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Final Report

Field Test Method to Determine Presence and Quantity of Modifiers in Liquid Asphalt

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SI (MODERN METRIC) CONVERSION FACTORS

Approximate Conversions to SI Units

Symbol	When You Know	Multiply By	To Find	Symbol
		Length		
in	inches	25.4	millimeters	mm
ft	feet	0.305	meters	m
yd	yards	0.914	meters	m
mi	miles	1.61	kilometers	km
		Area		
in^2	square inches	645.2	square millimeters	mm^2
ft^2	square feet	0.093	square meters	m^2
yd^2	square yard	0.836	square meters	m^2
ac	acres	0.405	hectares	ha
mi^2	square miles	2.59	square kilometers	km^2
		Volume		
fl oz	fluid ounces	29.57	milliliters	mL
gal	gallons	3.785	liters	L
ft^3	cubic feet	0.028	cubic meters	m^3
yd^3	cubic yards	0.765	cubic meters	m^3
		NOTE: volumes greater than 1000 L shall be shown in m^3		
		Mass		
oz	ounces	28.35	grams	g
lb	pounds	0.454	kilograms	kg
T	short tons (2000 lb)	0.907	megagrams (or "metric ton")	Mg (or "t")
		Temperature (exact degrees)		
°F	Fahrenheit	5 (F-32)/9 or (F-32)/1.8	Celsius	°C
		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	newtons	N
lbf/in^2	poundforce per square inch	6.89	kilopascals	kPa

Approximate Conversions from SI Units

Symbol	When You Know	Multiply By	To Find	Symbol
		Length		
mm	millimeters	0.039	inches	in
m	meters	3.28	feet	ft
m	meters	1.09	yards	yd
km	kilometers	0.621	miles	mi
		Area		
mm^2	square millimeters	0.0016	square inches	in^2
m^2	square meters	10.764	square feet	ft^2
m^2	square meters	1.195	square yards	yd^2
ha	hectares	2.47	acres	ac
km^2	square kilometers	0.386	square miles	mi^2
		Volume		
mL	milliliters	0.034	fluid ounces	fl oz
L	liters	0.264	gallons	gal
m^3	cubic meters	35.314	cubic feet	ft^3
m^3	cubic meters	1.307	cubic yards	yd^3
		Mass		
g	grams	0.035	ounces	oz
kg	kilograms	2.202	pounds	lb
Mg (or "t")	megagrams (or "metric ton")	1.103	short tons (2000 lb)	T
		Temperature (exact degrees)		
°C	Celsius	1.8C+32	Fahrenheit	°F
		Illumination		
lx	lux	0.0929	foot-candles	fc
cd/m^2	candela/m^2	0.2919	foot-Lamberts	fl
		Force and Pressure or Stress		
N	newtons	2.225	poundforce	lbf
kPa	kilopascals	0.145	poundforce per square inch	lbf/in^2

* 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)

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16. Abstract

Asphalt modified with styrene butadiene styrene (SBS) polymer and/or ground tire rubber (GTR) is widely used in the U.S. to enhance its performance. However, there are very few field tests developed to verify the content of modifier(s) in asphalt during construction.

In this study, a comprehensive literature review and a nationwide questionnaire survey were first conducted on available tests/tools and current agency practices for modifier detection and quantification in asphalt binders. Based on the findings from the review and survey, the Fourier transform infrared spectroscopy (FTIR) test by portable devices was chosen for further evaluation. A laboratory experiment was designed and conducted for this purpose, which included measurements with two portable and one desktop FTIR devices on two sets of SBS binders and two sets of GTR binders prepared in the laboratory and several binder samples from field paving projects.

It was found that the portable FTIR devices can give measurements very similar to those from a desktop FTIR spectrometer. For SBS-modified binders, the SBS content may be calculated from the peak height at 966 cm^{-1} of a sample’s absorbance spectrum, based on a standard curve calibrated for each type of asphalt. Estimation error, however, increases significantly for binder samples with more than 5 percent SBS. For GTR-modified binders, no firm conclusion can be made regarding the effectiveness of the FTIR test to quantify GTR content, although it seems promising that the baseline slope of a sample’s absorbance spectrum may be used as a predictor for GTR content. The library search function of the TruDefender FTX FTIR analyzer has a potential to quickly identify a binder sample (and therefore its polymer content) in the field, provided a suitable material library is used. Recommendations on preliminary implementation of portable FTIR devices and future study and evaluation are provided in the report.

17. Key Word
styrene butadiene styrene, ground tire rubber, modifier detection and/or quantification, Fourier transform infrared spectrometer, library search, asphalt binder

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EXECUTIVE SUMMARY

Asphalt binder modified with styrene butadiene styrene (SBS) polymer and/or ground tire rubber (GTR) is widely used in the U.S. and around the world to enhance binder performance, in turn enhancing the asphalt mixture performance. However, there are very few field tests developed to verify the content of modifier(s) in asphalt during construction. This study aims to identify and evaluate a practical tool and/or test 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.

A comprehensive literature review and a nationwide questionnaire survey were first conducted on the state of the art and state of the practice of tests related to modifier detection and/or quantification in asphalt binders. A number of potential tests were identified and analyzed, and 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 SBS or GTR modifiers in asphalt binders. A handheld TruDefender FTX FTIR analyzer and a portable Bruker Alpha FTIR spectrometer were included in the study. Two sets of SBS-modified binders and two sets of GTR-modified binders were prepared in the laboratory at various predetermined contents of modifiers and tested with both portable FTIR devices and a desktop FTIR spectrometer. Various ways of characterizing the absorbance spectrum features were explored to determine the best indicator to correlate with modifier contents. A number of binders from FDOT field paving projects were also measured by the two portable FTIR devices to test the effectiveness of selected absorbance spectrum features.

It was found that the two portable FTIR devices can give measurements very similar to those from a desktop FTIR spectrometer and are easier to operate.

