Bull. Environ. Contam. Toxicol. 30, 413–419 (1983)

Use of Fluorescence Spectroscopy for Monitoring Petroleum Hydrocarbon Contamination in Estuarine and Ocean Waters

W. A. Maher

Department of Physical and Inorganic Chemistry, The University of Adelaide, Adelaide, South Australia

It is recognized that repeated sublethal discharges of petroleum hydrocarbons into the marine environment may have long term ecological effects (CONNELL and MILLER 1981). Therefore a need exists for the rapid and accurate identification of contaminated waters to allow the extent of pollution to be assessed and sources of petroleum hydrocarbon inputs to be identified.

The presence of aromatic hydrocarbons in water samples provides a marker of petroleum pollution as all oils contain aromatic hydrocarbons while few if any biogenic aromatic hydrocarbons are produced in the marine environment (YOUNGBLOOD and BLUMER 1975).

Fluorescence spectroscopy has been used to obtain an estimate of the aromatic hydrocarbon contamination in extracts of seawater (KEIZER and GORDON 1973; LEVY and WALTON 1973; LAW 1978), sediments (HARDGRAVES and PHILLIPS 1975) and marine organisms (ZITKO 1970). This paper examines the use of fluorescence spectroscopy for the routine monitoring of petroleum hydrocarbon contamination in estuarine and seawaters.

EXPERIMENTAL

Equipment: All fluorescence measurements were made with a Perkin Elmer Model 3000 spectrofluorimeter.

Materials: All chemicals were of analytical reagent grade. Solvents were distilled before use. Crude and refined oils were obtained from commercial sources.

Sampling: A sampler constructed in our laboratory (MAHER et al. 1982) was used in this study; it consisted of a teflon inlet valve mounted onto a detachable glass bottle. The sampler opens and closes at the sampling depth, minimising the risk of contamination from the surface layer.

Extraction: Aromatic hydrocarbons were extracted from water samples (1 ℓ), after adjustment of pH to 4.0-5.0, by partitioning into 2 × 40 ml of methylene dichloride (KIEZER and GORDON 1973).

Extracts were dried over anhydrous sodium sulphate, the methylene dichloride removed under reduced pressure and the residue dissolved in 5 ml of n-hexane. Samples were stored at 2°C in the dark until analysed.

Analysis: The aromatic hydrocarbon content of the extracts were estimated by fluorescence emission spectroscopy. Solutions were excited at 300 nm, the emission scanned from 310-500 nm and the fluorescence emission intensity of the main peaks measured and reported as equivalents of m-terphenyl (λ_{em} 330 nm) and chrysene (λ_{em} 380 nm). The fluorescence emission of the reagent impurities was measured as the blank.

RESULTS AND DISCUSSION

Sampling: A problem in sampling subsurface water is avoiding contamination of the sampler as it passes through the surface layer and any oil slick present. The inner surfaces of the sample container must not come into contact with water other than the sample because of the ready adsorption of hydrocarbons onto surfaces (GORDON et al. 1974). The sampler employed in this study ensured that the collection bottle comes only into contact with the water being sampled as the sampler opens and closes at the sampling depth. Also an outer shield protects the sampling valve from contamination during the passage of the sampler through the surface and water column.

To determine if aromatic hydrocarbons were lost by adsorption onto the inner surface of the sampling bottles, bottles were emptied and rinsed after sampling with 100 ml of methylene dichloride. Subsequent analysis of the extract after evaporation of the solvent and dissolution of the residue in n-hexane showed that the amount of fluorescing material adhering to the inside walls of the bottles was negligible.

