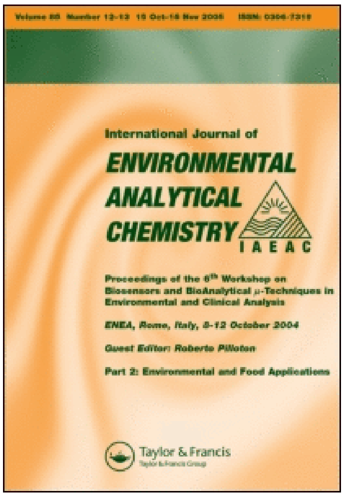

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INFLUENCE OF WEATHERING ON OIL SPILL IDENTIFICATION*

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IR, UV and fluorescence spectroscopy are applied to identify oil spills on the sea. In order to establish the influence of weathering, the samples of crude oil, motor oil, heavy and light gas oil were weathered up to 15 days. Samples were taken every few hours, and analysed.

The ratio of maximal absorbances were correlated with the time of the exposure. All ratios of maximal IR or UV absorbances decrease slowly with the weathering, so that identification of several oil samples was possible regardless of the time of weathering. Fluorescence spectroscopy cannot be applied if the samples contain only saturated hydrocarbons.

KEY WORDS: Oil spill, oil hydrocarbon, weathering, identification, spectroscopy.

INTRODUCTION

The dissemination of petroleum and petroleum products into the marine environment causes a number of serious pollution problems.[1] The estimation of the fate and impact of oil pollution on the marine environment requires sensitive, accurate, precise and simple analytical methods.[2]

Tracing and identifying an oil spill becomes difficult when a product is weathered, which is a complex process. When crude oil is released into the sea, immediate changes occur as a result of several processes. These include evaporation, dissolution, dispersion, photo-oxidation, biodegradation, emulsification and adsorption.[3] All these processes result in a changing composition. The analytical approach requires a selection of methods which are least affected by weathering.[4] These include: gas chromatography (GC),[5,6] gas chromatography/mass spectrometry (GC/MS),[7] fluorescence[2,8,9] and infrared spectroscopy,[10,11] thin-layer chromatography (TLC), liquid chromatography (LC),[13] emission spectroscopy,[4] ultraviolet absorption spectrometry,[14] laser Raman spectroscopy,[15] atomic absorption spectroscopy (AAS) and inductively coupled plasma spectroscopy (ICP).[16]

An analysis of various samples of oil spread on the surface of water is often required because of oil spillage problems. The object is to identify the oil for legal purposes and to provide information for inspection authorities. The method and the procedure to be used in any particular situation depend on the nature of the problem to be solved. In the case of oil spill identification the chosen method must

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*Partly presented at TNO Conference on Oil Pollution—Fate and Effects of Oil in Marine Ecosystems 1987, in Amsterdam.

be sensitive, fast and reliable.[16] To this end, we have selected fluorescence, infrared and ultraviolet spectroscopy.

EXPERIMENTAL

The influence of weathering on the analysis of oil was done in the first series of the experiments on two samples: crude oil_I ($d_{15°C}=0.860\,g/cm^3$) and motor oil ($d_{15°C}=0.867$). In the second series of the experiments, crude oil_{II} ($d_{15°C}=0.870\,g/cm^3$), heavy ($d_{15°C}=0.921\,g/cm^3$) and light ($d_{15°C}=0.832\,g/cm^3$) gas oil were weathered and analysed. The changes in hydrocarbon composition during the process of weathering were studied. The oil samples were spread on the sea surface, and samples taken in the first series for up to 139 hours. The samples in the second series were weathered for 15 days. The experiments were carried out on the Adriatic Sea at the coast near Zadar in August; 2 mm of oil slick was spread at a depth of about 1 m. The average temperature of the sea was 21 °C and the time of sunshine was 10 hours daily.

