Evaluation of Oven Simulation of Hot-Mix Aging by an FT-IR Pellet Procedure and Other Methods

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The long-established KBr pellet technique for IR analysis has been adapted for analyzing asphaltic materials. The procedure is highly reproducible and produces spectra that can be compared, with no normalization or other correction beyond normal background subtraction and baseline zeroing. Analysis of oven-aged and hot-mix asphalt samples by FT-IR, viscosity, penetration, and gel permeation chromatography provides comparisons for studies of asphalt aging. In a limited study, viscosity and penetration values for the hot-mix and for thin-film and rolling thin-film, oven-aged residues agreed quite well. However, the GPC and FT-IR analyses showed some significant differences.

A crucial element in understanding asphalt properties and performance lies in understanding the aging of asphalt materials. It is not enough to know the properties of the asphalt as it exists in the tank prior to being mixed with the aggregate for pavement, or even to know the hot-mix properties at the time the pavement is placed. Rather, the ultimate objective is to understand enough about asphaltic materials in order to understand the way their initial properties change over a period of time and the way these changes affect performance. Some asphalts age differently from others, more rapidly and in different ways; and a given asphalt may itself age differently with various aggregate materials or in different climatic environments.

Standard oven tests, the thin-film oven test (TFOT) and the rolling thin-film oven test (RTFOT), which are both ASTM standardized procedures, are commonly used to evaluate the relative aging of different asphalts. These tests have been designed to approximate the aging that occurs during the hot-mix aging process; they are based primarily on changes in asphalt viscosity due to the aging. The assumption implicit in the development of these tests is that if viscosity values are matched, then other properties are also matched and, in fact, the asphalt aging process has been duplicated.

It has been one of the objectives of this study to evaluate asphalt aging in these two oven tests and to compare them with the drum hot-mix process, not only with respect to viscosity and penetration but also with respect to measures of chemical composition, such as gel permeation chromatography and FT-IR. If this broader group of measurements is duplicated by the oven test, then the likelihood that these oven tests do in fact faithfully reproduce the hot-mix process is increased dramatically. Because the changes produced by aging in the asphalt FT-IR spectrum are relatively small, a significant portion of this effort has been directed at establishing a sensitive and highly reproducible FT-IR procedure that requires a minimum of normalization and background subtraction. This paper reports this FT-IR procedure and preliminary studies addressed at assessing differences between hot-mix and oven aging.

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FT-IR ANALYSIS OF ASPHALTS

Infrared analysis of asphalt continues to challenge asphalt chemists because of the complex nature and adhesive properties of asphalt that make sample preparation difficult. In general, the infrared spectra of substances are fairly easily determined if the sample is a gas, a liquid, or a solid. In this case, however, the asphalt sample is a material that is soft and sticky at room temperature and causes some problems in the course of sample preparation for infrared analysis.

Most researchers (*1–9*) have determined the spectra of asphalt samples in solution. This method uses solvent to dissolve asphalt; then the obtained solution is analyzed by IR. Because all solvents absorb strongly in at least several regions of the infrared spectrum, it is necessary to use more than one solvent to be able to get a complete spectrum of the asphalt sample. The most commonly used solvents in the solution method are carbon tetrachloride (CCl_4) and carbon disulfide (CS_2).

Unfortunately, this method has several problems. One difficulty that may arise is weak absorption bands in the asphalt sample that cause a low signal-to-noise ratio of the asphalt spectrum to remain after subtracting the solvent background. Increasing the asphalt absorption to improve this ratio can be achieved either by increasing its concentration in solution or by increasing the cell pathlength. Increasing the concentration, however, is limited by the necessity for a homogeneous solution and by the possible effects of the solute on the solvent spectrum (*10–12*). Increasing the pathlength is limited by the necessity of keeping the solvent absorption within the range of Beer's law in order to achieve quantitative solvent subtraction. Solvents such as carbon tetrachloride and carbon disulfide have some very strong absorption bands that reach detector saturation in very thin cells. Hence, multiple analyses with different solvents that have strong absorption bands at different frequencies are necessary to obtain a complete pic-

ture of the asphalt spectrum. There are also certain practical problems, such as deterioration of cell windows, caused by adsorbed water or solvent and difficulty in completely removing asphalt from the cell (*10–15*).

