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DISSOLVED/DISPERSED HYDROCARBONS IN SEAWATER, DETERMINED BY INFRARED AND FLUORESCENCE SPECTROSCOPY*

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Samples of sub-surface (1 m) and surface water were collected in the harbour of Las Palmas. These have been analyzed by infrared and by fluorescence spectroscopy in order to provide information on the levels of hydrocarbons generally present in the area. With the infrared method, the absorbance at 2925cm^{-1} has been measured and the values are given as API mixture equivalents. For the determination of total hydrocarbons by fluorescence spectroscopy, both the single-wavelength excitation fluorescence spectra which were used for the determination of the total concentration and the synchronous excitation spectra which give more structural information were recorded. The concentrations are given as chrysene equivalents. In all cases, high concentration levels of oil were detected. The results obtained from the two methods have been explained based upon the meteorological and oceanographic conditions.

KEY WORDS: Hydrocarbons, seawater, IR spectroscopy, fluorescence spectroscopy, oil-in-water.

INTRODUCTION

Currently, the detection and characterization of crude oil pollution in a variety of environments is of particular importance. Considerable difficulties are presented in selecting a single method, due to the variable nature of oil and the vast range of compounds, from gaseous hydrocarbons to bituminous compounds and from paraffinic to aromatic hydrocarbons. Furthermore, these components can vary both within different crude oils and, particularly, within oil wastes as a result of different processing conditions. It must be emphasised that this work deals with the overall discharge of oil-in-water and not with the determination of individual trace substances derived from crude oil.

Infrared spectrophotometry has been used as a satisfactory analytical method for the measurement and calculation of oil-in-water values.¹⁻² The method is based on the identification and quantitative measurement of absorptions due to the C—H stretching of CH, CH₂ or CH₃ groups within molecules.³⁻⁵ Of the three

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chemical groups indicated CH is the most characteristic for low-molecular-weight aromatic hydrocarbons. In the higher aromatic homologues the C atoms are partially or wholly substituted. For this reason, although the infrared method can provide data on the total levels of long straight-chain saturated hydrocarbons and cycloalkanes, the measurement of low-molecular-weight aromatic hydrocarbons and polynuclear aromatic hydrocarbons must be performed using other techniques.

The interest in monitoring polynuclear aromatic compounds has increased in recent years because of their carcinogenic nature and frequent occurrence in the environment. Synchronous excitation fluorescence spectroscopy (SEFS) has been applied in the identification and determination of these compounds, since the synchronous spectra provide considerably more structural information than the conventional spectra.⁶⁻¹⁰ The SEFS method entails the recording of spectra by simultaneously scanning the excitation and emission monochromators of a fluorescence spectrometer according to the procedure described by Lloyd⁶ and Frank and Gruenfeld.⁷ Use of the SEFS technique yields spectra of petroleum fraction and polynuclear aromatic compound (PAH) mixtures that are resolved according to the number of aromatic rings. Gordon and Keizer,¹¹ Harring¹² and Tanacredi¹³ demonstrated that the fluorescence of environmental water samples was caused by PAH constituents. SEFS emissions were therefore used in this study as an indication of PAHs.

In this work, the total hydrocarbon concentrations at different points in the harbour of Las Palmas have been determined by both infrared and fluorescence spectroscopy.

METHODS

The locations of the sites sampled between April and July, 1988 are shown in Figure 1. Seawater samples were collected at a depth of 1 m with a 2.8 l glass bottle, using a device built by us similar to the one described by Seldon, Sutcliffe and Prakash.¹⁴ We also collected surface water samples with a 1 l glass bottle using a special device, having two empty stoppered plastic bottles operating as a float which allowed us to take seawater at a depth of between 0 and 2 cm. In order to minimize the R/V contamination, a rubber dinghy was used and all the samples were taken just as the zodiac came to a halt in upwind position.

