"Fingerprinting" of oil by infrared spectrometry

1 AUTHOR:

James S Mattson

James S Mattson, PA

45 PUBLICATIONS   **791** CITATIONS

"Fingerprinting" of Oil by Infrared Spectrometry

James S. Mattson[1]

Gulf General Atomic Co., P. O. Box 608, San Diego, Calif. 92112

IN A PREVIOUS PAPER (*1*), the technique of infrared internal reflection spectrometry was employed to differentiate Santa Barbara Channel seepage oil from the blow-out oil originating from Platform A.   In this continuation of that study, it was felt that a determination should be made of the characteristic infrared spectra of a large sampling of crude oils and residual fuels, in order to see whether sufficient differences existed to warrant an attempt to set up a library of infrared "fingerprints" for use in identifying oil spills.   In an AEC-sponsored study, Bryan *et al.* (*2*) used neutron activation analysis to examine the trace element "fingerprints" of various oils. The oils used in this infrared study were the same as those employed in the activation analysis program (*2*).   Table I lists the sources of these 40 samples.

EXPERIMENTAL

Transmission infrared spectra of all 40 samples were obtained using silver chloride windows in Wilks Minicells (Wilks Scientific Corp., S. Norwalk, Conn.).   The spectrophotometer employed was a Hilger-Watts H-1200 (distributed by Wilks Scientific).   A special interface was designed and constructed for the H-1200 in order to record the spectra in digital format using a parallel-recording Mobark model 305 cassette incremental tape recorder (Mobark Instruments, Sunnyvale, Calif.).   Eight-bit binary characters were recorded, representing the ordinate in per cent transmittance every 2.66 cm^{-1} from 4000 to 2000 cm^{-1} and every 0.53 cm^{-1} from 2000 to 666 cm^{-1}.   The precision obtained from this system is about 1.7 cm^{-1} on the abcissa and 1% T on the ordinate.   The details of the mechanical and electronic design of the interface are presented in another paper (*3*).

The recorded digital spectra were read directly (using a Mobark 305 Reproducer) into a Sigma 2 computer, converted into arbitrary units proportional to absorbance, and smoothed using a 9-point smoothing routine (*4*).   Each spectrum was read into the computer individually and, after converting to absorbance and smoothing, was displayed on a visual display screen in front of the operator.   Using his best judgment, the operator would select the end points for integrating each peak (the points of maximum inflection), and the computer then proceeded to integrate the peak and correct for the (assumed linear) base line.   All peak areas

(1) J. S. Mattson, H. B. Mark, Jr., R. L. Kolpack, and C. E. Schutt, ANAL. CHEM., **42**, 234 (1970).

(2) D. E. Bryan, V. P. Guinn, R. P. Hackleman, and H. R. Lukens, "Development of Nuclear Analytical Techniques for Oil Slick Identification (Phase I)," Contract AT (04-3)-167, Division of Isotopes Development, USAEC, Clearinghouse for Federal Scientific and Technical Information, NBS, U.S. Dept. of Commerce, Springfield, Va. 22151.

(3) J. S. Mattson and A. C. McBride III, ANAL. CHEM., **43**, 1139 (1971).

(4) A. Savitzky and M. J. E. Golay, *ibid.*, **36**, 1627 (1964).

Table I.   Samples Used in Infrared Study[a]

Sample number	Sample description
	Crude oils
1	East Texas Field
2	El Morgan, Egypt
3	Wilmington, Calif.
4	Minas Field, Sumatra
5	Duri Field, Sumatra
6	Export, Neutral Zone, Saudi Arabia–Kuwait
7	Kuwait Export
8	Ceuta, East Shore, Lake Maracaibo, Venezuela
9	Mesa, Orinoco Basin, Venezuela
10	Timbalier Bay, Offshore Louisiana
11	Sarir, Sirte Basin, Libya
12	Agha Jari, Iran
13	Orita, Putumayo Basin, Columbia
14	Kuwait Export Blend
15	Arabian Light, Export Blend
16	Ward–Estes Field, Texas
17	Goldsmith Field, Texas
18	Kelly Snyder Field, Texas
19	Sprayberry (Trend Area), Texas
20	Headlee, Texas
	Residual fuel oils
21	Ceuta, see no. 8
22	Mesa, see no. 9
23	Timbalier Bay, see no. 10
24	Sarir, see no. 11
25	Minas, see no. 4
26	Agha Jari, see no. 12
27	Orito, see no. 13
28	Kuwait, see no. 14
29	Arabian Light, see no. 15
30	Gulf Oil, Philadelphia No. 6
31	Gulf Oil, Santa Fe No. 6
32	Gulf Oil, Vengref Meneg Bunker
33	Gulf Oil, Port Arthur No. 6
34	Gulf Oil, Caribbean 200 vis.
35	Gulf Oil, Vengref Meneg No. 6
36	Gulf Oil, Zakum
37	Gulf Oil, Nigerian
38	Gulf Oil, Cabinda
39	Gulf Oil, Oficina
40	Chevron, Sumatran

[a] Obtained from H. R. Lukens (*2*).

were then normalized to the area of the 1456 cm^{-1} CH$_2$ peak in an effort to correct for variations in sample thickness.