In this paper, the long-established KBr pellet procedure is adapted to asphalt analysis and the reproducibility of infrared absorption spectra for this method is shown.

EXPERIMENTAL METHODOLOGY

Asphalts, before and after aging, were evaluated using both physical and chemical properties. Physical properties measured were viscosity, at both 60 and 135°C (ASTM D2171-83), and penetration at 77°F (ASTM D5-83). These measurements are well known and widely used and provided the basis for the original development of the thin-film and rolling thin-film oven tests. Chemical characterization was performed by both GPC and FT-IR analyses. The GPC technique used is the method developed and reported previously (*16,17*). Analyses were made using a 500 Å and 50 Å column combination. Injections were 100 μl of a 7 weight percent solution in THF. The FT-IR analysis procedure is the KBr pellet procedure and is reported below. This procedure was chosen because of its quantitative nature, which allows direct comparisons between asphalts—in this case, comparisons between the unaged and aged samples without normalizations. Because both the GPC and FT-IR techniques have excellent reproducibilities, the authors are able to make these comparisons directly, allowing definitive conclusions about the changes that occur in these asphalts.

The scope of this study was quite limited in terms of the asphalt samples that were evaluated. Only two asphalts were studied from two different refiners: one, an Exxon AC-20 and the other, a Coastal AC-20. Both asphalts were placed in highways near College Station during the summer of 1987. At that time both tank asphalt and hot-mix samples, for which analyses are reported in this paper, were obtained. This study is ongoing; cores to be taken this year and in the future will provide data for in-service aging. The hot-mix process used in both cases is the drum process.

FT-IR EXPERIMENTAL APPARATUS AND PROCEDURES

Materials and Apparatus

The instrument used in this study for IR analyses was a Nicolet 60SX FT-IR single beam spectrometer. Potassium bromide was IR grade obtained from Fisher Scientific.

Pellet Preparation

Dry KBr powder was prepared for each batch of pellets. The KBr was oven-dried for 2 hr or more at 300°C to complete dryness, as verified by the absence of water IR absorption bands near 3,710 and 1,630 cm^{-1} in a pure KBr pellet. The dry KBr powder was stored in a desiccator until use.

Asphalt samples to be analyzed were collected and stored in a freezer (-20°C) for at least 2 hr before use. This cold storage was necessary to obtain a grindable and otherwise workable asphalt material that could be mixed with KBr powder to make pellets for IR analyses. Each asphalt sample was stored in its own closed container to avoid collecting moisture. Although water absorption by KBr is often mentioned as a difficulty with this technique (*10–14*), it was effectively controlled in this work, as by others (*18*), by proper sample preparation and background subtraction.

The asphalt-KBr mixture was prepared by accurately weighing the KBr and asphalt onto a sheet of aluminum foil. Dry KBr powder (0.975 g) and 0.025 g of asphalt were weighed to obtain a total mixture of 1.000 g. All amounts were adjusted to within 0.2 mg of the desired weight and weighed to a precision of 0.1 mg. The asphalt was weighed as quickly as possible to keep it at a low temperature, thereby maintaining its workability. The mixture was quantitatively transferred to a mortar and ground with a pestle for between 20 and 30 min to obtain a homogeneous mixture.

The amount of this asphalt-KBr mixture needed for one pellet was accurately weighed and placed between two highly polished, stainless steel dies inside a pellet press, where it was compressed at 25,000 psi for 1 min to make a small pellet approximately 0.5 in. in diameter. Prepared pellets were stored in a desiccator to prevent the KBr from absorbing moisture. A pellet of the same mass using pure KBr was similarly prepared for obtaining background comparisons.