For the samples used for infrared measurements, immediately following collection, two litres of seawater at a depth of 1 m and 1 liter taken at the surface were extracted in two independent 4-liter glass separatory funnels. Usually two to three extractions with 100 ml of carbon tetrachloride were carried out. The combined extracts were then concentrated in rotavapor at 340–360 mm Hg to 5 ml and spectra were recorded between 3200 and 2700 cm^{-1} using a 1 cm pathlength cell in a Perkin-Elmer 783 infrared spectrophotometer, some of which can be seen in Figure 2. A blank prepared following the same treatment was used in all cases as reference solution. The total hydrocarbon concentrations in seawater were determined by measuring the peak height at 2925 cm^{-1} and the values are given in

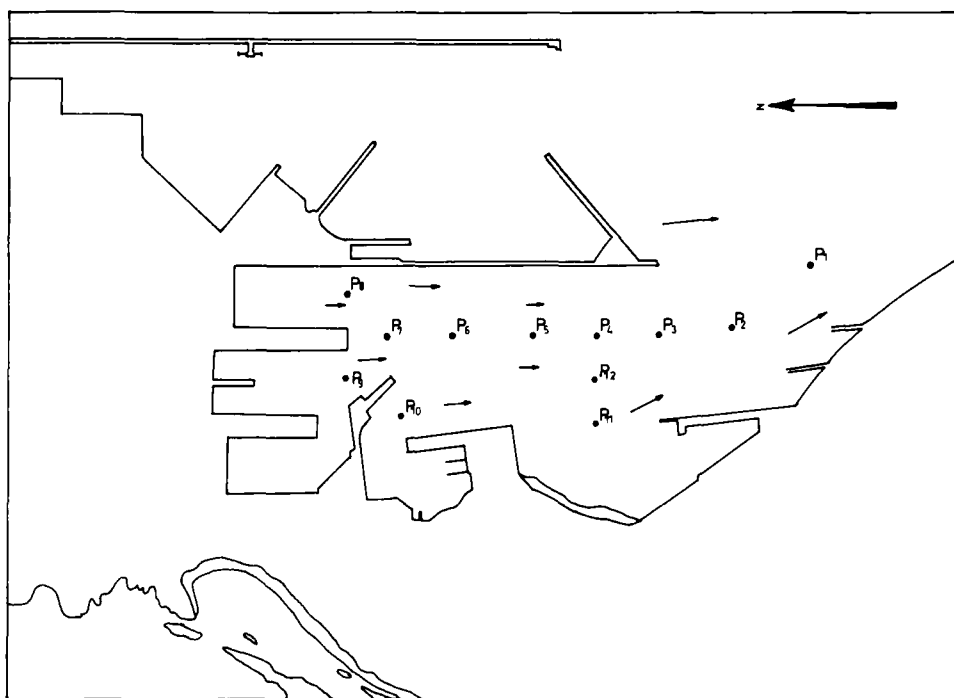


Figure 1 Area of investigation, location of sampling sites and flow of surface water in the harbour of Las Palmas.

toluene + isooctane + hexadecane mixture (API mixture) equivalents.¹⁵ The detection limit for this method was found to be on the order of $20 \mu\text{g l}^{-1}$, which is in the same range as described by the T90-114 AFNOR norm.¹⁵

For the samples used for fluorescence measurement, two liters of seawater at a depth of 1 m and 1 liter taken at the surface were transferred to two independent 4-liter glass separatory funnels. The procedure used was based on that adopted for the IGOSS project (IOC/WMO, 1984)¹⁶ and on that used by Gordon and Keizer.¹¹ Water samples were extracted three times with 100 ml of glass-distilled methylene chloride, and the extracts were combined. The final extract was then concentrated to dryness in a rotavapor and finally redissolved in 5 ml glass-distilled hexane. For each sample, a blank prepared according to the same method was used. The detection limit in this technique was found to be about $0.1 \mu\text{g l}^{-1}$. SEFS spectra of the hexane extracts were obtained by simultaneously scanning a fluorescence spectrometer excitation and emission monochromators and recording the fluorescence emission. Slit widths were set at 6 nm; excitation and emission monochromators were mechanically linked together at a difference of 23 nm, and the emission between 260 and 460 nm was recorded using a Perkin-Elmer MPF-44A fluorescence spectrophotometer with a 1 cm quartz cell. This technique, developed by Lloyd,⁶ allows the general types of aromatic compounds in a sample to be identified. In Figure 3, some of these spectra are shown.

