

Fluorescence Separation of Polyaromatic Hydrocarbons by Synchronous Resonance Fluorescence Method

by

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Fluorescence spectrophotometry has made a considerable application in analytical organic chemistry¹. Because of its sensitivity and selectivity, fluorescence is becoming increasingly important to characterize and to fingerprint crude oil especially at low concentration levels². The development of synchronous excitation fluorimetry³, in which excitation and emission wavelengths are varied together with the constraint that the difference between them is constant throughout the spectrum, has made fluorescence fingerprints to be obtainable from mixtures. Lloyd et al⁴ have applied it in petroleum products and forensic science to identify a number of polynuclear aromatic hydrocarbons. Recently, John and Soutar⁵ have showed it great promise as a diagnostic tool for the identification of crude oil. In order to employ this technique to petroleum exploration, we evaluate and compare the synchronous excitation fluorescence (SEF) and the synchronous excitation resonance fluorescence (SERF) as means of the fluorescence separation of the mixtures by using four known comparable fluorescence compounds: 9,10-diphenylanthracene (DPA), perylene (PL), tetracene (TC) and rubrene (RB) as shown in Figure 1 and Table 1.

DPA (Aldrich, 99.6% pure, gold label) and RB (Aldrich, m.p. 315° C) were used without further purification. PL and TC (both Aldrich) were recrystallized separately from ethanol several times until their fluorescence was correct. Fluorescence spectra were obtained on a Farrand MK-II or MK-I spectrophotometer.

The conventional emission and excitation spectra of DPA, PL, TC and RB are shown in Figure 2. The intensity of the fluorescence is a function of both the excitation and emission wavelengths. The efficiency of characterizing a mixture by either using a fixed excitation wavelength within the absorption band while scanning the emission frequencies or using a fixed emission wavelength within the emission band while scanning the absorption frequencies, is reduced, because

the serious overlap of the fluorescence spectrum and absorption spectrum of the components. By inspecting the emission and excitation spectrum of each compound, there is a characteristic overlap of the 0-0 band of each molecule, provided the geometry of the component is rigid-the configuration of the ground state is the same as that of the excited state. The SERF employs the variation of both emission and excitation, continuous increase or decrease of the excitation and emission wavelengths at the same speed while retaining at the same wavelength. It can be seen that only single emission peak appears for a pure compound as that in Figure 3. In this manner, the components of a mixture can be fluorescence resonance separated, as shown in Figure 4. Lloyd⁴ indicated that intervals of 23 nm were generally suitable for synchronous excitation spectra of polynuclear hydrocarbons in the region 400-500 nm. For comparison, this value was employed for those compounds chosen in this study. The results are shown with dotted lines in Figure 2 for the single compound and also in Figure 3 for the mixtures. Either Figure 2 or Figure 3 indicates that the SERF ($\Delta\lambda = 0$ nm) gives simpler fluorescence separation spectrum than that of SEF at $\Delta\lambda = 23$ nm. For instance the spectrum of SEF of DPA shown in Figure 2 is a single peak, whereas that of ESF of DPA provides two peaks.

The inner filter and energy transfer effects⁶ are very easily to mislead the identification of the components. The component of DPA in the four of three compounds mixture disappears from Figure 4. It can be explained that the DPA excited state is quenched completely by both PL and TC, but not RB at the arbitrary concentration for the mixture analyzed. In general, this phenomenon can be easily tested by the variation of the concentration of the suspected species. One other problem that might arise is that the Raleigh scattering prevails in the very dilute concentration. It is suggested that this effect be neglected in a very dilute solution for those molecules with high quantum efficiency.

We have used this method in conjunction with the traditional fluorescence methods in characterizing the samples from different geological locations and depths. Figure 5 shows some of the representative SERF spectra of samples from the various geological locations. The evaluation of the fluorescence method in petroleum exploration is under investigation.