Table II lists the absorption maxima used for the initial screening of the procedure.   The standard deviations given are for the peak locations in the entire set of 40 oils.   The fact that these deviations are quite small appears to indicate that these absorption bands are to be found fairly reproducibly in essentially all oils.

Table II. Absorption Maxima of 40 Oils Used in "Fingerprinting" Evaluation

Peak No.	Frequency average, cm^{-1}	Range cm^{-1}	Standard deviation cm^{-1}
1	1694	1680–1715	±7.5
2	1600	1594–1609	±3.3
3	1456	1446–1465	±3.2
4	1375	1372–1385	±2.6
5	1309	1302–1324	±5.5
6	1168	1155–1188	±6.8
7	1034	1031–1044	±2.8
8	874	864–893	±5.4
9	814	810–823	±2.6
10	747	741–756	±2.8
11	725	720–734	±2.6

Table III. Precision of Integration Method and Ranges of Peak Areas Observed for All 40 Samples

	(Based on 7 spectra of Sample 1) standard deviation		(Based on all 40 samples, normalized) Normalized peak areas	
Peak No.	Peak position, cm^{-1}	Peak area rel., %	Range, arb units	Ratio, max/min
1	±3.0	±29.2	0.0175 –0.0920	5.25
2	±1.5	±14.8	0.0370 –0.4140	11.18
3	±1.8	±2.8	1	1
4	±1.2	±2.9	0.1479 –0.3010	2.03
5	±2.0	±20.3	0.0093 –0.0329	3.54
6	±2.0	±5.5	0.0074 –0.0311	4.20
7	±1.2	±7.6	0.0068 –0.1896	27.88
8	±2.1	±8.9	0.0220 –0.1509	6.85
9	±1.4	±10.6	0.0076 –0.0920	11.86
10	±1.3	±9.3	0.0013 –0.0546	42.00
11	±0.9	±17.7	0.00011–0.0922	839

Table III lists the range of peak areas (normalized) observed and the ratios of the maximum observed areas to the minimum observed areas, as well as the standard deviations obtained after analysis of seven spectra of sample no. 1. The rather large standard deviations in peaks 1, 2, 5, and 11 are due to operator error in visually selecting integration end points.

Three of the eleven peaks were deleted from the final "fingerprint;" no. 3, obviously, as it was used in normalization; no. 4, because of the small variation in normalized area; and no. 5, because of its large relative standard deviation and small range of values. Peak no. 1 was retained, even though the relative standard deviation was very large, because of the observation (1) that this peak was very significant in determining the origin of different Santa Barbara Channel oils.

RESULTS AND DISCUSSION

The "fingerprint" was obtained by dividing the observed range for each of the peaks 1, 2, 6–11 into eight equal increments, numbering the increments from one to eight in order

Table IV. "Fingerprints" of the 40 Oil Samples of Table I

Crude oils		Residual fuel oils	
1.	72622341	21.	24655831
2.	53363412	22.	24614531
3.	53442351	23.	31532321
4.	22311124	24.	74214444
5.	75115563	25.	33111318
6.	22563541	26.	15776731
7.	33563621	27.	14644531
8.	23454531	28.	13854721
9.	63664521	29.	44866822
10.	62843431	30.	88758881
11.	42282433	31.	84364551
12.	12242421	32.	54586631
13.	33533431	33.	18547881
14.	32863522	34.	45575661
15.	11543522	35.	15356571
16.	22853421	36.	12431422
17.	21832321	37.	52423432
18.	32822321	38.	32312213
19.	21511211	39.	12333321
20.	11311115	40.	32212336

of increasing area, and then assigning the appropriate integer to each peak area observed for each oil. Thus an eight-character string is obtained, describing the intensities of the eight "fingerprint" peaks for that sample. Table IV lists these eight character "fingerprints." The only two samples having as many as five coincident characters are samples 17 and 18, which differ by only one digit in each of three peaks. Whether this is mere coincidence or is indicative of the same source is not known; however, both samples do come from Texas oil fields.

SUMMARY

Infrared "fingerprinting" of oils can be carried out simply and rapidly. There exist sufficient differences between the fingerprints of oils from different sources that the technique could be a promising one in the identification of oil spills. Additional studies of the variability of the fingerprint with natural aging must be carried out to determine the extent to which the method can be applied. These studies are currently under way.

ACKNOWLEDGMENT