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Identification of Oil Pollution Sources in Harbour Waters

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Gas chromatography, infrared spectroscopy and UV-fluorescence analyses were made to establish the similarity of oil samples from the harbour waters and their suspected source. Results showed that 5 out of 7 samples tested were of the same origin while the other two were of different origin.

International Maritime Organisation (IMO) has prohibited release of oil and its products within 50 nautical miles from the shore[1]. Using proper tagging techniques, it should be possible to match an oil spill to one of the reference samples and the source of pollution could then be traced. It is well known that gas chromatography, infrared spectroscopy and fluorescence spectroscopy can be used for finger printing oil spills and pin point the source[2-4]. The purpose of this study is to identify the source of oil spills, occurring in Marmagoa harbour waters, using appropriate techniques.

Materials and Methods

Seven oil samples were received from the Marmagoa Port Trust. These samples, collected from and around the ships, were classified as (I) *Ship M.V. Bellary*: 1, oil sample from engine tank; and 2 and 3, water samples around the ship and (II) *Ship M.V. Homi Bhaba*: 4, oil sample from cargo tank; 5, oil sample from slop tank; 6, engine room bilge sample; and 7, water sample around the ship. These samples were then analysed by gas chromatography, infrared spectroscopy and UV-fluorescence.

Gas chromatography— All samples were dissolved in spectroscopic grade hexane and dried over anhydrous sodium sulphate to remove moisture. After decanting, the supernatant liquids were subjected to silica-gel column chromatography. Excess solvent was evaporated under reduced pressure and 5 μl of this was injected into a Perkin Elmer model 3920-B gas chromatograph. All samples were run under identical conditions using a 12′ stainless steel column with inner diameter $\frac{1}{8}''$. The filling material of the column was XE-60 (7%), DC200 (4%) and QF on CW 80/100. The gas used was ultra-pure helium with a flow rate of 35 ml. min^{-1}. A thermal conductivity detector was used for the experiments.

Infrared spectroscopy—This method involves recording infrared spectra of oil samples dried by the same procedure used for gas chromatography. Solvent hexane was removed prior to spectral studies by evaporation and spectra were recorded in the region 4000-400 cm^{-1} on a Pye-Unicam Infragraph.

UV fluorescence—After treatment as described earlier, an aliquot of the sample was placed in a 1 cm quartz cuvette. The wavelength of excitation was kept constant at 310 nm and the scanning was performed from 600 to 310 nm to determine the peak wavelength of emission on a scanning spectrofluorometer (Turner model 430).

Results and Discussion

Gas chromatography—Fig. 1 gives gas chromatograms of samples alongwith retention time of the peaks. The peak heights on the chromatograms are only qualitative and not quantitative. Similarity of chromatograms between sample 1 and samples 2 and 3 is very clear. The retention times of the peaks are also similar. However, in the case of samples 2 and 3 the peaks are not as sharp as those in sample 1. This may be due to weathering process such as evaporation, dissolution and degradation of oil during the interval between its release in the harbour water and collection of samples[6].

Chromatograms of samples 4 and 5 are totally different from the remaining two samples 6 and 7. A remarkable similarity is noted between the chromatograms of the samples 6 and 7. The retention time of the peaks in the two differs very little. The chromatogram of sample 7, though