Analyses were made of both the blank and asphalt-KBr pellets. Prior to analysis, the instrument sample compartment was purged with nitrogen for at least 20 min. Subtraction of the blank KBr pellet spectrum from the asphalt-KBr spectrum corrected for any moisture that might have been absorbed by the KBr. All baselines were adjusted to have zero absorption at 600, 1,800, and 4,000 cm^{-1}.

Spectra Reproducibility

Figure 1 is an overlay of three spectra for the entire IR region obtained for a Coastal AC-20 asphalt. The high degree of

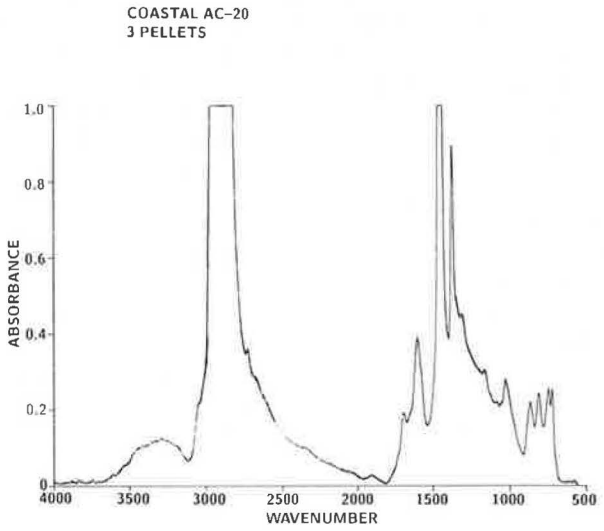

FIGURE 1 Reproducibility of three asphalt FT-IR analyses over the range from 600 to 4,000 cm^{-1} using 300-mg pellets.

reproducibility obtained for these three pellets is shown in increasingly more detail for the 600- to 1,800-cm^{-1} region in Figure 2, and for the carbonyl region in Figure 3. In Figure 1 the small spectra differences in the region between about 3,600 cm^{-1} and 3,200 cm^{-1} may be attributed to the instrument's small signal-to-noise ratio and lack of complete removal of moisture by the nitrogen purge. The carbonyl (1,675 to 1,750 cm^{-1}) and sulfoxide (950 to 1,050 cm^{-1}) regions, which are of particular importance to asphalt aging, show excellent reproducibility.

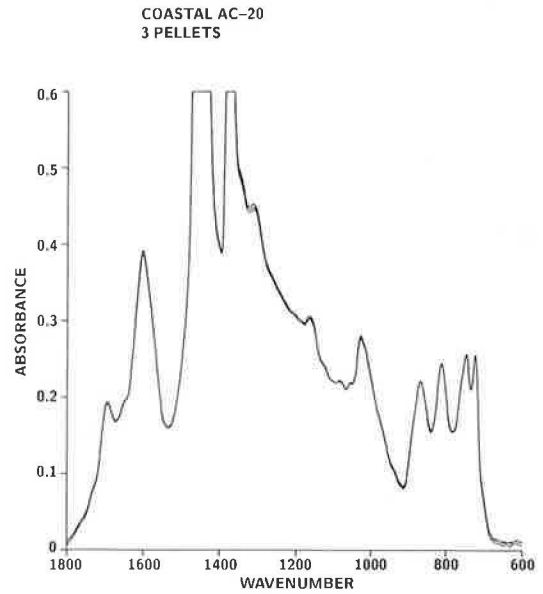

FIGURE 2 Reproducibility of three asphalt FT-IR analyses over the range from 600 to 1,800 cm^{-1} using 300-mg pellets.

