Report No. BDV25-977-20

Final Report

Field Test Method to Determine Presence and Quantity of Modifiers in Liquid Asphalt – Followup Data Analysis

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August 2015

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Approximate Conversions to SI Units							
Symbol	When You Know	Multiply By	To Find	Symbol			
Symbol	When rou know	Length	TOTING	Symbol			
in	inches	25.4	millimeters	mm			
ft	feet	0.305	meters	mm m			
yd	vards	0.303	meters	m			
mi	miles	1.61	kilometers	km			
	mics	Area	Niemeters	NIII			
in²	square inches	645.2	square millimeters	mm ²			
ft ²	square feet	0.093	square meters	m ²			
yd ²	square vard	0.836	square meters	m²			
ac	acres	0.405	hectares	ha			
mi ²	square miles	2.59	square kilometers	km ²			
		Volume		NII			
fl oz	fluid ounces	29.57	milliliters	mL			
	gallons	3.785	liters	1			
gal ft ³	cubic feet	0.028	cubic meters	m ³			
yd ³	cubic yards	0.765	cubic meters	m ³			
yu		mes greater than 1000 L s	hall be show n in m^3				
		Mass					
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T	short tons (2000 lb)	0.434	megagrams (or "metric ton")	Mg (or "t")			
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·F	Fahrenheit	5 (F-32)/9	Celsius	C°			
		or (F-32)/1.8					
		Illumination					
fc	foot-candles	10.76	lux	lx			
fl	foot-Lamberts	3.426	candela/m ²	cd/m ²			
		Force and Pressure or	Stress				
lbf	poundforce	4.45	new tons	Ν			
				1.5			
lbf/in ²	poundforce per square inch	6.89	kilopascals	kPa			
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SI (MODERN METRIC) CONVERSION FACTORS

* SI is the symbol for the International System of Units. Appropriate rounding should be made to comply with Section 4 of ASTM E380. (Revised March 2003)

TECHNICAL REPORT DOCUMENTATION PAGE

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7. Author(s) Qing Lu and Lukai Guo			8. Performing Organization Report No.			
9. Performing Organization Name and Address Department of Civil and Environme	ental Engineering		10. Work Unit No. (TRAIS)			
College of Engineering University of South Florida, Tampa	a, FL 33620	11. Contract or Grant No. BDV25-977-20				
 ^{12.} Sponsoring Agency Name and Address Florida Department of Transportation 605 Suwannee Street, MS 30, Tallahassee, FL 32399 		13. Type of Report and Period Covered Final Report				
			June 2015 – August 2015 14. Sponsoring Agency Code			
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EXECUTIVE SUMMARY

Under the contract grant number BDV25-977-06, a research project was conducted to identify and evaluate a practical tool to perform field testing of modified binders and/or mixtures for styrene-butadiene-styrene (SBS) or ground tire rubber (GTR) modifier detection and/or quantification. After the completion of the project, an additional test tool, Agilent Handheld ExoScan 4300 FTIR Spectrometer, was identified and so required evaluation and comparison with results from the completed project.

In this study, the Agilent Handheld ExoScan 4300 FTIR Spectrometer was evaluated in a way similar to that for the other portable FTIR devices included in the completed project, and its results were compared with those from the other FTIR devices.

It was found that the Agilent Handheld ExoScan 4300 FTIR Spectrometer can capture absorbance spectra similar to those from other portable FTIR devices and can read absorbance spectrum from asphalt mixture samples. The variability in test data of the Agilent Handheld ExoScan 4300 FTIR Spectrometer, however, is higher than that of the TruDefender FTX FTIR spectrometer.

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CHAPTER 1 INTRODUCTION

Under the contract grant number BDV25-977-06, the University of South Florida (USF) completed a research project for the Department of Florida Transportation (FDOT) to identify and evaluate a practical tool and/or test one currently available or one that can easily be developed to perform field testing of modified binders and/or mixtures for modifier detection and/or quantification.

