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# Detection and evaluation of hydrocarbons in source rocks by fluorescence microscopy

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**Abstract**—In pursuing the detection of hydrocarbons in sedimentary rocks by conventional petrological methods, an attempt has been made to correlate standard fluorescence parameters with the quality and quantity of hydrocarbons present in crushed rocks embedded in epoxy resin. The capacity of the embedding resin, commonly used in the preparation of petrographic samples, to extract and physically fix hydrocarbons is recognized. This phenomenon permits one to measure monochromatic fluorescence parameters, *I* 546 and *Q* (u.v.) 650/500, on the trapped hydrocarbons and to correlate these parameters with selected geochemical data.

The potential application of using these petrological parameters to evaluate oil quantities and qualities is tested using real case studies. It is also shown that it is possible to directly detect the mature zone in each case.

*Key words*—crude oil, epoxy resin, fluorescence, geochemistry, hydrocarbon, maturation, petrology, reservoir, source rock

## INTRODUCTION

Oil is normally present in source rocks having entered the maturation zone (oil window). However, it is also found in other sedimentary rocks due to its migration. In this study, novel petrographic techniques are used to identify such occurrences of oil.

Fluorescence properties of hydrocarbons have been investigated by many authors, viz. Ottenjann (1980), Bertrand *et al.* (1986), Hagemann and Hollerbach (1986), Martinez and Connan (1989). It has been established clearly that the fluorescence of hydrocarbons is related to the distribution of $\pi$ electrons in aromatic rings and conjugated double bonds. During u.v. excitation $\pi$ electrons are excited from one orbital to the other, and upon returning to their ground state, emit photons (radiation) in the visible spectrum (Lin and Davis, 1988).

In the present investigation an attempt has been made to establish relations between fluorescence parameters and oil qualities (in terms of chemical composition) and quantities, bearing in mind that the methodology employed differs from others in that it attempts to profit from the following: (1) recognition that hydrocarbons are *extracted* and trapped by the epoxy resin in which rocks are embedded, (2) hydrocarbons become detectable by fluorescence excitation, and (3) the monochromatic measurements can be carried out by routine methods and equipment similar to those used for vitrinite reflectance.

Nevertheless, our concern is presently not directed at economic aspects of oil fields, but instead at the relevance of micro-impregnations or micro-neogenerations detected by optical microscopy which may be applied to petroleum prospecting.

## METHODOLOGY

### *Sample preparation*

Most of the samples studied were whole rock cuttings already in a granular form. Mild crushing (<2 mm) was only necessary when the size was too big or irregular. The cuttings were washed, dried, and visible contaminations were removed. The clean granular samples of whole rocks were then *embedded* in an epoxy resin (EPOFIX†) and polished according to routine petrographic methods (polished blocks). The epoxy resin behaves as an extractor of hydrocarbons, favouring a physical readjustment of this fluid phase into the embedding resin itself, without a chemical reaction. In addition, *crude oil* samples were mounted on a slide (single drop) and covered with a lamella (cover slip). In some cases, each oil was mixed with embedding resin in various proportions (0.5–4.0%) so that their properties, in such an embedding medium, could be studied. With reference to the latter point, other embedding resins were also tested and produced similar results.

### *Hydrocarbons*

On mixing the rock samples with the epoxy resin, the hydrocarbons which may be present in the rock particles are partly extracted and easily detected under fluorescence. Since the embedding resin is very low fluorescing (*I* 546 = 6%), and once it is mixed

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†This epoxy resin-hardner kit is supplied by STRUERS.

Table 1. Classification of hydrocarbons (HC) present in rocks crushed and embedded in epoxy resin, as observed under fluorescence and reference to measurements

| | | measurements |
|---|---|---|
| automorph HC | drops | Q 650/500 |
| | films | Q 650/500 |
| | exsudates (complex) | not measured |
| | non-spherical HC | not measured |
| dissolved HC in-resin | | I 546 and Q 650/500 |

with a sample containing hydrocarbons, the resulting fluorescence properties are taken to be those from the hydrocarbons themselves.