Choice of reference standards: The application of fluorescence spectroscopy to the estimation of aromatic hydrocarbons in extracts required the choice of a reference standard, as the composition of oils and hence the concentration and emission intensity of fluorescing components vary widely. The fluorescence emission spectra of several crude oils and refined oil products (Figures 1 and 2) were examined to determine any common features. The results showed that oils can be classified into two groups. (a) Oils containing predominately two and three ringed aromatic compounds with a fluorescence emission maximum at approximately 330 nm (Figure 1 b, d, e, f and 2 c, d, e, f). (b) Oils containing aromatic compounds with three or more rings with a fluorescence emission maximum at approximately 380 nm. It would therefore appear meaningful to report results as the fluorescing material present at 330 nm and 380 nm. Two pure compounds which fluoresce at the wavelengths of maximum fluorescence of the oils, m-terphenyl ($\lambda_{max} \sim 330$ nm) and chrysene ($\lambda_{max} \sim 380$ nm), were selected as reference standards. An emission monochromator slit width was chosen to produce single emission peaks for the reference standards without resolving detail.

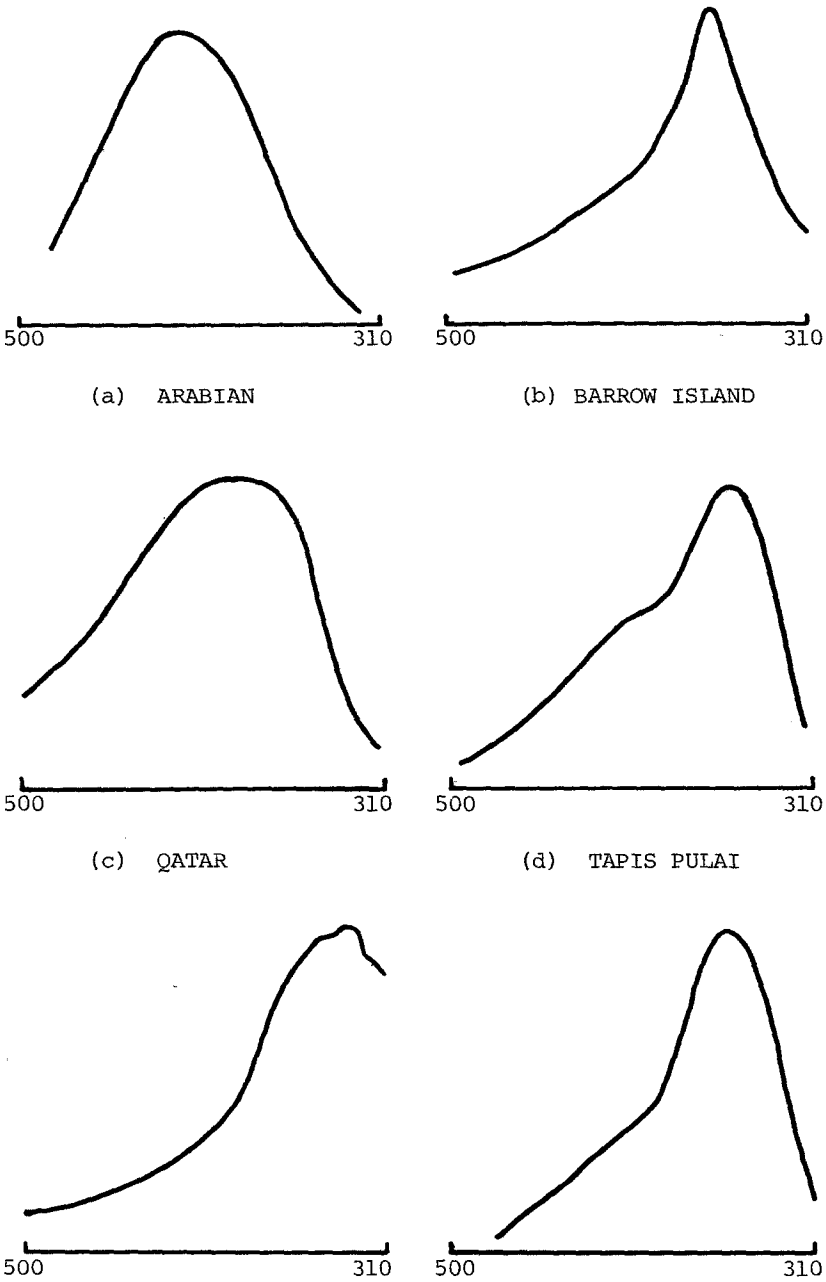

Fig. 1. Fluorescence emission spectra of crude oils .