Ratio of Infrared Absorbances (*RIA*)

The samples were analysed on a Perkin–Elmer Model 257 IR spectrophotometer, in chloroform as solvent. The maximal absorbances were measured at 720, 810, 1375 and $1600\,cm^{-1}$. The following RIA were calculated: 720/1375, 810/1375, 810/720, 1600/1375, 1600/720 and $810\,cm^{-1}/1600\,cm^{-1}$, as proposed by Kawahara *et al.*[17,18] and modified by Mattson *et al.*[19,20] and applied several times by our group.[16]

Ratio of Ultraviolet Absorbances (RUA)

The samples were measured on a Pye Unicam SP 8000 UV spectrophotometer using n-hexane as a solvent. The UV absorbances were measured between 200 and 400 nm. The maxima at 248, 267 and 278 nm in the first series of the experiments were measured and their RUA were calculated for 248/267 and 248/278 nm (see ref. 21). In the second series of the experiments the RUA at 228/256 were determined.

Ratio of Fluorescence Spectroscopy (RFS)

The spectrometer used was a Carl Zeiss Specord M 40. As a standard Rhodamine B in ethyleneglycol (103 mg/l) was used. A WK 38 yellow filter was applied, which has a cut-off at $27548\,cm^{-1}$. The samples were dissolved in chloroform.

RESULTS AND DISCUSSION

RIA

The maximal absorbances were chosen according to the hydrocarbon structure: signals at 720, 810, 1375 and $1600\,cm^{-1}$ correspond to the paraffinic, naphthenic, methyl group and aromatic structure, respectively.

Table 1 Ratios of IR absorbances (RIA, cm^{-1}/cm^{-1}) for two oil samples

Sample	*Time (h)*	*720*	*810*[a]	*810*[b]	*1600*	*1600*	*810*
		1375	*720*	*1375*	*1375*	*720*	*1600*
Crude oil_1	39	0.463	0.400	0.185	0.333	0.720	0.555
	48	0.489	0.388	0.190	0.554	1.130	0.342
	66	0.458	0.385	0.180	0.290	0.632	0.608
	88	0.493	0.340	0.168	0.402	0.816	0.416
	91	0.448	0.369	0.165	0.379	0.846	0.436
	115.5	0.503	0.333	0.168	0.369	0.733	0.454
	139	0.508	0.320	0.163	0.305	0.600	0.533
Motor oil	20	0.432	0.056	0.024	0.079	0.184	0.303
	39	0.346	0.067	0.023	0.016	0.048	1.400
	48	0.551	0.048	0.026	0.092	0.166	0.286
	70	0.362	0.048	0.017	0.043	0.119	0.400
	73.5	0.523	0.043	0.022	0.134	0.255	0.166
	88	0.363	0.042	0.015	0.054	0.150	0.277
	98	0.418	0.028	0.012	0.069	0.166	0.166
	116	0.425	0.040	0.017	0.085	0.200	0.200
	139	0.388	0.030	0.012	0.036	0.092	0.333

[a] RIA_1
[b] RIA_2

The values of RIA for the crude oil_1 and motor oil samples are shown in Table 1. Also based on previous experiments, two main ratios were chosen, 810/720 (RIA_1) and 810/1375 (RIA_2), in order to correlate with the time of weathering. During the weathering of crude oil as well as motor oil a slow decrease of the ratios occurs (Figures 1 and 2). The statistical analysis of the correlation studied proved to be linear, as was also shown previously:[16]

$$\mathrm{RIA} = -aw + b$$

The values of coefficients a and b for both samples, as well as the corresponding standard deviations are shown in Table 2. It is evident that in spite of the influence of weathering the samples can be identified. The main ratios of IR absorbance decrease so slowly that RIA_1 and RIA_2 can serve as a tool to identify the source of marine pollution caused by mineral oil regardless of the age of an oil spill. Also according to our previous experiments,[16,22] the method can be successfully applied to identify the source of oil slick. The values of RIA_1 and RIA_2 (Table 1) are sufficiently different from sample to sample to distinguish one oil from the other, regardless of their age. The same results were obtained when different crude or motor oils were weathered.

