

# Determination of Petroleum Hydrocarbons in Sediment Samples from Bombay Harbour, Dharamtar Creek and Amba River Estuary

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## INTRODUCTION

The surface sediment samples were collected by van Veen grab sampler during premonsoon, monsoon and postmonsoon seasons from Bombay harbour, Dharamtar creek and Amba river estuary. Moisture content of the samples ranges from 36 to 67.5 %. Samples were analysed for petroleum hydrocarbon using UV - Spectroscopy. Bombay High (BH) crude and Saudi Arabian Mix (SAM) crude were used as reference standards. Calibration curves were used for determination of petroleum hydrocarbon in the samples. The values of petroleum hydrocarbons in the sample residues using BH crude as reference standard were 3 to 4 times higher than the values obtained with reference to SAM crude. Relative amounts of aliphatic unsaturated and aromatic unsaturated constituents in the samples were determined by taking the ratio of absorbance at 256 nm to that of 223 nm and the ratio ranges from 0.5 to 1.0. The nature of constituents in the petroleum hydrocarbon residues was established by gas chromatographic technique. Chromatograms of samples from different stations exhibit different features indicating presence or absence of paraffinic peaks.

## EXPERIMENTAL

### Reagent

Analytical grade potassium hydroxide, hexane, sodium sulphate (anhydrous) and methanol were used for extraction of petroleum hydrocarbon. Methanol and hexane were redistilled before use. Double distilled water was used for preparation of solutions. Analytical grade silica gel with particle size 0.063 - 0.125 mm was used for the extraction. Hexane (spectroscopic grade) was used for spectroscopic determination.

### Apparatus

Samples were analysed on UV - Vis spectrophotometer Perkin - Elmer Lambda 5 model at 256 nm for petroleum hydrocarbon content. The nature of the constituents of petroleum hydrocarbons was established by using Perkin Elmer Sigma 2000 capillary column gas chromatograph.

### Sample location

Station locations were selected from the area of Amba river estuary, Dharamtar creek and Bombay harbour. The locations were selected in such a way that they represent entire area under consideration. Stations are shown in figure 1. At each sample location, sampling has been done during premonsoon, monsoon and postmonsoon seasons (Table 1).

Table 1. Physical parameters of sampling

Sample number	Station number	Season	Date of collection	Depth, m
1A	1	Postmonsoon	Dec 4, 1984	9.0
2A	2			7.5
3A	3			6.0
4A	4			7.25
5A	5			8.0
6A	6			5.50
1B	1	Premonsoon	April 30, 1985	10.0
2B	2			10.5
3B	3			6.0
4B	4			6.0
5B	5			7.0
6B	6			5.0
1C	1	Monsoon	July 25, 1985	11.0
2C	2			14.0
3C	3			6.0
4C	4			7.0

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5C	5	8.0
6C	6	6.0

### Sampling procedure

The surface sediment samples were collected in December 1984, April 1985 and July 1985 from six stations. The samples were collected by using van Veen grab sampler. After retrieval of the sampler, water was allowed to drain off avoiding disturbing the surface layer of the samples. The sediment samples were taken carefully from the hatch at the top of the sampler. The samples were transferred in the aluminium foil and immediately frozen in a thermo-isolated box cooled with ice. Then they were preserved in a refrigerator at -20 °C.

### Analytical procedure

**Determination of moisture content:** A clean watch glass was put into the oven at 105 °C for 2 hr using a pair of pincers. The watch glass was removed from the oven and put into a dessicator to cool. The empty watch glass was then carefully weighed on an analytical balance. The watch glass was removed from the pan and the sediment (~ 20 - 25 gm) was placed on the watch glass. The watch glass alongwith the sediment was carefully weighed and placed in drying oven at 105 °C for 24 hr. It was removed from the drying oven and placed in a dessicator to cool. Then the watch glass was weighed. The loss in weight of sediment was taken as moisture content in sediment.

