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A Rapid, Nondestructive Technique for Infrared Identification of Crude Oils by Internal Reflection Spectrometry

Qualitative Differentiation of Crude Oils Originating from Natural Seepages and Platform "A" in the Santa Barbara Channel

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A rapid, direct, and qualitative internal reflection spectroscopic (IRS) technique requiring no sample pretreatment for the identification and differentiation of crude oils and tars is presented. The sample may either be a liquid or mixed with a solid substrate. As IRS is relatively more sensitive than transmission spectroscopy over an extended portion of the infrared, the use of IRS results in a better sample spectrum. The results of this study show that differentiation of crude oil samples originating both from Platform "A" and from natural seepages in the Santa Barbara Channel is possible, based upon the presence of carbonyl and carbon monoxide-like bands observed only in the natural seepage samples.

THERE are several places on the coast of the Santa Barbara Channel and in the channel where natural seepages of oil and tar exist. In the course of the investigation into the effects of the oil blowout, it was necessary to develop a differentiation technique which would enable the investigators to identify the oil on sediment and beach samples and differentiate that which originated from natural seepages from the oil which came from the blowout.

A specific analytical method for the rapid and accurate differentiation and identification of oils and tars was needed for this and similar instances. From experience gained in the course of this study, it should be pointed out that special analytical problems arise. Often these oil slicks are found on the water surface only as thin films, and it is the material which collects on beach sand, soil, and marine sediment which is most often available for analysis. The problems of oxidation and of the evaporation of low molecular weight components, or the aging processes, must also be taken into account. There is insufficient information available on biological degradation of the oils and tars, and this must be considered an unknown factor at this time. Until more information is obtained concerning such processes, samples taken are stored frozen until just before analysis. Thus the technique to be employed must not only be fast, easy to interpret, and not subject to procedural error, but it must also be directly applicable to samples which are mixed with sand, sediment, or other solid substrates.

The best candidate for these determinations was infrared spectrometry, as all of the oil and tarry materials of interest can be well fingerprinted by their infrared spectra. An in-

frared analysis method has been suggested as the solution to a similar problem (1), and transmission infrared analysis has long been employed in the petroleum industry in similar determinations on mixed hydrocarbon systems.

The type of sample encountered in natural systems does not always lend itself to simple transmission spectroscopic investigation. Oil and tar samples encountered in these situations are often mixed with a solid substrate, and the oils and tars themselves may contain insoluble weathered or oxidized components which must be included in the final analysis.

Kawahara (1) employed an extraction step to separate oils and asphalts from beach sands, using chloroform as the solvent, which is evaporated by gentle heating, leaving a thin film of the sample on an IR-transparent plate. In a study in this laboratory of the applicability of this technique (1) to the analysis of crude oils, the evaporation of the solvent had the added effect of selectively evaporating low molecular weight portions of the sample. Upon heating a chloroform-crude oil sample as recommended (1) over a 10-minute period, the infrared absorbance ratio of aromatic to aliphatic CH groups increased by 50%, and that for CH_2 to CH_3 groups increased by 20%. Also, a sample prepared as directed (1) and run several times in succession on a Perkin-Elmer 337 spectrophotometer underwent such changes with time due to heating by the infrared source that the absorbances of all the bands decreased nonuniformly from 20 to 100% over a period of 30 minutes. After 30 minutes of exposure, the 720 cm^{-1} peak (CH_2) completely disappeared, while the 2925 cm^{-1} band decreased by only 20%. Thus, any method which exposes a crude oil sample to direct heating such as this destroys the validity of the absorbance measurements, and leaves in doubt the validity of any ratios of these absorbances.