For SBS-modified binders, the portable FTIR spectrometers can detect a generally linear increase in height or area of a characteristic peak at 966 cm^{-1} or 699 cm^{-1} of the absorbance spectrum when the SBS content increases. The peak height at 966 cm^{-1} can be used as a good indicator in a linear standard curve to calculate SBS content. For SBS binders with different base asphalt, however, different standard curves should be generated and used. Moreover, the variance of FTIR measurements increases with increasing SBS contents. Therefore, either the application of FTIR device to SBS quantification should be limited to asphalt binders with low SBS contents (less than 5 percent), or the number of test repetitions should be significantly increased.

For GTR-modified binders, the existence of carbon in GTR caused the spectrum baseline to tilt up to the low wavenumber end. This feature was discovered to be useful in predicting GTR content in one set of GTR binder samples, but not in the other set. The effectiveness of using spectrum baseline slope for GTR quantification still needs further verification.

The library search function of a portable FTIR analyzer may be used to quickly identify a test sample in the field. Once the absorbance spectra of a set of standard binders with a range of polymer contents were pre-scanned and saved into a material library of the portable FTIR analyzer, there was a high chance that the analyzer could correctly identify a test sample by comparing its spectrum with those in the library. In this study, a user-defined small library was used and the FTIR analyzer generally identified a test sample through library search. Whether or not the library search function could work with a large binder library needs to be evaluated in further studies.

It is recommended that portable FTIR test devices, particularly the TruDefender FTX FTIR analyzer, may be used preliminarily in the field to estimate polymer contents in modified binders, along with a follow-up study to further evaluate its effectiveness, define scope of use limits, and to develop standard test procedures.

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CHAPTER 1 INTRODUCTION

Asphalt binder modified with styrene butadiene styrene (SBS) polymer and/or ground tire rubber (GTR) is widely used in the U.S. and around the world to enhance binder performance, in turn enhancing the asphalt mixture performance. In Florida, the Florida Department of Transportation (FDOT) currently produces about five million tons of asphalt mix each year, of which approximately 60% contains an asphalt binder modified with SBS and/or GTR.

The asphalt binder is the most expensive component of an asphalt mixture. In Florida, using a modified binder, as opposed to an unmodified binder, results in a cost increase of about $8 - $10/ ton of asphalt mix. Ensuring that the asphalt mixture actually contains these modifiers during mixture production is essential, not only to ensure good performance, but also to make certain that all contractual specification requirements are being met and that the additional cost of the binder is warranted.

Currently, a variety of tests have been developed or applied to detect the existence or to quantify the content of modifier in asphalt binders. These tests, however, are mostly conducted in a laboratory environment. The laboratory equipment and expertise required for these tests are not suitable for field use. Different from laboratory tests, a field test needs to be easy (in terms of sample preparation and test procedure), quick (in terms of testing and data analysis time), and portable (in terms of mobility of test equipment). Unfortunately, there are very few, if any, field tests of asphalt binder that meet these requirements.

A simple field test, therefore, needs to be researched and/or developed to allow field personnel to determine the presence and possibly the quantity of SBS and GTR modifiers in asphalt binders in order to verify that these high performance binders are received as specified.

The objectives of this study include:

(1) to perform a literature review and a survey on the state of the art and state of the practice of tests related to modifier detection and/or quantification in asphalt binders, and
(2) to identify and evaluate a practical tool and/or test 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.

In this study, a comprehensive literature review and a nationwide questionnaire survey were first conducted on available tests/tools and current agency practices for modifier detection and quantification in asphalt binders. Based on the findings of the review and survey, the Fourier transform infrared spectroscopy (FTIR) test by portable devices was chosen for further evaluation. A laboratory experiment was designed and conducted for this purpose, which included two portable and one desktop FTIR devices. Based on the experiment results, the validity of the portable FTIR devices for field use was discussed and recommendations for further evaluation/implementation of the FTIR test were provided.

CHAPTER 2 LITERATURE REVIEW

Current tests for detecting and/or quantifying modifiers in asphalt binders can be roughly divided into two categories: those based on mechanical performance of asphalt binders/mixtures and those based on non-mechanical performance of asphalt binders.

For the first category, eight test procedures are covered in the review, with their theories and sample results from earlier studies.

For the second category, the review focuses on the following methods:

- Spectrum methods: Fourier transform infrared spectrometer (FTIR) and Raman spectrometer tests
- Chromatography method: gel permeation chromatography (GPC) test
- Thermal methods: differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA)
- Micro-vibration method: nuclear magnetic resonance (NMR) test

Since the non-mechanical tests are mainly based on molecular physics or quantum chemistry, they are generally more reliable and accurate than the mechanical tests. For this reason, more review efforts were put into the non-mechanical tests, covering the theories behind them, their history of development and application both in and outside the asphalt pavement field, the details of test operations, and their limitations and equipment costs, to help decide on how potentially these tests could be further developed or refined for field use.

2.1 Mechanical Tests

Since the use of SBS or GTR modifier changes the mechanical properties of asphalt binders, any test that measures the mechanical properties of asphalt binders or asphalt mixtures may be used to detect the existence of modifiers. For example, the Superpave binder tests including rotational viscometer (RV) test, dynamic shear rheometer (DSR) test, bending beam rheometer (BBR) test, and direct tension test (DTT), measure binder responses to loading at various temperatures and loading rates. By comparing the mechanical responses of an unknown modified binder to those of a known unmodified asphalt binder, the presence of modifiers may be detected. The key mechanical properties that may be measured include viscosity, elastic stiffness, permanent deformation resistance, tensile strength, and fatigue cracking resistance. Correspondingly, there are a variety of tests that can be potentially used for modifier identification and/or quantification. For example, in 2011, one research group from University of Malaya did several basic mechanical tests (ductility test, elastic recovery test, penetration test, and dynamic shear rheometer test) to examine the relationship between modifier contents and modified asphalts' performance. Some of the results are shown in Figure 4-1 (Mashaan et al., 2011).

In this section, eight relevant laboratory tests are involved:

1) Repeated Creep Test,
2) Static Creep Test,
3) Elastic Recover Test,
4) Flexural Fatigue Beam Test,
5) Flow Number Test,
6) Flow Time Test,

7) Binder Fracture Energy Test,
8) New Creep / Recovery Test with Laser Interferometry Application.