For the determination of total hydrocarbon concentrations by fluorescence, the

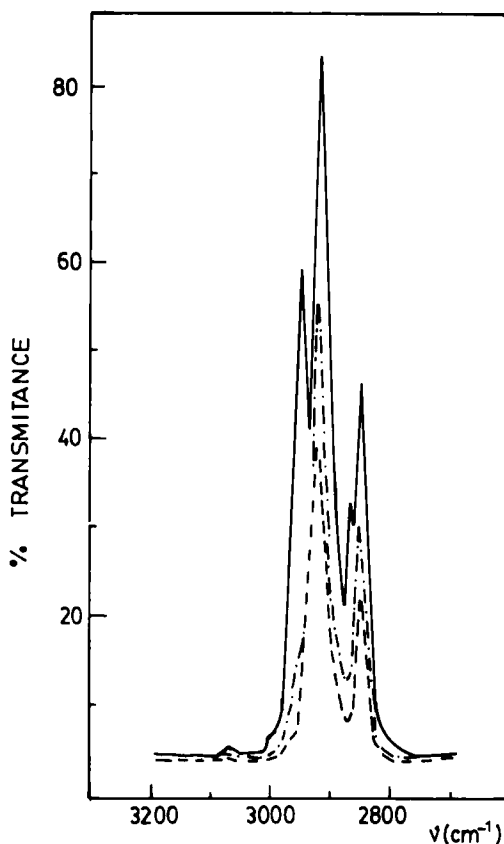


Figure 2 Infrared spectra of some carbon tetrachloride extracts exhibited by most of the samples.

fluorescence intensity of the different samples was determined using the conventional single-wavelength excitation fluorescence method.¹⁶ The sample was excited at 310 nm, as can be seen in Figure 4, which also shows the chrysene spectrum. The fluorescence intensity was then measured at 362 nm; the concentration values are given as chrysene equivalents.

DISCUSSION

The port of Las Palmas is mainly commercial and has 10 km of berthing area with sea depths of between 10 and 22 m. It has two points of entrance known as the Outer Port and Inner Port; the latter which has a width of 700 m has been studied in the present work (Figure 1). Las Palmas Bay is sheltered by the winds coming from three quadrants, and the prevailing winds blow in a northeastern and northeastern-northwestern direction. The sampling points were chosen to study the levels and the diffusion of hydrocarbons in the Inner Port. In Table 1, the different meteorological conditions and physico-chemical properties are shown for the three