Using a crude oil sample either after extraction or from a sample of pure crude oil, it is possible to obtain a conventional transmission spectrum either in solution or as a neat film between two IR-transparent plates. Figure 1 is an example of one such spectrum run in CCl_4 on a natural seepage sample. This figure is included for the purpose of making a side-by-side comparison of transmission vs. IRS technique. The major problems inherent in transmission spectroscopy are illustrated by this Figure. One problem is the lack of relative

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(1) F. Kawahara, *Environ. Sci. Technol.*, **3**, 150 (1969).

sensitivity at lower energies, due to the inverse wavelength dependence of the absorption coefficient in transmission spectroscopy (2, 3). This inverse wavelength dependence is evident in the equation:

$$\frac{T}{T_o} = \exp\left(-\frac{4\pi n\kappa d}{\lambda}\right) \qquad (1)$$

where n is the refractive index of the sample, κ is the attenuation index (2) of the sample, d is the cell thickness, and λ is the *in vacuo* wavelength. In Equation 1, the absorption coefficient, α, of the Beer-Lambert relationship, $T/T_o = \exp(-\alpha Cd)$, where C is the concentration of a solution of the absorbing species, is expressed by:

$$\alpha = \frac{4\pi n\kappa}{\lambda} \qquad (2)$$

As Figure 1 illustrates, the inverse wavelength dependence of the absorption coefficient leads to a relative decrease in sensitivity at longer wavelengths. The use of thicker films is precluded by the requirement that the intensity of the most intense band be held below one, as absorbance values greater than one are too high to be of value in accurate infrared analyses (4). The optical null design of most infrared spectrophotometers severely distorts their linearity at absorbances greater than one (5). Another significant factor observed in Figure 1 is the absorption of CCl_4 between 810 and 715 cm^{-1}, cutting off all of the available energy in that region, a region of considerable significance in the analysis of petroleum hydrocarbons.

The problems inherent in transmission spectrometry, with both solutions and neat films, are circumvented by the use of internal reflection spectrometry (IRS) (6). IRS can be utilized to analyze samples admixed with particles without any of the adverse effects (scattering, high losses of energy, interfering bands, adsorption of water by KBr, etc.) associated with transmission methods (7-9).

Not only is IRS suitable for the analysis of a wider range of samples than is transmission spectrometry, but internal reflection spectra exhibit greater relative sensitivity in the low energy region of the infrared, as IRS eliminates the inverse wavelength dependence of the absorption coefficient as observed in transmission spectrometry. Just as Equation 1 describes the attenuation of the sample beam in transmission spectrometry, an expression can be written to describe the attenuation of the reflected beam in IRS. This equation is, provided that the actual thickness of the sample is $\gg \lambda$,

$$\frac{R}{R_o} = \exp\left(-\frac{4\pi N n\kappa b(\lambda)}{\lambda}\right) \qquad (3)$$

(2) M. Born and E. Wolf, "Principles of Optics," 3rd ed., Pergamon Press, New York, N. Y., 1965, p 611.
(3) A. Prostak, Ph.D. Thesis, University of Michigan, 1968.
(4) W. J. Driscoll in "Progress in Infrared Spectroscopy, Vol. I," H. A. Szymanski, Ed., Plenum Press, New York, N. Y., 1962, pp 125–42.
(5) L. E. Tufts and A. Davis, *ibid.*, pp 151–65.
(6) N. J. Harrick, "Internal Reflection Spectroscopy," Interscience, New York, N. Y., 1967.
(7) J. S. Mattson, H. B. Mark, Jr., and W. J. Weber, Jr., ANAL. CHEM., 41, 355 (1969).
(8) J. S. Mattson, H. B. Mark, Jr., and W. J. Weber, Jr., "Proc. 20th Mid-America Symposium on Applied Spectroscopy," Plenum Press, New York, N. Y., 1970, in press.
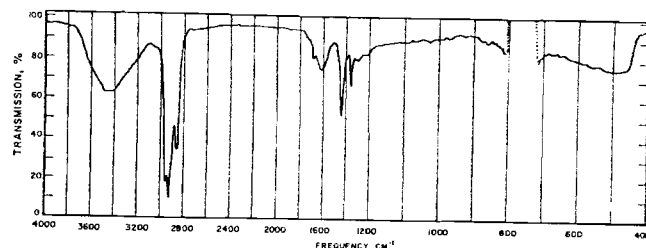(9) J. S. Mattson and H. B. Mark, Jr., *Environ. Sci. Technol.*, 3, 161 (1969).