A portion of the hydrocarbons appear as *automorph* hydrocarbons, whilst another portion is *dissolved* or mixed with the embedding epoxy resin (Table 1). These categories have been described and illustrated in detail by Alpern *et al.* (1992). As a brief summary, automorph hydrocarbons are categorized as drops and films; drops are clearly spherical in form and variable in size. Their color ranges from green to yellow-brown. Films appear as coatings of, or stuck to particles and with varying thickness. Their fluorescence color also varies from green to yellow-brown. On the other hand, the dissolved hydrocarbons category is comprised of those which mix with the embedding epoxy resin giving it a fluorescence color also dependent on their chemical composition: greenish for saturated oils and yellow for the aromatic ones.

### *Optical analysis*

The petrographic equipment used for the fluorescence measurements is comprised of a Leitz microscope (MPV Combi) with reflectance and fluorescence attachments. Ultraviolet fluorescence conditions were obtained with a HBO 100 W mercury lamp, an UG1 excitation filter ($I = 365$ nm), a K430 barrier filter and a TK400 dichroic mirror. The intensity of the embedding epoxy resin was measured at $I = 546$ nm, using an uranyl-glass as a standard. The size of the field measured on the embedding resin was 100 $\mu m^2$, and a minimum of 50 measurements were recorded for each sample. Although the ratio of $Q = 650/500$ in u.v. light may be measured both for the hydrocarbons (films, drops), when present, and for the embedding resin, in the present study it was only done on the epoxy embedding resin. The above measurements were carried out using a 50× oil immersion objective, and the spectral fluorescence of the free crude oils were performed using water immersion.

## APPLICATIONS TO PETROLEUM PROSPECTING

### *Correlation of Q (u.v.)650/500 with oil quality*

$Q$ (u.v.)650/500 measurements were carried out on 10 selected oils which reported wide variations in chemical composition (Table 2).

A good positive correlation was obtained between $Q$ (u.v.)650/500 and the percentage of aromatics (ARO) plus heavy products (HP = resins + asphaltenes) (Fig. 1). That is to say that aromatic oils are more red shifted than saturated oils. This was confirmed by spectral fluorescence measurements (using a water immersion objective) that showed aromatic oils had $\lambda$max values at longer wavelengths than saturated oils (e.g., Fig. 2).

Since our routine methods are carried out on rock samples embedded in epoxy resin, the crude oils were mixed with resin and fluorescence measurements were performed. The resulting correlation between the color, expressed by $Q$, and quality, as SAT/(ARO + HP), remain excellent with $r = -0.957$ (Fig. 3). It should be noted that, for each crude oil, the $Q$ values obtained on each of the different concentrations of oil mixed with the epoxy resin, were so similar that the average $Q$ value was considered representative. This last point was a valid argument in favour of

Table 2. The genetic nature and chemical composition of ten crude oils

| Oil No. | Genetic character | Saturated (%) | Aromatic (%) | Resins + asphaltenes (%) | Density |
|---|---|---|---|---|---|
| 1 | Marine | 82.0 | 14.0 | 4.0 | 0.81 |
| 2 | Continental | 84.9 | 12.9 | 2.2 | 0.87 |
| 3 | Marine | 26.7 | 56.3 | 16.9 | 0.97 |
| 4 | Marine | 58.8 | 29.0 | 10.8 | 0.93 |
| 5 | Marine | 88.5 | 11.5 | — | 0.79 |
| 6 | Marine | 63.0 | 33.1 | 3.9 | 0.81 |
| 7 | Marine | 42.0 | 27.0 | 31.0 | 0.90 |
| 8 | Marine | 28.0 | 47.0 | 25.0 | 0.87 |
| 9 | Marine | 63.3 | 29.3 | 7.4 | 0.80 |
| 10 | Marine | 60.0 | 22.0 | 18.0 | 0.83 |