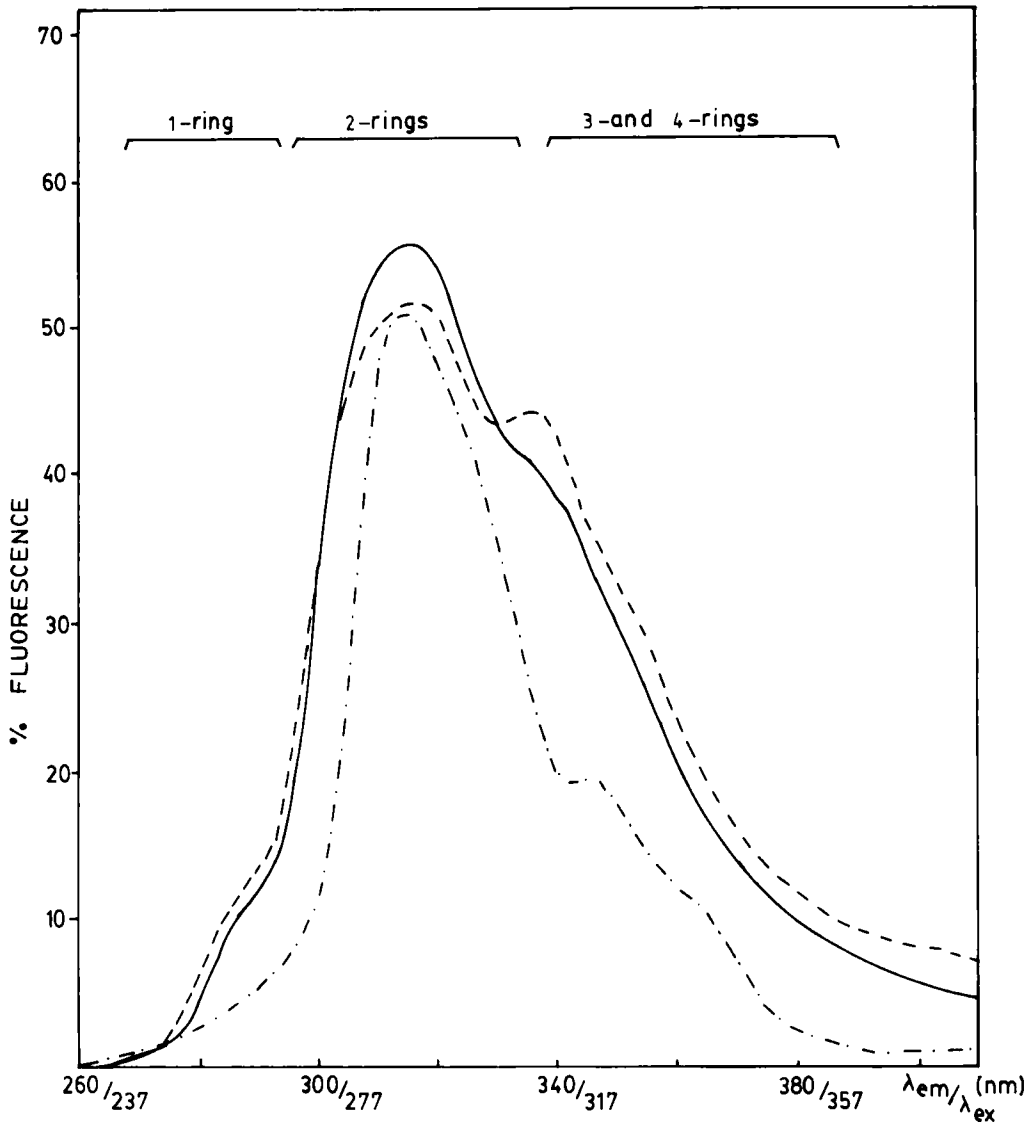


Figure 3 Fluorescence synchronous spectra of the three types of spectra exhibited by samples.