A cknowledgement

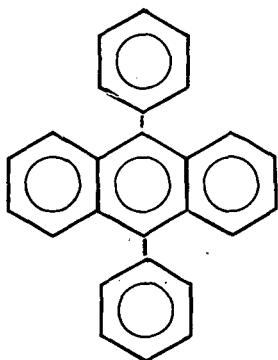
We thank the Exploration and Exploitation Research Center, Chinese Petroleum Corporation for financial support of this work. We also like to express our deep appreciation to Mr. T.H.Chow and his group fellows for providing samples from different geological locations and depths.

REFERENCES

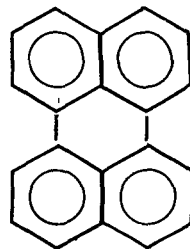
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Table 1: The photophysical Data of the Taken Polyaromatic Hydrocarbons

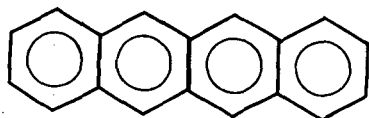
Compound	Energy of Singlet	Quantum Yield	Stokes Loss
9,10-diphenyl-anthracene (DPA)	395 nm	0.84	1820 cm ⁻¹
Perylene (PL)	435 nm	0.94	1400 cm ⁻¹
Tetracene (TC)	490 nm	0.40	1330 cm ⁻¹
Rubrene (RB)	545 nm	~ 1.00	1370 cm ⁻¹



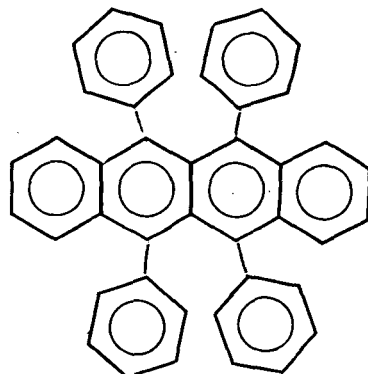
9,10-diphenylanthracene
(DPA)



Perylene (PL)



Tetracene (TC)



Rubrene (RB)

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Figure 1: The Structures of the Taken
Polyaromatic Hydrocarbons