Tests 1 through 6 were discussed or verified by one research group at the University of Texas at El Paso. One project of Virginia DOT by Diefenderfer also verified Test 3. University of Florida developed Test 7 in 2013 and verified the identify function on binder modifier. Test 8 was initially developed by Dongre et al. and presented at the 49th Petersen Asphalt Research Conference in 2012.

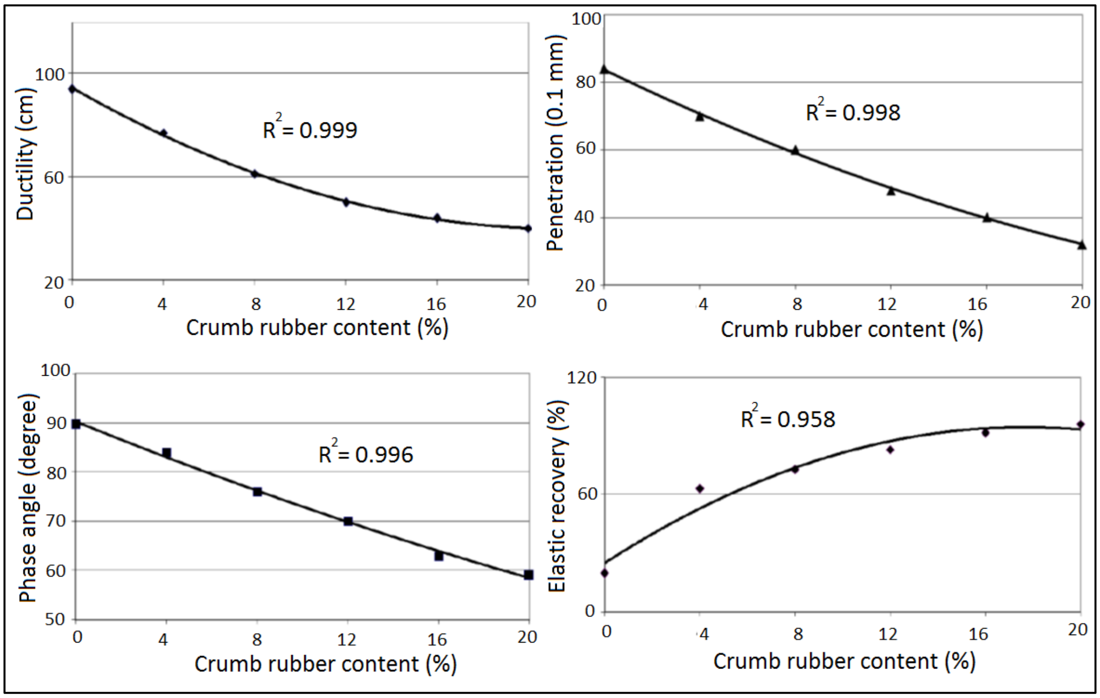


Figure 2-1 Physical and Rheological Properties at Different Crumb Rubber Contents (Mashaan et al., 2011)

2.1.1 Repeated Creep Test (RCT)

Because of the presence of viscous components in asphalt binders, asphalt pavements do not regain their original shape after traffic load removal, which causes rutting. This viscoelastic property of binders varies with the presence of binder modifiers. The repeated creep test can generate accumulated permanent strain to simulate the repeated impact from traffic load and then evaluate permanent deformation (rut depth). Based on variations in permanent deformation of different asphalt binders, the presence of binder modifier can be identified (Hrdlicka et al., 2007). It is worth pointing out that Federal Highway Administration (FHWA) proposed repeated creep test to indirectly detect the presence of modifiers (Sugandh et al., 2007).

A study from TxDOT conducted repeated creep tests under eight stress levels (25, 50, 100, 400, 800, 1600, and 3200 Pa) and three temperatures (52, 64, 76ºC), and found that asphalt modified with SBS and tire rubber (TR) had significantly less accumulated strain than unmodified asphalt, and their accumulated strain non-linearly depends on temperature, as shown in Figure 4-2 (Hrdlicka et al., 2007). In other words, this difference exhibited more significantly at a higher temperature (76ºC).

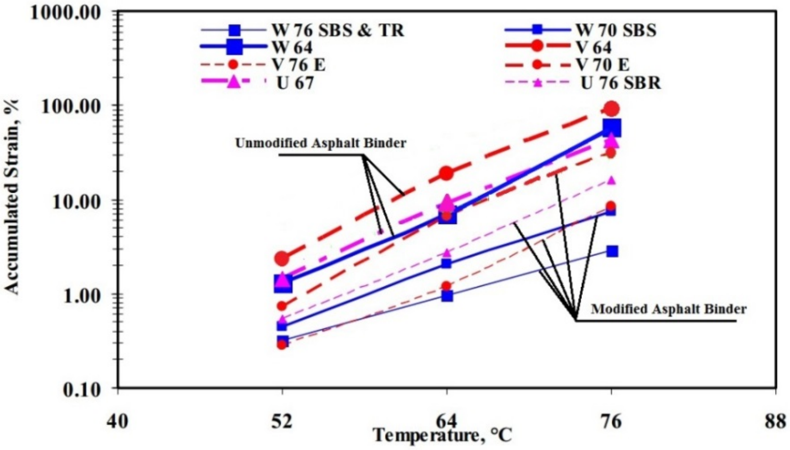


Figure 2-2 Accumulated Strain at a Shear Stress of 100 Pa at the End of the Test for Unaged Binder (Hrdlicka et al., 2007)

2.1.2 Static Creep Test (SCT)

Opposite to repeated creep test, the static creep test applies a constant axial compressive load, as described in Tex-231-F. The temperature set in this test is 40 to 60ºC. This test measures and records the axial deformations with Linear Variable Differential Transducers (LVDT) and their corresponding loads. Normally, the static creep test results contain three parameters: total strain, creep stiffness, and permanent strain (Sugandh et al., 2007).

