

## SOME STUDIES ON TAR PILLETS AT VERAVAL COAST (GUJARAT)

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### ABSTRACT

Infrared spectroscopic (IR) analysis indicated that the tar pillets contain saturated hydrocarbons particularly higher homologues of *n*-paraffins, unsaturated and carbonyl type of polar compounds. Gas chromatographic (GLC) fingerprint pattern and high asphaltene contents revealed that the residue might have originated from residual fraction of a crude oil such as fuel oil. Its fingerprint pattern and paraffin profile did not match with those of Bombay High Crude residue.

Key-words: Beach pollutants, tar pillets, Gujarat

Oil residues such as tar residues and tar balls on the beaches along the west coast of India first reported in 1970, is a common feature during August to October every year (Reddy and Singbal, 1973; Dwivedi, Desai, Parulekar, Josanto and George, 1974). Attempts were made in the past to characterise the residues and to trace their sources based on thin layer chromatography (Reddy and Singbal, 1973; Dwivedi, Desai, Parulekar, Josanto and George, 1974). The paper presents the results of a more detailed investigation on the tar pillets collected from Veraval Beach (Gujarat) during August, 1984.

Tar pillets from 1 m<sup>2</sup> area of a thick patch were hand picked and weighed (1710 g). Randomly selected pillets (2 g) were dissolved in carbon tetrachloride (GR, Sarabhai, 200 ml). The solution was dried over anhydrous sodium sulphate and filtered through a thick cotton plug. The solvent was removed at 30°C/200 mm Hg to obtain a dark brown semisolid (V) with a m.p. 210°C/10 mm and yield of 1.38 g (69.2%). Wax and asphaltene contents of the purified sample were determined by the procedures reported by the Institute of Petroleum Standardization Committee (1970) and Javes and Liddell (1958) respectively.

Samples were scanned in a Perkin Elmer 983 g Infrared Spectrophotometer in the form of thin liquid films on sodium chloride discs in the range of 4000-600 cm<sup>-1</sup>. Gas chromatographic analysis (GLC) was performed on Perkin Elmer, Sigma 2000 Gas Chromatograph using 40 m x 0.25 mm ID fused silica glass capillary (FSOT) column with bonded methyl silicon phase. Flame ionisation detector (FID) and split injector system were maintained at 350°C. The split ratio was 1:70. Nitrogen (100 ml/min) was used as carrier gas. Column temperature was programmed between 80 and 300°C at the rate of 10°C/min.

Although post monsoon occurrences of tar residues along west coast of India have been reported, no information is available pertaining to the Veraval region. The sandy beach at Veraval was found littered with tar pillets mainly concentrated on the intertidal area over a stretch of nearly 2 km during August 1984. The spread was not even and the denser areas yielded more than 2000 mostly oblique shaped pillets of different sizes per  $\text{m}^2$  area weighing 1710 g indicating severity of the deposition. These soft brown pillets might have been derived from floating oil residues such as crude oil sludge, weathered crude oil or fuel oil. It is necessary to distinguish tar balls from tar pillets. They did not belong to tar ball category which are hard and round in shape and well mixed with sand and vegetation.

Close similarity of the IR spectrum with those of the purified samples (V) indicated that the pillets might have originated from an identical source. The IR spectrum (Fig.1) exhibited strong absorption bands around 2900, 1460

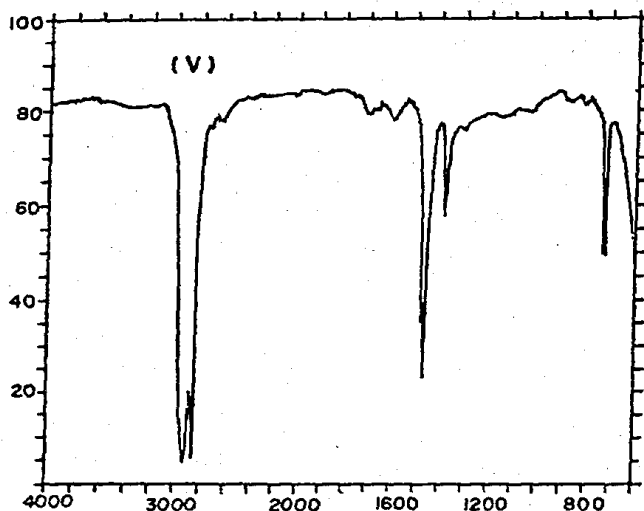


Fig.1. Representative Infrared Spectrum (IR) of purified sample of tar pillets (V)

and 1375  $\text{cm}^{-1}$  and very weak bands in 1800-1600  $\text{cm}^{-1}$  region. The absorptions at 1800-1600  $\text{cm}^{-1}$  revealed the presence of carbonyl compounds (Silverstein, Bassler and Morrill, 1981) possibly resulting from photo-oxidation and microbial reactions which transform hydrocarbons into polar compounds such as ketones and aldehydes (Freearge, Hotchard and Parker, 1970). The intense doublet at 730-720  $\text{cm}^{-1}$  in the spectrum arose from methylene rocking vibrations.