After a comprehensive literature review and a nationwide questionnaire survey, the Fourier transform infrared spectrometer (FTIR) test was determined to be the one most worthy of further evaluation and development from a practical point of view. A laboratory study was then conducted to investigate the effectiveness of portable FTIR devices to identify and quantify styrene butadiene styrene (SBS) polymer or ground tire rubber (GTR) modifiers in asphalt binders. Three different brands of portable FTIR devices available on the market were identified, including

- TruDefender FTX handheld FTIR analyzer from Thermo Scientific,
- Alpha FTIR spectrometer from Bruker Corporation, and
- Handheld ExoScan Series (4100, 4200, 4300) FTIR spectrometer from Agilent Technologies.

However, only the first two were included in the study. The Agilent ExoScan Series FTIR spectrometer was not included due to the inability of the investigators to acquire one during the project (Lu et al., 2015).

After the completion of the project, Agilent Technologies offered a full demonstration of their Handheld 4300 FTIR Spectrometer to FDOT on June 11, 2015. To fully evaluate the recommended types of portable / handheld FTIR spectrometers from BDV25-977-06, the data from the FDOT demonstration were acquired, analyzed, and compared with the other two sets of data.

This report summarizes the analysis results of the data acquired from the demonstration of the Agilent Handheld 4300 FTIR Spectrometer. Specifically, it compares the absorbance spectra from the three portable FTIR spectrometers, and evaluates the precision and reliability of the Agilent 4300 Handheld FTIR Spectrometer for detecting and quantifying SBS and GTR modifiers in asphalt binders and mixtures.

CHAPTER 2 TEST SAMPLES AND PROCEDURES

2.1 Test Samples

The same set of samples included in the BDV25-977-06 study were supplied by the investigators and used during the Agilent Handheld 4300 FTIR Spectrometer demonstration. Specifically, the samples include two sets of SBS modified binder samples and two sets of GTR modified binder samples:

- 1) First set of SBS binder samples with SBS contents of 0, 1, 3, 5, 7, 9, and 10 percent (by mass of binder), were prepared by USF using a PG 67-22 base asphalt and a 10 percent SBS binder, both from Mariani Asphalt;
- 2) Second set of SBS binder samples with SBS contents of 0, 1, 2, 3, 4, 5, and 10 percent (by mass of binder), were prepared by Ergon Asphalt and Emulsions;
- 3) First set of GTR binder samples with GTR contents of 0, 5, 10, 15, and 20 percent (by mass of binder), were prepared by USF using a PG 52-28 base asphalt and MicroDyne 400-TR (40 mesh) from Lehigh Technologies Inc.;
- 4) Second set of GTR binder samples with GTR contents of 0, 5, 10, 15, and 20 percent (by mass of binder), were prepared by USF using a PG 52-28 base asphalt and Microgrind GTR (40 mesh) from Global Tire Recycling.

Details of the original sample preparation can be found in the BDV25-977-06 report (Lu et al., 2015). For this demonstration use, the residual samples from the previous study were reheated until fluid at 350°F and poured into small tin cans for transportation and testing.

2.2 Test Procedures

The FTIR test using the Agilent Handheld 4300 FTIR Spectrometer was conducted by an Agilent technician at the FDOT State Materials Office. The test procedures were simple. Unlike TruDefender FTX handheld FTIR analyzer or Alpha FTIR spectrometer, the Agilent Handheld 4300 FTIR Spectrometer did not use an anvil to press test samples against the crystal. Instead, the technician just used his fingers to gently press a small sample onto the crystal. This simple step made the testing process significantly quicker than the other two portable FTIR devices. Similar to all other FTIR devices, a background scan was also required before each FTIR test.

One important change in the FTIR testing during this demonstration was the number of scans, which could be subjectively set by users. In this study, the technician set the device to perform 64 scans per sample, which was twice the number of scans used by Alpha FTIR spectrometer in the previous study. For the TruDefender FTX handheld FTIR analyzer, the number of scans used varied by scan modes, such as quick scan and library scan.

