

Quantitative Functional Group Analysis of Asphalts Using Differential Infrared Spectrometry and Selective Chemical Reactions—Theory and Application

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An analytical method is described for the rapid quantitative analysis of seven highly polar chemical functional groups present in asphalt or formed in asphalt during oxidative aging. The method employs infrared spectrometry combined with the specialized use of selective chemical reactions and differential spectra for quantification of the analytical absorption bands of interest. The naturally occurring functional groups determined are carboxylic acids and their salts, 2-quinolone types, phenolics, and pyrroles; those formed on oxidation are ketones, anhydrides, small amounts of acids, and sulfoxides. Several selected applications of the functional group analysis as applicable to composition-related problems in asphalt technology are presented.

The chemical analysis of asphalts continues to challenge asphalt chemists because of the wide variety of molecular types and structures present and their relatively high molecular weight. Molecular types in asphalt range from nonpolar, non-aromatic hydrocarbons to highly aromatic hydrocarbons the molecular structures of which contain varying amounts of certain so-called heteroatoms, predominantly oxygen, nitrogen, and sulfur, together with parts-per-million amounts of metals such as vanadium and nickel (1). These heteroatoms are often associated with polar, strongly interacting chemical functionality or functional groups that have a disproportionately large effect on asphalt properties (1–3).

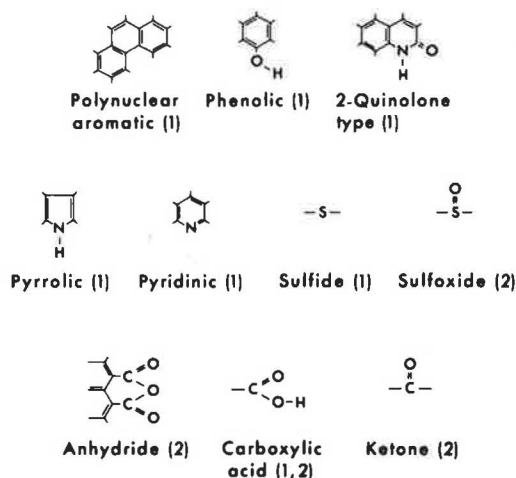
Because the number of molecules in asphalt with different chemical structures and reactivities is extremely large, determination of asphalt composition by separation of asphalt into its molecular components is generally considered impractical if not impossible by present-day techniques. However, if the different chemical functionalities that compose and dominate the properties of the various asphalt molecules are considered, the number of types of functionalities that need be considered quickly narrows to a manageable number (1). Examples of some of the more important chemical functionalities that are an integral part of large asphalt molecules are shown in Figure 1 (1). Many asphalt molecules of different composition will have similar chemical functionalities, which in turn produce similar effects on physical properties.

The principal cause of age hardening and embrittlement of asphalt used in pavements is the atmospheric oxidation of

certain asphalt molecules with the formation of highly polar and strongly interacting chemical functional groups containing oxygen (1–6). Thus, the ability to identify and quantify asphalt chemical functionality provides an important tool for assessing the effects of composition on asphalt properties and, thus, the performance of the asphalt in service.

During the past 20 years, the author and co-workers have conducted research related to the identification and characterization of the polar, heteroatom-containing chemical functionality in asphalt. Infrared spectrometry has been a rewarding technique in this research because it can be applied to complex mixtures without prior separation.

Earlier researchers who explored infrared spectrometry for the characterization of asphalts found the technique useful in determining the general chemical structural types present (7–9); however, the strongly associating polar functionalities present were never adequately identified or characterized. The inability to adequately characterize these polar functionalities resulted from several inherent problems, such as overlapping and ill-defined absorption bands, and the shifting and broadening of absorption bands from hydrogen bonding.



(1) Naturally occurring

(2) Formed on oxidative aging

FIGURE 1 Examples of important chemical functionalities present in asphalt molecules.

These inherent problems have been overcome by the combined use of selective chemical reactions and differential spectrometry. A selective solvent system is also used to break up hydrogen bonding, eliminating the complicating effects of hydrogen bonding on the spectra. The development and evaluation of this technique are described in several papers (10–12). The technique has been used extensively in the author's laboratories for the quantitative characterization of asphalt chemical functionality.

In this paper, the current practice of the functional group analysis is presented and applications of the technique are described. The chemical functionalities quantitatively determined include carboxylic acids (and independently their salts), anhydrides, ketones, 2-quinolone types, sulfoxides, pyrrolids, and phenolics. Structural formulas for these functional types are shown in Figure 1. With the exception of basic nitrogen compounds in asphalts (predominantly pyridine types), which do not yield readily to infrared analysis, these functionalities make up the important polar heteroatom-containing functionalities initially present in asphalts or formed during oxidative aging (1).

EXPERIMENTAL METHODOLOGY

Theory

As previously mentioned, the most polar and strongly interacting functional groups in asphalts occur in relatively small amounts and their infrared absorption bands are often complicated by hydrogen bonding and overlap with other strong absorption bands, making their detection difficult and their quantitative assessment virtually impossible without the use of special techniques. Phenolic and pyrrolic groups in asphalt are hydrogen-bonding functionalities. Thus, in neat asphalts or in solutions of asphalts in typical infrared spectral solvents, an equilibrium exists between the free absorption bands of these functional groups and their hydrogen-bonding bands (the latter bands overlap), which is dependent on their concentration, the characteristics of the solvent (if used), and the basicity of components in the asphalt with which the acidic hydrogen of the functionalities interacts (13,14).

Two other important, naturally occurring functionalities are carboxylic acids and 2-quinolone types. These functionalities are extremely strong hydrogen bonders. Not only do they form dimers in neat asphalt or nonpolar spectral solvents such as carbon tetrachloride, but they interact strongly with each other to form a mixed dimer, yielding six absorption bands, of which five overlap and become virtually indistinguishable (15,16).