RUA

Maximal UV absorbances were measured at 248, 267 and 278 nm. Table 3 shows

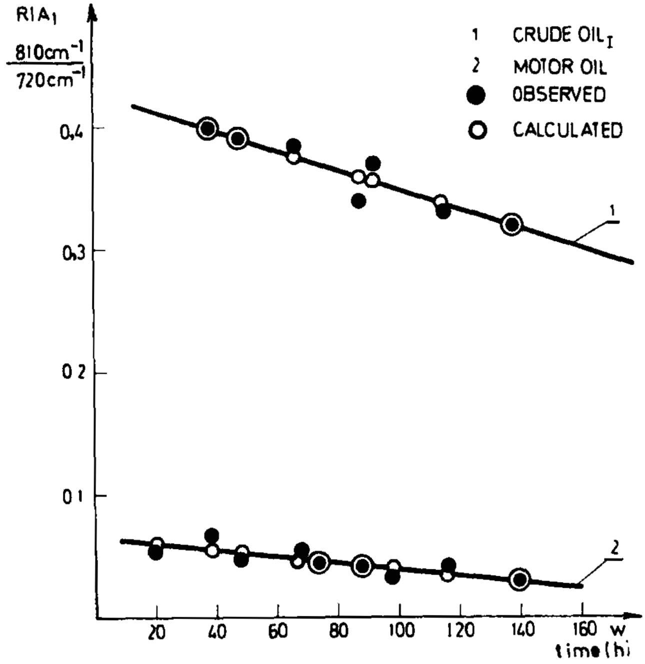

Figure 1 Correlation of 810/720 RIA and the time of weathering (w).

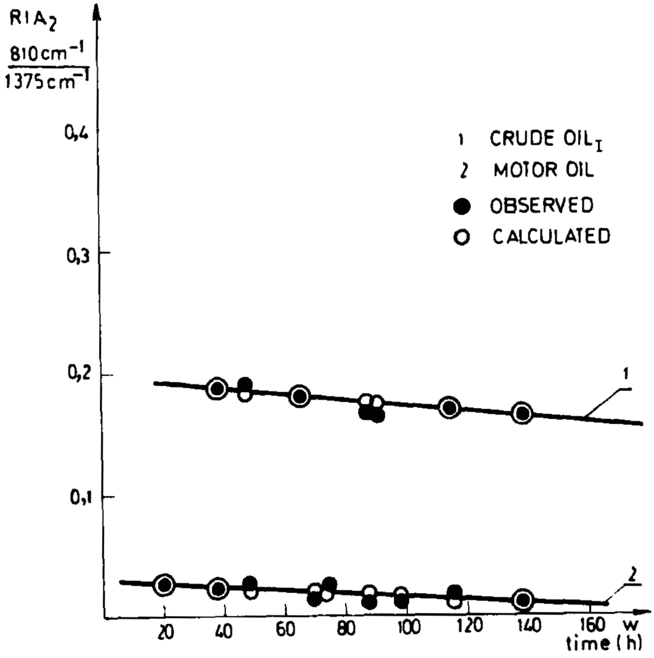

Figure 2 Correlation of 810/1375 RIA and the time of weathering (w).

Table 2 The coefficients a and b with standard deviations for linear relationship of weathering time (w) and RA (RIA, RUA and RFI) ratios

Sample		$RA = -aw + b$		
		a	b	s
Crude oil$_I$	RIA$_1$ (810/720)	$7.79\cdot10^{-4}$	0.427	0.0100
	RIA$_2$ (810/1375)	$1.85\cdot10^{-4}$	0.190	0.0062
Motor oil	RIA$_1$ (810/720)	$2.67\cdot10^{-4}$	0.065	0.0070
	RIA$_2$ (810/1375)	$1.16\cdot10^{-4}$	0.027	0.0030
	RUA$_1$ (248/267)	0.059	17.319	1.1001
	RUA$_2$ (248/278)	0.033	9.616	0.7318
	RFI$_1$ (25900/26800)	$1.96\cdot10^{-3}$	1.295	0.0273
	RFI$_2$ (22800/25900)	$8.49\cdot10^{-3}$	1.463	0.0783
Light gas oil	RUA (228/256)	0.073	3.077	0.0778
Crude oil$_{II}$	RUA (228/256)	$6.39\cdot10^{-3}$	1.551	0.0220
Heavy gas oil	RUA (228/256)	$3.21\cdot10^{-3}$	1.014	$9.23\cdot10^{-3}$