CHAPTER 3 RESULTS AND ANALYSIS

3.1 Comparison of Portable FTIR Spectrometers

3.1.1 Comparison of Portable FTIR Spectrometers' Specifications (Hardware)

The general specifications of the three portable FTIR devices are summarized in Table 3-1. The weights and sizes of these FTIR portable devices show that TruDefender FTX is the most convenient one for use in field testing. The available spectral ranges show that Alpha FTIR can scan a wider range of chemical compositions. For scanning specimens with rough surfaces, such as asphalt mixtures, the attenuated total reflectance (ATR) collection optics on all the three FTIR devices can be replaced by a diffusion reflectance accessory from their individual companies.

	TruDefender FTX	ExoScan 4300	Alpha FTIR	
Weight (lb.)	3.1	4.8	13	
Size (inch)	$8.9 \times 4.5 \times 2.1$	N/A	8×11	
Spectral Range (cm ⁻¹)	4,000 - 650	5000 - 650	7500 - 375	
Spectral Resolution (cm ⁻¹)	4	4	2	
Collection Optics	Solid Diamond Crystal ATR	Solid Diamond Crystal ATR	Solid Diamond Crystal ATR	
Diffusion Reflectance Accessories	Available	Available	Available	

Table 3-1 Specifications of Three Portable FTIR Spectrometers

3.1.2 Comparison of Portable FTIR Spectrometers' Data Analysis Methods (Software)

Based on the hardware specifications, all the three FTIR portable devices should be able to capture the characteristic peaks for asphalt binder and SBS contents based on their spectral range and spectral resolution. However, considering their built-in mobile software (not the analysis software on a separate computer), TruDefender FTX and ExoScan 4300 both have competitive advantages.

The main method to identify a sample material by TruDefender FTX is via library search, which may be enhanced by adding additional material spectra through its library scan (Lu et al., 2015). To quantify sample elements, TruDefender FTX has to rely on external software (e.g., OMNIC, the one developed by Thermo Scientific) installed on a separate computer for analysis. In other words, the quantitative analysis with TruDefender FTX is neither truly real time nor mobile.

However, ExoScan 4300 overcomes this limitation via its powerful built-in "Microlab Lite Synchronize" software. Depending on the Synchronize function, ExoScan 4300 itself can work as a mobile computer to perform the quantitative analysis (Agilent Technologies, 2013).

For Alpha FTIR, all spectrum analysis work has to be performed on a separate computer.

Thus, the proper selection of a portable FTIR device would depend on users' purpose. If the FTIR device is only required to collect material spectra in the field, one can pick any of these three FTIR devices. If quantification in the field through material library search function is required, both TruDefender and ExoScan 4300 can be selected. If quantification in the field through more advanced models (e.g., the quant model in OMNIC) is required, ExoScan 4300 can be used.

3.2 Comparison of Results from Portable FTIR Spectrometers

3.2.1 Comparison of Results Based on SBS-Modified Asphalt Samples

The BDV25-977-06 report revealed the similarity of spectra captured using the Bruker and the TruDefender portable FTIR spectrometers (Lu et al., 2015). In this report, the spectra from Agilent Handheld 4300 FTIR Spectrometer was added and compared with those from the other two portable FTIR spectrometers. One example of comparison results is shown in Figure 3-1Error! Reference source not found. It can be seen that the spectra of the same asphalt binder scanned via these three FTIR spectrometers are consistent with each other. That is, all characteristic peaks of the SBS modified asphalt binder were all captured by these three FTIR spectrometers. Similar results were also observed from other asphalt binders.

For quantitatively testing the accuracy of Agilent Handheld 4300 FTIR Spectrometer, the typical indicators of SBS contents on asphalt binder spectra were compared. Since the previous study found that the indicators' variances increased significantly for SBS binders with more than 5 percent SBS, those high percentage SBS specimens were triply sampled and scanned by the Agilent Handheld 4300 FTIR Spectrometer. Given the previous uniform outputs from the TruDefender FTX and Alpha FTIR spectrometers using the indicator of PA966/PA1455, the values of PA966/PA1455 obtained from spectra of USF samples and Ergon samples using the Agilent Handheld 4300 FTIR Spectrometer are plotted against SBS contents, along with results from the other two portable spectrometers, as shown in Figure 3-2 and Figure 3-3.