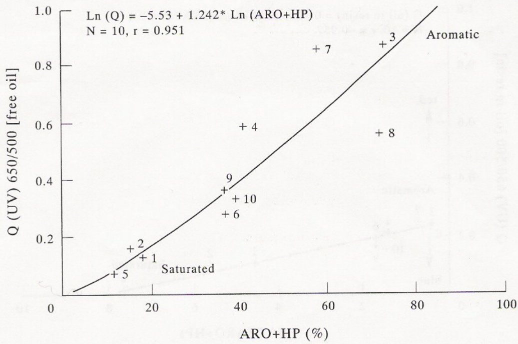



Fig. 1. Correlation between optical parameter $Q$ (UV) on free oil (slide) and oil quality (ARO + HP%) for 10 selected oils.

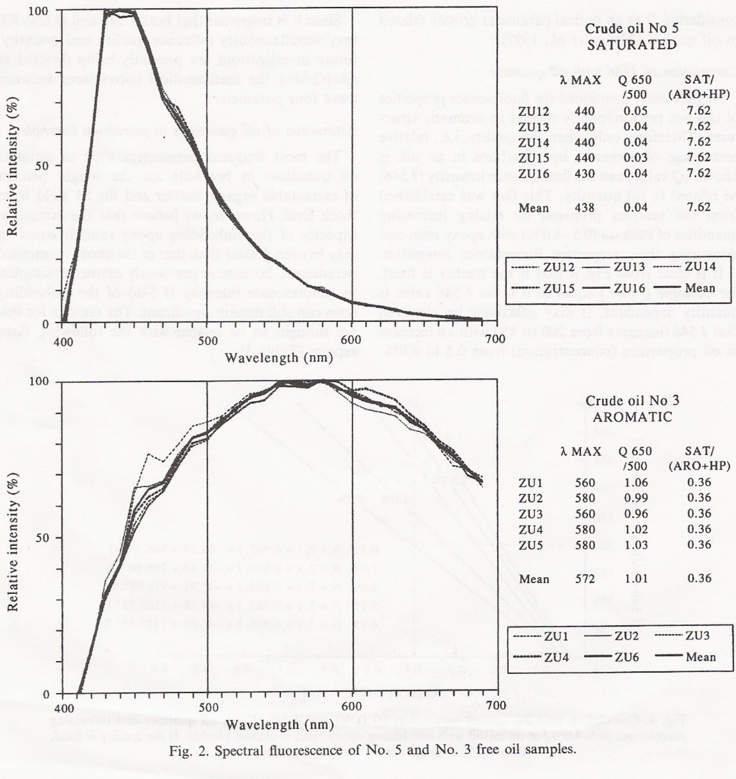



Fig. 2. Spectral fluorescence of No. 5 and No. 3 free oil samples.

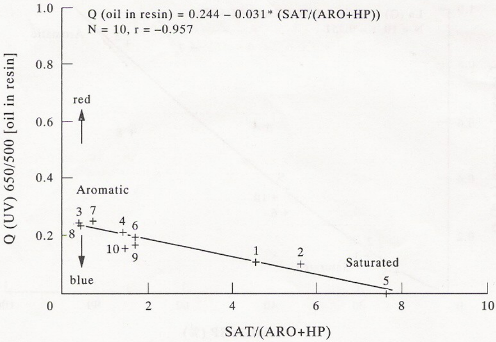



Fig. 3. Correlation between $Q$ (UV) of embedding epoxy resin mixed with 1% oil (polished block) and oil quality [SAT/(ARO + HP)].

considering $Q$ as an optical parameter grossly related to oil quality (Alpern *et al.*, 1992).

*Correlation of I546 with oil quantity*

As previously mentioned the fluorescence properties of oils are predominantly related to aromatic structures. Therefore, only when the quality, i.e., relative percentage of aromatic hydrocarbons in an oil, is known ($Q$ value) can the fluorescence intensity ($I$ 546) be related to oil quantity. This fact was established from the samples prepared by mixing increasing quantities of each oil (0.5–4.0%) with epoxy resin and measuring their respective fluorescence intensities.

