

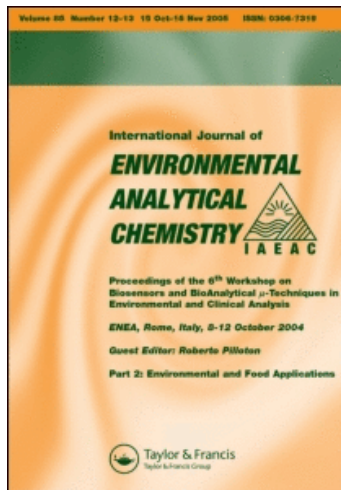
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Publisher Taylor & Francis

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## International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713640455>

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**To cite this Article** Fayad, Nabil M. , Siddiqui, M. Nahid and Iqbal, S.(1988) 'Effects of Solvent and Humic Materials in Fluorimetric Determination of Oil Hydrocarbons in Marine Sediments', International Journal of Environmental Analytical Chemistry, 33: 2, 123 – 129

**To link to this Article:** DOI: 10.1080/03067318808081230

**URL:** <http://dx.doi.org/10.1080/03067318808081230>

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# Effects of Solvent and Humic Materials in Fluorimetric Determination of Oil Hydrocarbons in Marine Sediments

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*(Received 13 August 1987; in final form 28 October 1987)*

Serious interferences were found to occur during the fluorimetric determination of oil hydrocarbons in marine sediments. The presence of trace quantity of methylene chloride in the sediment extracts was found to considerably enhance the fluorescence intensity of chrysene. While the presence of humic materials, naturally existing in sediment, in some cases completely quench the fluorescence. This study suggests that a great precaution should be taken when fluorescence spectroscopy is applied to such determinations.

**KEY WORDS:** Oil hydrocarbon, sediment, humic material, solvent effect, quenching, fluorescence spectroscopy.

## INTRODUCTION

The estimation of the fate and impact of oil pollution on the marine environment requires the development of sensitive, accurate, precise and simple analytical methods for the determination of oil hydro-

carbons in marine samples. Oil hydrocarbons contaminating the marine environment may persist in the sediment for several years. This results in the continuous exposure of the marine life and demonstrates the dangerous effects of oil pollution. Therefore, monitoring of oil hydrocarbon levels in the sediments represents an essential step in oil pollution studies. At present, several analytical techniques are used for the determination of oil hydrocarbons in sediments. These techniques include GC, LC, GC/MS, IR, UV, and fluorescence spectroscopy.<sup>1</sup> Unfortunately, no single standard method for the measurement of oil hydrocarbons in sediment exists. This has resulted in great difficulties in comparing the analytical results from various laboratories. The technique of fluorescence spectroscopy is simple, quick, sensitive and requires relatively inexpensive instrumentation. However, it has some inherent limitations, especially when it is applied to the determination of oil hydrocarbons in marine samples.

The present paper discusses some of the problems encountered when fluorescence spectroscopy was applied to the determination of oil hydrocarbons in marine sediments from the Arabian Gulf.

## EXPERIMENTAL

### Sample preparation and analysis

All solvents used in this study were of high purity "distilled in glass" and used without further purification. Silica gel (60–200 mesh), and alumina (neutral) were also of high purity.

Sediment samples were collected from several locations along the Saudi coast of the Arabian Gulf. The samples were collected in glass jars capped with hexane washed aluminum foil liners and kept in a deep freeze until analysis. Frozen sediment samples were allowed to air dry over night before these were ground using a porcelain mortar. The dry sediment samples were sieved using 16 mesh sieve. Sediment samples (20 grams each) were soxhlet extracted for 6 hours using a 100 ml of methylene chloride as a solvent. The extract was evaporated to 15 ml using a Kuderna Danish (K–D) concentrator. The methylene chloride was replaced with hexane by the addition of 10 ml of hexane to the concentrator and the solvents were evaporated again to 1 ml. The sample extract was cleaned up to