This test was conducted by TxDOT to verify whether its results can be the indicators of modifier binders' presence. They found that, although total strain and permanent strain of modified binder did not satisfy the acceptance criteria, all these three parameters (total strain, creep stiffness, and permanent strain) can indicate the modified binder presence, depending on their significant differences from those of unmodified binders, as shown in Figure 4-3 and Figure 4-5 (Sugandh et al., 2007).

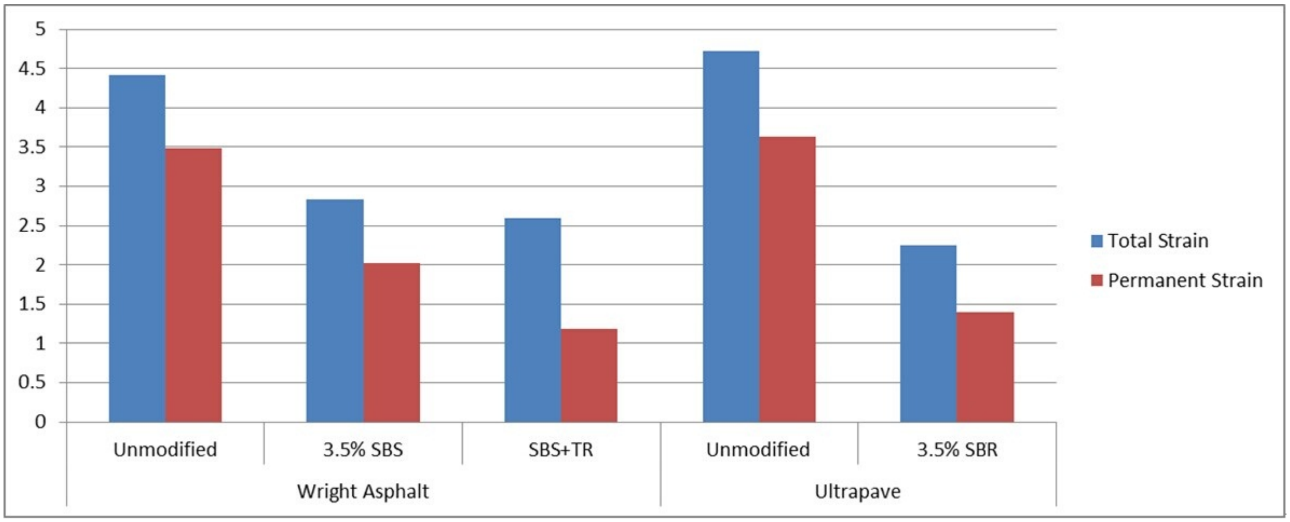


Figure 2-3 Static Creep Test Results of Total Strain and Permanent Strain (unit: %)

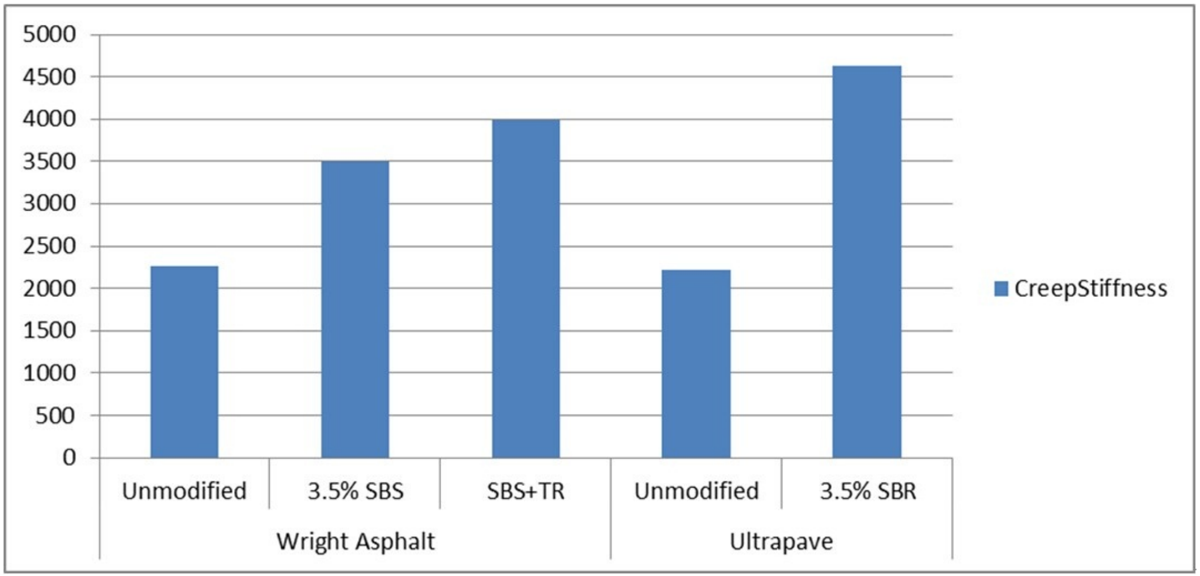


Figure 2-4 Static Creep Test Results of Creep Stiffness (unit: lb/in^2)

2.1.3 Elastic Recovery Test (ERT)

Similar to the repeated creep test, the elastic recover test is also based on the binders' viscoelastic property, but using different test procedure and indicator. As mentioned in Tex-539-C, this test uses ductilometer to pull the clips at a rate of 50 mm/min till the sample elongation reaches 200 mm, then stops pulling and cuts the sample at center. After sample relaxing for around 1 hour, the elastic recovery is calculated.

ERT is the only mechanical test which has been included in AASHTO standards for modifier quantification, presented in AASHTO T301. In 2006, Diefenderfer validated the use of ERT as quantification tools for polymer contents, as illustrated in Figure 2-5.

In the following year, TxDOT conducted ERT to predict pavement rutting. They found that elastic recovery was dramatically increased from 30% to 50% in the presence of modifier. They stated that, at 10ºC, more than 45% elastic recovery can firmly indicate the presence of modifier (Hrdlicka et al., 2007).