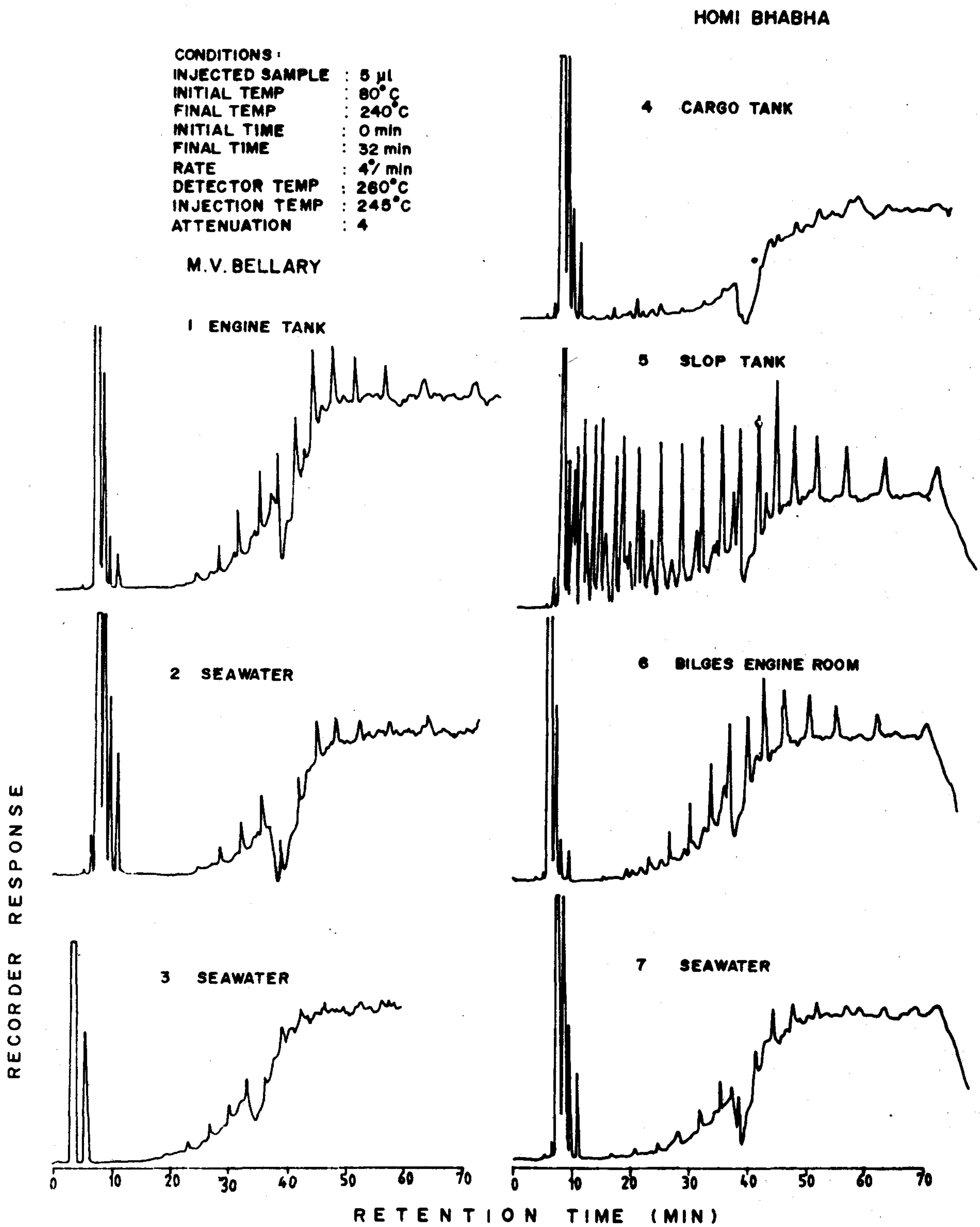

Fig. 1 – Gas chromatograms of samples

showing pattern similar to that of sample 6 indicates a little difference in the overall pattern which may be due to eventual dissolution and degradation of oil in the sea[6].

Infrared spectroscopy—In infrared spectroscopy, commonly the absorbance ratios at several wavelengths are examined to establish similarities between the samples. Fig. 2 depicts the spectra of the samples 1-7. The ratios of 3 IR-bending frequencies which are usually considered as key ratios for identification and characterisation of petroleum hydrocarbons have been calculated and presented in Table 1. For samples 1 and 3, all 3 IR ratios have very much similar values. However, for sample 2, the 1st and 3rd ratios could not be calculated because of insignificant peak-heights. It can be presumed that this is due to the presence of some impurity in one of the samples collected from the harbour water.

A good similarity was observed between samples 6 and 7 as regards the first ratio. Variation in the other 2 ratios is probably due to the degradation of the unsaturated hydrocarbons on its release into water. Although there are some similarities in the 3rd ratio, in samples 4 and 5, no attempt is made for detailed explanations as their chromatograms clearly indicate their different origin.

UV fluorescence—Spectra of all the samples are presented in Fig. 3. Emission peaks of samples are 356 nm for sample 1 and 358 nm for samples 2 and 3. The similarity between the emission peak wave length of the hexane extracts of all the 3 samples is remarkable. The hexane extracts of samples 4 to 7 have their maximum emission at 400 nm indicating the similarity in their sources of aromatic hydrocarbons.