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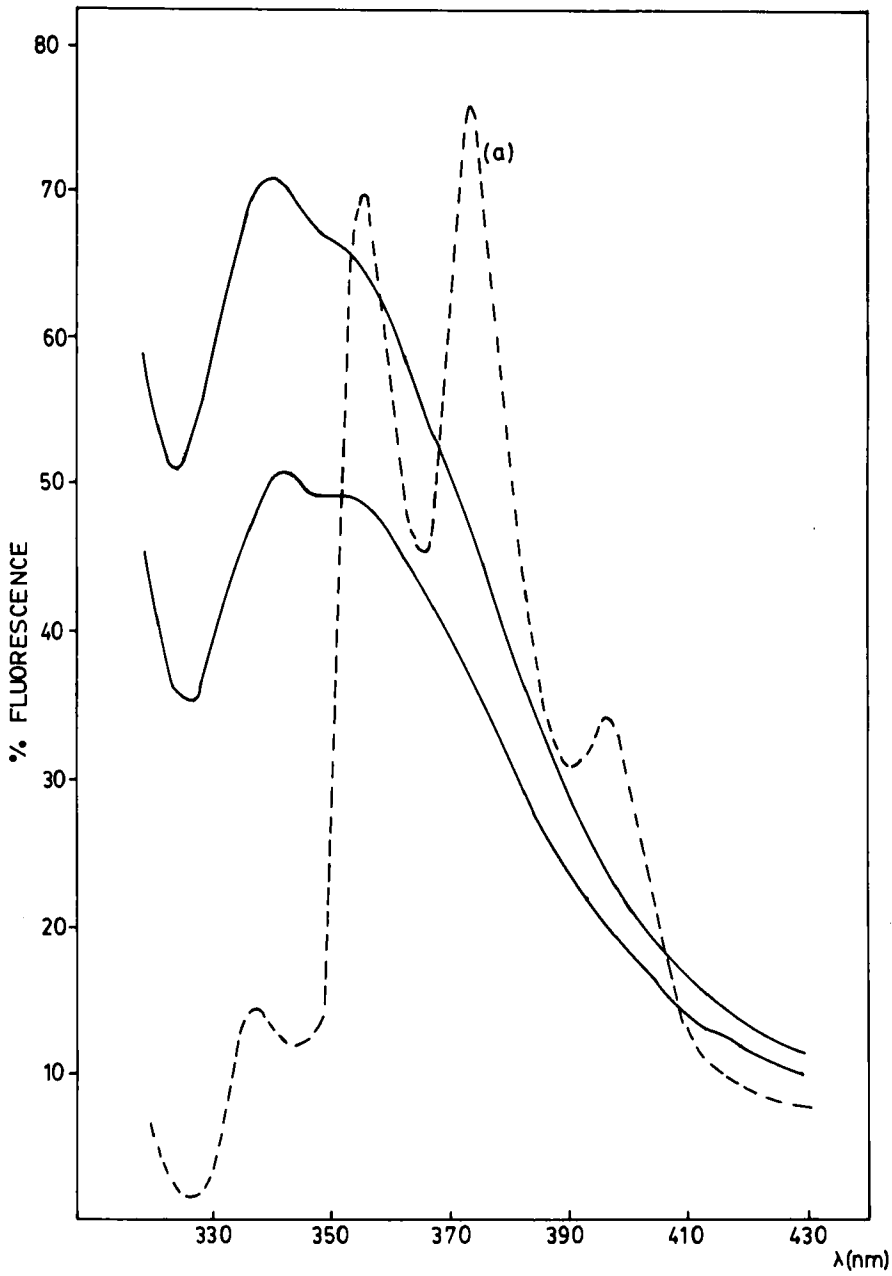


Figure 4 Fluorescence emission spectrum of chrysene (a) ($4.5 \mu\text{gml}^{-1}$) and of the two types of spectra exhibited by samples.

Table 1 Meteorological conditions and physical-chemical properties for the three sampling days

<i>Property</i>	<i>21-4-88</i>	<i>31-5-88</i>	<i>5-7-88</i>
Wind direction	N	NW	NW
Wind velocity (Km/h)	2.0	21.0	17.0
Pressure	1016.2	1018.2	1016.0
Air temperature	20.2	22.0	22.9
Water temperature (surface)	19.2	21.42	22.27
Water temperature (1 meter)	19.66	21.31	22.15
Salinity (%) (surface)	36.38	36.47	36.49
Salinity (%) (1 meter)	36.38	36.48	36.44

Table 2 Concentration of total hydrocarbons ($\mu\text{g}\cdot\text{l}^{-1}$) as API mixture equivalents determined by infrared spectroscopy

<i>Date</i>	<i>21-4-88</i>		<i>31-5-88</i>		<i>5-7-88</i>	
<i>Depth</i>	<i>Surface</i>	<i>1 m</i>	<i>Surface</i>	<i>1 m</i>	<i>Surface</i>	<i>1 m</i>
P ₁	794	262	887	790	905	605
P ₂	702	209	1086	797	953	672
P ₃	698	198	968	637	874	613
P ₄	621	276	690	636	1564	715
P ₅	698	325	889	832	955	754
P ₆	721	351	1297	1004	1021	673
P ₇	682	460	971	942	1220	611
P ₈	799	698	815	807	995	668
P ₉	810	596	985	759	1254	740
P ₁₀	562	391	1025	822	1054	781
P ₁₁	298	208	798	714	978	821
P ₁₂	281	126	658	565	1028	739

sampling days. In Tables 2 and 3, the results based on the infrared and fluorescence measurements, respectively, are shown.