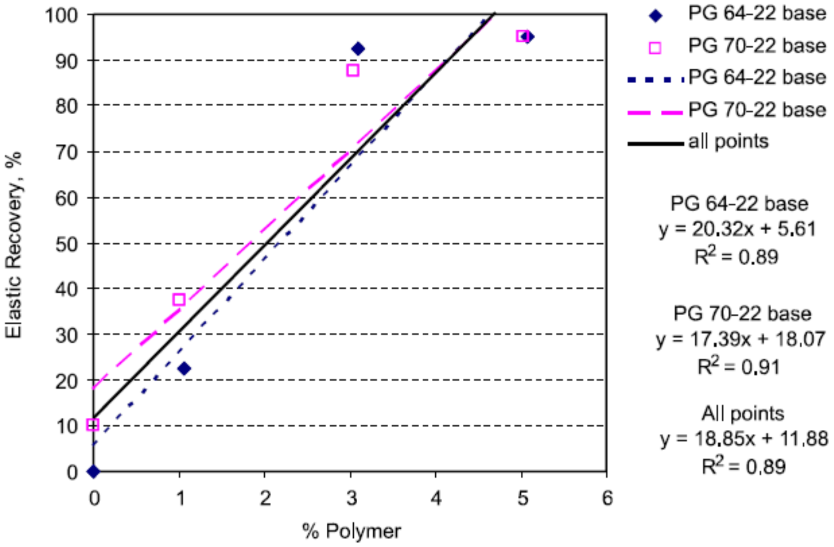


Figure 2-5 Calibration Curves of Polymer Content for Elastic Recovery (Diefenderfer, 2006)

2.1.4 Flexural Fatigue Beam Test (FFBT)

In the flexural fatigue beam test, an asphalt beam is repeatedly impacted by a sinusoidal load with fixed maximum tensile strain (or stress) at beam bottom. After the flexural stiffness of beam drops 50%, researchers record the number of loads, which is defined as fatigue life cycle (Sugandh et al., 2007).

Another program in Texas conducted the flexural fatigue beam test under different tensile strain levels with different mix types (unmodified, 3-5% SBS, SBS +GTR). It found that, with the presence of modifier, the fatigue life of mixes was significantly increased at fixed strain levels, in comparison with unmodified binder, as shown in Figure 2-6. They also recommended that the termination criterion of this test should be set as 15-20% for capturing “dip” on flexural stiffness change (Sugandh et al., 2007).

2.1.5 Flow Number Test (FNT)

With a similar experimental principle of the repeated creep test, a flow number test applies a haversine axial compressive load to samples (Sugandh et al., 2007). The strain is calculated based on permanent axial deformation, which is normally monitored with actuator LVDT. The flow number is defined as the number of load repetitions when the slope of change in permanent strain reaches minimum (Witczak et al., 2002).

One TxDOT study performed the flow number test under a test temperature of 54ºC and 210 kPa stress level. It was found that the permanent strain of less than 1% represented the presence of modifier (Sugandh et al., 2007), as shown in Figure 2-7.

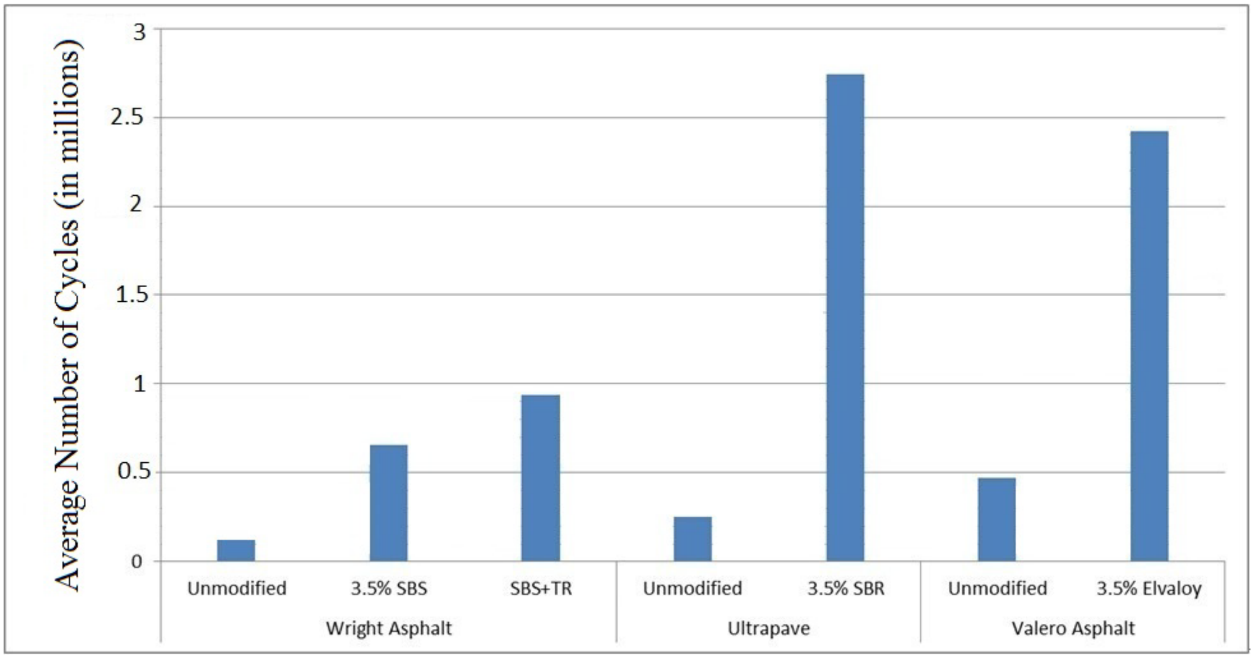


Figure 2-6 Comparison of Numbers of Life Cycles from Unmodified and Modified Asphalt (Sugandh et al., 2007)