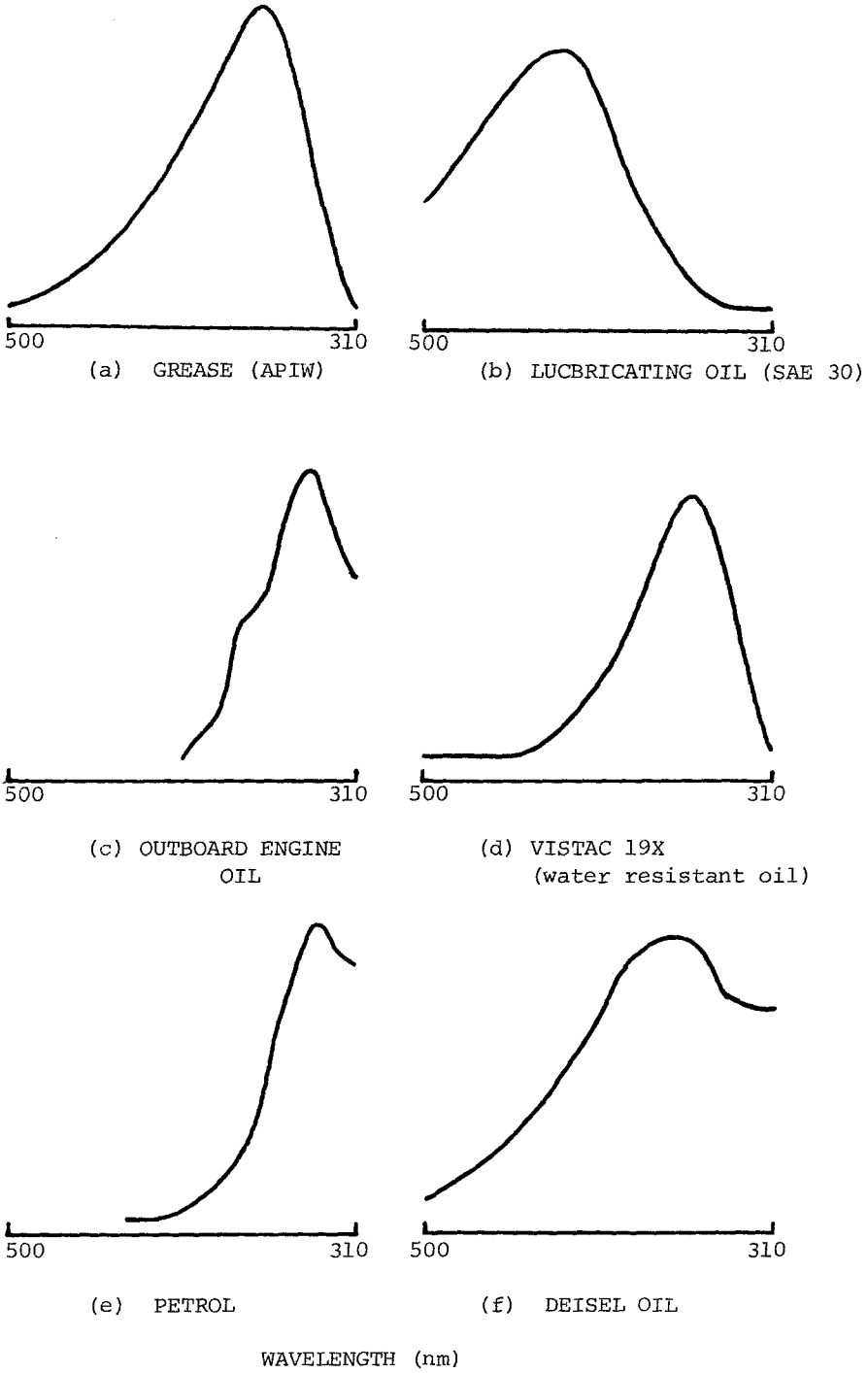

Fig. 2. Fluorescence emission spectra of refined oils

Evaluation of procedure: One litre samples of seawater were spiked with 1 µg of either Tapis Pulai crude, Barrow Island crude or lubricating oil and analysed by extraction and spectrofluorimetry. Recoveries of all oils were greater than 95% and the relative standard deviation ranged from less than 2% for the Barrow Island crude and lubricating oil to 3% for the Tapis Pulai crude.

Interferences: The suitability of using fluorescence spectroscopy to estimate the concentration of petroleum aromatic hydrocarbons in extracts depended on the effect of other dissolved components on the background fluorescence. Several compounds that are commonly found in estuarine and seawaters were added to 1 litre samples of seawater and the blank remeasured (Table 1). The results show that the compounds tested cause no significant increase in the fluorescence emission of the blank.

Table 1. The effect of dissolved organic compounds on the fluorescence emission of the blank. (Temperature 20°C, Salinity 20‰ S).

Compound	Concentration (µg/ℓ)	Change in fluorescence emission of blank %	
		330 nm	380 nm
Humic acid (disodium salt)	5000	1.2	0.8
Chlorophyll pigments (seaweed extract)	5000	2.1	2.8
Detergent (containing optical brighteners)	10000	-0.7	-0.3

Application to pollution source monitoring: Water samples were collected from locations near potential sources of petroleum hydrocarbon inputs (Table 2).

The fluorescence emission intensity of extracts at 330 nm and 380 nm varied depending on the source of petroleum hydrocarbons. Measurement at 330 nm gives a better measurement of petroleum discharges near the boat marina and sewerage inlet. Measurement at 330 nm and 380 nm is more suitable for monitoring potential inputs from oil refineries and storm water drains.