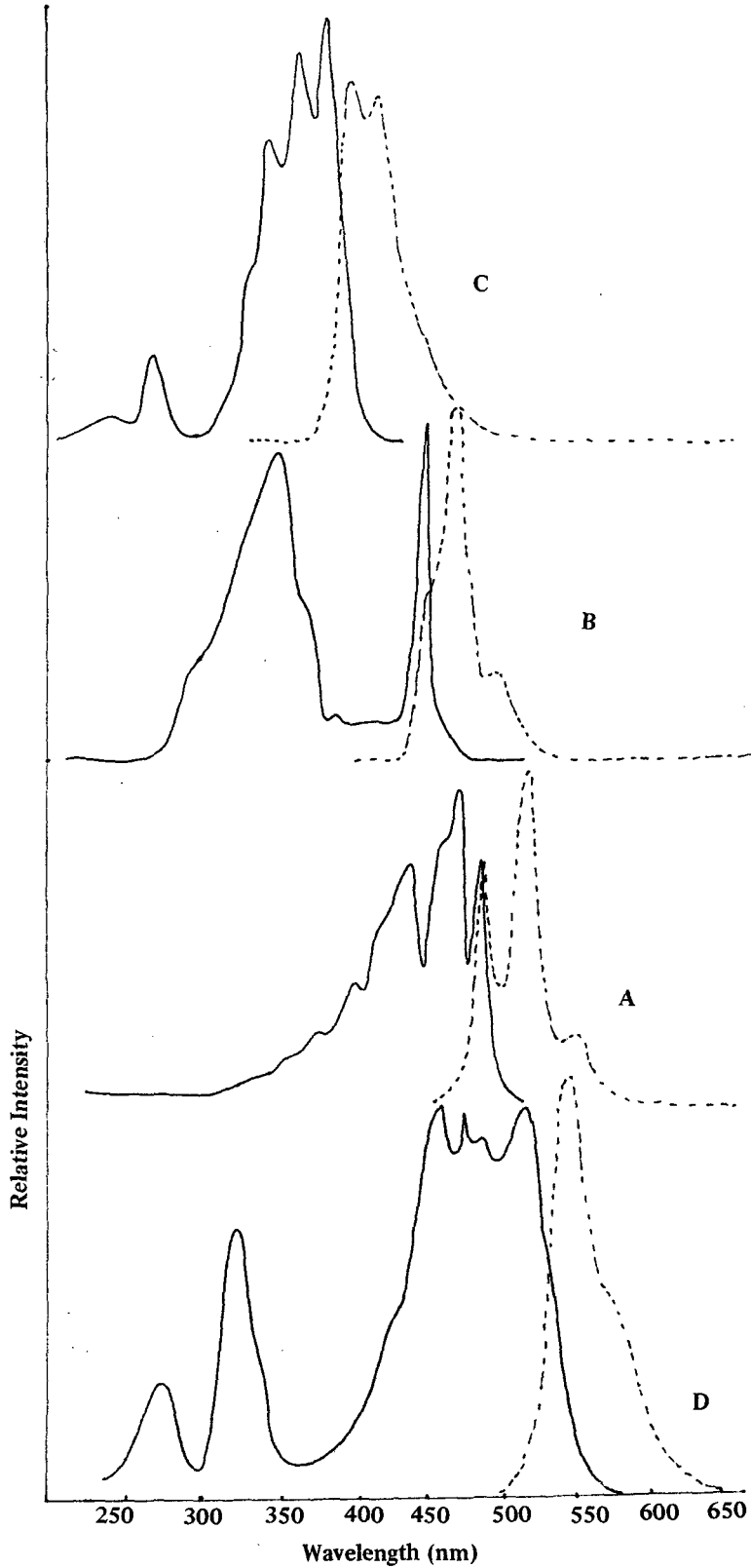


Figure 2. The Conventional Emission (Dotted Lines) and Excitation (Solid Lines) Spectra.