As results, the outputs from the Agilent FTIR spectrometer are generally consistent with those from the TruDefender FTX and Alpha FTIR spectrometers. For a total of 14 different SBS binder samples, the results from 12 of them are located within or very closely to the ranges of results from the TruDefender FTX and Alpha FTIR spectrometers, with the two exceptions of 9% SBS USF sample and 3% SBS Ergon sample (note that the outputs of 5% SBS Ergon sample and 10% SBS Ergon sample are regarded as acceptable because two results of three repetitions are within those ranges). However, a general trend can be observed that the results from TruDefender FTX and Alpha FTIR spectrometers are closer to each other than the Agilent FTIR

spectrometer results. The higher variation in the Agilent FTIR spectrometer results might result from changes in binder samples due to aging and resampling disturbance, different FTIR test procedure (e.g., gentle pressing of samples onto crystal), and possible differences in measurement accuracy of the FTIR devices. The results from the three portable FTIR devices are in close match with the results from the desktop FTIR device for the USF samples, but higher for the Ergon samples. The exact reason for the latter is unknown.

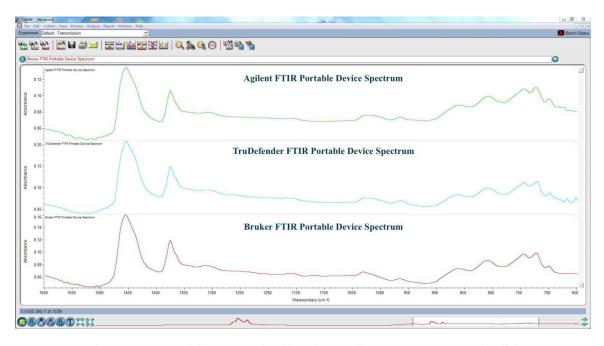


Figure 3-1 Comparison of Spectra of USF Binder Sample with 10% SBS from Three Portable FTIR Devices

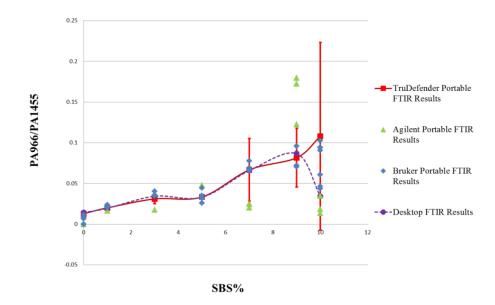


Figure 3-2 Results from Three Portable FTIR Devices Based on USF Samples

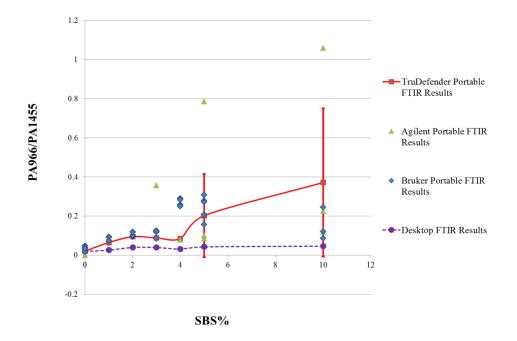


Figure 3-3 Results from Three Portable FTIR Devices Based on Ergon Samples

3.2.2 Comparison of Results Based on GTR-Modified Asphalt Samples

The BDV25-977-06 report showed that, for the GTR sample from Lehigh Technologies Inc., the slope of the tilted spectrum baseline (between 1093 cm⁻¹ and 1268 cm⁻¹ wavenumbers) increased with the GTR content in GTR-modified binders. Both the desktop Nicolet 6700 FTIR spectrometer and the TruDefender FTX FTIR analyzer confirmed a finding: the relationship between GTR content and spectrum baseline slope can be potentially fitted by a quadratic curve. This study uses the Agilent FTIR spectrometer results to further verify this finding and, meanwhile, to test the accuracy of the Agilent FTIR spectrometer in detecting GTR contents. The results are shown in Figure 3-4.