Table 2. Estimation of aromatic hydrocarbon concentrations in estuarine and seawaters near potential sources of petroleum hydrocarbons.

Source	Temp °C	Salinity ‰ S	Concentration (ng/ℓ) as m-terphenyl	as chrysene
Adjacent oil refinery	23	34.6	1200	900
Boat marina	22	32	2700	800
Adjacent sewerage discharge	24	29	186	69
Adjacent stormwater drain	21	4	1400	1200
River input	21	19	176	114
Seawater*	23	35	< 50	< 50

* pristine environment

Conclusions

1. This study has shown that if fluorescence spectroscopy is to be used to monitor petroleum contamination of estuarine and seawaters, the fluorescence emission of extracts should be measured at least at two wavelengths (330 nm; 380 nm) to allow the detection of fuel oil, lubricating oil and crude oil inputs.

2. A preliminary clean up of extracts is not usually required thus the measurement of the fluorescence emission of water extracts provides a rapid means of monitoring petroleum hydrocarbon contamination.

REFERENCES

CONNELL, D.W. and G.J. MILLER: C.R.C. Crit. Rev. Environ. Control 11, 37 (1981).

GORDON, D.C., P.D. KEIZER and J. DALE: Mar. Chem. 2, 251 (1974).

HARDGRAVE, B.T. and G.A. PHILLIPS: Environ. Pollut. 8, 193 (1975).

KEIZER, P.D. and D.C. GORDON: J. Fish. Res. Bd. Canada 30, 1039 (1973).

LAW, R.J.: Mar. Pollut. Bull. 9, 321 (1978).

LEVY, E.M. and A. WALTON: J. Fish. Res. Bd. Canada 30, 251 (1973).

MAHER, W.A., I. KEENE and J.D. SMITH: (1982) (to be published).

ZITKO, V.: Bull. Environ. Contam. Toxicol. 5, 559 (1970).

YOUNGBLOOD, W.W. and M. BLUMER: Geochim. Cosmochim. Acta 39, 1303 (1975).

Accepted January 12, 1983