remove any fluorescent material of indigenous origin that may interfere during the measurement. The clean up procedure involved the elution of the sample extract through a chromatographic column (0.9 cm ID and 30 cm long) containing 1.5 grams of alumina over 4.5 grams silica gel. The sample extract was applied to the column top, and eluted with 25 ml of methylene chloride/hexane mixture (3/7 V/V). The eluent was concentrated to less than 5 ml in K-D concentrator. The concentrate was then quantitatively transferred to a 5 ml capacity volumetric flask and the volume completed to the mark with hexane. With each set of samples extracted, one procedure blank was included. All measurements were made using a 1 cm silica cell. Chrysene was used as a standard for oil hydrocarbon determinations. The fluorimetric measurements were carried out using a Shimadzu Model RF 540 fluorescence spectrophotometer at an excitation wavelength of 267 nm and the emission was recorded at 382 nm.

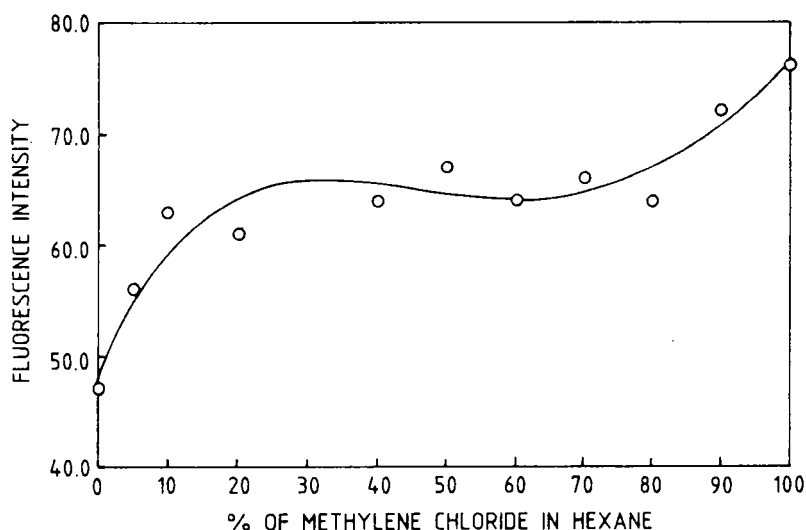
## RESULTS AND DISCUSSION

Results obtained from the analysis of control sediment samples collected from KFUPM beach have shown that the extraction and the cleaning procedure applied in this study were very effective. A recovery of 90% at 37.5 ng/g level was obtained. However, the following phenomena were noticed and found to greatly affect the analytical results.

### Solvent effect

Fluorescence properties of many organic compounds are very sensitive to the polarity of the surrounding environment. The emission spectra of fluorophores are normally shifted to a longer wavelength (Red shift) as the polarity of the solvent increases. This red shift is often, but not always, accompanied by decrease in the fluorescence intensity of the fluorophore.<sup>3</sup> During this study, it was noticed that no such shift in the emission spectra of chrysene standard occurs when the solvent changed from hexane to methylene chloride. However, the quantum yield obtained when methylene chloride used as solvent was very high as compared to hexane. It was also

found that the presence of small quantities of methylene chloride in the hexane considerably enhances the fluorescence intensity as is shown in Figure 1. Each point in Figure 1 represents the average of eight determinations. The standard deviation obtained for all the determinations ranges between 0.2 and 0.7. A mixture of polar and nonpolar solvent such as methylene chloride/hexane is normally used for eluting the aromatic hydrocarbons during the column chromatographic clean up procedure of the sediment extracts.<sup>2</sup> The concentration of the aromatic hydrocarbons in the sediment will be mistaken if the ratio of methylene chloride/hexane is changed during the final concentration step due to the large difference in the boiling points of the two solvents. In order to avoid any problems in the quantitation of oil hydrocarbons by this technique, great care should be given to the types and proportions of the solvents used in the final measurements. And also the solvent used in the final extract should be the same as those used in the preparation of the calibration standards.



