ANALYSIS AND CHARACTERIZATION OF TAR COLLECTED IN NEW PASS, SARASOTA BAY

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Suggested reference Pierce RH. 1982. Analysis and characterization of tar collected in New Pass, Sarasota Bay June 30, 1982. Sarasota County Environmental Services. Mote Marine Laboratory Technical Report no 51. 8 p. Available from: Mote Marine Laboratory Library.

CONCLUSIONS

The tar collected in New Pass, Sarasota Bay on June 30, 1982 was found to be representative of material recently (<1 month) discharged from oil tankers cleaning oily residual from oil storage tanks. Two types of tar were observed, one exhibiting greater weathering (older) than the other. Both tar samples contained crude oil with the older sample showing a high percentage of a refined, residual petroleum distillate mixed in, Although exact identification of the oil source would require a source sample, comparison of the tar ball data with that for IXTOC oil and tar formed from IXTOC oil shows that the origin of these tar balls was not the IXTOC oil spill.

METHODS

Collection

Four tar balls were collected from New Pass, Sarasota Bay June 30, 1982 (all were associated with Sargassum), placed in aluminum foil and frozen until analyzed.

One large tar ball (8 cm diameter) and three smaller tar balls (ca. 4-5 cm diameter) were collected. The large tar ball was characteristic of relatively non-weathered tar with a homogenous flexible texture throughout. The smaller tar balls exhibited more extensive weathering with a hard, dry exterior covering the softer interior. Because the two different types of tar were observed, a representative of each type was analyzed in duplicate.

Analysis

Two equal portions of each tax ball were collected from the interior (ca. 0.5 g of tar) for duplicate analysis. Hydrocarbons were dissolved in benzene, leaving the benzene-insoluble residue (asphaltene). The asphaltene content was determined by weighing after solvent evaporation.

The hydrocarbon portion was separated into aliphatic and aromatic fractions by column chromatography using silica gel and alumina. Both fractions were analyzed by glass capillary gas chromatography with flame-ionization detectors relative to internal standards o-terphenyl and 5α-androstane for qualitative and quantitative determinations. The aromatic fraction was also subjected to gas chromatographic-mass spectrometric analysis to

RESULTS

The gas chromatographic fingerprint of the aliphatic hydrocarbon fraction for each tar ball is shown in Figure 1. These chromatograms show that the two tar balls were of distinctive composition. The first tar ball (#1) is representative of a crude oil that has undergone short-term weathering (<1 month) as evidenced by loss of the normal alkane hydrocarbons containing up to 14 carbons. The second tar ball (#2) is representative of slightly weathered crude oil mixed with a heavy refined petroleum product (e.g., #6 fuel oil). This tar exhibits the same short-term weathering characteristics as #1.

Specific information obtained from these chromatograms for characterization is given in Table 1 along with those observed for several representative petroleum products. These data show the tar balls to be of similar composition relative to the key indicators, yet not identical to any *of* the selected petroleum products shown.

TABLE 1. Characteristics of the Aliphatic Hydrocarbon Fraction of Tar Balls and Select Petroleum Samples.

Sample	n-alkane Series	Most Abundant n-alkanes	Prist./Phy.	C_{17}/Prist.	C_{18}/Phyt.
Tar ball #1	C_{18}-C_{35}	C_{15}-C_{19}	0.8	2.4	1.7
Tar ball #2	C_{13}-C_{35}	C_{15}-C_{19}	0.9	2.0	1.8
#6 Fuel oil	$<C_{13}$-C_{33}	C_{20}-C_{24}	1.7	3.2	8.0
Venezuelan crude	$<C_{13}$-C_{35}	C_{15}-C_{19}	2.3	1.0	2.2
S. Louisiana crude	$<C_{13}$-C_{31}	C_{11}-C_{15}	2.1	0.7	1.1
IXTOC crude	$<C_{13}$-C_{35}	C_{12}-C_{16}	0.8	2.9	2.1
IXTOC tar ball	$<C_{13}$-C_{35}	C_{18}-C_{22}	0.4	3.2	2.4
Kuwait crude	$<C_{12}$-C_{33}	C_{13}-C_{14}	0.6	5.6	2.8

The aromatic hydrocarbon gc fingerprint is shown in Figure 2. These chromatograms show essentially identical patterns. Additional information regarding the aromatic fraction was obtained by GC-MS and is given in Table 2. This was performed only on one tar ball, due to the similarity of the GC-FID traces. These specific parameters