It is clear from Fig. 4 that if the quality is fixed, for example $Q$ (u.v.) equal to 0.4, the $I$ 546 value is quantity dependant. It may effectively be observed that $I$ 546 increases from 200 to 450 with an increase in oil proportion (concentration) from 0.5 to 4.0%.

Since it is suspected that both $I$ 546 and $Q$ 650/500 may simultaneously influence quality and quantity, future investigations are presently being directed at establishing the mathematical correlations between these four parameters.

*Estimation of oil quantities in petroleum boreholes*

The most frequent parameters used to estimate oil quantities in borehole are the weight percent of extractable organic matter and the S1 yield from Rock Eval. However, we believe that the extraction capacity of the embedding epoxy resin is equal or may be even greater than that of the above mentioned parameters, because in previously *extracted* samples, the fluorescence intensity ($I$ 546) of the embedding resin can still remain significant. The reasons for this are thought to be related with the following three aspects (Table 3):

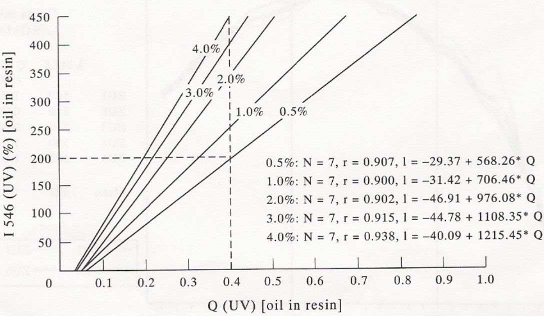
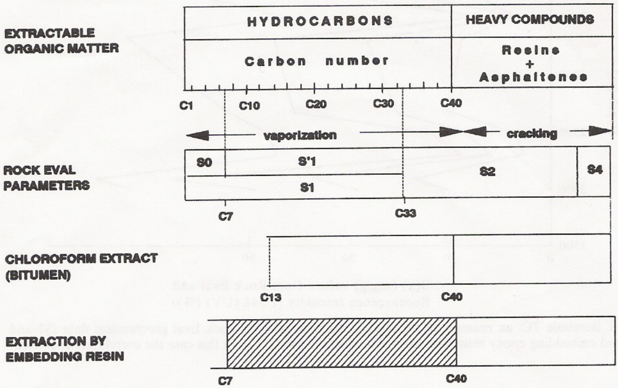



Fig. 4. Correlation between optical parameters [$Q$ (UV) and $I$ 546 (UV)], oil qualities and increasing percentages (0.5–4.0%) of oil mixed with embedding epoxy resin (polished blocks). If the quality is fixed, then $I$ 546 is proportional to hydrocarbon percent.

Table 3. Comparison between the extraction capacity of the embedding epoxy resin and geochemical tools (after Espitalié *et al.*, 1985, modified). The shaded area corresponds to the HC optically detected




(1) It is known that the S1 yield does not correspond to the total free hydrocarbons in rocks, but only to the volatile fraction, typically containing <33 carbons.

(2) Gas bubbles, perhaps belonging to S0, are often included in oil drops visibly trapped in the embedding epoxy resin.

(3) The fact that the C33+ fraction is included in the S2 yield and not in the S1 yield, explains the existing correlations between *I* 546 and S2 (Fig. 6). This is so because the embedding epoxy resin is capable of separating and fixing at least a part of the C33+ fraction.

In testing the application of the routine fluorescence parameters, three real case studies are presented. In borehole CA1 (Fig. 5) the correlation between *I* 546 and S1 is excellent with $r = 0.934$. In borehole TC (Fig. 6) the correlation is a little lower, $r = 0.89$, but the variations with depth are very similar between *I* 546 and the Rock Eval yield data. In the Paris basin (Fig. 7), Toarcian oil shales are clearly detected and the correlation between *I* 546 and selected geochemical data is again very high ($r = 0.954$). The above examples infer that within a given section the oil quality seems to be relatively constant since the correlations between *I* 546 and geochemical data are rather good.

