

## Characterisation & Source Identification of an Oil Spill by Infrared Spectroscopy & Gas Chromatography

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An oil spill on a beach in Bombay was characterised for the source identification. Presence of fractions having bp as low as 135°C and very weak IR absorption bands in 1800-1700  $\text{cm}^{-1}$  region indicated that the spill was of recent origin. High wax (60%), asphaltene (10%) and iron (131 ppm) and other properties revealed that the spill was derived from a tanker sludge. The comparison of the gas chromatographic fingerprint pattern of the spill with several crude oils being handled by Bombay Port revealed that the pattern was superimposable with that of the Bombay High crude. However, the spill did not seem to have originated from the well-blowout in the Bombay High offshore oilfield.

Increasing transportation of petroleum products and offshore oil exploitation rendered marine environment around Bombay vulnerable to oil pollution<sup>1-4</sup>. Although minor spillages of oil largely go unnoticed, the spill observed (24 Aug. 1982) in the Nepean Sea area (South Bombay) attracted much attention by virtue of its occurrence within few days from the blowout in the Bombay High region. It was feared that the source of the spill was in the blowout. It was therefore of interest to investigate the spill to trace its source.

### Materials and Methods

The spill sample (10 g) which was collected by skimming and preserved in pre-cleaned glass bottle in deep freeze was dissolved in dichloromethane (200 ml, bp 39-41°C). Water from the mixture was removed using separatory funnel. The organic layer after drying over anhydrous sodium sulphate and filtering through a cotton plug was evaporated at 30°C/200 mm to obtain a brown semisolid (NS; bp  $\geq$  135°C, yield 6.4 g).

Wax and asphaltene contents were determined as 60 and 10% respectively by known procedure<sup>5</sup>. The iron content was estimated by atomic absorption spectrophotometry after ashing the sample<sup>6</sup>.

PMR spectrum was scanned in the region 0-15 delta using  $\text{CDCl}_3$  as a solvent on Varian-XL100 FT using TMS as the internal standard. IR spectrum of the sample was scanned in 4000-600  $\text{cm}^{-1}$  region as liquid film using NaCl discs on Perkin Elmer-983G. Gas chromatographic analysis was performed on Perkin Elmer-Sigma 3B using OV-17 (5%) phase on Chromasorb W-HP. Injector and flame ionisation detector (FID) were maintained at 350°C. Carrier gas (nitrogen) flow was 50  $\text{ml min}^{-1}$ . Column temperature was

programmed 60-300°C at the rate of 12°C  $\text{min}^{-1}$  and further isothermal at 300°C for 20 min.

### Results and Discussion

It was evident from a sharp and intense singlet at 1.2 delta and weak signals around 0.35 delta in PMR of purified sample (NS; Fig. 1) that it had paraffinic character<sup>7</sup>. Complex pattern of some minor peaks around 1.4-3 delta was also observed. The spectrum resembled the PMR pattern of paraffin mixture isolated from crude oil<sup>6</sup>. In addition to several sharp and intense absorption bands around 2900, 1462 and 1378  $\text{cm}^{-1}$  in IR of NS (Fig. 2), a sharp doublet around 730-720  $\text{cm}^{-1}$  was quite prominent supplementing the hydrocarbon origin of the spill<sup>8</sup>. The doublet in particular was more significant as it reflects on the composition of the sample. This type of doublet is also observed in the IR of commercial white wax and number of samples containing high wax residues, and arises

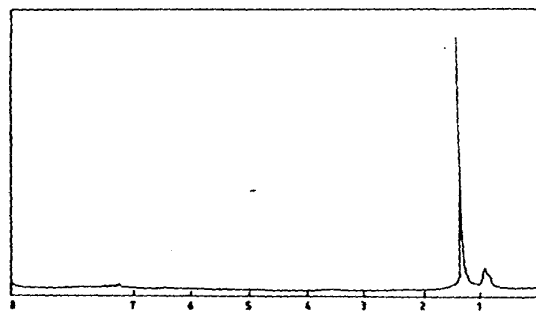


Fig. 1 — Proton magnetic resonance spectrum (PMR) of the spill sample NS

from the methylene rocking vibrations due to the alignment of the *n*-paraffins into polymeric crystalline structure as in polythelene<sup>9</sup>. The presence of high waxy residue in *NS* as suggested by the doublet was confirmed by determining the wax content which was as high as 60%. Among the variety of crude oil residues, generally a crude oil sludge from the tankers contains high wax<sup>10,11</sup>. Also a tanker sludge is expected to be contaminated with iron rust due to its contact with the bunkers<sup>11,12</sup>. The iron content of *NS* was 131 ppm which was higher than the levels (0-100 ppm) in crude oils and their residues. Hence, it appeared that the spill was a tanker sludge.

Following the procedure of Kawahara and Ballinger<sup>13</sup> for the identification of the category of the spill, the IR transmittance ratio of  $810\text{ cm}^{-1}/720\text{ cm}^{-1}$  was plotted against the ratio of  $810\text{ cm}^{-1}/1375\text{ cm}^{-1}$  for lubricating oils (Nos 30 and 40), various crude oils, commercial white wax and *NS* (Fig. 3). *NS* lies far away from lubricating oils and crude oils but falls closer to the commercial wax because of its high wax content again supporting the view that the spill was a tanker sludge.