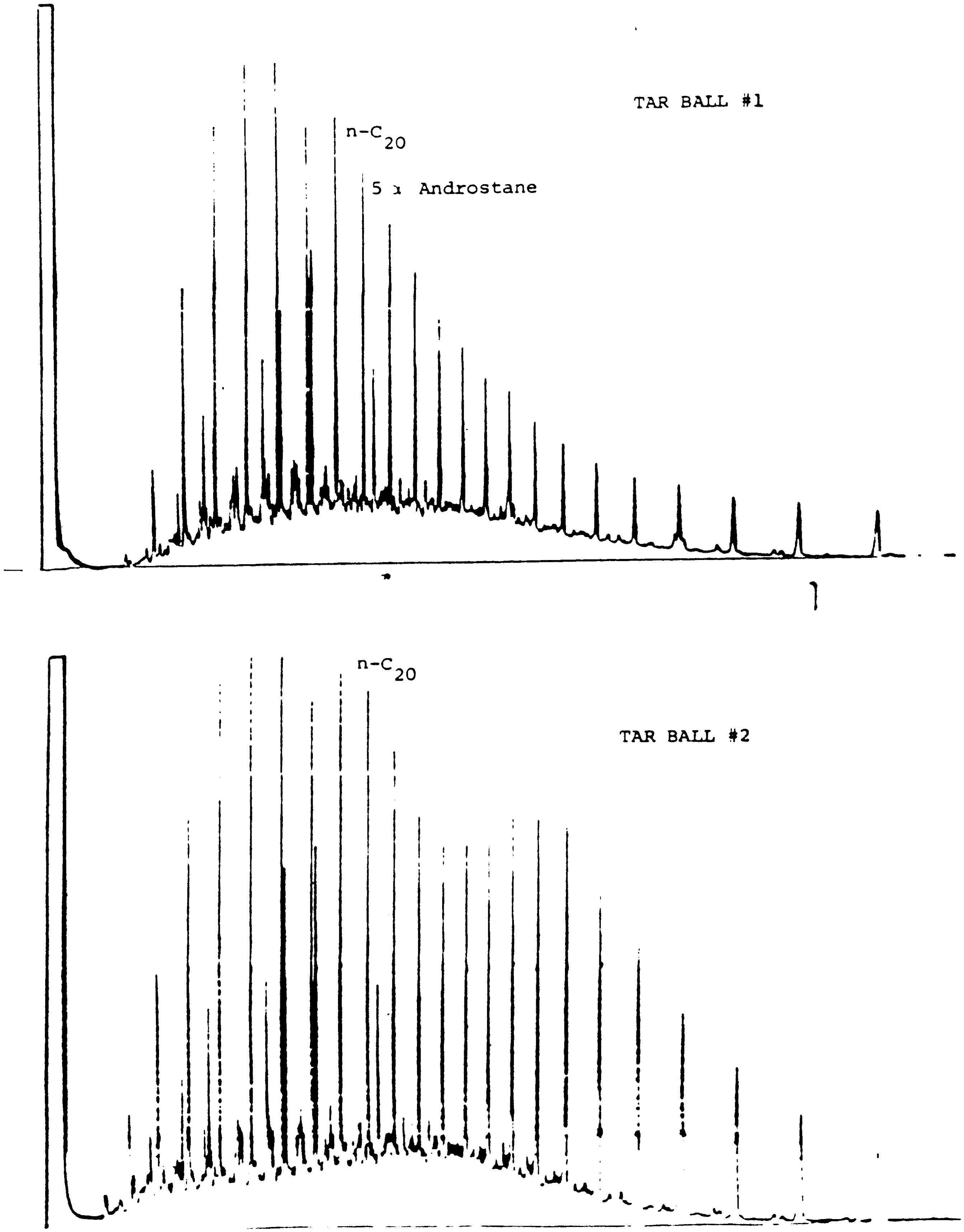

Figure 1. GC-FID Fingerprint of Aliphatic Hydrocarbons from Tar Balls. Temp. Prog. 100-280°C at 8° min. Glass Capillary Column, 30x X 0.25mm. SE-30

