of crude oils and expressing them in terms of contour diagrams is successful in distinguishing the oils from each other even when they have been exposed moderately to environmental weathering effects. The method used can be easily modified to work in remote sensing since it depends mainly on collecting the fluorescence signal only from the surface of the oil without any need for sample preparation. This is an

attractive feature that major petroleum companies, oil tanker companies and environmental agencies would find valuable to fight oil spill acts.

Acknowledgement

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References

- ASTM (1978) Book of Standards, p. 720, D3650-78.
- Bentz, P. (1976). *Anal. Chem.*, **V48**, 454A.
- Camagni, P., G. Colombo, C. Koeehler, A. Pedrini, N. Omenetto, and G. Rossi. (1988) *IEEE Transac. Geosci. and Rem. Sens.* **GE-26**, 22-26.
- Camagni, P., G. Colombo, C. Koeehler, A. Pedrini, N. Omenetto, P. Qi, and G. Rossi. (1991) *App. Opt.*, **V 30**, 26-35.
- Cook, T.E., R.E. Santini, and H.L. Pardue, (1977) *Anal. Chem.*, **V49**, 871.
- Eastwood D., S.H. Fortier, and M.S. Hendrick, (1978). *Am. Lab.*, **V10**(3), 45.
- Fantasia, J.F., T.M. Hard, and H.C. Ingrao (1971). Report No. DOT-TSC- USCG-71-7, Transportation Systems Center, Dept. of Transportation, Cambridge, Mass.
- Fantasia, J.F. and H.C. Ingrao (1974). *Proc. of the 9th Intern. Symp. on Remote sensing of the environment, 15-19 April 1974*, Paper 10700-1-X, 1711-1745.
- Giering L.P. and A.W. Hornig, (1977) *Am. Lab.*, **V9**(11), 113.
- Hegazi, E., A. Hamdan, and J. Mastromarino, (2001) *App. Spec.*, **55**(2), 202.
- Hegazi, E. A. Hamdan, and J. Mastromarino, (2003), US patent number 6,633,043.
- Lloyd, J.B.F., (1971). *J. Forens. Sci. Soc.* **V11**, 83 also 153 and 235
- Lloyd, J.B.F., (1974). *Analyst*, **V99**, 729.
- Measures, R.M., H.R. Houston, and D.G. Stephenson, (1974), *Optical Engineering*, **13**, 494-550.
- Measures, R.M., J. Garlick, H.R. Houston, and D.G. Stephenson (1975). *Can. J. Remote Sensing*, **1**, 95-102.
- Parker, C.A., (1968). *Photoluminescence of Solutions*, Elsevier, New York.
- Porro, T.J. and D.A. Terhaar (1976). *Anal. Chem.*, **V48**, 1103A.
- Quinn, M.F., A.S. Al-Otaibi, P.S. Sethi, and F. Al-Bahrani, (1994) *J. Int. Rem. Sen.* **V15**, 2637-2358.
- Shen, J., R.J. Engen, and N.K. Saadeh (1984). *Arab. J. Sci. Eng.*, **v. 10**, 63.
- USCG (1977) Oil Spill Identification System, Chemistry Branch, U.S. Coast Guard R&D Center, Report No. DOT-CG-D-52-77
- Warner, M., G.D. Christian, E.R. Davidson, and J.B. Callis, (1977) *Anal. Chem.*, **V49**, 564.

بصمات طيفية للبتروول الخام المعرض لعوامل التعرية

عزت حجازي

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المستخلص. تم تطبيق طريقة جديدة حائزة على براءة إختراع في تحديد البصمات الطيفية للبتروول الخام المعرض لعوامل التعرية الطبيعية. تعتمد هذه الطريقة على قياس أطيف الفلورة في شرائح زمنية قصيرة داخل البروفائل الزمني لنبضة الليزر. ويتم تكوين البصمات على هيئة رسومات كمنثورية تربط الشدة الضوئية لأطيف الفلورة بالطول الموجي للفلورة المنبعثة وأيضا بزمن الشريحة التي تم عندها قياس الأطيف. وقد استخدت في هذه الدراسة الأنواع الخمسة للبتروول الخام الذي تسوقه المملكة العربية السعودية وهي، البتروول الخفيف الممتاز، الخفيف جدا، الخفيف، المتوسط، والثقيل. تم تكوين خمسة بصمات طيفية لكل نوع من البتروول تحت خمسة ظروف طبيعية: (١) بدون تعرية، (٢) تعرية بواسطة ماء البحر، (٣) تعرية بواسطة التبخر بالرياح، (٤) تعرية بواسطة أشعة الشمس، و (٥) تعرية بواسطة جميع هذه العوامل معا. وقد وجد أن البصمات الطيفية تشير إلى وجود نمط يتغير بطريقة منتظمة بالنسبة لنوعية البتروول حتى في وجود عوامل التعرية. وهذا يجعل من هذه التغيرات المنتظمة وسيلة فعالة في تحديد نوعية البتروول المسكوب في البحار ومن ثم ربطها بالسفينة التي تسببت في سكبها. هذه الورقة تشرح الطريقة التي استعملت لقياس أطيف الفلورة الزمنية وتبين البصمات الطيفية المميزة لكل عينة بتروول وتعطي أيضا نتائج رقمية تربط المساحة تحت المنحنيات بنوعية البتروول.