- A: Tetracene
- B: Perylene
- C: 9,10-Diphenylanthracene
- D: Rubrene

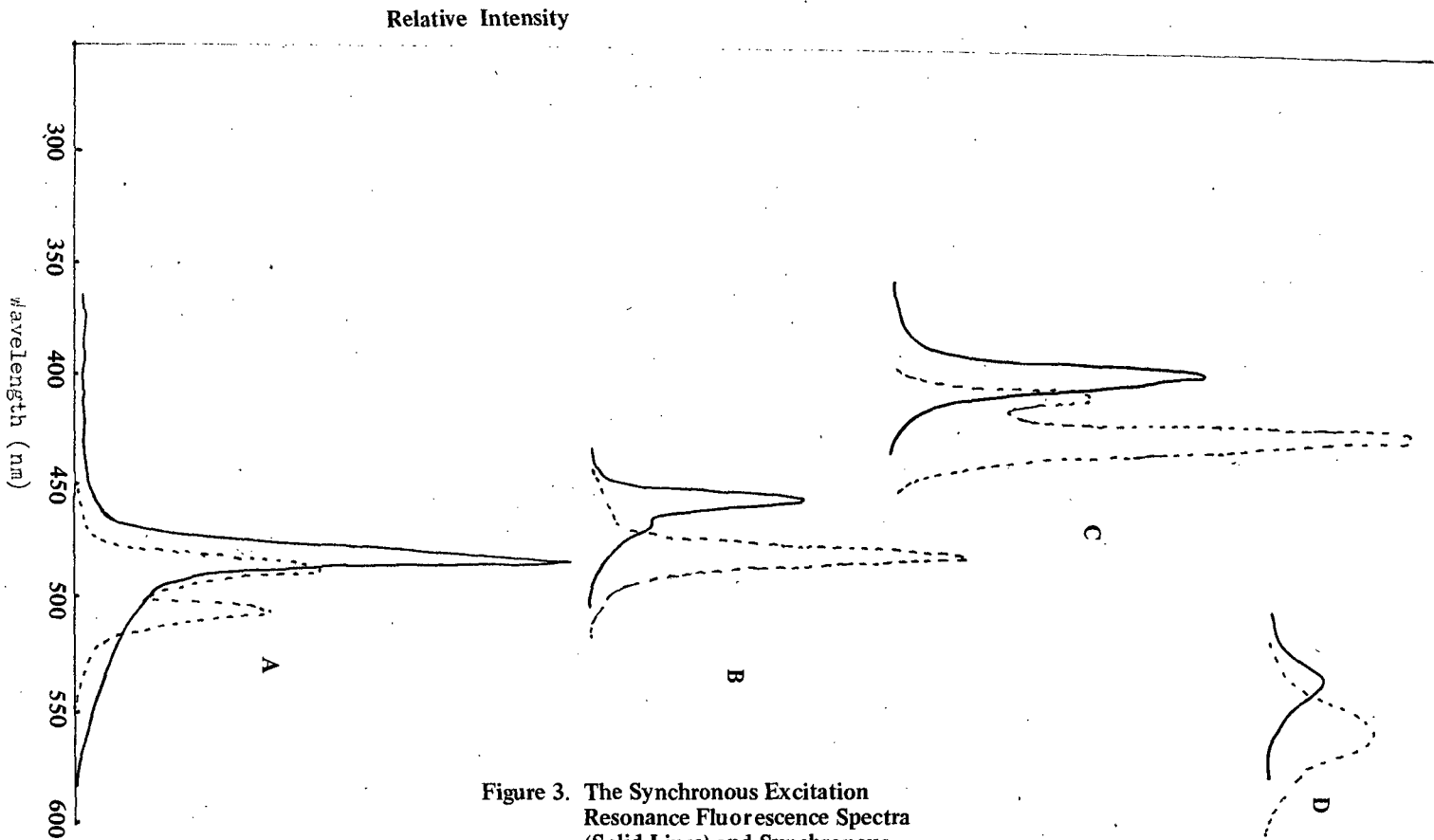


Figure 3. The Synchronous Excitation Resonance Fluorescence Spectra (Solid Lines) and Synchronous Excitation Fluorescence Spectra (Dotted Lines, $\Delta\lambda = 23\text{nm}$).