As can be seen from Figure 3-4, the results from the Agilent Handheld 4300 FTIR Spectrometer also reveals a quadratic relationship between GTR content and spectrum baseline slope. The data points are consistent with those from the other two FTIR devices, although with some offsets. The various sample pressing methods used by these portable FTIR devices probably caused these offsets due to different contact conditions between ATR crystals and sample specimens.

For asphalt binders with GTR from Global Tire Recycling, just like other FTIR devices, the Agilent FTIR spectrometer did not capture any significant characteristic peak or slope to quantify the GTR contents either, even after using different probe accessories.

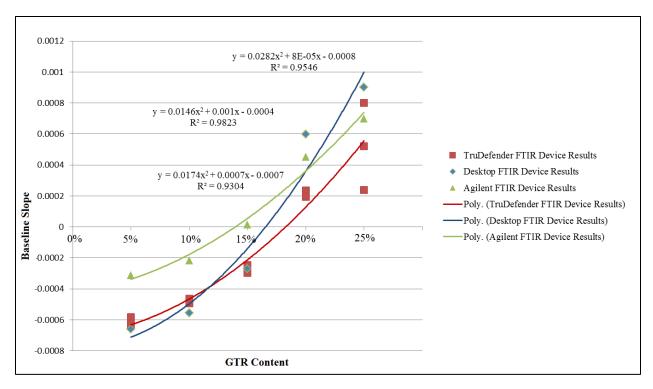


Figure 3-4 GTR Content in MD Samples vs. Slope of Spectrum Baseline

3.2.3 Comparison of the Fitted Linear Regression Models Based on Different FTIR Handheld Devices

The BDV25-977-06 report shows that some characteristic peaks can be proper indicators to quantify the SBS content in modified asphalt binders, such as peak height at 966 cm⁻¹ or peak area at 966 cm⁻¹ divided by peak height at 1455 cm⁻¹. To verify the reliability of these linear relationships, this study also builds simple linear regression models and compares their linearity with previous results. It is worth pointing out that, given the limited number of tests done on binder samples with 10% SBS and high variability in indicator values, the spectra scanned from these binder samples were not used in estimating the regression models.

Figure 3-5 through Figure 3-8 show the linear regression models estimated from results of both the TruDefender FTX and the Agilent 4300 FTIR spectrometer for various indicators. It can be seen that the estimated parameters in these linear regression models are consistent, which indicates the similar performance of the two portable FTIR devices and the reliability of these quantification functions. However, there were some offsets between these two linear functions. Also it can be seen that the variability of the Agilent 4300 FTIR spectrometer data is significantly higher than that of the TruDefender FTX FTIR spectrometer. These differences might be caused by the different contact conditions between specimens and the crystal ATR during the test.

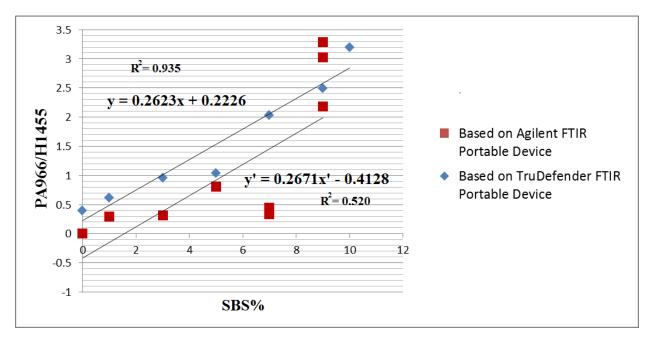


Figure 3-5 PA966/H1455 vs. SBS Content (USF Samples)

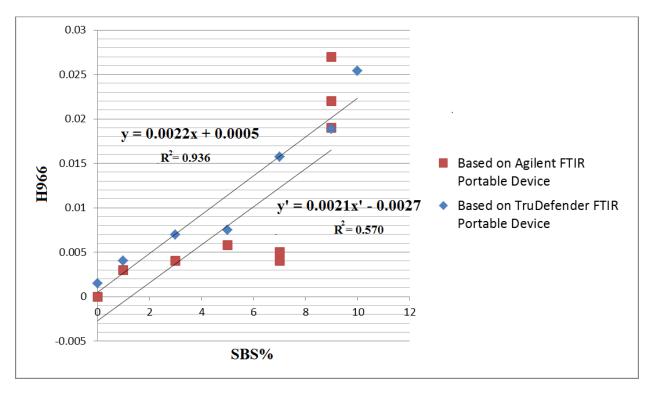


Figure 3-6 H966 vs. SBS Content (USF Samples)