Infrared spectra in the carbonyl region become further complicated in oxidized (aged) asphalts because of the intense ketone band formed. This band has the same absorption frequency as does the acid dimer, making the two indistinguishable. The free (nonhydrogen-bonded) acid band is also lost in the shoulder of the strong ketone band (4,10,11). Determination of anhydrides formed on oxidative aging is also virtually impossible from typical infrared spectra because their absorption bands are also masked by the strong ketone absorption band, making them often undetectable (5,10).

To overcome the problems just described and to obtain

spectra suitable for quantitative analysis, several specialized techniques and procedures are employed. Tetrahydrofuran (THF) solvent is used to eliminate the interference from hydrogen bonding on the carbonyl absorption region in the determination of ketones, carboxylic acids, anhydrides, and 2-quinolones. This solvent is a cyclic ether having a strongly electronegative oxygen within the molecule. Because of its electron-donating properties, THF associates with the acidic hydrogen of carboxylic acids and 2-quinolone types, thus preventing dimer and mixed-dimer formation. The unassociated carbonyl group is therefore made available for characterization.

Advantage is taken of the hydrogen bonding of phenolic and pyrrolic functionality with THF in the analysis of these functional groups. Details of this analysis will be discussed later. Because THF has strong absorption bands in the frequency ranges used in the determinations, solvent compensation must be used.

With the problems of hydrogen bonding eliminated, the problem of overlapping bands in the carbonyl absorption region (about 1800–1600 cm^{-1}) is addressed by using selective chemical reactions and differential infrared spectrometry. The techniques applied are as follows. To reveal the absorption band of interest and eliminate from the spectra other bands with absorption at the same frequency, the asphalt sample is treated with a selective reagent that eliminates, or shifts to another frequency, the absorption band of interest. A differential spectrum is then taken with the treated sample in one beam and the untreated sample in the other beam of a double-beam infrared spectrophotometer. This procedure reveals the absorption band of the functionality of interest in the differential spectrum and nulls or cancels out all other absorption bands in the same region. Quantitative analysis is then applied, as will be described in the paper, to the absorption band of interest.

Examples of Spectra Used

Examples of the spectra used in the functional group analysis, together with a description of the pertinent selective chemical reactions, will be discussed next.

To provide background for the discussion of the differential spectra, the spectra in carbon disulfide (CS_2) of 5 percent weight by volume solutions of asphalts, before and after oxidative aging, are shown in Figure 2. [Spectra in this and other examples in this paper were taken in 1.0-mm sealed cells using a Perkin-Elmer Model 983G double-beam diffraction-grating infrared spectrophotometer. All spectra are compensated (nulled) for solvent absorption. The instrument was operated in the linear absorbance mode to facilitate quantification of the absorption bands.] The small absorption bands at about 3610 cm^{-1} and 3480 cm^{-1} result from the free (nonhydrogen-bonded) OH and NH absorption of the phenolic and pyrrolic functional groups, respectively. The broad absorption between about 3100 cm^{-1} and 3400 cm^{-1} results from hydrogen bonding of additional amounts of these functional groups. Note the decrease in intensity of the free absorption bands and the increase in the hydrogen-bonding bands in the spectrum of the oxidized sample (Spectrum B) compared with the unoxidized sample (Spectrum A).

The carbonyl region between about 1900 cm^{-1} and 1600

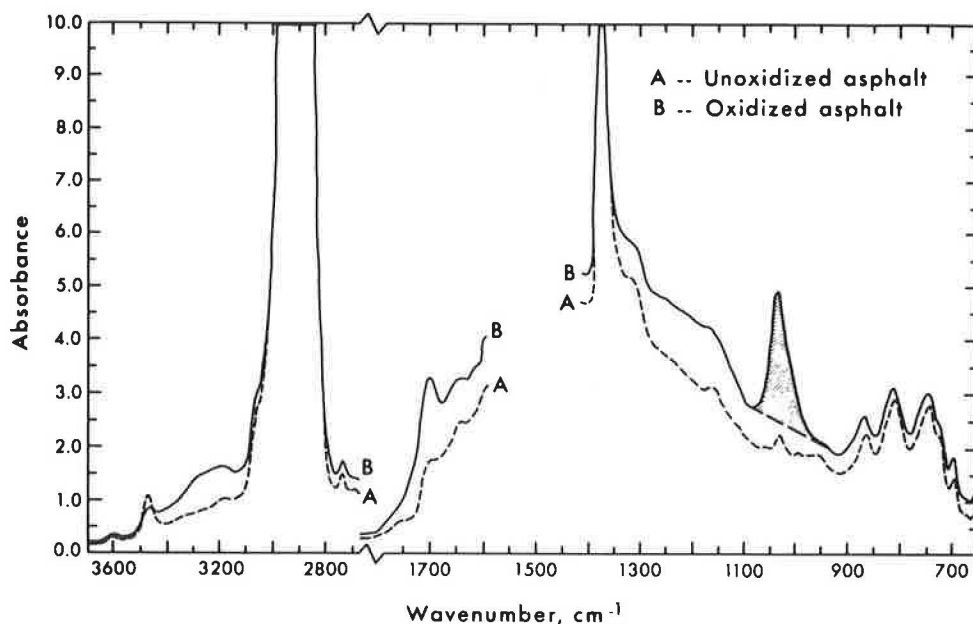


FIGURE 2 Spectra of CS_2 solution of unoxidized and oxidized asphalt (solvent compensated).

cm^{-1} in Figure 2 is of particular interest because it contains the absorption bands for carboxylic acids, 2-quinolone types, ketones, and anhydrides. No ketones or anhydrides are present in the spectrum of the unoxidized asphalt (Spectrum A). The small shoulder at about 1700 cm^{-1} is from dimerized or hydrogen-bonded carboxylic acids and the shoulder at about 1640 cm^{-1} is from dimerized 2-quinolone types and mixed dimers of 2-quinolone types and carboxylic acids. Again, it is apparent that this carbonyl spectrum has little value for quantitative analysis of the functional groups mentioned.