The results show that (1) samples 1 to 3 (*M.V. Bellary*) have similar characteristics in all the 3 modes of analyses and (2) samples 6 and 7 (*M.V. Homi Bhabha*) show similarity of origin while the other 2 samples are different.

Gas chromatography, IR spectroscopy and UV fluorescence, apart from vanadium/nickel ratio by atomic absorption spectrometry, are the only an-

Table 1 — Infrared Ratios of Oil Samples

Ratios of IR-bending frequencies	Sample No. 1	2	3	4	5	6	7
$\frac{720\ cm^{-1}}{1375\ cm^{-1}}$	0.24	—	0.25	0.21	0.28	0.26	0.25
$\frac{810\ cm^{-1}}{1375\ cm^{-1}}$	0.24	0.21	0.25	0.21	0.28	0.30	0.23
$\frac{810\ cm^{-1}}{720\ cm^{-1}}$	1.00	—	1.00	1.00	0.95	1.10	0.95

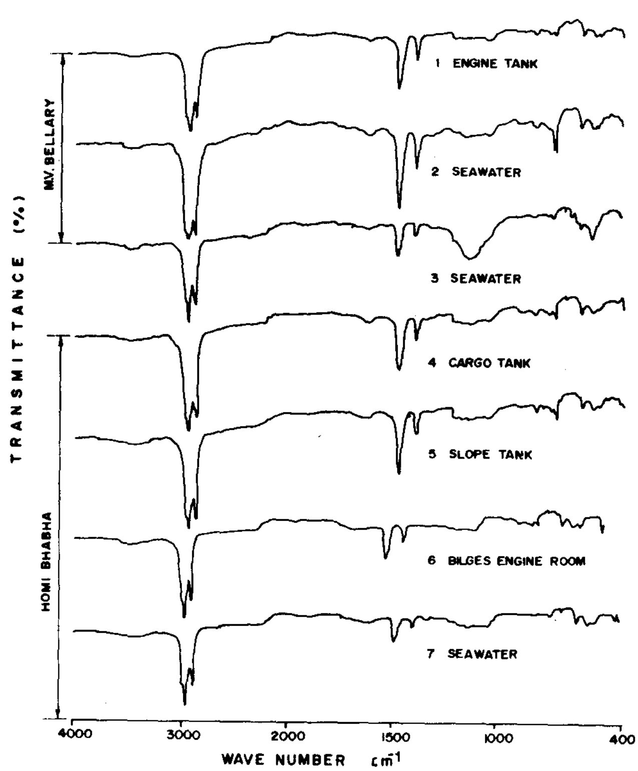

Fig. 2 — IR spectra of samples

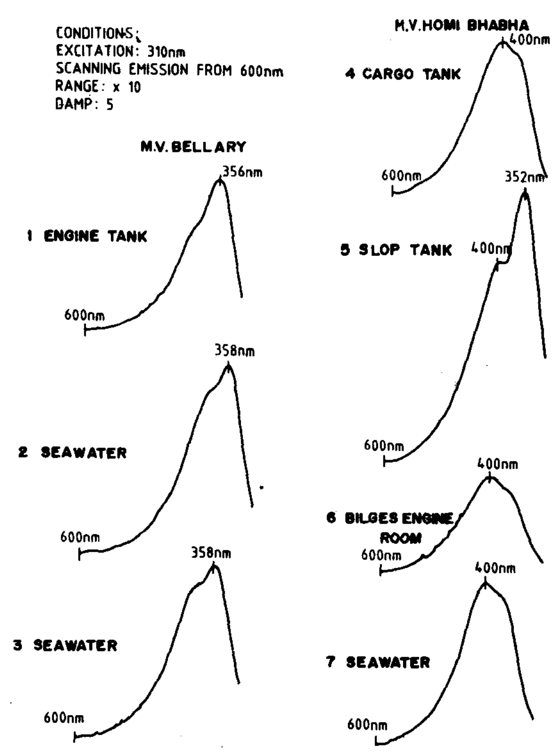

Fig. 3 — UV fluorescence spectra of samples

alytical methods to establish sources and similarities for oil spill.

Acknowledgement

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