**Extraction of petroleum hydrocarbons:** The weight sediment (~ 50 gm) was taken in a clean and dried 250 ml round bottom flask. Redistilled methanol (100 ml) and potassium hydroxide (3 gm) were added to

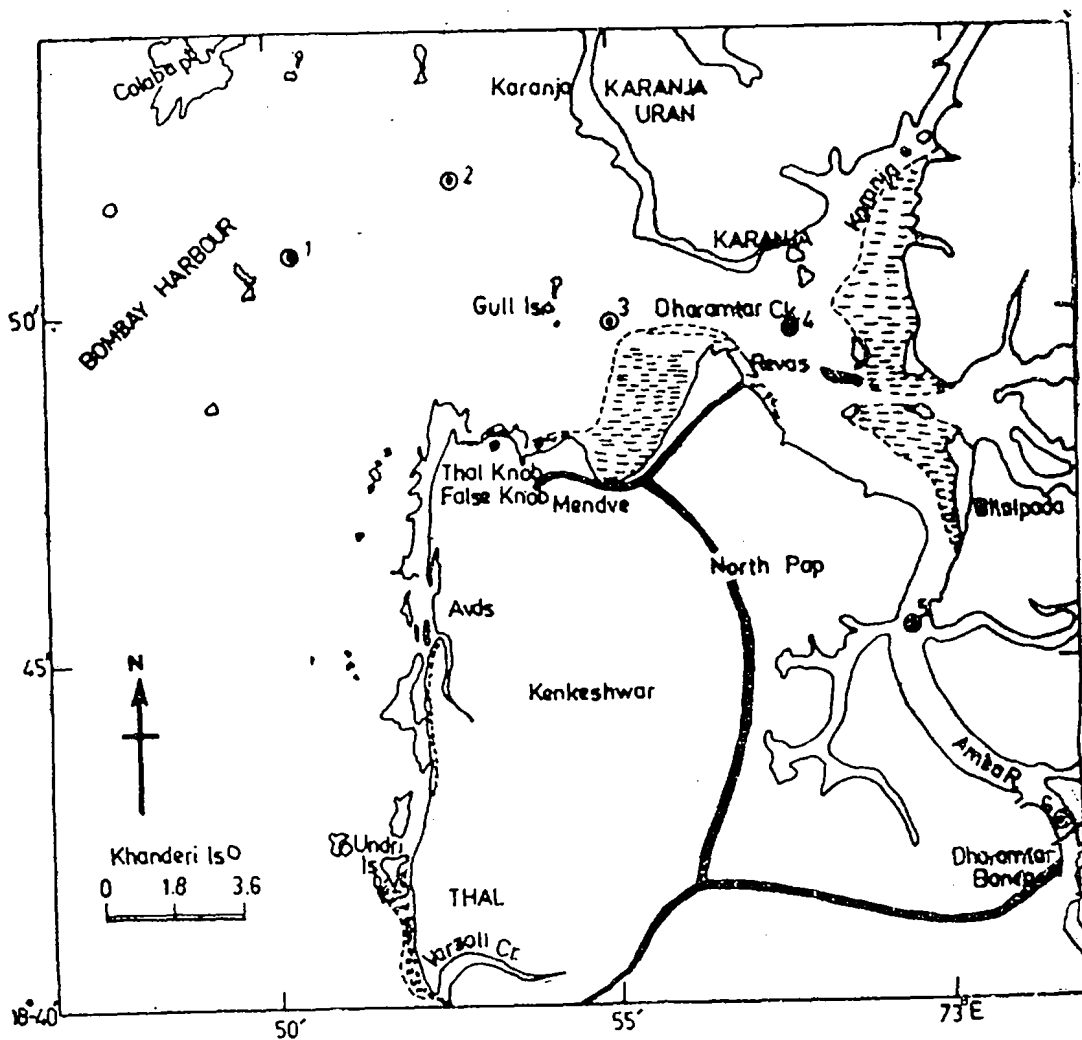


Figure 1. Map of Bombay Harbour, Dharmter creek and Amba river showing location of sampling

it. The mixture was refluxed for 1.5 hr. The flask was then cooled to room temperature and the mixture was filtered through Whatman filter paper no. 41. The filtrate was transferred to a separating funnel and extracted with 25 ml of redistilled hexane twice and dried over anhydrous sodium sulphate. The hexane fraction was evaporated to dryness to obtain brownish semisolid.

**Cleanup of extract :** A Pasteur pipette (ID - 0.8 cm, length - 4.5 cm) with a cotton plug was filled with activated silica gel (0.5 gm). The column was rinsed three times with redistilled hexane. Then the sample was loaded on the top of the column using minimum quantity of hexane. It was eluted with hexane (12 ml). The hexane extract was evaporated to dryness at  $\pm 0$  °C to obtain a yellow residue. The experimental blank and standards namely Bombay High (BH) crude residue (BP > 100 °C) and Saudi Arabian Mix (SAM) residue (BP > 100 °C) were also run under identical conditions.