Table 3 Ratio of UV absorbances (RUA, nm/nm) of a motor oil sample

Time (*h*)	*248/267*	*248/278*
20	16.56	9.93
39	14.00	8.00
48	15.00	7.50
70	14.30	7.53
73.5	11.99	6.50
88	12.88	5.89
98	11.60	6.52
116	10.20	6.60

the RUA for 248/267 (RUA$_1$) and 248/278 (RUA$_2$) for all samples of motor oil during weathering (w); RUA$_1$ and RUA$_2$ decrease during the weathering.

The coefficients a and b as well as the standard deviations obtained by polynomial regression are shown in Table 2. Figures 3 and 4 illustrate the correlations shown in Table 2. As the absolute value of coefficient a is lower for the correlation of w and RUA$_2$ (0.033) than w and RUA$_1$ (0.059), it is preferable to use RUA$_2$, i.e. the ratio 248/278. As the motor oil and other petroleum products are mixtures of numerous hydrocarbons and additives, it is not possible to assign the various maxima to specific compounds. That is why it is not possible to define the exact wavelength of the maximums to be used for RUA. The smallest absolute value of the statistical parameter a will define the best ratio of UV maximal absorbances.

The results of the experiments of weathering carried out in the second series with the crude oil, and the heavy and light gas oils analysed by UV are shown in Table 4 and Figure 5. The coefficients a and b as well as the standard deviation obtained by polynomial regression are shown in Table 2. The RUA 228/256 values decrease slowly, so that the differences between the samples are evident, even when

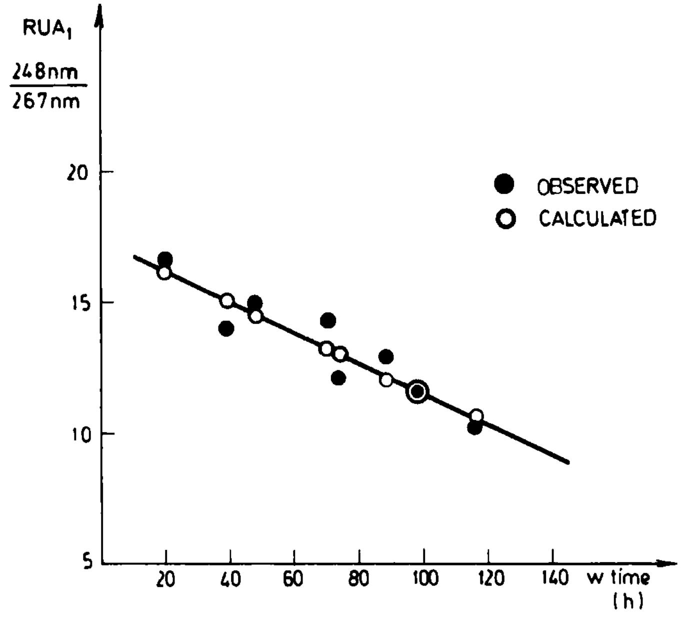

Figure 3 Correlation of 248/267 RUA and the time of weathering (*w*) for motor oil samples.