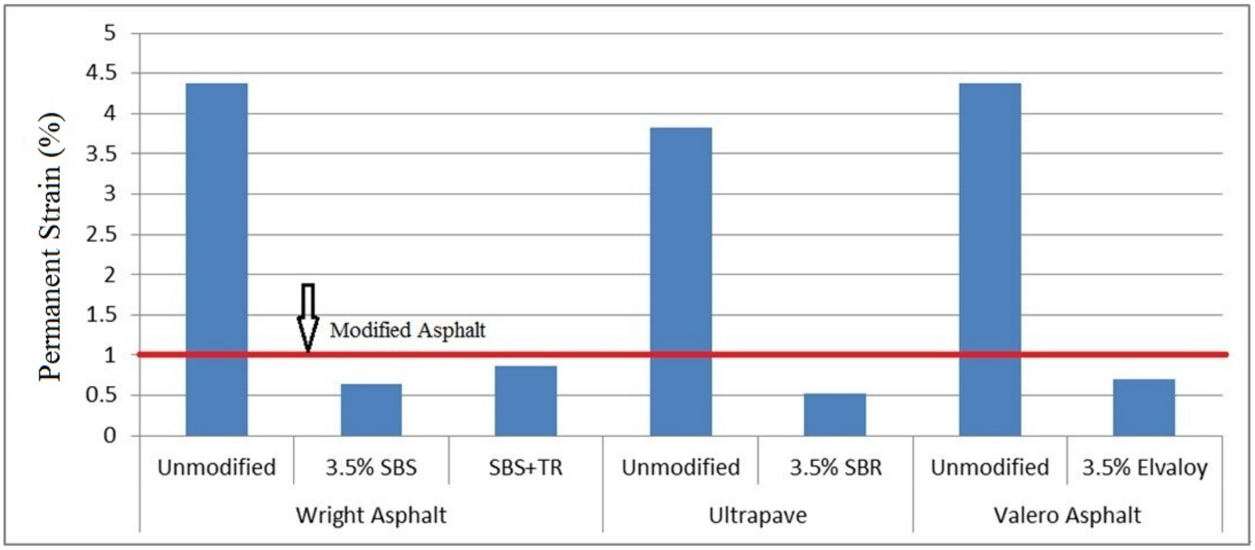


Figure 2-7 Flow Number Test Results (Sugandh et al., 2007)

2.1.6 Flow Time Test (FTT)

Opposite to the flow number test, the stress levels applied in a flow time test are fixed, which is deemed as a variation of the static creep test. Similar to flow number definition, flow time measures the time of load when the slope of change in permanent strain reaches minimum (Sugandh et al., 2007).

TxDOT also performed the flow time test under a test temperature of 54ºC and 210 kPa stress level. They stated that the less than 7000 µ in. /in. of total axial strain could identify the presence of modifier, as shown in Figure 2-8 (Sugandh et al., 2007).

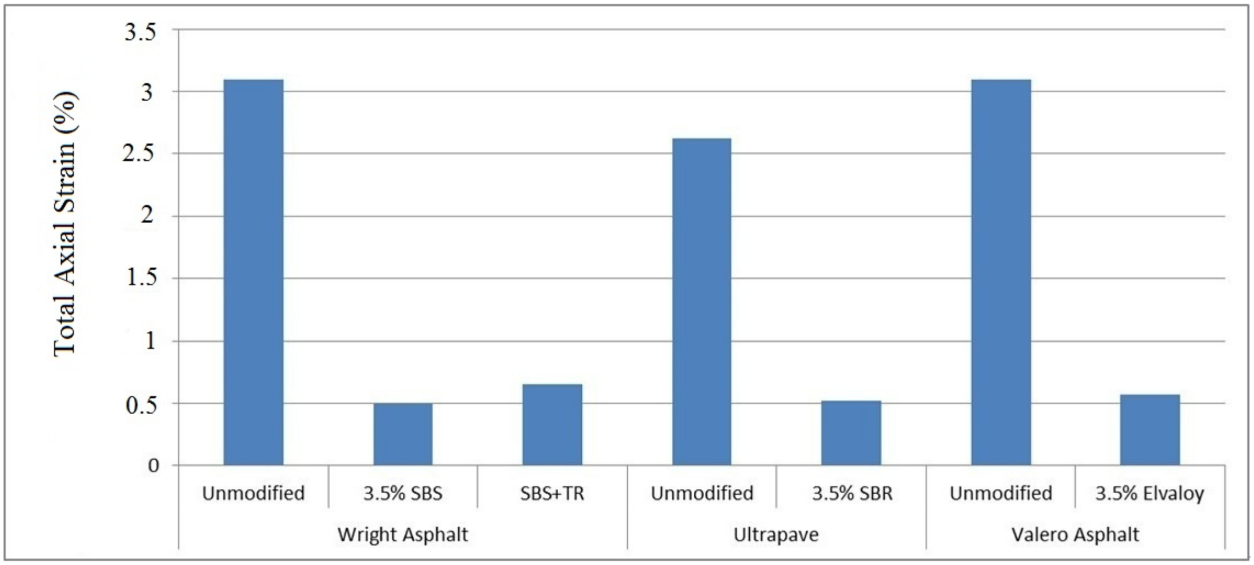


Figure 2-8 Flow Time Test Results (Sugandh et al., 2007)

2.1.7 Binder Fracture Energy Test (BFET)

BFET uses a MTS servo-hydraulic testing machine to provide a stable testing environment. The sample, which is fixed at the lower loading head, is pulled by upper loading head until rupture happens at a temperature of 15ºC (Roque et al., 2013). This test requests the specimen to be suspended vertically to avoid from bending or twisting. Through the BFET, the plot of stress vs. strain and each specimen’s fracture energy can be obtained.

FDOT conducted a BFET to evaluate seven asphalt binders. Based on the stress-strain curves, researchers found that SBS modified asphalt binder has a distinct second stress peak at all loading rates, accompanying with high fraction energy. The neat binders did not display a second peak and the GTR modified binders displayed deflections. Thus, researchers stated that the BFET firmly can be an indicator of the SBS modifier presence (Roque et al., 2013).

2.1.8 New Creep / Recovery Test with Laser Interferometry Application

In 2012, based on the strains and elastic recovery, Dongre et al. initially used laser interferometry to measure the creep and recovery loading which was induced by a computer controlled air jet in the field to quantify the binder content. The main steps can be summarized in Figure 2-9 (Dongre et al., 2012).