**Spectroscopic determination :** The residue (after column chromatography) was transferred to 10 ml volumetric flask and diluted with n-hexane (spectroscopic grade). Standard solutions (10 ml) of reference standard samples, namely BH crude and SAM crude were prepared. Samples were analysed on UV/Vis spectrophotometer. Absorbance values were plotted against concentration for reference standards, and factors were determined to find the concentration of samples.

## RESULT AND DISCUSSION

### Quantitative determination of petroleum hydrocarbon

Values of the residues in comparison with SAM residue and BH crude were found from the calibration curves (Figures 2a and 2b). BH crude oil locally manufactured and heavily transported in harbour area and hence there is every likelihood that the contamination might have been caused by BH crude (NEERI, 1985; Sen Gupta and Quasim, 1985). Therefore BH crude was chosen as a standard. The values of petroleum hydrocarbons in the sample residues in comparison with BH residue were 3 to 4 times higher to the values obtained with reference to SAM crude. This may be due to lower aromatic contents in the BH crude oil. In the monsoon season the environmental temperature is comparatively low and currents are towards the shore (Gouveia and Kurup, 1977). There are heavy disturbances in the sediments and coastal traffic

is also minimum. Thus less contamination in surface sediment was anticipated. Among the three seasons, lowest concentration was found for samples collected during monsoon (Table 2).

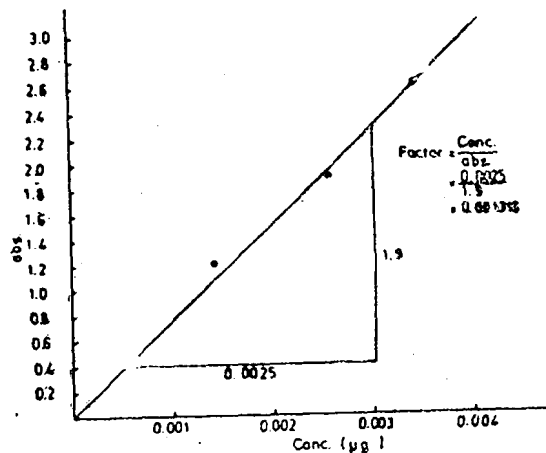


Figure 2a. Calibration curve of Saudi Arabian mixed residue as reference standards

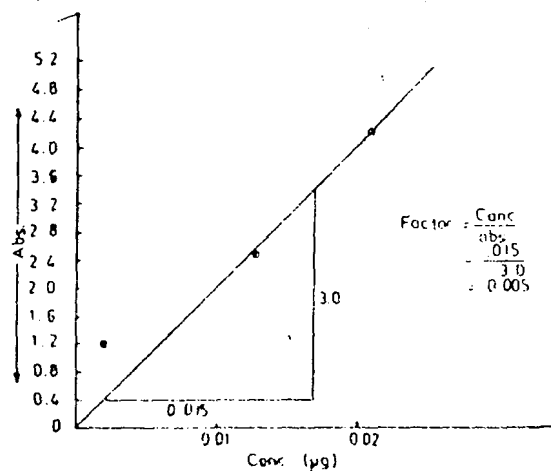


Figure 2b. Calibration curve of Bombay High crude residue as reference standards

In postmonsoon season offshore current starts and then there is much dilution of coastal water by freshwater. Therefore no increase in contamination of surface sediment is anticipated. Actually very moderate values have been obtained for the concentration of petroleum hydrocarbons. In premonsoon season, the higher environmental temperature causes quick evaporation of low boiling fraction of a petroleum spill. Consequently, the residue becomes heavy and sinks (Conomos, 1975). Additionally, the sea is also calm and there is no disturbance in the sediments. There-

**Table 2. Gravimetric spectroscopic analysis of surface sediments**

Sample number	Moisture content, %	Petroleum hydrocarbon concentration, $\mu\text{g}/\text{gm}$ , with reference to	
		BH	SAM
1A	59.4	-	-
2A	53.64	175.83	51.36
3A	56.16	10.85	2.85
4A	56.12	38.25	10.07
5A	57.32	8.83	2.32
6A	36.03	N.D.	N.D.
1B	63.11	49.16	12.94
2B	65.63	58.48	15.39
3B	58.41	46.96	12.36
4B	52.40	22.63	5.96
5B	57.19	47.48	12.91
6B	57.55	57.38	05.36
1C	67.54	7.90	2.08
2C	62.85	32.66	8.60
3C	56.71	2.31	6.07
4C	59.93	24.34	6.41
5C	50.19	N.D.	N.D.
6C	60.20	29.00	7.63

fore, there are less chances of the residue travelling towards shore; and the contamination in the surface sediments could be more. The concentration of petroleum hydrocarbons in summer is comparatively higher than that in monsoon and postmonsoon seasons.