Figure 1. Transmission spectrum of Carpenteria seepage crude oil, 4.71% in CCl_4, 0.1 mm NaCl
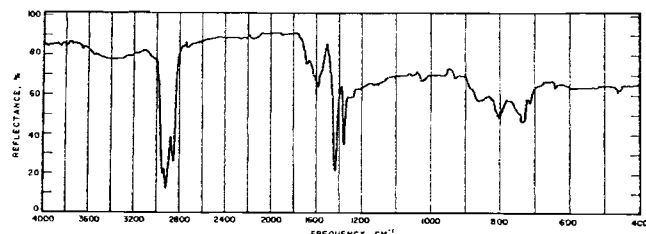

Figure 2. Internal reflection spectrum of Carpenteria crude oil
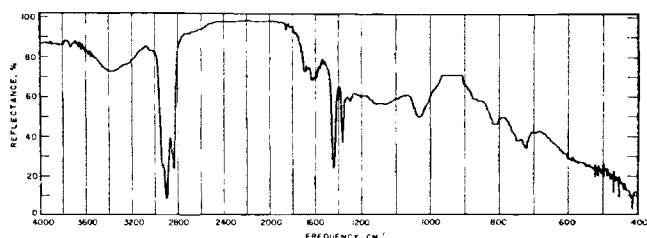

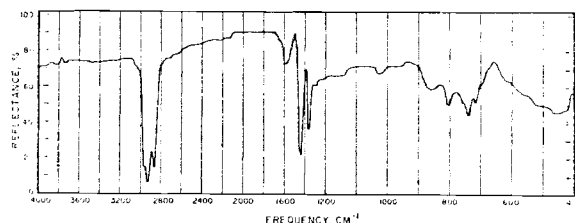Figure 3. Internal reflection spectrum of Coal Oil Point crude oil

Figure 4. Internal reflection spectrum of crude oil from Platform A21 in the Santa Barbara Channel

where N is the number of reflections, and $b(\lambda)$ is the effective optical thickness (6) as a function of wavelength. $b(\lambda)$ can also be expressed as $b' \cdot \lambda$, as the effective thickness varies linearly with wavelength for systems where the exponent in Equation 3 is $\ll 1$. This reduces Equation 3 to:

$$\frac{R}{R_o} = \exp(-4\pi N n\kappa b') \qquad (4)$$

The effective thickness constant b' is a complicated function of the optical constants and geometry of the IRS system (6). A discussion of these relationships is presented by Harrick (6) for nonabsorbing systems and by Hansen (10) for the general case.

Figure 2 is the IRS spectrum of the same crude oil used for Figure 1. Figure 2 appears to show enhancement of the absorption bands at longer wavelength relative to those at shorter wavelengths, when compared with the transmission spectrum in Figure 1. It should be noted that in Figure 2 the

(10) W. N. Hansen, *J. Opt. Soc. Amer.*, 58, 380 (1968).

absorbance of the 2925 cm⁻¹ CH₂ band is 0.90, well within the range of 0.1 to 1.0 considered (5) to be a necessity for infrared analysis. It should also be noted that several bands are observed in the region masked by CCl₄ in Figure 1, at 805, 735, and 715 cm⁻¹.

EXPERIMENTAL

A Wilks Model 45C micro-sampling IRS accessory (Wilks Scientific Corp., S. Norwalk, Conn.) was employed, mounted in the sample compartment of a Perkin-Elmer 337 infrared spectrophotometer. The Model 45C is compensated for atmospheric absorption by a matched path length reference beam mirror system. The 45 series accessory was chosen over previously employed systems (7–9) because it employs a smaller, less expensive crystal (5 × 12.5 mm) and requires much less sample (ca. 5–10 mg of solid sample). In studies involving beach sand and sediments, the polish of a KRS-5 crystal deteriorates with only a few samples, and repolishing then becomes necessary. This type of IRS accessory operates at a fixed angle of incidence of 45°, and is capable of yielding 5, 11, 15, or 23 reflections depending on the thickness of the crystal employed. More complete discussion of IRS techniques are presented by Harrick (6) and Wilks (11–13), and a discussion of experimental considerations in the handling of particulate samples in IRS is presented in another paper (8).