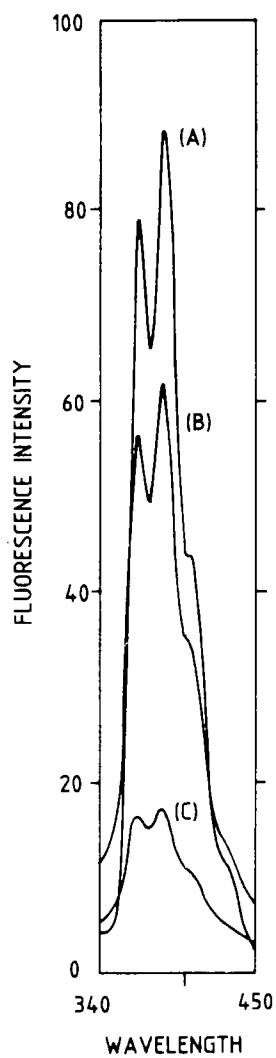
**Figure 1** Effect of methylene chloride content on the fluorescence intensity of chrysene.

### Fluorescence quenching

During the analysis of various sediment samples, it was noticed that some of the sample extracts suppress the fluorescence intensity. In some instances, a 100% decrease in the fluorescence intensity was noticed. Variations in the suppression intensity were also noticed with sediment samples collected from the tidal and intertidal zones of the same location. As is shown in Figure 2, sediment samples collected from the intertidal areas suppress the fluorescent intensity more than those collected from the tidal areas. This indicates that the concentration of the materials responsible for fluorescence quenching in the intertidal sediment samples were more than the others. Attempts were made to determine the identity of the materials responsible for the quenching effects. It is known that the presence of some trace metals like copper, lead, cadmium and manganese results in the fluorescence quenching.<sup>3</sup> The trace metals contents of those samples which shows variable quenching effects were measured using ICAP Jerall Ash 9000 system. No difference in the concentration of various trace metals was noticed. The extracts of various sediment samples were analyzed with capillary gas chromatography equipped with a FID detector. Again no difference in the chromatographic patterns of various samples were noticed. Total organic carbon (TOC) analyses of various sediment samples showed that the TOC content is higher in those samples which pose pronounced quenching effects on the fluorescence intensity of chrysene. This may indicate that the materials responsible for fluorescence quenching are humic materials of high molecular weights which are not volatilized at the injection port temperature of the gas chromatograph.

Unfortunately, a wide variety of substances act as fluorescence quenchers. Many aliphatic and aromatic amines are good quenchers for most unsubstituted aromatic hydrocarbons like chrysene.<sup>3</sup> These amines may originate from the humic substances usually existing in the marine sediment. Also, the phenomenon of fluorescence quenching has been used by several investigators<sup>4,5</sup> to study the binding of polyaromatic hydrocarbons to humic materials.

In addition to the above problems, fluorescence spectroscopy has some inherited limitations when it is applied to the analysis of oil hydrocarbons in environmental samples. It requires the use of a

**Figure 2**

standard calibration mixture which contains the same component as the sample under investigation. This kind of standard dose does not exist so far. Thus the comparisons of the results between different laboratories in various parts of the world becomes very difficult. The technique does not give information about the alkane and the cycloalkane contents of the samples which represents about 60% of the constituents of crude oil. The technique may be successfully applied in systems where no matrix effects occur, such as in the initial screening of seawater following an oil spill. Also it can find applications to the determination of oil hydrocarbons in bioassay studies which deals with the effects of oil on marine organisms.

Based on the analytical results obtained and other inherent limitations discussed above, we suggest that great precautions should be taken when fluorescence spectroscopy is applied for the determination of oil hydrocarbons in marine sediment.

### Acknowledgement

This work was supported by the Research Institute of the King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia.

### References

1. R. C. Clark, Jr. and D. W. Brown. In: *Effect of petroleum on arctic and subarctic marine environment and organisms*, Vol. 1 (D. C. Malins, ed.) (1977) p. 54.
2. UNESCO, The determination of petroleum hydrocarbons in sediments, manual and guide No. 11. Report prepared by the Intergovernmental Oceanographic Commission (IOC) of Unesco (1982).
3. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Plenum Press, New York, 1983).
4. J. F. McCarthy and B. D. Jimenez, *Environ. Sci. & Tech.* **19**, 11 (1985).
5. T. D. Gauthier, E. C. Shane, W. F. Guerin, W. R. Seikz and G. L. Grant, *Environ. Sci. & Tech.* **20**, 20 (1986).