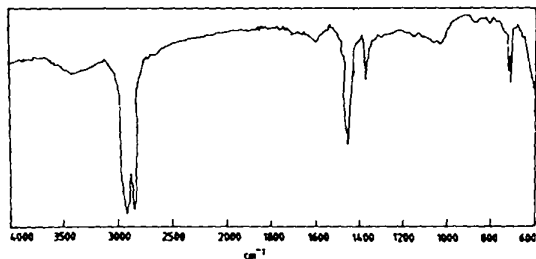


Fig. 2 — Infrared spectrum (IR) of the spill sample *NS*

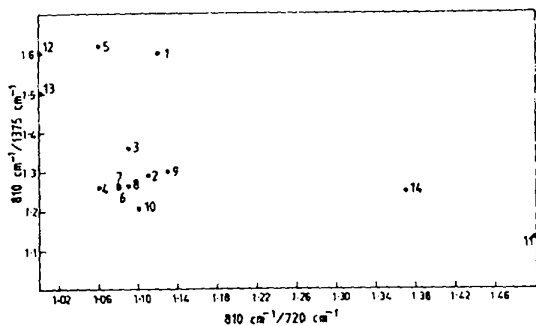


Fig. 3 — Relation of various virgin crudes (1-9), Bombay High Crude (10), Commercial white wax (11), lubricating oil No. 30 (12) and No. 40 (13) and spill sample: *NS* (14) involving two ratios of infrared transmittances

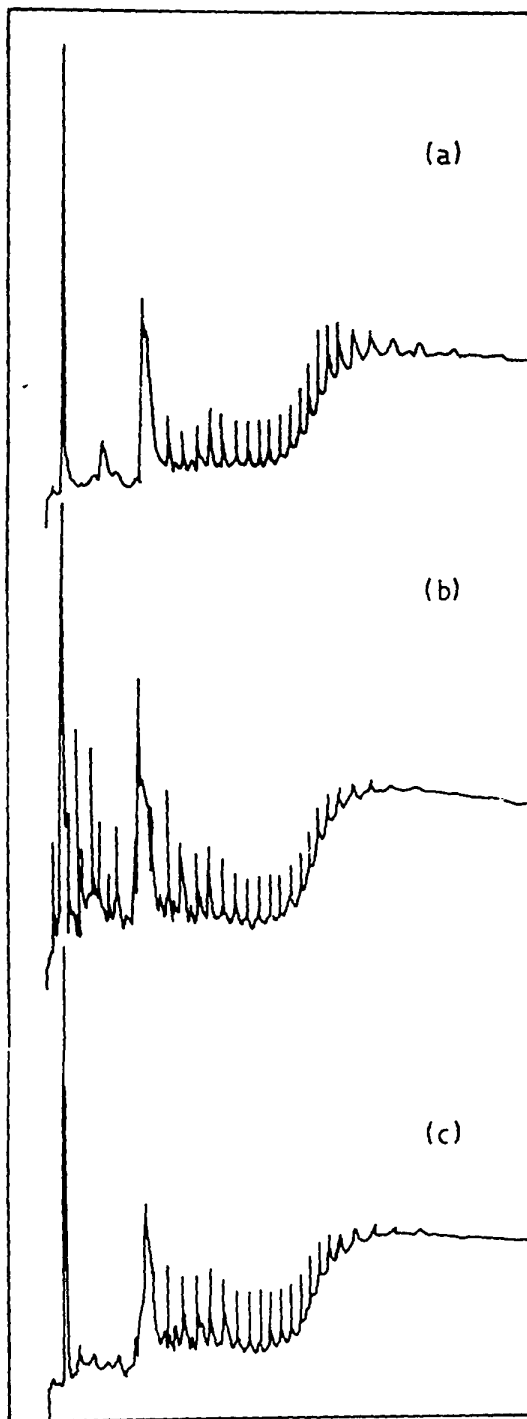


Fig. 4 — Representative gas chromatograms of (a) spill sample *NS*, (b) virgin Bombay High crude and (c) residue of Bombay High crude above 135°C

Comparison of gas chromatograms obtained under identical instrumental parameters of a number of crude oils which are being transported along the west coast of India revealed that the pattern of *NS* matched well with the chromatogram of Bombay High crude and its residue obtained after removing low boiling fractions up to 135°C (Fig. 4). Similar comparison of IR is difficult as IR absorptions are very sensitive to even minor variations in the composition<sup>10,14</sup> and hence the preparation of equivalent samples for matching is extremely difficult. During the present investigation, rapid settling of sludge of Bombay High crude along the walls and the bottom of the container was observed. The virgin oil shows a weak doublet at 730-720 cm<sup>-1</sup> in the IR spectrum the intensity of which varies after storing for a few days. Typically, the settled sludge yielded a stronger doublet in 730-720 cm<sup>-1</sup> region while it almost disappeared in the IR of the liquid portion.

From the foregoing discussion, it is considered that the spill was from a tanker sludge and that the tanker was carrying Bombay High crude prior to the discharge of sludge. The spill does not seem to have originated from the well blowout for the following reasons. Studies on the probable movement of a hypothetical oil spill in Bombay High region have revealed that the slick would take 7-22 days to reach the shore depending on the onshore component of the currents<sup>15</sup>. Hence, any spill coming from Bombay High should be highly emulsified due to rough sea conditions during the monsoons (June-August)<sup>16</sup> and not likely to contain low boiling components (up to 250°C) as the same are expected to have lost within a day of the spill<sup>17</sup>. Chemical changes are also expected due to the photo-oxidation of hydrocarbons transforming them into polar compounds containing hydroxyl and carbonyl groups<sup>18</sup>. The field sample *NS* had lower range of boiling point (135°C) and the absorptions around 1800-1700 cm<sup>-1</sup> in the IR spectrum pertaining to carbonyl compounds were either very weak or absent.

It is therefore reasonable to consider that the spill was a tanker sludge derived from Bombay High crude.

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