- A: Tetracene
- B: Perylene
- C: 9, 10-Diphenylanthracene
- D: Rubrene

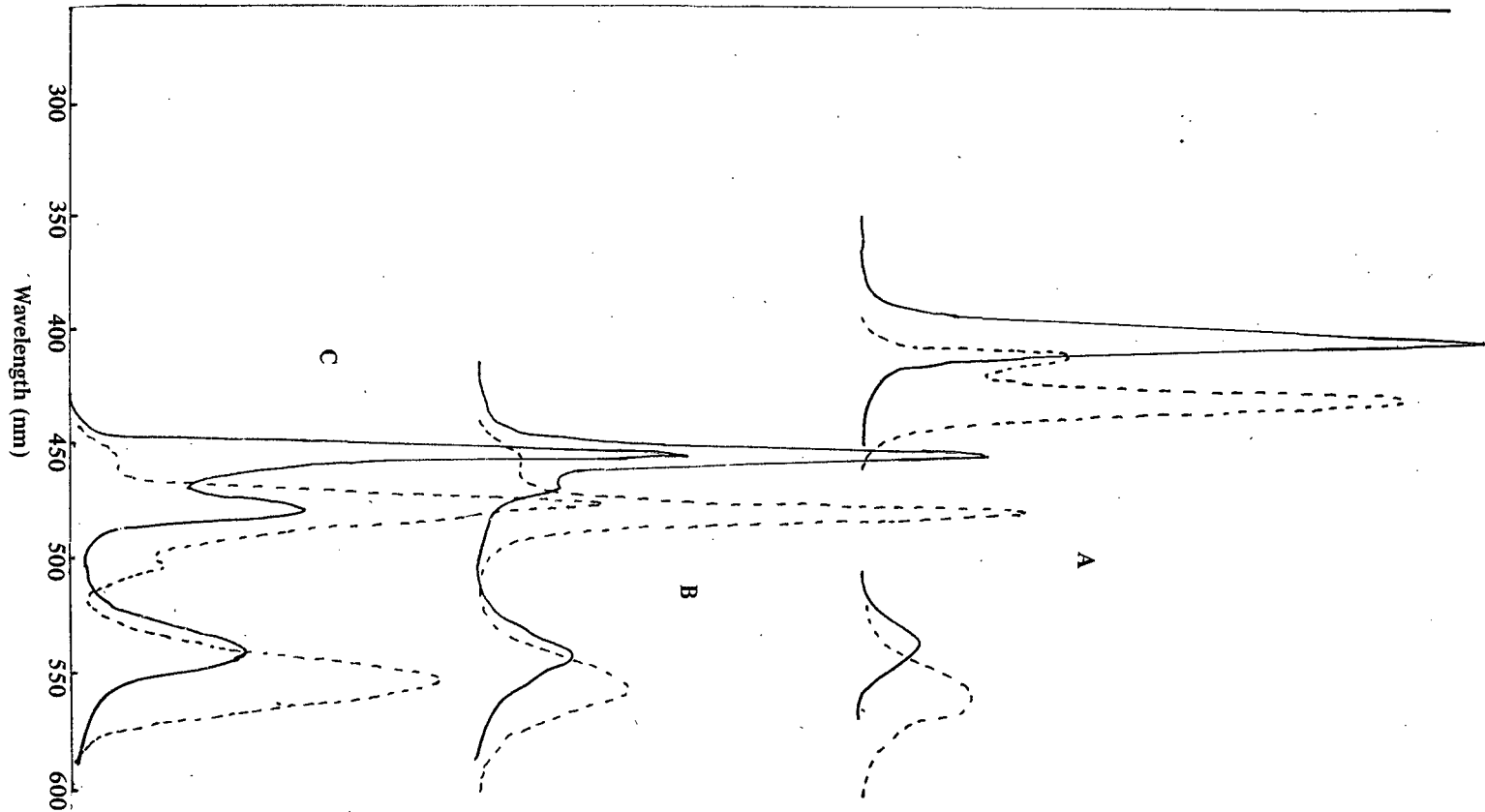


Figure 4. The Synchronous Excitation Resonance Spectra (Solid Lines) and Synchronous Excitation Fluorescence Spectra (Dotted Lines, $\Delta\lambda=23\text{nm}$)

- A: Rubrene + 9, 10-Diphenylanthracene
 B: Rubrene + 9, 10-Diphenylanthracene + Perylene
 C: Rubrene + 9, 10-Diphenylanthracene + Perylene + Tetracene