Spectrum B needs to be considered for the oxidized asphalt. The strong absorption at about 1700 cm^{-1} results primarily from the development of ketones, the major functional group formed from hydrocarbon oxidation in asphalts (1,4). The acid dimer band, apparent in the unoxidized asphalt, has completely merged with the ketone band and is not discernible. Furthermore, absorption bands for anhydrides, discussed later, are also present but not discernible in the 1700-cm^{-1} absorption band. Although the 1700-cm^{-1} absorption region in the CS_2 spectra of the oxidized asphalt is not useful for the quantitative determination of the functional groups of which it is comprised, the net change in absorption at 1700 cm^{-1} can be a useful technique for following relative changes in the level of asphalt oxidation, and was so used by early investigators (8).

Finally, the band at 1030 cm^{-1} in the spectrum of the oxidized asphalt is of interest because it results from the oxidation of sulfide moieties in asphalt molecules to sulfoxides during oxidative aging (6). Because there are no interfering bands in this region, and hydrogen bonding is not a complicating factor, the intensity of this band can be used directly for the quantitative determination of sulfoxides. The spectrum between 2700 cm^{-1} and 1900 cm^{-1} is not shown in Figure 2 because there are no significant absorption bands in this region in asphalts. Also, the asphalt absorption bands between 1600

cm^{-1} and 1400 cm^{-1} are not shown because strong absorption by the solvent, CS_2 , in this region negates their detection.

The balance of the spectra discussed were taken as 5 percent wt/vol solutions in THF. As previously mentioned, THF eliminates hydrogen-bonding complications in the carbonyl region. Spectra shown in Figure 3 were taken by using the same asphalts as were used for the spectra in Figure 2. Spectra of the unoxidized and oxidized asphalts are shown before and after selective chemical reactions.

The spectra of the unoxidized asphalt will be considered first. Spectrum C for the untreated asphalt shows the free acid carbonyl absorption at about 1730 cm^{-1} , having shifted from its hydrogen-bonded dimer, which was observed at about 1700 cm^{-1} in the CS_2 spectrum of Figure 2. The broad hydrogen-bonded band seen at about 1640 cm^{-1} in the CS_2 spectrum has also been resolved by the solvent THF to yield the free carbonyl absorption of 2-quinolone types at about 1685 cm^{-1} . The broad band centering at about 1600 cm^{-1} , missing in Figure 2 because of strong CS_2 absorption, results primarily from aromatic carbon-carbon double bonds with a minor contribution from carbon-nitrogen double bonds.

Spectrum D resulted from treatment of the asphalt with triphenyltin hydroxide (TPTH). TPTH, the selective reagent used to react with carboxylic acids in their determination, complexes with free acids and shifts their carbonyl absorption frequency in THF from about 1730 cm^{-1} to about 1640 cm^{-1} (11). Evidence of this can be observed by comparing Spectra C and D.

Spectra E, F, and G in Figure 3 were obtained using the oxidized asphalt. The increase in carbonyl absorption in the 1700-cm^{-1} region from ketones (4) and anhydrides (5) formed on oxidation is apparent. Spectrum E was obtained on the untreated asphalt. Spectrum F was obtained after treatment with TPTH and shows the loss of carboxylic acid carbonyl in

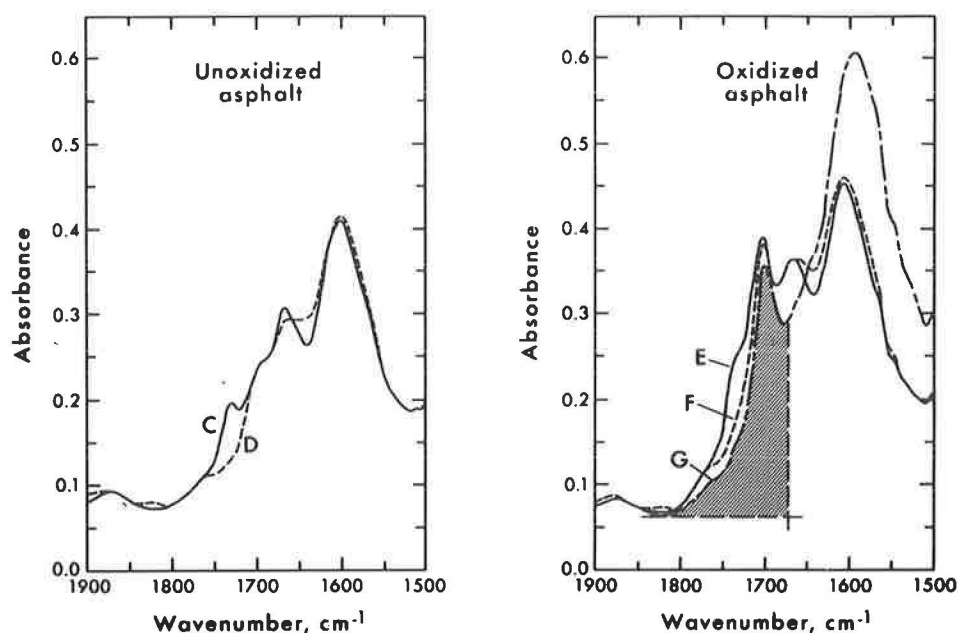


FIGURE 3 Examples of infrared spectra used in functional group analyses: (C) untreated; (D) TPTH treated; (E) untreated; (F) TPTH treated; (G) NaOH treated (solvent compensated).

the 1730-cm^{-1} region. Spectrum G was obtained on the sample after treatment with sodium hydroxide (NaOH), which, in addition to reacting with acids, reacts with the acid anhydrides to convert them to their sodium salts. Loss of anhydride carbonyl absorption in the 1700- to 1800-cm^{-1} region is evidenced by comparison of Spectra F and G. NaOH treatment shifts the carbonyl frequency to 1580 cm^{-1} , characteristic of their acid salts. Comparison of Spectra E and G also indicates that NaOH eliminated the 2-quinolone-type absorption at about 1685 cm^{-1} , this by forming the sodium salt of the tautomeric hydroxy form of the 2-quinolone carbonyl (10,15). After reaction with NaOH, the balance of the carbonyl absorption remaining at 1695 cm^{-1} in Spectrum G (less background absorption) results from ketones formed on oxidation (4).