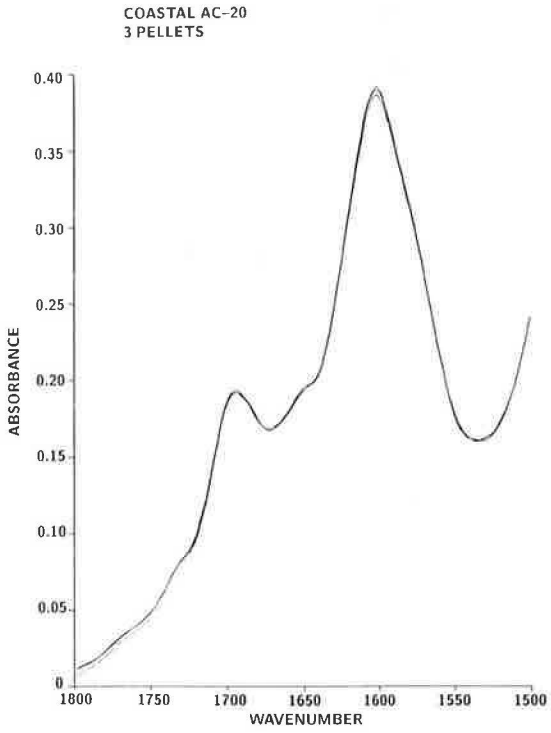

FIGURE 3 Reproducibility of three asphalt FT-IR analyses over the range from 1,500 to 1,800 cm^{-1} using 300-mg pellets.

Pellet Thickness

The lack of IR absorption of potassium bromide allows a wide range of pellet thickness, thereby providing a convenient means of adjusting the level of sample absorption. Weak absorption bands can be increased to good signal-to-noise ratios by using thick pellets; strong absorption bands can be kept within Beer's law by using thin pellets. By contrast, adjustments to the asphalt concentration in the KBr mixture are limited. Too low a concentration jeopardizes homogeneity; too high a concentration produces an unworkable mixture. The concentration of 2.5 weight percent used in this study was chosen to optimize workability.

RESULTS AND DISCUSSION

Figures 4 through 7 contain the viscosity, penetration, GPC, and IR analyses for both asphalts for the thin-film oven test. Viscosities at 60 and 135°C are shown in Figure 4 for the tank asphalts (0 time), for 5 hr of aging (the standard oven time), and for 14 ½ hr, an extended period to observe larger changes in the asphalt. For measurements at both 60 and 135°C, significant increases in viscosity with the amount of aging time were observed, as expected. During the test period, the Coastal asphalt underwent considerably more aging than the Exxon, at least according to the thin-film oven test at 60°C. Both asphalts began as AC-20 grade asphalts with viscosity near 2,000 poise. By the standard oven time, however, the Coastal asphalt viscosity increased to more than 6,000, whereas the Exxon was around 4,000. After aging for 14 hr, the divergence is even more evident, with the Coastal asphalt at 24,000 but the Exxon at only about 10,000. This divergence is not exhibited at 135°C, however, indicating that the Coastal aged asphalt has a larger viscosity temperature susceptibility than does the Exxon. Concerning the extracted hot-mixes for these two asphalts, the viscosities at both 60 and 135°C match very well the standard thin-film oven test viscosity. Penetrations for both the Coastal and Exxon un-aged and aged asphalts are shown in Figure 5. Penetrations for the asphalt extracted from hot-mix samples are also shown. In this case, both asphalts compare very well with respect to penetration, in spite of their differences in viscosity. Hot-mix penetration values, especially for the Coastal, do not agree with TFOT values as well as they do for the viscosities, however.

GPC profiles for the two asphalts are shown in Figure 6. The profile for the tank asphalt is shown, as well as profiles for two aging times in the thin-film oven test. Finally, the hot-mix profile also is overlaid for comparison. There are clear differences in each of the curves, with the 14 1/2-hr aged sample showing a significant growth in the large molecular size (LMS) region (material eluted between 20 and 25 min) for both asphalts. The standard time samples also show growth in the LMS region but not nearly so much as the extended time. Profiles for the asphalt extracted from the hot-mix for both asphalts show a larger LMS than for the standard time, especially for the Coastal asphalt. In fact, in this case the hot-