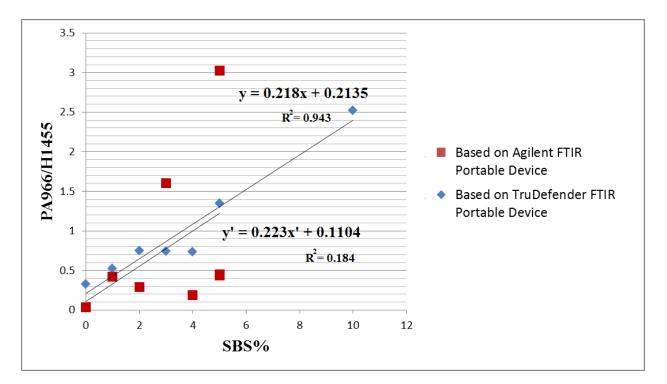


Figure 3-7 PA966/H1455 vs. SBS Content (Ergon Samples)

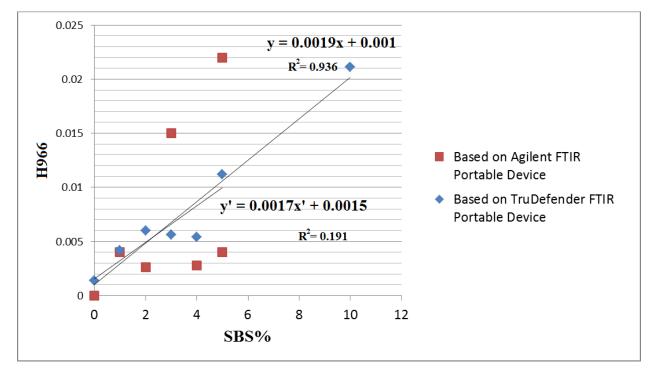


Figure 3-8 H966 vs. SBS Content (Ergon Samples)

3.2.4 Updated Verification of Prediction Models Using Binder Samples from Field Projects

The BDV25-977-06 project examined the effectiveness of prediction models for SBS content developed from USF samples measured by the TruDefender FTX FTIR analyzer, using a number of binder samples from FDOT field projects, whose exact polymer contents were unknown. During this stage of work, the approximate polymer contents of those binders were further estimated by FDOT technicians, as shown in Table 3-2. Moreover, the results from Ergon samples were combined with those from USF samples to build linear prediction models. The predicted SBS contents based on two linear models developed by two spectral indicators, PA966/H1455 and H966, are also summarized in the Table 3-2.

Sample ID	Binder Grade	Estimated SBS%	Estimated GTR%	PA966 /H1455	H966	Estimated SBS% by PA966/ H1455	Estimated SBS% by H966	Comment
FA	PG 52-28 with RAP / RAS	Unknown	Unknown	0	0	0	0	Binder Extraction
FB	PG 52-28	0	0	0.415	0.001	0.887	0.143	
FC	PG 67-22	0	0	0.368	0.001	0.699	0.143	
FD	PG 76-22 (PMA)	2-4	0	1.843	0.012	6.611	5.381	
FE	PG 76-22 (ARB)	1-2	Min 7	0.413	0.001	0.879	0.143	
FF	Unknown	0	0	0	0.006	0	2.524	Fog seal; polymer emulsion residual
FG	PG 76-22 (HP)	7-8	0	1.884	0.015	6.775	6.810	
FH	ARB-12	0	12	0.470	0.002	1.108	0.619	
PolyH P	PG 76-22 (HP)	7-8	0	2.338	0.018	8.595	8.238	
15572	PG 58-22	0	0	0.435	0.001	0.968	0.143	
15589	PG 76-22 (PMA)	2-4	0	2.204	0.016	8.058	7.286	
15447	PG 76-22 (ARB)	1-2	Min 7	1.478	0.011	5.148	4.905	
15473	PG 76-22 (PMA)	2-4	0	1.515	0.01	5.296	4.429	
15476	PG 82-22 (PMA)	3-6	0	2.255	0.016	8.262	7.286	
15539	ARB-5	0	5	0.414	0.001	0.883	0.143	
15487	ARB-12	0	12	0.212	0.001	0.074	0.143	