Although the spectra in Figure 3 clearly show the effect of the selective chemical reactions on the chemical functionality, the spectra are not in the most convenient form for quantitative analysis. To clearly delineate the absorption band affected by the selective chemical reaction and eliminate adjacent interfering absorption bands, differential spectra are used. Examples of those used in the functional group analysis are shown in Figure 4. These will be discussed as the quantification of band areas for each functional group is described.

Quantification of Absorption Band Areas

The areas under the absorption bands of interest, shown as shaded areas in the spectra, are used to evaluate the concentrations of functional groups. Guidelines for determining the boundaries of the band areas for each functional group will be detailed next.

Carboxylic Acids and Their Salts

Differential Spectrum H, Figure 4, shows the 1730-cm^{-1} carboxylic acid band (shaded area) for asphalts. The spectrum was obtained with the TPTH-treated sample in the spectrophotometer sample beam and the untreated sample in the reference beam. The corresponding TPTH complex band appears at 1640 cm^{-1} . A baseline is drawn, as indicated in the figure, which defines the band area. Should the asphalt contain salts of carboxylic acids (whose broad carbonyl absorption bands between 1500 cm^{-1} and 1600 cm^{-1} are masked by the broad 1600-cm^{-1} aromatic absorption band), they can be determined by difference as follows. Both carboxylic acids and their salts react with silylating reagent to form silyl esters with an absorption frequency at about 1715 cm^{-1} . Thus, an aliquot of the untreated asphalt is routinely silylated by treatment with a mixture of hexamethyldisilazane and trimethylchlorosilane (10,11), and a differential spectrum of the silylated versus the TPTH-treated spectra is obtained (Spectrum J). Because the acid concentration calculated from the area of the corresponding silyl ester band includes both free acids and acid salts, the difference between the acid concentrations calculated from Spectra J and H corresponds to the amount of acid salts present. In the example shown in Figure 4, the difference was zero and thus no acid salts were present.

2-Quinolone Types

The silylation reaction just described is also used to determine the 2-quinolone types (10). The 2-quinolones can undergo tautomerization by migration of the hydrogen on the nitrogen

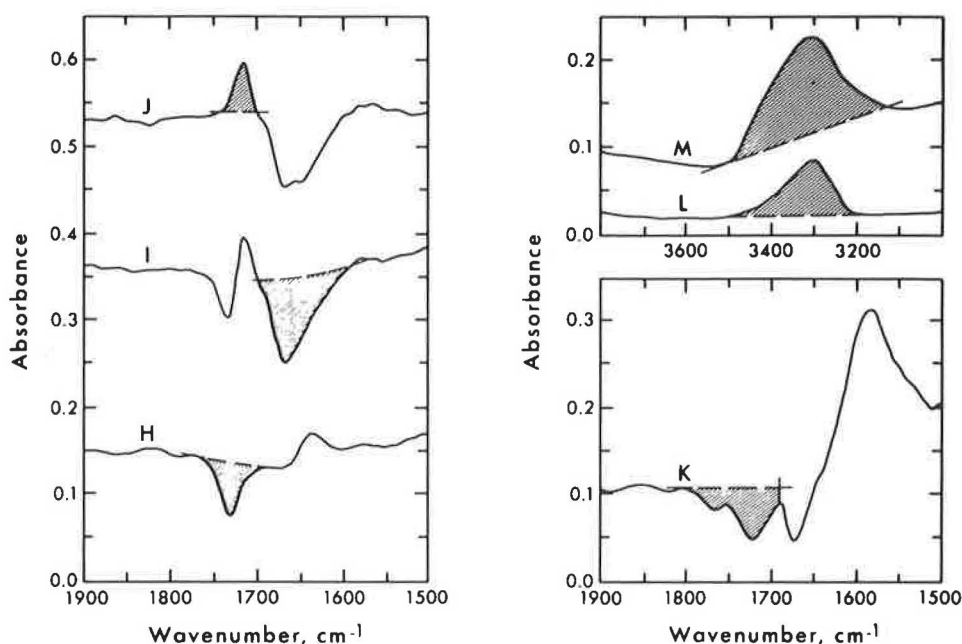


FIGURE 4 Examples of differential infrared spectra used in functional group analysis: (H) TPTH treated versus untreated; (I) silylated versus untreated; (J) silylated versus TPTH treated; (K) NaOH treated versus TPTH treated; (L) NaOH treated versus solvent; (M) untreated versus solvent.

atom (see Figure 1) to the carbonyl oxygen with the simultaneous movement of the carbon-oxygen double bond to the bond between the carbon and nitrogen to form a hydroxy-quinoline. This hydrogen is acidic and readily reacts with the silylation reagent to form the silyl ether, thus destroying the carbonyl group with a corresponding loss of 2-quinolone carbonyl absorption. The band area of the 2-quinolones (band peak at about 1680 cm^{-1}) is therefore determined, as shown in Spectrum I, from the differential spectrum of the silylated versus unsilylated samples.