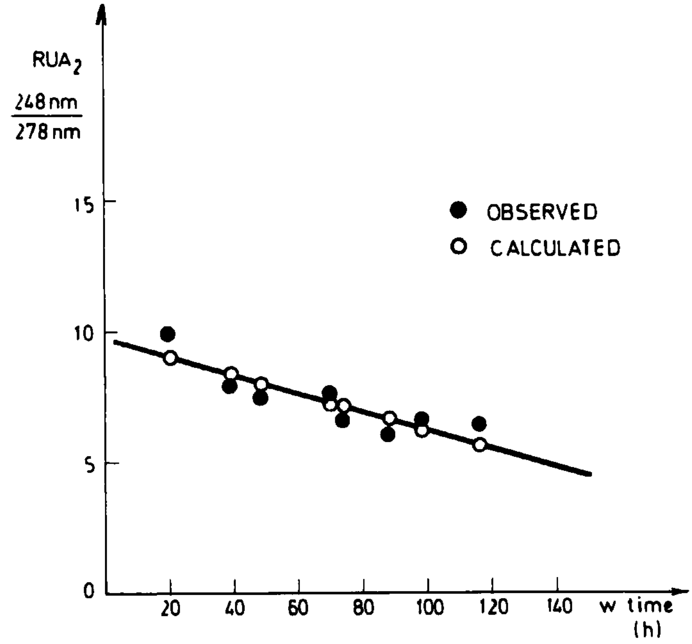

Figure 4 Correlation of 248/278 RUA and the time of weathering (*w*) for motor oil samples.

Table 4 Ratio 228/256 RUA for three oil samples

Time (days)	*Crude oil$_{II}$*	*Heavy gas oil*	*Light gas oil*
2	1.533	1.000	2.888
5	1.538	1.007	2.724
10	1.465	0.986	2.428
15	1.465	0.962	1.922

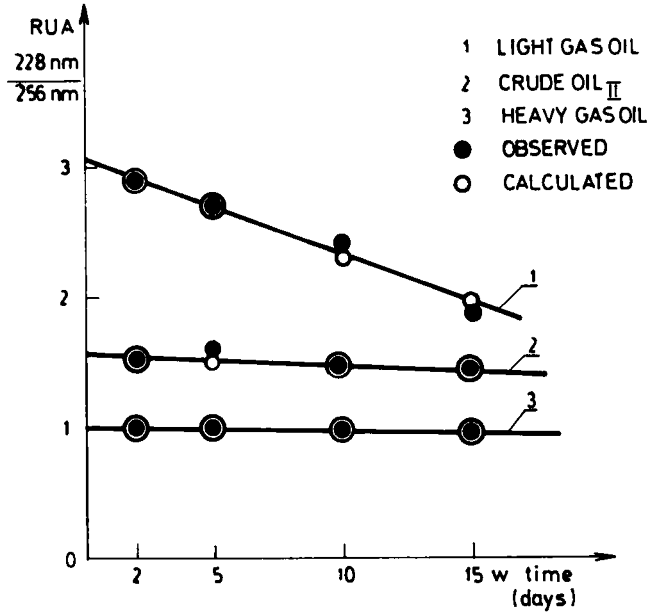

Figure 5 Correlation of 228/256 RUA and the time of weathering (*w*).

the oil slick is spread on the surface of the sea during 15 days. Our experience in several cases confirm Levy's findings,[21] that ratios of UV absorbances can serve as a tool to identify the source of oil pollution, regardless of the ageing of the spread oil.

RFI

Fluorescence spectroscopy is considered a powerful tool when identifying oil spills. The method is extremely sensitive for naturally fluorescing oil components and additives. Many of the naturally fluorescing materials present, such as the polynuclear aromatic hydrocarbons are not particularly volatile nor soluble, so that fluorescence spectra are relatively stable to weathering.[9]

In the first series of experiments the motor oil sample showed emission maxima at 22800, 25900 and 26800 cm^{-1}. Under the same conditions, the crude oil sample, as well as the samples of the second series gave rather smooth fluorescence

Table 5 Ratios of fluorescence spectroscopy (RFI, cm^{-1}/cm^{-1}) for weathered motor oil sample

Time (*h*)	RFI_1 *25 900/26 800*	RFI_2 *22 800/25 900*
20	1.250	1.350
39	1.200	1.100
48	1.190	0.940
70	1.200	0.820
73.5	1.140	0.920
88	1.160	0.810
98	1.106	0.600
116	1.030	0.530
139	1.020	0.220

spectra without any characteristic peaks. In other words, RFI could only be calculated for motor oil weathered samples (Table 5 and Figures 6 and 7).