 Table 3-2 Approximate and Predicted SBS Contents in Binder Samples for Verification

If one percent difference from the possible SBS content ranges is deemed acceptable, the prediction results highlighted in green represent acceptable estimations while red represents unacceptable estimations. As can be seen, among the 16 binder samples, the linear functions developed from combining USF samples and Ergon samples produced unacceptable prediction

results for 5 of them, which are mainly PG 76-22 and PG 82-22 binder samples. These observations are also displayed in Figure 3-9 and Figure 3-10, in which error bars are used to represent the ranges of estimated SBS contents. These large prediction errors are likely due to the difference in asphalt sources of USF samples (PG 67-22 base asphalt) and test binder samples.

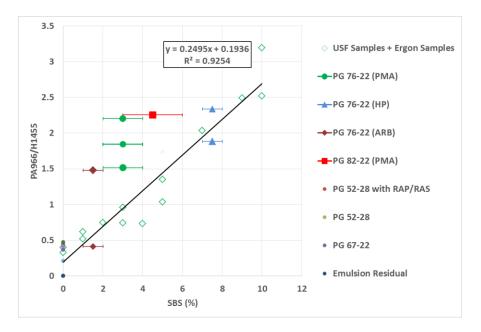


Figure 3-9 Quantification Results of Binder Samples with Unknown Polymer Contents Using PA966/H1455

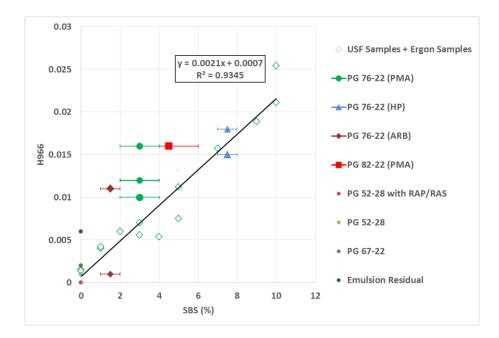


Figure 3-10 Quantification Results of Binder Samples with Unknown Polymer Contents Using H966

3.3 Possibility of Using Agilent Portable FTIR Device on Mixture Samples

This study also attempted to use the Agilent FTIR device to directly scan asphalt binders in mixture samples. Differing from previous trials with the TruDefender FTX handheld FTIR analyzer on mixture samples, the Agilent 4300 Handheld FTIR Spectrometer showed better potential performance in scanning asphalt binder on rough aggregate surfaces, due to two of its advantages: (1) its special design for field use makes its interface to contact mixture's rough surface easier; (2) during the test, the diamond ATR interface was replaced with a diffuse reflectance spectroscopy (DRS) accessory, which, theoretically, could limit the scattered light emitted back to the air for more precisely capturing the incident beam via short light path (SHIMADZU, 2015). As a result, in this study, the Agilent 4300 Handheld FTIR Spectrometer was able to get the binder spectra from mixture samples, which were not captured by the TruDefender FTX handheld FTIR analyzer with ATR interface in the previous study.

The spectra scanned from mixture samples are shown in Figure 3-11. Although the spectra obtained by ATR and DRS exhibit differences, it can be seen that DRS can capture some characteristic peaks for asphalt binder at 1455 cm⁻¹ and SBS at 699 cm⁻¹, but not for SBS at 966 cm⁻¹. In this case, especially for the peaks locating within 750 cm⁻¹ to 650 cm⁻¹, weak peaks become stronger in the diffuse reflectance spectrum. After Kubeika-Munka conversion (K-M), the characteristic peaks (699 cm⁻¹, etc.) become more significant for SBS quantification, but without capturing additional characteristic peaks (966 cm⁻¹, etc.).