Caution should be exercised in drawing the baseline for band area quantification because trace amounts of water—if present in the hygroscopic solvent, THF—give a strong, broad absorption band at about 1640 cm^{-1} . Because silylation destroys this water band, any water in the untreated sample solution will erroneously add to the intensity of the 2-quinolone band in the differential spectrum. Additional details on the effect of water on the analysis, and how to cope with the water problem in THF, can be found elsewhere (10).

Anhydrides

Anhydrides produced on oxidation in asphalts are of a stereospecific type and form at the 1,8-bridgehead position of a naphthalene ring structure in the asphalt molecule (5). They yield a doublet infrared band with a major peak at 1725 cm^{-1} and a minor peak at 1765 cm^{-1} . The area of the anhydride band is determined from the differential spectrum of the NaOH-treated sample versus the TPTH-treated sample (Spectrum K). The TPTH-complexed sample is used in the reference beam to eliminate carboxylic acid absorption. With the potentially inter-

fering carboxylic acid absorption eliminated from both samples, a clean anhydride band is displayed in the differential spectrum.

Care must be exercised in the preparation of the NaOH-treated sample to ensure complete hydrolysis and avoid artifact formation. Reference can be made to the description of the original method for details and discussion of the NaOH hydrolysis procedure (10). Several factors must be considered when determining the boundary constraints of the anhydride band area. If 2-quinolone types are present in the asphalt, a peak may appear at about 1680 cm^{-1} . The 2-quinolone reaction with NaOH is not always quantitative with the hydrolysis conditions used, causing the intensity of this band in the differential spectrum to vary. The 2-quinolone band also tends to overlap with the major anhydride band.

Further, the strong acid salt band at 1580 cm^{-1} , if sufficiently intense, may also tend to pull up the baseline that defines the boundaries of the low-frequency side of the 1725-cm^{-1} band. In most cases, this latter effect is not a significant problem but should be considered when baseline boundaries are judged. In most cases, a horizontal baseline drawn from the high-frequency side of the 1765-cm^{-1} band to a point midway between the 1725-cm^{-1} anhydride band and the 1680-cm^{-1} 2-quinolone-type band, as shown in Spectrum K in Figure 4, adequately defines the anhydride band.

Phenolics and Pyrrolics

Both the phenolic and pyrrolic functionalities have an acidic hydrogen atom (see Figure 1) that hydrogen bonds with the

oxygen of the THF solvent molecule to form broad, intense bands, both centering at the same frequency at about 3300 cm^{-1} , which makes differentiation of the bands impossible. However, NaOH reacts with phenolics, but not pyrrolics, to form the sodium salt of the phenolic group with the elimination of the phenolic OH band from the spectrum. Therefore, Spectrum M of the untreated asphalt contains the absorption of both phenolic and pyrrolic functionalities, and Spectrum L of the NaOH-treated asphalt reflects absorption of only the pyrrolic functionality. Thus, the shaded area in Spectrum L is used to calculate pyrrolic NH, and the difference between the amount of shaded area in Spectra L and M is used to calculate phenolic OH. Traces of water in the samples (which is not present if the samples are properly prepared and handled) produce an intense interfering doublet band at about 3470 cm^{-1} and 3550 cm^{-1} .

Ketones

The shaded area in Spectrum G in Figure 3 is used to calculate ketone concentration. Because differential spectra are not used for quantification of this functional group, defining the boundaries of the band is difficult, and changes have been made in the procedures initially reported (10). The shaded area is defined by two intersecting boundary lines, the first drawn horizontally from the high-frequency side of the band shoulder at about 1830 cm^{-1} and the second drawn vertically at 1670 cm^{-1} , as shown in Figure 3. The boundary at 1670 cm^{-1} was chosen after careful analysis of many spectra and differential spectra at different levels of ketone content. The area defined by the boundaries must be corrected for nonketone background absorption.

The background absorption can be determined from analysis of the spectrum of an unoxidized, NaOH-treated sample, after correcting for small amounts of ketone artifact that may be present. Often, however, an unoxidized sample is not available. It has been found that the correction ranges from about 5.0 to $8.0 \int A_{\nu} dv$ units (defined later) over the range of less-polar, low-aromaticity asphalts to more-polar, high-aromaticity asphalts, respectively, with $6.5 \int A_{\nu} dv$ units being typical (6.5 units is equivalent to 65 squares on chart paper that is divided into 0.01 absorbance units on the ordinate and 10 wave numbers on the abscissa). Uncertainties in estimating background absorption may sometimes cause a small determinant error in the calculation of ketone concentration.

Sulfoxides

The shaded area of Spectrum B in Figure 2 is used to calculate sulfoxide concentration. Estimation of this area is usually straightforward; however, finely suspended mineral matter, sometimes present in asphalts recovered from asphalt-aggregate mixtures, can produce broad absorption centering at about 1078 cm^{-1} . This absorption can shift the high-frequency shoulder of the sulfoxide band and increase its apparent intensity (6). If contamination is suspected, a solution of the asphalt should be centrifuged to remove the mineral matter.

Calculations and Sample Handling Routine

Calculations

The apparent integrated absorption intensity (B), in units of $\text{L mol}^{-1}\text{cm}^{-2}$, of an infrared absorption band obtained on a spectrophotometer having a nonmonochromatic energy source and finite slit width is defined as follows (17):

$$B = 1/cl \int \ln(T_0/T)_{\nu} dv$$

where

- c = concentration of functional group type (mol L^{-1});
- l = cell path length (cm);
- ν = absorption frequency (cm^{-1});
- T_0 = incident radiation; and
- T = transmitted radiation.

The area under the absorbance versus absorption-frequency curve for the absorption bands of interest is represented by the term $\int \ln(T_0/T)_{\nu} dv$. The term $\ln(T_0/T)$ is equivalent to the commonly used term "absorbance," designated by the notation A .