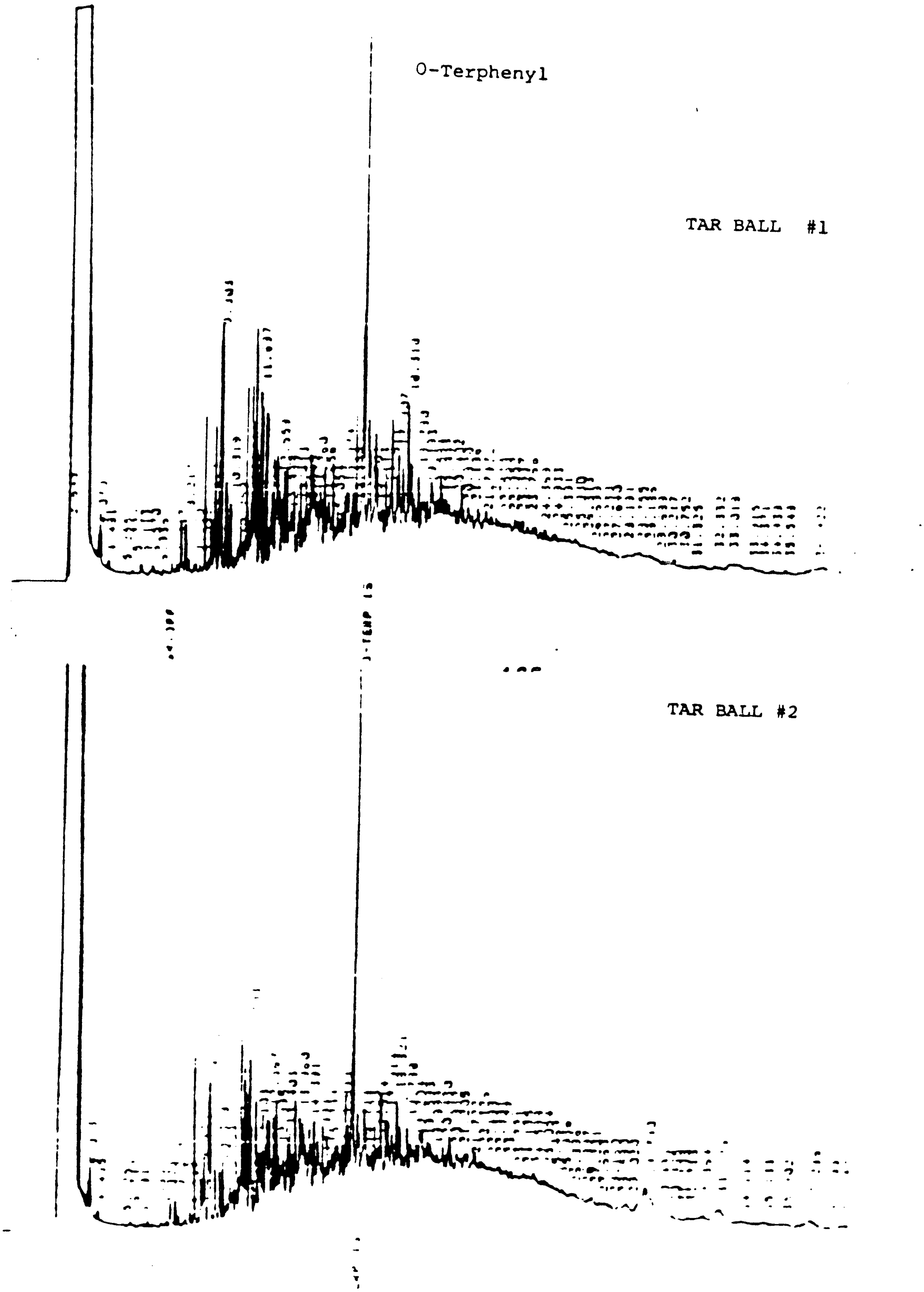

Figure 2. GC-FID Fingerprint of Aromatic Hydrocarbons from Tar Balls.
Temp. Prog. 100-280°C at 8° min. Glass Capillary Column, 30x X 0.25mm, SE-30

do not change greatly with weathering, thus indicating that the tar did not originate from IXTOC or Kuwait oil.

TABLE 2. GC-MS Analysis of Aromatic Hydrocarbons from Tar Ball and Select Petroleum Samples.

	$(C_1+C_2+C_3)P^1$ / P	$(C_1+C_2+C_3)D^2$ / D	C_1P/C_1D	C_2P/C_2D	C_3P/C_3D
Tar Ball #1	22.0	41.6	0.58	0.57	0.83
Kuwait Crude	18.7	65.9	0.41	0.10	0.10
IXTOX Crude	6.1	4.7	0.81	1.00	0.55

P^1 = Phenenthrene

D^2 = Dibenzothiophene

Concentrations of the trace metals Ni, Fe and Zn were determined for a sample of IXTOC oil and the two tar balls (Table 3). Although the trace metal concentration may change with weathering, the ratio of one metal to another should remain relatively characteristic of the petroleum source material. Because metals are predominantly associated with the asphaltene (benzene-insoluble) fraction, this function was determined for each tar ball and is reported in Table 3. These data show that the tar balls may be of common origin, but that they show no similarity to the IXTOC crude oil.

TABLE 3. Trace Metals in Tar Balls and IXTOC Crude Oil.

	Asphaltene	Ni	Fe	Zn	Ni/Fe	Ni/Zn
Tar Ball #1	38%	0.12	21.8	0.11	0.006	1.1
Tar Ball #2	8%	0.10	1.8	0.01	0.06	10.0
IXTOC Crude		0.03	0.1	0.003	0.30	10.0

The results indicate that these tar balls are physically and chemically distinct, yet may represent a common crude oil source with one of the tar samples having become mixed with a refined residual oil product. The bimodal distribution of n-alkane hydrocarbons observed in the GC-FID chromatogram for this tar ball (#2) is representative of two or more petroleum products mixed during oil tanker discharge *of* waste from their holding tanks. The predominance of a heavy refined oil is supported by the high boiling n-alkanes and the very low asphaltene (benzene-insoluble) fraction.

Although the internal portions of both tar balls represent approximately the same degree of weathering, the surface of #2 was more weathered than #1, indicating longer contact with the elements.