Samples of crude oils employed in these analyses were simply smeared on the surfaces of a 2-mm thick, 5-reflection KRS-5 crystal, and a conventional IRS spectrum run (6, 9, 11–13). Samples of sediments and sands are run in the same manner, using a 0.5-mm thick, 23-reflection crystal for additional sensitivity. No chemical treatment of any kind is required.

RESULTS AND DISCUSSION

Through some strange coincidence, the authors had obtained some samples of natural seepage crude oil several months before the blowout from two locations within a few miles east and west of Platform A21.

The sample from Platform A21 was taken about a month after the blowout, directly from the well. All three of the samples were obtained without solid material mixed with them, so that it would be possible to treat them as standards. Because it was not originally known that they would be used for this purpose, none of the samples were kept frozen. However, no significant changes were observed in their spectra after long exposure to the mild temperatures and conditions of the authors' laboratory. They were kept in sealed containers for most of the time.

IRS spectra of the three samples are shown in Figures 2–4. Figure 2 is the Carpenteria seepage, Figure 3 the Coal Oil Point seepage, and Figure 4 the sample from Platform A21. Table I lists the bands observed in the spectra and their respective functional group assignments.

The most obvious qualitative difference between the natural seepage oils and that from Platform A21 is in the carbonyl band at 1700 cm⁻¹. In Figure 4, the Platform A21 sample, there is no trace of a carbonyl absorption at 1700 cm⁻¹, while both of the natural seepage samples exhibit C=O bands of significant intensity at this frequency. A separate run of spectra 2 and 3, using another 337, showed a band at 2200 cm⁻¹

Table I. Band Assignments, Crude Oils

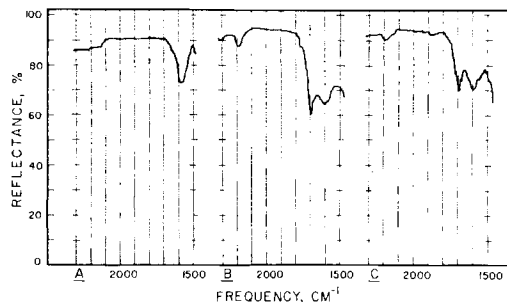|			
3100–3600 cm⁻¹	water	1450 cm⁻¹	>CH₂
3050	aromatic CH	1375	—CH₃
2950	—CH₃	1030	>S=O or PO₄ (?)
2925	>CH₂	860	aromatic CH
2850	>CH₂	805	aromatic CH
1700	>C=O	735	aromatic CH
1600	aromatic CC	715	long chain —CH₂—

Figure 5. 2300 to 1500 cm⁻¹ regions of spectra of all three samples, showing 2200 cm⁻¹ peak obscured by filter change in Figures 2 and 3

A: Platform A21 sample, B: Coal Oil Point seepage sample, C: Carpenteria seepage sample

which had been obscured by the filter change in the first spectrometer. Figure 4 was obtained on this second instrument and did not exhibit this 2200 cm⁻¹ band. Figure 5 reproduces the 2300–1500 cm⁻¹ region of these three spectra, showing both the C=O band at 1700 cm⁻¹ and the band at 2200 cm⁻¹. The 2200 cm⁻¹ band in the seepage oils corresponds to the carbon–oxygen bond similar to that in carbon monoxide, and is most likely some kind of oxidation product. The qualitative differences observed in the seepage samples vs. the sample of oil from Platform A21 represent significant differences in the extent of oxidation of the two types of samples. It is possible that the close proximity of the seepage sources to the ocean bottom and to the atmosphere has resulted in this oxidation over the long term, or that biological activity is responsible for the oxidation. The possibility that oxidative changes took place in the laboratory was not immediately ruled out, but the sample from Platform A21 did not undergo these changes after storage under similar conditions for five months.