The significant difference in the binder spectra obtained from mixture samples and from binder samples indicates that the Agilent Handheld 4300 FTIR Spectrometer may be used on mixture samples to detect SBS in asphalt binders. Further evaluation is needed to determine its potential to quantify SBS content.

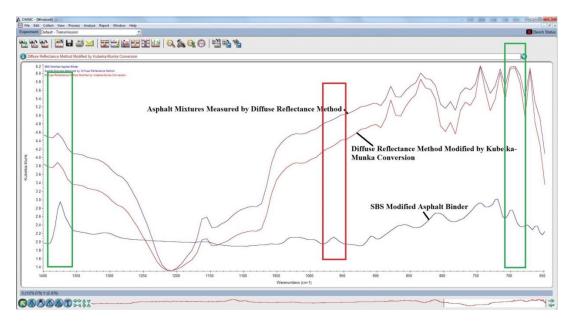


Figure 3-11 Spectra by DRS on Asphalt Mixtures

CHAPTER 4 CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

This study evaluated the performance of the Agilent Handheld 4300 FTIR Spectrometer using the same two sets of SBS binder samples and two sets of GTR binder samples that were tested in the BDV25-977-06 research project. The spectra captured by the Agilent Handheld 4300 FTIR Spectrometer were compared with those from other portable FTIR devices that were evaluated in the BDV25-977-06 project. Moreover, this study also attempted to scan asphalt mixture samples by the Agilent Handheld 4300 FTIR Spectrometer with a diffuse reflectance spectroscopy (DRS) accessory. The following conclusions are obtained:

- 1. With the same specifications, Agilent Handheld 4300 FTIR Spectrometer can capture absorbance spectrum similar to those from other portable FTIR devices (i.e., the TruDefender FTX handheld FTIR analyzer and the Bruker Alpha FTIR spectrometer).
- 2. The prediction models of SBS contents by spectral indicators, including H966 and PA966/H1455, are similar for the Agilent Handheld 4300 FTIR Spectrometer and the TruDefender FTX handheld FTIR analyzer. The variability of the Agilent Handheld 4300 FTIR Spectrometer data, however, is higher than that of the TruDefender FTX handheld FTIR analyzer, which is likely due to different contact conditions between specimens and ATR crystal during testing.
- 3. Unlike the TruDefender FTX handheld FTIR analyzer, the Agilent Handheld 4300 FTIR Spectrometer, with the crystal ATR accessory replaced by a diffusion reflectance accessory, can read absorbance spectra of asphalt mixture samples. The obtained spectra from mixture samples, however, are significantly different from those from binder samples. The Agilent Handheld 4300 FTIR Spectrometer may be used on mixture samples to detect SBS in asphalt binders. Quantification of SBS content by the Agilent Handheld 4300 FTIR Spectrometer on mixture samples needs further evaluation.

4.2 Recommendations

The conclusions of this study are based upon a limited number of binder samples and test replications. The same recommendations in the BDV25-977-06 report apply here. That is, a follow-up study should be conducted prior to or along with the preliminary implementation, with the following suggestions:

- A portable FTIR device should be acquired for use for a sufficient period of time.
- A variety of asphalt binders that are commonly used in FDOT asphalt paving projects should be included in the study. For each type of binder, a set of calibration binders (i.e., same asphalt but with different polymer contents) should be carefully prepared in the laboratory, preferably by the same organization or operator, to make sure that they are uniformly mixed and contain the labelled polymer contents.

REFERENCES

Lu, Q., Gunaratne, M., and Guo, L. *Field Test Method to Determine Presence and Quantity of Modifiers in Liquid Asphalt*. Report No. BDV25-977-06, University of South Florida, 2015.

Agilent Technologies. *MicroLab Software Operation Manual*. http://www.chem.agilent.com/Library/usermanuals/Public/0020-410.pdf, 2013.

SHIMADZU. *ABC's of the Diffuse Reflection Method*. http://www.shimadzu.com/an/ftir/support/ftirtalk/talk1/intro.html, Copyright 2015.