As stations 1 and 2 are located in Bombay harbour, one of the busiest ports in the country, very high concentrations of petroleum residue were anticipated at these stations (Clark and MacLeod, 1977). But the values (sample no. 1 to 17) obtained were not high enough to indicate pollution. Lot of drazing activities and ship movement may be causing disturbances in the surface sediments. Besides, the channel is comparatively narrow, therefore there is possibility of the spill, if any, travelling to the shore. Sediments from stations 3 and 4 located near the mouth of Amba river yielded lower concentrations of petroleum hydrocarbons. Stations 5 and 6 have been located in the Amba river estuary. There is no much urban or industrial activities on the bank of the river. Therefore, the contamination input through the river water is minimum. The harbour area is highly contaminated (NEERI, 1985; Rokade *et al.*), and the tidal inflow in the estuary should lead to the contamination. However, minimum contamination was found in the sediments. This may

be possibly due to the following factors. The floating oil residue may be reaching the shore before it sinks. Lot of clay carried by freshwater may be freshly depositing on the estuarine sediments causing the burial of pollutants.

#### Relative amount of unsaturated aliphatic and aromatic constituents

The UV spectra of samples were recorded at 233 and 256 nm. The ratio of absorbance at 256 nm to that of 223 nm were calculated for the two standards, namely SAM crude and BH crude. The ratio of absorbance at 256 nm to that of 223 nm for former is 0.59 while for latter it is 0.26. This indicates that BH crude contains more of aliphatic unsaturated constituents. It has been found that the values of the ratio for all the samples were in the range of 0.5 to 1.0 (Table 3). It has been observed that value of only sample 3 matches with SAM standard. In most of the samples the aromatic contents seem to be more which may indicate original composition of crude oil.

**Table 3. Ratio of absorbance of 256 nm to absorbance at 223 nm**

Sample number	Ratio of absorbance at 256 nm/223 nm
1	0.6666
2	0.6666
3	0.5833
5	0.6429
6	0.7692
7	0.5000
8	0.8000
9	0.7391
10	0.6957
11	0.7391
12	0.8333
16	1.0000
17	0.7141
SAM	0.5872
BH	0.2621

#### Gas chromatographic analysis

Gas chromatographic technique was employed for determination of the nature of constituents in the petroleum hydrocarbon residues as the method affords high discrimination in correlating petroleum products (Ehrhardt and Blumer). Representative gas chromatograms of sample no. 1 to 17 from all the stations are shown in figure 3. Characteristic chromatograms

were obtained for the residues of the samples 6 and 12 from station 1. In both the chromatograms peaks pertaining to the high boiling fractions are distinct indicating that the residue is weathered. The chromatograms of samples 1, 7 and 13 are comparatively simple and do not include distinct features. It seems that the residues are originated from an oil which may be containing lesser concentration of paraffins. The non-similarities in the patterns suggest that they may not be from the same source (Page *et al.*, 1988). A bulgy peak appeared in chromatogram of sample 13 indicates that the residue has mixed origin. The chromatogram of sample 8 consists of several peaks of paraffins, indicating that the sample is not much weathered (Adlard *et al.*; Rokade *et al.*, 1986).

The chromatograms of samples 2 and 14 from the

same station do not indicate good percentage of paraffins; possibly, they might have been originated from a spill which may be containing less paraffins (Jeffery, 1977; Kadam). Chromatograms of sample 9 of station 4 yielded a typical pattern of moderately weathered crude oil (Meyer and Takeuchi, 1979). The other two chromatograms for sample 3 and 15 corresponding to station 4 contain mainly unresolved complex mixture. The chromatograms of samples 10 and 16 indicate that the residue contains high boiling paraffins. In both the chromatograms intermittent broad peaks have been observed. Probably they may be having origin other than petroleum oil. The chromatogram of sample 10 indicates that the residue may be containing lesser percentage of paraffins, as equally spaced paraffinic peaks are not seen in the chromatogram. The chroma-