Although the purpose of their study is to quantify the asphalt binder, since modified asphalt has outstanding performance with less generated strains and more elastic recovery, this method could be further developed to measure the contents of modifiers in asphalt binders.

Moreover, the method initially developed by Dongre et al. provides a great hint for other researchers: based on these significantly different physical properties between modified and unmodified asphalts, using some devices to measure these physical properties in the field may have the potential to measure modifier content quickly and easily.

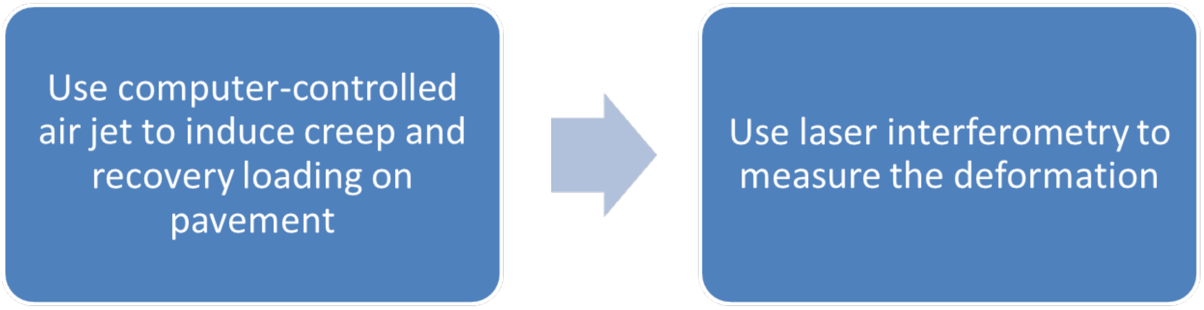


Figure 2-9 Procedures of New Creep / Recovery Test with Laser Interferometry Application

2.1.9 Summary of Mechanical Tests

Since the mechanical properties of asphalt binders are significantly changed by SBS or GTR modifier, many mechanical tests could detect the existence of modifiers based on the performance of asphalt binders. Previous studies on creep test, elastic recover test, flexural fatigue beam test, flow test, and binder fracture energy test have shown that several types of strains (total strain and permanent strain), creep stiffness, elastic recovery, viscosity, and fatigue life can be the indicators of modifier existence. Based on these outstanding indicators, applying or even inventing some portable equipment to quantify the modifier's content in the field may be possible, such as creep or recovery test induced by air jet and measured by laser interferometry.

Since the test developed by Dongre et al. is only based on the creep and elastic recovery properties, other properties might also be considered to develop new tests for quantifying modifiers in the field.

However, because the different modifiers might change the binder's performance to the same extent, very few tests can identify the specific modifier types. Currently, among these mechanical tests, elastic recovery test is the only one which has been included in AASHTO standards for modifier quantification, as presented in AASHTO T 301.

2.2 Non-Mechanical Tests

Compared to mechanical test, non-mechanical tests are more reliable and accurate, because most non-mechanical tests are based on molecular physics or quantum chemistry. However, these non-mechanical tests also require researchers to be more skilled and to understand the test's theory. Thus, this section specifically introduces the theory behind each test, the history of each test, and the details of test operation. Since these tests were developed with different initial purposes and to various extents, the review not only focuses on the current practice or research of detecting and quantifying modifiers, but also involves other asphalt-polymer related studies outside the asphalt pavement field as further references. Finally, this section summarizes the development of each test and lists the limitations and costs of tools to decide how potentially these tests could be further developed or refined.

2.2.1 Fourier Transform Infrared (FTIR) Spectrometer Test

2.2.1.1 Theory of FTIR test

When infrared light irradiates a specimen, waves at certain energy levels are absorbed by atomic or molecular bonding. Since energy absorption varies with different atom or molecule structures, the peak value and the wavelength of absorption band in the absorption spectra can be used to identify specimen's ingredients. For the quantification of these ingredients, the ratio of peak values on adsorption bands is linearly proportional to the contents of corresponding ingredients (Wei et al., 1994; Curtis et al., 1995; Diefenderfer, 2006; Ling et al., 1997; Ma and Yuan, 2012; SHRP, 2012).

2.2.1.2 Background

In 1957, the first low-cost FTIR spectrometer, whose wavelength range is from 2.5 µm to 15 µm, was invented by Perkin-Elmer. As the material of prism was improved (rock-salt, potassium bromide, cesium iodide), the upper limit of FTIR spectrometer was extended from 15 µm to 50 µm (Wikipedia, 2014[a]). It is worth pointing out that all FTIR spectrometers were originated from Michelson interferometer in 1887 (Wikipedia, 2014[b]).

For quantifying the modifiers in asphalts, there have been numerous relevant studies since 1991.

In 1991, He and Button published one paper, named "Methods to determine polymer content of modified asphalt," in *Transportation Research Record*. However, they failed to develop a successful FTIR procedure because of its accuracy limitation (He & Button, 1991).

In 1992, Choquet and Ista tried different sampling techniques using tetrachloroethylene and carbon disulfide and found that tetrachloroethylene could not be used as a solvent because its absorption bands are very close to 966 cm^{-1}. Moreover, they checked the calibration curves of polymer and asphalt, which should be 698 cm^{-1} and 1376 cm^{-1}, respectively (Choquet & Ista, 1992).

In 1994, Wei et al. from Michigan State University performed FTIR tests to characterize asphalt binders and stated that the combination of HP-GPC and FTIR could be used to capture the nature of asphalt and polymers, with quality control. Similar to the previous study done by Choquet and Ista, they also used the ratio of the 965 cm^{-1} adsorption band to the 1375 cm^{-1} band as an indicator to estimate the modifier content, expressed as the following linear regression model (Wei et al., 1994):

$$Ratio = 0.064 \times polymer\ content + 0.037 \qquad (unaged)$$
$$Ratio = 0.051 \times polymer\ content + 0.079 \qquad (aged)$$

In the next three years, one study group from Auburn University successfully estimated the polymer contents in asphalt through FTIR tests in 1995 (Curtis et al., 1995) and extended FTIR tests to quantify crumb rubber content, with the same method used for styrene-butadiene rubber (SBR) and SBS in 1997 (Ling et al., 1997). The asphalt absorption brand they used was also 1375 cm^{-1}, which was the same as Wei et al. used.