Taking into account the infrared data based on API mixture equivalents, the concentration values for the different points are a function of the depth (surface or 1 m depth), the sampling day, and the position of the points in the sampling grid. In addition, the effect of the wind is very significant and as a rule, it can be considered that the concentration decreases from point 7 to point 1 and from the surface to a depth of 1 m under the meteorological conditions studied. At points 5 and 6, high concentrations are found, which is an agreement with the flow of surface water in the Inner Port shown in Figure 1.

The infrared method has proven to be a very satisfactory and easy method for determining the total hydrocarbons concentrations, mainly the concentration of long straight-chain saturated hydrocarbons and cycloalkanes in seawater. No important influence on the absorbance measured was observed when a clean-up using a Florisil column¹⁵ was carried out for the samples analyzed. Taking 10 liters of water in a special sampling bottle and determining the concentration for

Table 3 Concentration of total hydrocarbons ($\mu\text{g}\cdot\text{l}^{-1}$) as chrysene equivalents determined by fluorescence spectroscopy

Date	21-4-88		31-5-88		5-7-88	
Depth	Surface	1 m	Surface	1 m	Surface	1 m
P ₁	3.85	2.20	2.50	2.42	3.95	2.16
P ₂	5.21	2.32	3.69	3.21	4.79	2.37
P ₃	6.35	2.10	2.81	2.74	4.96	2.10
P ₄	3.89	1.90	2.74	1.07	2.54	1.86
P ₅	3.25	1.89	5.40	1.40	2.46	1.99
P ₆	3.26	2.30	6.12	2.27	3.54	2.53
P ₇	2.89	2.25	4.94	3.63	3.50	2.50
P ₈	1.98	2.16	3.09	2.85	2.51	2.30
P ₉	4.31	2.96	6.58	3.04	5.83	3.86
P ₁₀	2.98	2.10	3.02	2.25	3.93	2.29
P ₁₁	2.57	1.95	1.95	1.69	2.47	1.81
P ₁₂	2.10	2.35	1.96	1.54	2.61	2.77

the corresponding 10 samples of 1 liter of seawater, the magnitude of the analytical error was determined to have a relative standard deviation of 0.12%.

In the infrared spectrum (Figure 2), a weak peak at about 3080cm^{-1} which is due to the CH stretching vibration mode in aromatic hydrocarbons is observed. However, this peak is difficult to quantify using this technique. For this reason we have also used fluorescence spectroscopy for the determination of the total petroleum hydrocarbons. Previous authors who have discussed the use of fluorescence spectroscopy to this end, state that it is a general detection method for aromatic compounds. A correlation between both techniques is almost impossible because different compounds are determined and because the ratio between long-chain saturated hydrocarbons, cycloalkanes and polynuclear aromatic hydrocarbons generally is not constant. The aromatic compounds have widely varying fluorescence characteristics depending upon their structure. Lloyd⁶ has demonstrated that the wavelength of maximum emission is a function of the ring number. In Figure 3 it can be observed how both the surface and 1-m depth samples have pronounced peaks in the 310–330 nm region, which is indicative of the presence of naphthalenes, and also lower peaks in both the 280–290 nm and 340–380 nm regions, the former due to benzene and the latter corresponding to three- and four-ring compounds. For the routine quantitative analyses, we have used the emission measured at 362 nm corresponding to two-, three- and four-ring aromatics, because all the samples had more relevant peaks in this range than in the other one (Figure 4), and because the former range is recommended by the IOC Manuals and Guides No. 13.¹⁶

The values obtained as chrysene equivalents are shown in Table 3. All the values at a 1-meter depth are in the $1\text{--}3\mu\text{g}\cdot\text{l}^{-1}$ range, while higher concentrations were obtained for the surface water depending mainly on wind strength. Again, higher values are found at points 5, 6 and 7 and also at the furthest points 1, 2 and 3. This can be explained by taking into account the flow of surface water and the presence of a diesel station on the sport wharf near points 1–3.

Taking into account the interest in monitoring polynuclear aromatic hydrocarbons because of their occurrence in the environment, the fluorescence method appears to offer a sensitive analytical technique in the estimation of the aromatic fraction in petroleum residues in seawater. It is important to bear in mind the limitations of the method if comparisons are made with estimates based on infrared or other analytical techniques.

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