In Figures 2–4, there are some semi-quantitative differences observed in the region below 1200 cm⁻¹. There is a strong band observed at 1030 cm⁻¹ in the Coal Oil Point spectrum, while the Carpenteria and Platform A21 samples show much less absorption in this area. The three aromatic CH bands at 860, 805, and 740 cm⁻¹ and the (long-chain) CH₂ band at 715 cm⁻¹ show slightly different relationships in all three samples, and these relationships could be incorporated into a computer program to differentiate the oils on the basis of their characteristic spectra. A discussion of the lack of applicability of the quantitative absorbance ratio (I) technique for the differentiation of oil samples of this type is discussed in Appendix I. The amount of absorption in the 600–400 cm⁻¹ region varies with each sample, but this is again too subtle a difference for observing differences by eye, and would be relevant in terms of a computer aided search of fingerprint spectra. The inorganic substrates found in sediment samples also show strong absorption in the 600–400 cm⁻¹ region.

(11) "Internal Reflection Spectroscopy, Vol. I," Wilks Scientific Corp., S. Norwalk, Conn., 1965.
(12) P. A. Wilks, Jr., *Appl. Spectrosc.*, **22**, 782 (1968).
(13) P. A. Wilks, Jr., *ibid.*, **23**, 63 (1969).

It should be pointed out that the same spectra as shown in Figures 2–4 were obtained after mixing the oil samples with solid substrates such as diatomaceous earth. This illustrated that the presence of solid materials in the oil samples does not change the qualitative nature of the spectra obtained by IRS.

The results of the above investigation appear to be quite promising, in that a method for the identification and differentiation of oils and tarry pollutants has been demonstrated to be feasible. The differentiation of the natural seepage materials from the blowout oil on the basis of oxidation products seems quite valid. The use of IRS in examining similar environmental samples is strongly indicated over any type of transmission technique. The use of IRS requires some additional care in the selection of the IRS crystal and geometry to be employed, but these considerations are adequately understood (6–9, 11–13).

There is no question that a specific qualitative examination of the whole spectrum in these situations is to be preferred over a quantitative or semi-quantitative method of data reduction involving certain absorbance ratios. There are simply too many chances for error introduced through aging and biological processes. This IRS technique can be employed to make a thorough study of these aging and biological processes, and such an investigation should be finished before the technique outlined in this paper can be adopted as a standard method. This investigation is currently underway.

APPENDIX I

Data Treatment. Kawahara (*1*) has suggested that a more quantitative approach to the identification and differentiation of oils and tars is feasible, and that such an approach should be employed in preference to a qualitative examination of the entire spectrum. If it is assumed to be possible to neglect the effects of weathering and biodegradation of the samples, there may be some value inherent in calculating the ratios of absorbances for some of the bands present in the crude oil spectra. Because of the inherently greater sensitivity of IRS in the longer wavelength region, reflectance absorbance determinations measured from IRS spectra automatically provide a substantial increase in accuracy over similar determinations made from transmission spectra. However, several problems arise.

The data reduction technique employed by Kawahara (*1*), involving the placement of a baseline by connecting the points of maximum transmittance at the edges of a peak, is not sufficiently accurate for complex spectra and cannot be employed in the study of oils, tars, asphalts, etc. For single isolated peaks this technique is applicable provided certain conditions on the spectral slit width are satisfied, but this is not the case in the types of analyses reported here and by Kawahara (*1*). There are two problems which must be considered in the determination of absolute infrared absorbances (*4*). These are spectral slit width function deconvolution, and the separation mathematically of overlapping bands.

Kawahara (*1*) employed a Perkin-Elmer 137 infrared spectrophotometer in his studies of oil and asphalt. The P-E 137 has a spectral slit width of from 20 to 50 cm⁻¹ (*14*), depending on wavelength. The Perkin-Elmer 337 used in these studies of the California crude oils has a much narrower spectral slit width, varying from 2 to 6 cm⁻¹ (*14*). (These spectral slit widths apply to the normal mechanical slit width settings on both instruments.) It is possible to obtain accurate measure-

ments of peak absorbances without resorting to slit function deconvolution only for the case where the true band half-width (band width at half maximum) exceeds the spectral slit width by a factor of 10 (*4*). In the oil and asphalt spectra reported by Kawahara (*1*) the ratio of the band half-width to the spectral slit width varied from about 1 to 3. In the spectra reported here, in Figures 1–4, the ratio varies from about 10 to over 30, well above that necessary for accurate absorbance determinations without slit function deconvolution.