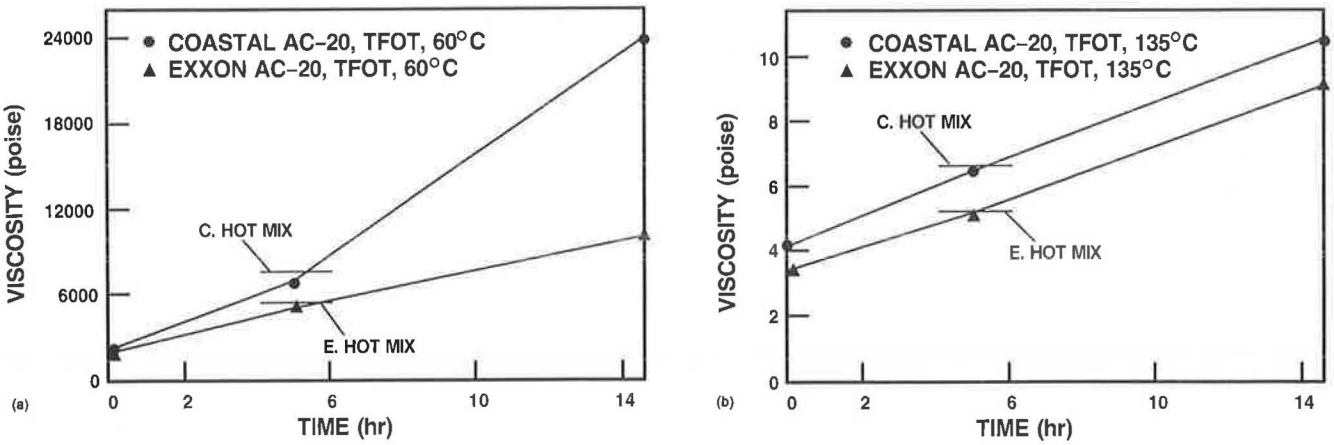

FIGURE 4 Effect of TFOT aging on two asphalts' viscosities at (a) 140°F (60°C) and (b) 275°F (135°C).

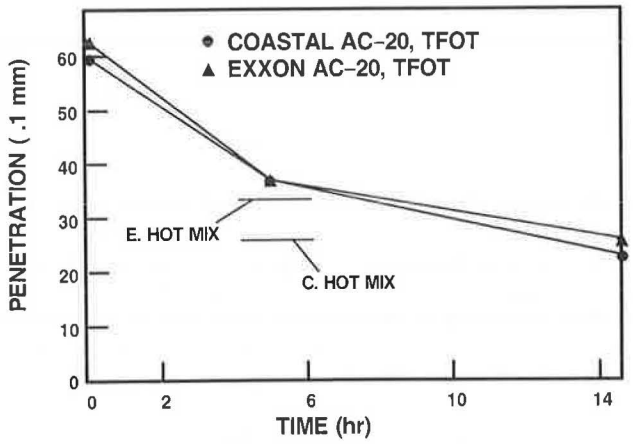

FIGURE 5 Effect of TFOT aging on two asphalts' penetrations at 77°F.

mix asphalt compares more favorably with the 14 1/2-hr oven-aged sample than it does with the standard time sample. For the Exxon asphalt, however, the hot-mix asphalt and the standard oven-aged asphalt are in much better agreement.

Figure 7 contains similar comparisons for FT-IR analyses. Compared with the GPC profiles, an interesting reversal of the asphalts' behavior for the carbonyl region of the spectra (Figures 7a and 7b) is evident. Again, dramatic differences between the tank asphalt and the 14 1/2-hr oven-aged asphalt are apparent, with the standard time and the hot-mix asphalt spectra lying in between. For this analysis, however, the Coastal hot-mix agrees much better with the standard 5-hr oven test than does the Exxon, in contrast to the comparison of the two asphalts for the GPC analysis. Similar results were observed for the sulfoxide region shown in Figures 7c and 7d. Similar studies with a broader range of asphalts will be necessary to show the extent to which this observation is important.