Although it may not be possible to identify the source of a beach pollutant by GLC alone, some general information about the possible type of

source can be obtained. On the basis of GLC, several workers have categorised tar residues on beaches as those derived from crude oil residue, tanker sludge, residual fuel oil and residues from distillation fractions (Brunnock, Duckworth and Stephens, 1968; Ramsdale and Wilkinson, 1968; Koons and Monaghan, 1973; Morris and Butler, 1973; Jeffrey, 1977; Jeffrey, 1980). Comparison of gas chromatogram of V with the literature data and fingerprint pattern of residual fuel oil reported by Jeffrey (1980) revealed that the residue belonged to the residual fuel oil category (Fig.2). Absence

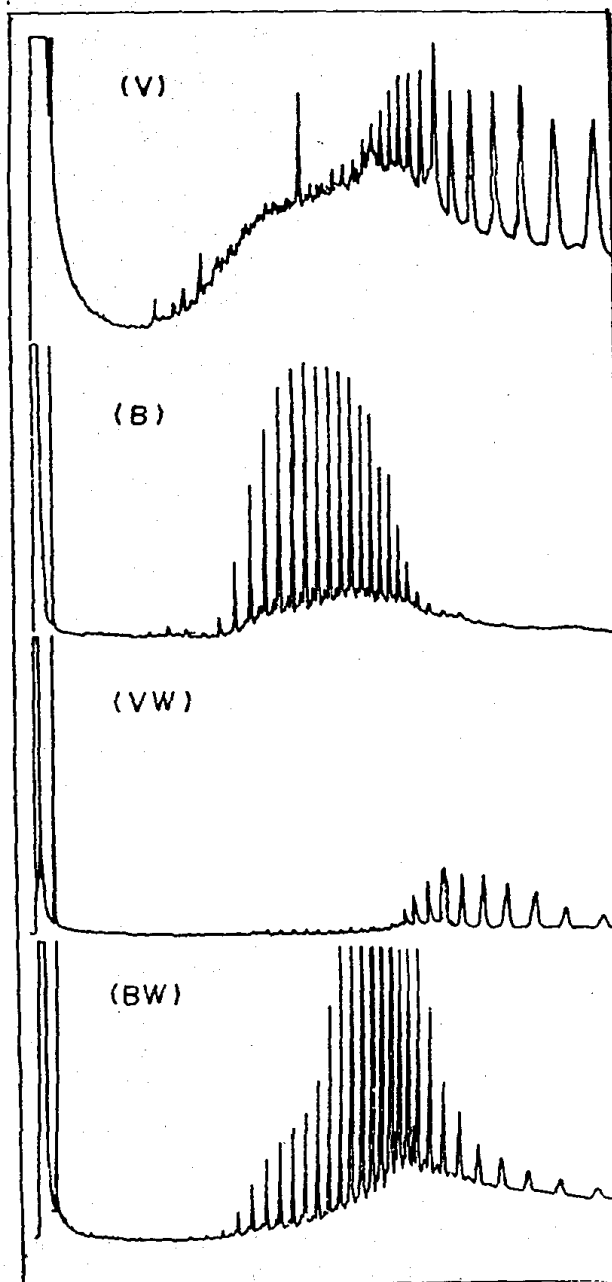


Fig.2. Gas chromatograms of purified sample of tar pillets (V), Bombay High Crude Residue (B), wax of purified sample of tar pillets (VW) and wax of Bombay High Crude Residue (BW).

of peaks corresponding to the low boiling paraffins in the chromatogram and wax and asphaltene contents (13 and 36% respectively) also support this view (Brunnock, Duckworth and Stephens, 1968). These type of spills generally occur as a consequence of a ballast tank, the pumping of bilge and corrosion of tanker (Brunnock, Duckworth and Stephens, 1968).

It is notable that paraffin constituents which are generally present in crude oil residues were not observed in the gas chromatogram of V. Though it is possible that they might have been consumed by microbes, Koons and Monaghan (1973) reported that the action of these microbes on pelagic tar would be only moderate. Further the presence of polar constituents in V is not significant as seen from the IR spectrum in frequency ranges of  $3600-3400\text{ cm}^{-1}$  and  $1800-1700\text{ cm}^{-1}$ . High m.p. ( $210^{\circ}\text{C}/10\text{ mm}$ ) of the residue and the absence of paraffins suggest that the lower homologues of paraffins might be absent in the parent oil itself. It is generally feared that the west coast of India is being polluted by Bombay High Crude. Therefore, attempts were made to match the tar residue (V) with the residue of Bombay High Crude. As a requirement, laboratory sample (B) was prepared by washing Bombay High Crude with water and distilling off the fraction by boiling upto  $210^{\circ}\text{C}/10\text{ mm}$ . Gas chromatogram of B yielded a systematic fingerprint pattern above the unresolved envelope (Fig.2). Profiles of fingerprint patterns of these chromatograms as well as their paraffin profiles did not match with each other (Fig.2). In addition, the wax and asphaltene contents of B (3 and 9% respectively) also differ substantially. These preliminary tests did not suggest any identity between residue of Bombay High Crude (B) and the tar sample (V).

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