The problem of separating overlapping bands is of a much more serious nature both in the treatment of spectra in this paper and in Kawahara's study. In making the peak absorbance measurement of a band which is adjacent to another strong, overlapping band, it is not possible to employ a baseline drawn between the two points of maximum transmittance on either side of an absorption maximum (*4, 5*). Instead, it is necessary to solve a set of inhomogeneous linear equations for the true absorbances, of the form:

$$A_1^{\text{apparent}} = a_{11}A_1 + a_{12}A_2 + \ldots + a_{1n}A_n$$
$$A_2^{\text{apparent}} = a_{21}A_1 + a_{22}A_2 + \ldots + a_{2n}A_n$$
$$\ldots \qquad \ldots \qquad \ldots \qquad \ldots \qquad \ldots \tag{4}$$
$$A_n^{\text{apparent}} = a_{n1}A_1 + a_{n2}A_2 + \ldots + a_{nn}A_n$$

where the apparent absorbances are made up of contributions from all of the overlapping bands, and are measured from the I_o line. One method of determining the coefficients in (4) involves the assumption of a Lorentzian band shape (*15, 16*), for which the intensity of a band at a frequency ν is related to the band half-width δ such that the coefficient a_{ij} of Equation 4 is given by

$$a_{ij} = \frac{(\delta/2)^2}{(\nu_i - \nu_j)^2 + (\delta/2)^2} \tag{5}$$

With the problems associated with the mixture of compounds present in crude oils, tars, etc., where several different species are contributing to individual broad bands, the Lorentzian band shape is not truly applicable. A better approach to this problem is arrived at through the coefficients derived by Cabana and Sandorfy (*17*), where it is not assumed that symmetry exists, and the band shape is best determined by using the left and right half band widths at $^1/_8$, $^1/_4$, $^1/_2$, and $^3/_4$ of the band maximum. The coefficients a_{ij} above can be computed by the Cabana-Sandorfy method, but this involves the use of a high speed digital computer and the computational technique begins to become overwhelmingly important, thus attaching unwarranted significance to the numbers obtained in this way. The spectra and the nature of samples encountered in this type of work do not generally warrant quite that level of sophistication.

One can understand the effect of using a mathematical band separation in the magnitude of a given band absorption by comparing the values obtained for the three overlapping bands at 860, 805, and 740 cm⁻¹ of Figure 2. These bands were treated according to a Lorentzian band shape (*15, 16*) and by Kawahara's baseline treatment. For the band separation, the problem in this case reduces to the matrix solution of

$$\begin{pmatrix} 0.080 \\ 0.127 \\ 0.125 \end{pmatrix} = \begin{pmatrix} 1.000 & 0.200 & 0.045 \\ 0.265 & 1.000 & 0.129 \\ 0.064 & 0.129 & 1.000 \end{pmatrix} \begin{pmatrix} A_1 \\ A_2 \\ A_3 \end{pmatrix}$$

(14) R. Gore, Perkin-Elmer Corp., private communication, August 1969.

(15) W. Kauzmann, "Quantum Chemistry," Academic Press, New York, N. Y., 1957, p 567.
(16) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York, N. Y., 1955, p 342.
(17) A. Cabana and C. Sandorfy, *Spectrochim. Acta*, **16**, 335 (1960).

Table II. Absolute Band Intensities, Carpenteria

Band, cm^{-1}	$A_{\text{Lorentzian}}$	A_{Kawahara}	$\dfrac{A_{\text{L}} - A_{\text{K}}}{A_{\text{K}}}$, %
860	0.057	0.044	30
805	0.099	0.074	34
740	0.111	0.055	100

where the Lorentzian coefficients were obtained from the solution of Equation 5. The observed half band widths are $\delta_1 = 60$ cm^{-1}, $\delta_2 = \delta_3 = 50$ cm^{-1}. [The spectral slit width for a Perkin-Elmer 337 in this region is about 3 cm^{-1} (*14*).] The results of this computation, shown in Table II, clearly show that the use of absorbance measurements as suggested by Kawahara (*1*) as a quantitative method of differentiation of such species could lead to erroneous results and that only a highly sophisticated computerized data reduction system which utilizes the total spectrum should be employed in this manner.