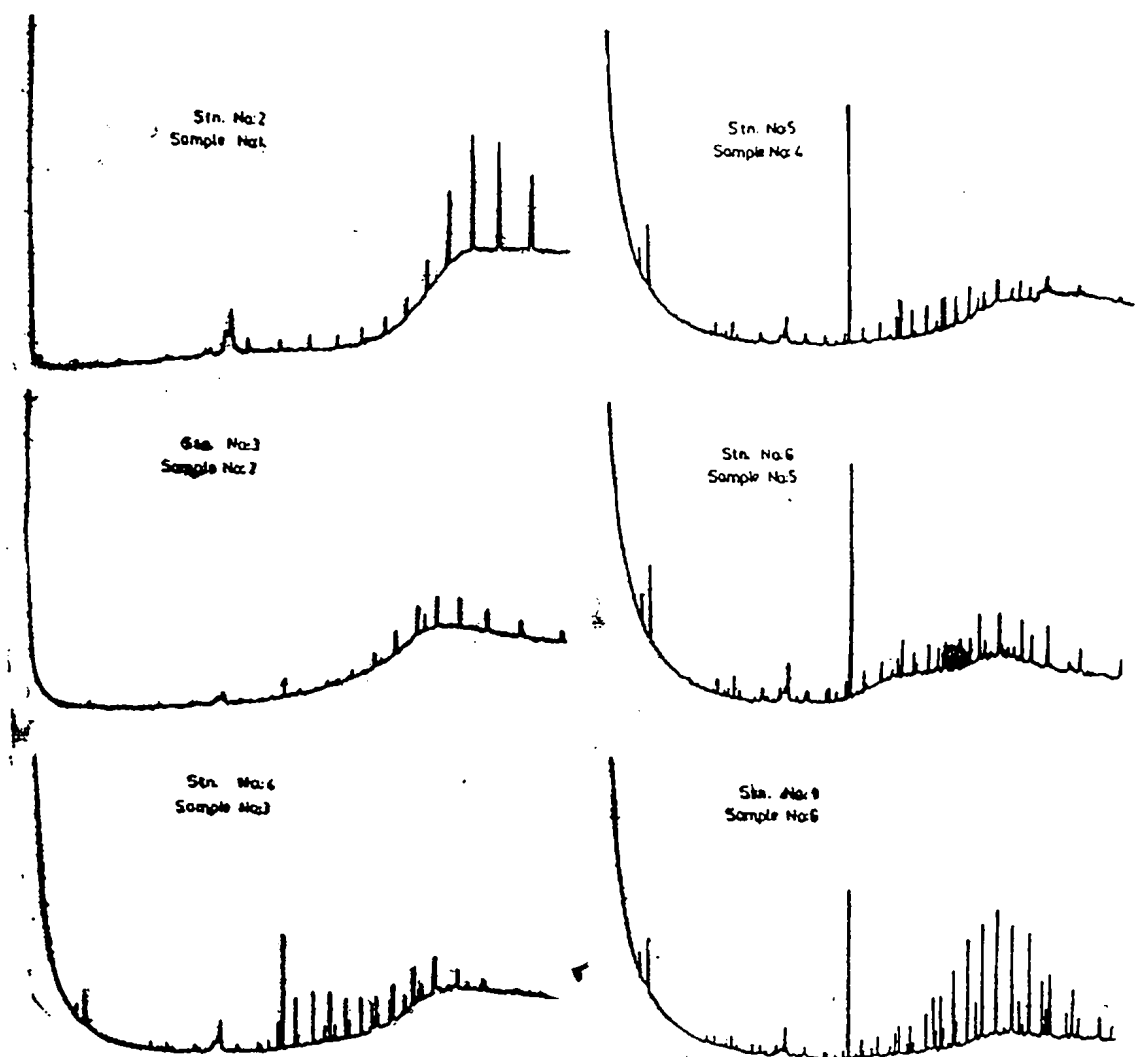


Figure 3. Gas chromatograms of different samples from different stations

tograms of samples 11 and 17 of station 6 consist of paraffinic peaks. The chromatogram of sample 5 is entirely different but has close similarity with chromatogram of sample 4. The chromatograms of residues of samples collected in postmonsoon season from stations 4, 5 and 6 closely resemble each other indicating that they have possibly originated from the same source spill. The sample obtained from station 3 in premonsoon also has same characteristics.

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