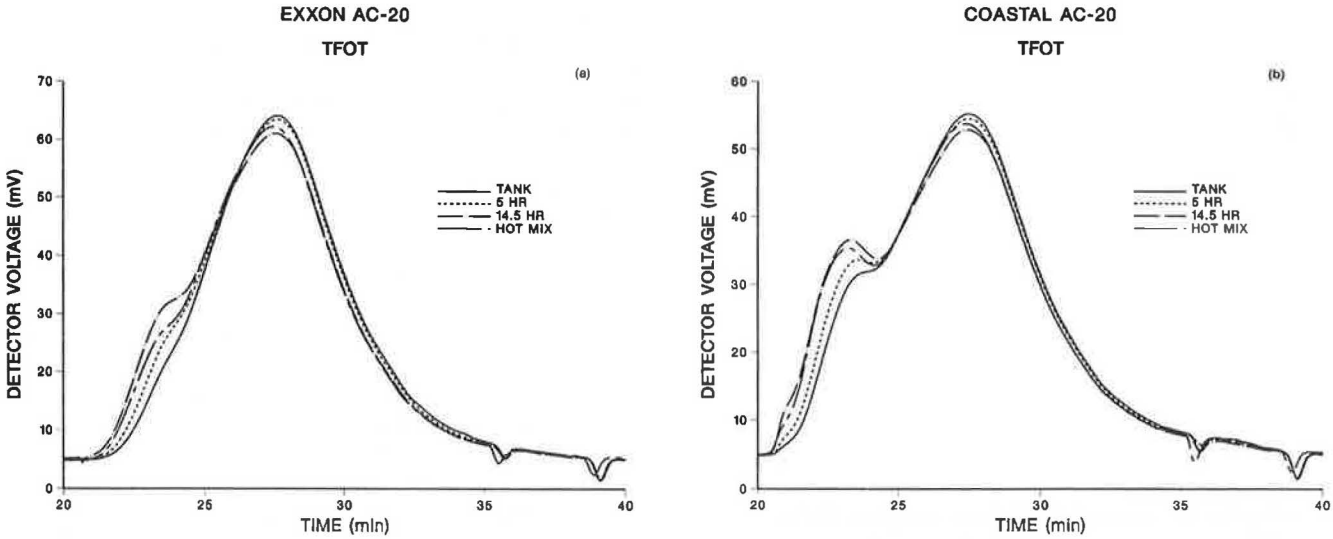

FIGURE 6 Effect of TFOT aging on GPC chromatograms for (a) Exxon AC-20 and (b) coastal AC-20 asphalt samples.