In the author's work, the band area, $\int A_{\nu} dv$, was estimated by counting squares on the recording chart paper. The concentrations of functional group types in the neat asphalt were then estimated by using the equation

$$c = \int \Delta A_{\nu} dv / B_l \times 1.05/0.05$$

The solutions measured contained 50 mg of asphalt in 1.00 ml of solvent; therefore, assuming the volumes of asphalt and solvent to be additive, the term 1.05/0.05 corrects for sample dilution by the solvent.

Values of B used in the calculations are given in Table 1 and were obtained by averaging values determined for sets of model compounds in THF solutions. Values reported here may differ slightly from those reported earlier because a different

TABLE 1 VALUES OF APPARENT INTEGRATED ABSORPTION INTENSITY (B) USED TO ESTIMATE COMPOUND-TYPE CONCENTRATIONS IN ASPHALT

Functional Type	B, $\text{L mol}^{-1}\text{cm}^{-2}$
Carboxylic acids	10 500
Silyl esters of carboxylic acids	8300
Anhydrides	26 000
Ketones	6000
Sulfoxides	4900
2-Quinolone types	27 000
Phenolics	13 000
Pyrrolics	12 000

spectrophotometer was used (10). When absorption bands of the model compounds were narrow, baseline expansion was used to increase the accuracy of the band area determinations.

Sample Handling Routine

Time and labor efficiency require a carefully planned sequence for handling samples. By using the routine described in the following paragraphs, a complete analysis (not including band area determinations) can be completed in about 1 1/2 hr.

The initial method was developed using 0.250-gm samples processed in 25-ml Erlenmeyer flasks (10). The author is currently processing 0.0500-gm samples in 10-ml Erlenmeyer-shaped reaction flasks. These flasks are equipped with a screw cap top containing a Teflon®-lined silicon rubber disc, which permits accessing the sample flask with a hypodermic syringe to add solvent or withdraw sample. The disc seal also prevents solvent evaporation and exposure of the THF to water vapor in the air. If one intends to conduct the determination, the published procedures and details of reagent preparations should be consulted (10,11). Briefly, the samples are handled as follows.

Four 0.0500-gm samples are weighed into four flasks to which a boiling chip has been added. One flask is capped with the Teflon®-faced disc (Teflon® side toward flask) to which 1.00 ml of CS₂ is added with a hypodermic syringe while venting the flask with an additional hypodermic needle. This sample is used to obtain the spectrum in CS₂. To the remaining three flasks 3 ml of benzene is added, and in addition 0.15 ml of 0.5 N NaOH is added to one of the flasks. The benzene is then boiled off in a hood on a hot plate having a surface temperature of about 145°C.

Immediately after evaporation of the benzene from the two untreated asphalts, vacuum is applied momentarily to the flasks to remove last traces of benzene and the flasks are capped with Teflon®-faced discs. After the condensation of water on the sides of the flask containing the NaOH-treated sample, the water is washed back into the flask with a syringe charged with 1 to 2 ml of benzene and the mixture again boiled down, this time allowing any remaining water to be expelled. To assure complete removal of water from the sample and residual NaOH, an additional 3 ml of benzene is boiled from the sample, and the flask is capped as previously described. By using a hypodermic syringe, exactly 1.00 ml of TPTH reagent in THF is added to one of the untreated samples and 1.00 ml THF is added to the remaining two flasks to yield sample solutions ready for infrared analysis (11).

Four 1.00-mm sodium-chloride-sealed cells for use in the analysis of the samples in THF and two additional cells for analysis of the samples in CS₂ are recommended. Separate cells are recommended for the CS₂ spectra (one for the sample and one for solvent compensation) because cells used with the THF solutions gradually become contaminated and must be cleaned when interference becomes significant in the 1500-cm⁻¹ to 1900-cm⁻¹ region. (Successive treatment of the cell with glacial acetic acid followed by pyridine often provides effective cleaning.) A variable path-length cell is used in the reference beam for THF compensation when needed.

All spectra shown in Figure 3 should be run consecutively in the same cell to allow spectra comparisons without minor baseline shifts caused by variations in cell transmittancy or minor differences in peak heights caused by variations in cell thickness. Remaining solutions of each sample are used to fill an additional cell to be used for differential spectra. The remaining portion of the untreated sample, not used to fill the cells, is transferred to a small, capped vial and silylated (10). The differential spectra needed, as shown in Figure 4, are then determined.

SELECTED APPLICATIONS OF THE METHOD

The potential applications of the functional group analysis in composition-related asphalt technology are numerous and the technique is used extensively in the author's laboratory. A few examples of its application have been selected to demonstrate its utility.

Kinetics and Chemistry of the Cure of Metal-Complex-Modified Asphalt

A modified asphalt paving composition marketed under the name Chemkrete is being evaluated and used by a number of transportation agencies. The modification consists of pretreatment of the asphalt with a metal complex, preferably of manganese, which induces a rapid reaction of the asphalt with atmospheric oxygen after mixture preparation. After rapid cure in the field, the mixture exhibits increased compressive strength. Functional group analyses were used in an investigation of the metal-induced reaction (18). Results indicated that the reaction during the Chemkrete cure produced the same oxidation products (ketones and anhydrides) that are formed during normal oxidative aging and that the metal complex acted as a catalyst to increase the rate of reaction with atmospheric oxygen.

The kinetics of the curing reaction were studied and evidence was presented that the manganese catalyst was inactivated after completion of the curing period (18). More recent chemical studies of the curing reaction have confirmed the manganese inactivation and have elucidated the chemical mechanism of the inactivation. Summary details are shown in Figure 5. These data demonstrate the application of the functional group analysis. Complete details of the study will be published elsewhere. In this work, the asphalt was cured as a thin film of asphalt in Ottawa sand briquets in a 45°C air oven. Void space in the briquets was 30 to 40 percent, which allowed ready access of oxygen.