It is evident that RFI 25900/26800 should be preferred to 22800/25900, the coefficients a being $1.96 \cdot 10^{-3}$ and $8.49 \cdot 10^{-3}$, respectively (Table 2).

Fluorescence analysis of our samples shows that only the motor oil contains a considerable quantity of aromatic hydrocarbons and that crude oil samples, and heavy and light gas oils obtained from the same crude oil mainly contain saturated hydrocarbons (alkane and cycloalkane content of about 60%). That is why we agree with Fayad *et al.*,[2] who suggested that great caution should be taken when applying fluorescence spectroscopy for the determination of oil hydrocarbons in the marine environment.

CONCLUSIONS

Three relatively simple methods were applied in order to identify an oil spill on the sea: infrared, fluorescence and ultraviolet spectroscopy. The influence of weathering on the reliability of these methods was examined. The use of IR and UV maximal absorbances ratios can successfully be applied, regardless of the weathering of the oil spill. Fluorescence spectroscopy must be applied with much caution, because samples which mainly contain saturated hydrocarbons do not give an adequate response. Especially in complicated cases, one should preferably apply all three techniques.

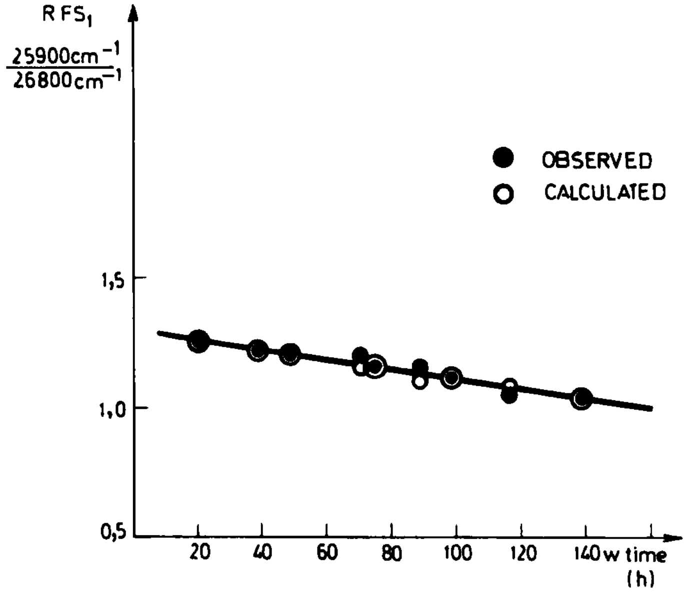

Figure 6 Correlation of 25 900/26 800 RFI and the time of weathering (*w*) for motor oil samples.

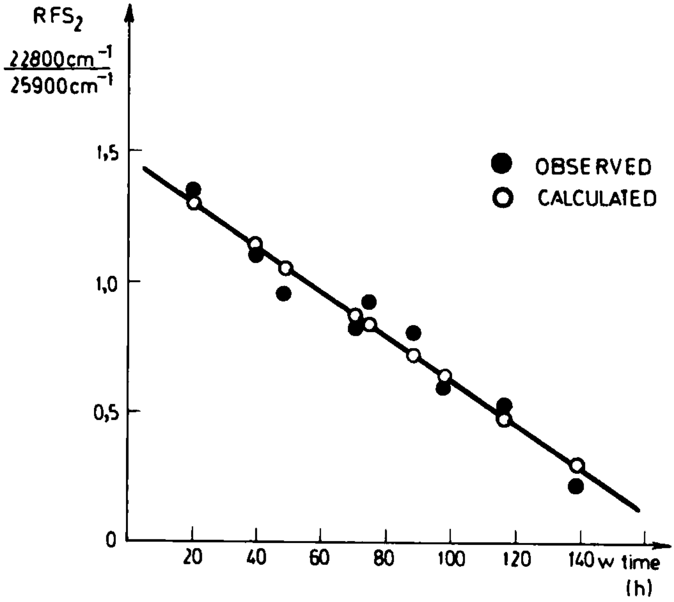

Figure 7 Correlation of 22 800/25 900 RFI and the time of weathering (*w*) for motor oil samples.

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