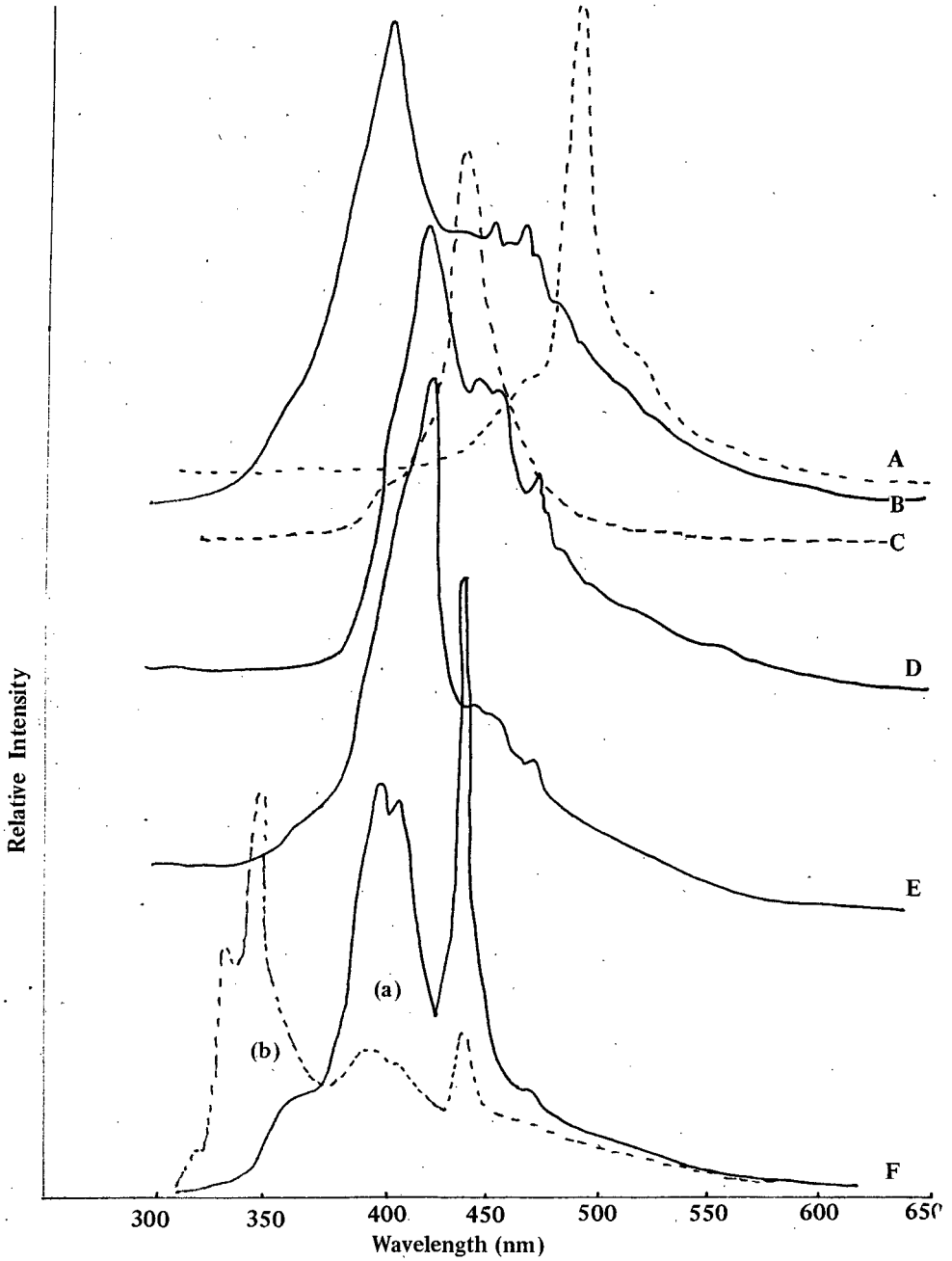


Figure 5. The Synchronous Excitation Resonance Fluorescence Spectra of the Samples from the Various Geological Locations.

- A: No.7
- B: 3365 meter
- C: 3340 meter
- D: 3281 meter
- E: 3726 meter
- F: 935-951 meter . (a) Concentrated
(d) Diluted.

芳香碳氫混合物的同步共振螢光分離

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中文摘要

本文介紹同步共振螢光光譜的原理與應用。同步共振螢光技術，乃同時掃瞄激發和發射光的波長，以記錄發射光（即螢光）的訊號。9,10 = 苯基蒽（DPA），派錄寧（PL），聯四苯環（TC）及路卜寧（RB）可用此技術，予以螢光分離。所可能干擾的因子，亦在文中予以討論。