As can be observed in Figure 5, during the first 24 hr of the curing period, the major reaction product formed was ketones from the air oxidation of hydrocarbon components of asphalt molecules. No measurable changes in the concentrations of anhydrides and free or complexed acids were observed. The active form of manganese used in the asphalt modification is a complex of the manganese ion with high molecular weight carboxylic acids. The TPTH reagent used in the functional

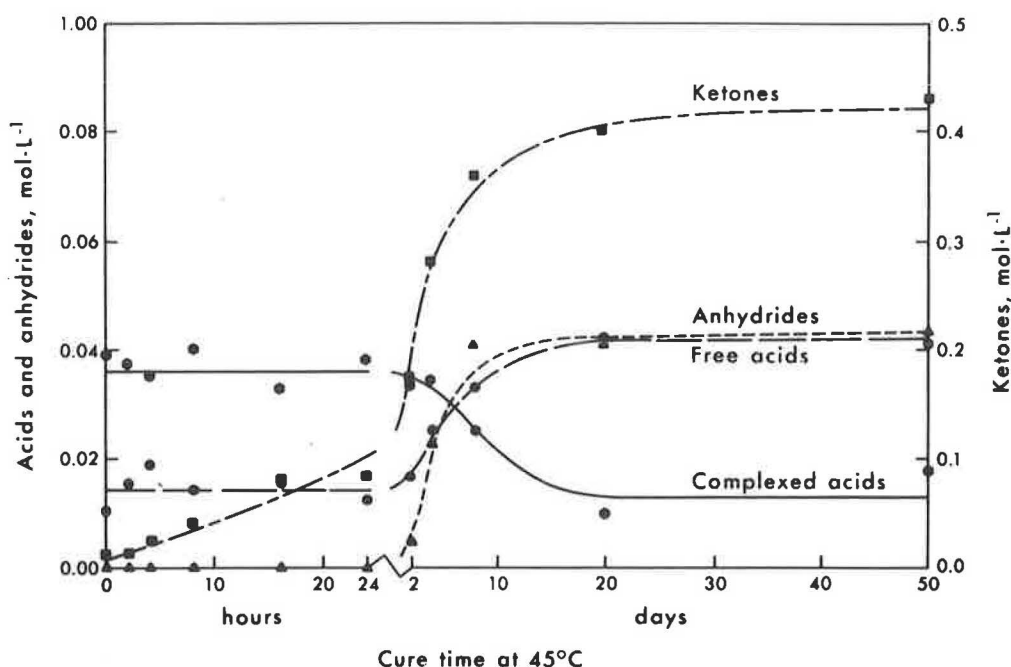


FIGURE 5 Changes in chemical functionality during cure of metal complex-modified asphalt.

group analysis was able to differentiate between the complexed acid and excess free acid present, thus providing a measure of the amount of active manganese present.

By the end of 2 days of cure, significant changes were observed in all the functionalities being monitored. Anhydrides, the formation of which is always preceded by a induction period, were beginning to form at a ketone content of between 0.3 and 0.4 mol L⁻¹. With the formation of anhydrides there was a simultaneous decrease in the manganese-complexed acids together with a corresponding increase in free acids.

Based on additional evidence, too comprehensive to present here, liberation of free acids from their manganese complex results from complexation of the manganese with a stereospecific diketone. This diketone is formed simultaneously with the stereospecific anhydrides (previously described) from the oxidation of asphalt molecules having alkyl substituents in the 1,8-bridgehead position of a naphthalene ring component of the molecules (5). The key intermediate, based on earlier evidence obtained in the author's laboratory, is believed to be a 1,8-ketone hydroperoxide, which decomposes on a statistical basis to form either the anhydride or the stereospecific 1,8-diketone. The diketone then forms a strong complex with manganese, freeing its complexed acids and destroying its catalytic activity as an oxidation catalyst in asphalt.

After 20 days (Figure 5) the catalytic reaction was complete and all the manganese was inactivated, as evidenced by the abrupt cessation of ketone and anhydride formation. Based on the loss of one carboxylic acid molecule from one manganese upon the formation of the diketone complex, the amount of acids found liberated exactly equaled the amount of manganese known to be present. Approximately one mole of acid per mole of manganese still remained complexed with the manganese following its inactivation.

The author has proposed that upon complex formation between the manganese and the first stereospecific diketone, the complex with the remaining acid is occluded within an agglomerate or micelle of polar asphalt molecules. The functional group analysis technique not only made it possible to follow the chemistry of the metal-induced curing reaction as changes in physical properties were followed, but also provided additional confirmation of the mechanism of anhydride formation in asphalt.

Carboxylic Acid Salts as a Contributor to Pavement Moisture Damage

Several years ago a state transportation agency experienced a sudden onset of moisture damage in a newly constructed pavement. The granite aggregate used had produced pavements that had performed satisfactorily in the past. The asphalt used in the troubled mix was examined by functional group analysis together with an asphalt that had performed satisfactorily with the granite aggregate. Results are given in Table 2.

A high concentration of carboxylic acid salts, indicative of caustic treatment during processing of crude stock with a high acid content, was found in the asphalt that produced the moisture-sensitive pavement. Caustic treatment of the crude during processing was found to be the case. Fundamental studies of the asphalt aggregate interaction by using the functional group analysis together with additional model compound studies have indicated that carboxylic acid salts are concentrated and strongly adsorbed at the asphalt-aggregate interface, but are also easily displaced from certain aggregate types by water (20). Thus, a strong indication of the cause of the moisture damage problem in the pavement in question was rapidly identified by using the functional group analysis.