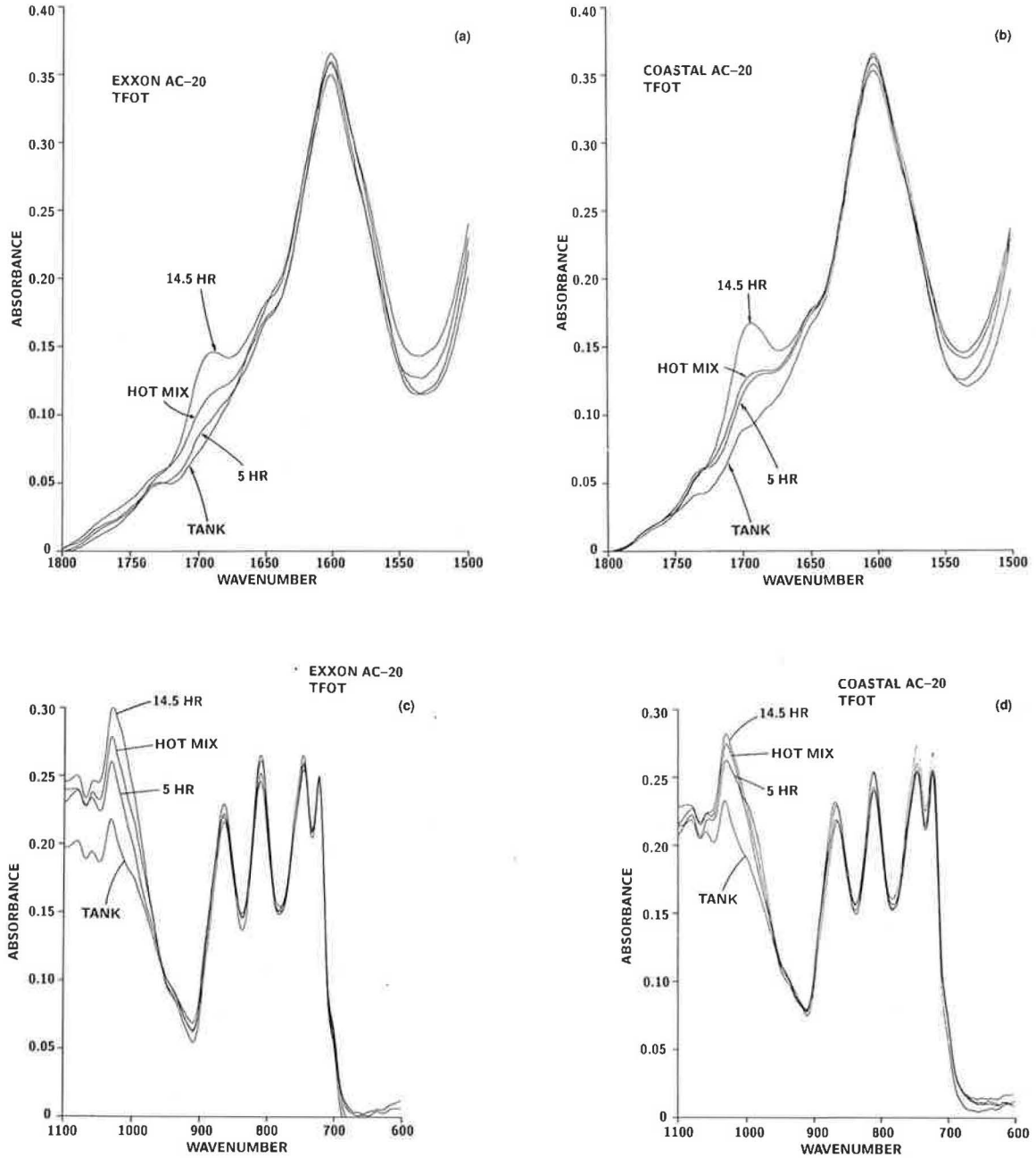

FIGURE 7 Effect of TFOT aging on FT-IR spectra for (a) Exxon AC-20 carbonyl region, (b) coastal AC-20 carbonyl region, (c) Exxon AC-20 sulfoxide region, and (d) coastal AC-20 sulfoxide region.

Results for the RTFOT are essentially identical to those for the TFOT by both physical and chemical measures.

CONCLUSIONS

The KBr analysis procedure produces spectra that can be compared directly, with no normalization or other correction beyond normal background subtraction or baseline zeroing. Very accurate reproducibility is possible using the pellet technique because of the weighing precision and the minimal background compensation of the KBr. Handling the asphalt quantitatively is made possible by freezing. The lack of IR absorption by potassium bromide also allows a wide range of pellet thickness, thereby providing a convenient means of adjusting the level of sample absorption. Weak absorption bands can be increased to good signal-to-noise ratios by using thick pellets; strong absorption bands can be kept within Beer's law by using thin pellets.

The work on asphalt aging has been a limited study comparing rolling thin-film oven test to hot-mix aging. As such it has involved only two asphalts, both AC-20 grades, and one hot-mix sample for each one. Consequently, conclusions are limited by the small sampling.

Within the bounds of these restrictions, however, certain conclusions appear appropriate. First, the thin-film and rolling thin-film oven tests appear to produce the same aging results measured not only with respect to viscosity and pen-

etration but also with respect to gel permeation chromatography and FT-IR. The extent of aging and the manner in which aging occurs appear to be identical in the two oven tests. Second, with respect to the viscosity tests, it is concluded that both oven tests are very good predictors of hot-mix aging. With respect to penetration, they appear to be moderately good predictors. Third, and in contrast with the viscosity measurements, the oven tests underpredict hot-mix aging with respect to both GPC and FT-IR analyses for both asphalts. The apparent extent of additional aging in the hot-mix, however, depended on the asphalt and the analysis being used in the evaluation. Furthermore, GPC and IR analyses did not agree on which asphalt aged more in the hot-mix.

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