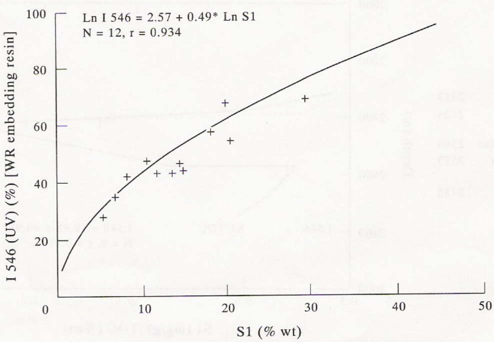



Fig. 5. Borehole CA 1: correlation between *I* 546 of the whole rock (WR) embedding epoxy resin (polished block) and S1 from Rock Eval.

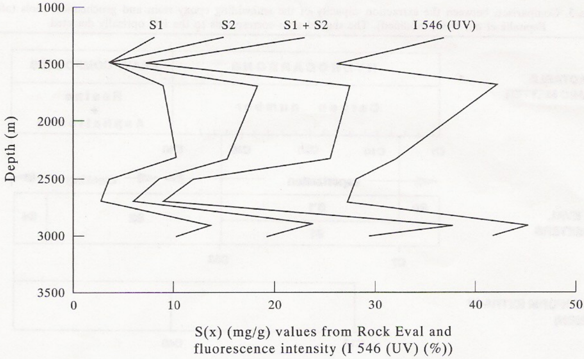



Fig. 6. Borehole TC: an example of the relation between selected Rock Eval geochemical data (S1 and S2) and embedding epoxy resin fluorescence intensity [*I* 546 (UV)]. In this case the correlation coefficient between *I* 546 and S1 is 0.89.

## CONCLUSIONS

Liquid hydrocarbons occur frequently in sedimentary rocks. They may be trapped and fixed in the embedding resin during routine petrographic sample preparation. These hydrocarbons may be revealed by fluorescence excitation of polished resin plugs, and characterized by two simple fluorescence monochromatic parameters [*I* 546 and *Q* (u.v.) 650 nm/500 nm]. They provide information with respect to the oil quantities and qualities (in terms of chemical composition) of the rock. *Q*, expressing the fluorescence color, is more related to the oil quality and the correlation with the proportion of aromatic hydrocarbons is good. In borehole case studies *I* 546 shows also good correlations with S1 yield from Rock Eval.

The simple procedures followed in our investigation not only permit evaluations of oil qualities and quantities, but can also detect thermally mature zones. Thus, the hydrocarbon fluorescence properties of epoxy embedded rocks provide an alternative maturation parameter which supplements conventional indirect methods such as spore coloration, vitrinite reflectivity, Thermal Alteration Index (TAI), etc.

Although our investigation provides a direct method of detecting mature zones it is still necessary to distinguish source rocks from reservoirs. The latter is accomplished by careful microscopic observations.

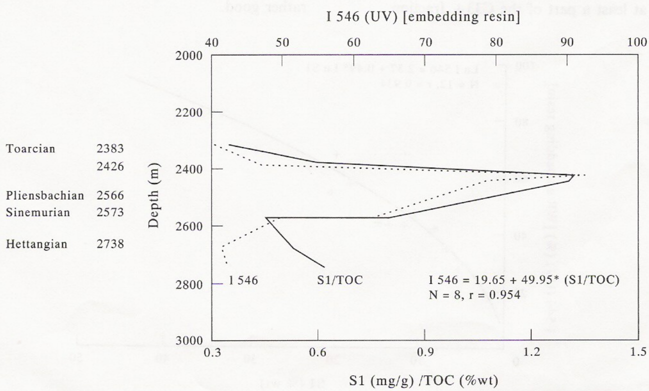



Fig. 7. Variations with depth and correlation between optical [*I* 546 (UV)] and geochemical parameters (S1/TOC) for the Paris Basin.

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