TABLE 2 FUNCTIONAL GROUP ANALYSIS OF ACID FUNCTIONALITY OF ASPHALT FROM MOISTURE-SENSITIVE AND SATISFACTORY PAVEMENTS

Asphalt source	Carboxylic acids (mol L ⁻¹)		
	Free	Salts	Total
Moisture sensitive pavement	0.013	0.082	0.095
Satisfactory pavement	0.017	None	0.017

Fundamental Studies of the Chemistry of the Asphalt-Aggregate Interaction

By using the analysis technique described in this paper together with techniques for isolating the chemical functional groups that form the bond between asphalt molecules and mineral aggregate surfaces, those chemical functional groups that form the asphalt-aggregate bond have been identified (19). In addition, their relative tendency to be concentrated at the aggregate surface and their relative tendency to be displaced by water have also been quantitatively assessed (12,19,20). An example of some of the data obtained in one of the studies referenced is given in Table 3 (12). These data are averages for a number of different asphalt-aggregate systems in which the relative concentrations of the various functional groups were found to vary considerably from one system to another. However, the data are indicative of general behavior.

All of the different types of polar functionality present were

found to be concentrated at the asphalt-aggregate interface, with carboxylic acids and anhydrides being concentrated 30- and 14-fold, respectively. Many of the strongly adsorbed functionalities concentrated at the aggregate surfaces were also selectively displaced by water. Correlation of these results with the performance of corresponding asphalt-aggregate mixtures in actual pavements and in laboratory moisture damage testing provided a rational explanation for the sensitivity of the pavement mixtures to moisture-induced damage (12).

Analysis of Fractions from Corbett-Type Separation

As the final example of the application of the functional group analysis, the determination of the chemical functionality of fractions from a Corbett-type separation (ASTM Method D-4124) is given in Table 4.

TABLE 3 RELATIVE TENDENCY OF CHEMICAL FUNCTIONALITY IN ASPHALTS TO BE CONCENTRATED AT THE AGGREGATE SURFACE AND TO BE DISPLACED BY WATER

Functional group type	Average	Average water
	concentration ratio ^a	displacement ratio ^b
Ketone	1.2	0.65
Carboxylic acid	30	2.1
Anhydride	14	3.5
2-Quinolone	5.4	3.1
Sulfoxide	2.6	2.5
Pyrrolic	0.27	low
Phenolic	4.1	low

^aConcentration at asphalt-aggregate interface divided by concentration in bulk asphalt

^bConcentration in water-displaced fraction divided by concentration at asphalt-aggregate interface

TABLE 4 DISTRIBUTION OF FUNCTIONAL GROUPS IN FRACTIONS FROM CORBETT-TYPE SEPARATION

	Concentration in fraction (mol L ⁻¹)				
	Whole		Naphthene		Polar
	asphalt	Saturates	aromatics	aromatics	Asphaltenes
Ketones	0	0	0	0.11	Trace
Carboxylic acids	0.027	0	0	0	0.034
Anhydrides	0	0	0	Trace	Trace
2-Quinolone types	0.021	0	0	0.023	0.046
Sulfoxides	0.019	0	Trace	0.12	0.09
Pyrrololics	0.17	0	0	0.21	0.23
Phenolics	0.035	0	0	0.055	0.075

Note: Yield of fractions, based on whole asphalt were: saturates, 9.9%; naphthene aromatics, 25.3%; polar aromatics, 38.1%; asphaltenes, 21.6%; loss (which should be added to polar aromatics), 5.1%.

Virtually no oxygenated polar functional groups were found in the saturates or naphthene aromatics fractions. This was not unexpected because asphalt molecules containing polar, heteroatom-containing functionality would not be expected to be displaced from the alumina chromatographic adsorbent with the solvents (heptane and benzene) used. A concentration of 0.11 mol L⁻¹ ketones was found in the polar aromatics fraction. Because virtually no ketones were present in the whole asphalt, and only a trace of ketones was found in the reactive asphaltenes, the ketones found in the polar aromatics were probably formed as artifacts by adsorbent-promoted oxidation of this fraction during separation. The absence of carboxylic acids in the polar aromatics fraction was at first surprising because the whole asphalt contained significant acids, and significant amounts of acids were found concentrated in the asphaltenes that were precipitated from the asphalt before the chromatographic separation. However, functional group accountability indicated that only 28 percent of the carboxylic acids present could be accounted for in the asphaltene fraction. It is apparent that most of the carboxylic acids present in the original asphalt were lost during analysis by irreversible adsorption on the alumina column during fractionation. This adsorption probably accounts for most of the weight loss during fractionation, as noted at the bottom of Table 4.

The 2-quinolone types in the whole asphalt were accounted for by the combined amounts found in the polar aromatic and asphaltene fractions. In the analysis of other asphalts not reported here that were low in acids, some 2-quinolone types were irreversibly adsorbed on the alumina, suggesting competitive adsorption between carboxylic acids and 2-quinolones, with the acids being most strongly adsorbed. The combined sulfoxides found in the asphaltenes and polar aromatics exceeded the concentration found in the initial asphalt, again suggesting the formation of oxidation artifacts that are pro-

duced on the chromatographic column. Sulfoxides are the most easily formed oxidation product in asphalt (6). Their formation during separation is supported by the fact that they occur in higher concentration in the polar aromatic fraction than in the asphaltene fraction, the latter never having had contact with the adsorbent. Finally, within the limits of accuracy and precision of the determinations, the pyrrololics and phenolics present in the whole asphalt were accounted for in the combined polar aromatic and asphaltene fractions.

SUMMARY

The combined use of differential infrared spectrometry and selective chemical reactions provided the basis for the development of an analytical method for the quantitative analysis of important chemical functionality naturally present in asphalt or formed in asphalt on oxidative aging. The method can be applied to the solution of a variety of composition-related problems in asphalt technology.

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