In 2001, Masson et al. performed a series of mid-IR tests, called the rapid FTIR method, to quantify the styrene-butadiene type copolymers in bitumen. They observed that the average absorptivity for polystyrene and polybutadiene blocks were 699 and 966 cm^{-1}, respectively, and found that adding bitumen could slightly change the absorptivity (Masson et al., 2001).

In 2005, AASHTO published one standard of test for polymer content in asphalt binders, coded as AASHTO T 302-05. This standard became the most popular and even the unique standard for modifier quantification based on its chemical features until GPC became another standard in this field in 2013.

In 2006, Diefenderfer from Virginia Transportation Research Council verified AASHTO T 302-05 as the quality assurance test of polymer-modified binders using FTIR (Diefenderfer, 2006). The FTIR calibration curves of polymer content plotted by Diefenderfer were shown in Figure 2-10. Based on these linear regression models for different asphalt grades, it is safe to say that, for each asphalt grade, the polymer content is almost linearly proportional to IR peak ratio. However, these regression models with different coefficients also showed that this test should rely on the specific referred samples of different asphalt grades, which might cause potential errors.

In 2012, Strategic Highway Research Program (SHRP) completed one comprehensive study on field spectroscopy devices used to identify and quantify the construction materials. FTIR is introduced in that SHRP report specifically (SHRP, 2012). They also plotted similar calibration curves, as shown in Figure 2-11. This study verified AASHTO T 302 and confirmed Diefenderfer’s conclusion: the coefficients on these simple linear regression models change with specific binder materials.

Since the sample extracted from field may be aged, the polymers’ signals might be changed after aging. In 2013, one research supported by Swedish Transportation Administration showed that aging does not affect the peak locations of EVA and styrene, but can slightly decrease the butadiene signal at 966 cm^{-1} (Lu et al., 2013). This finding shows that FTIR test might allow for aged samples.

In summary, FTIR spectrometer started to develop in 1957 after its price decreased. The wavelength range in FTIR was ranged from 2.5 µm to 50 µm. In 1990s, numerous studies had interest in developing FTIR to measure the modifier content in modified asphalt. Finally, one relevant standard, T 302-05, was published in 2005 by AASHTO. However, because of the sample preparation requirement, the test currently is still difficult to perform in the field.

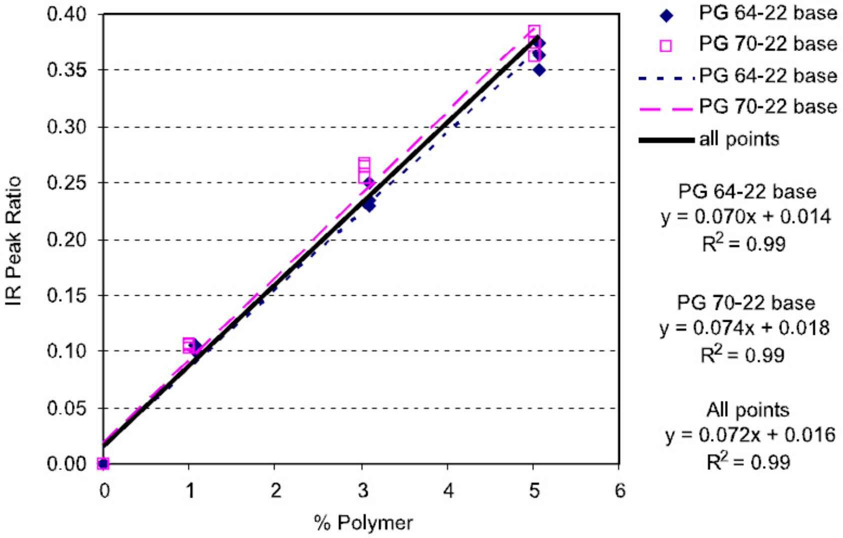


Figure 2-10 Calibration Curves of Polymer Content from FTIR (Diefenderfer, 2006)

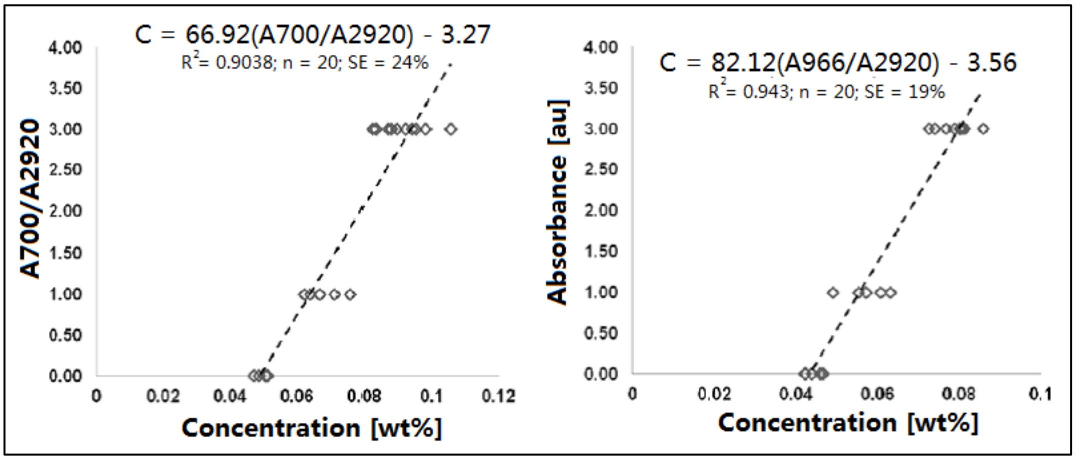


Figure 2-11 Calibration Curves of Polymer Content by SHRP (SHRP, 2012)

2.2.1.3 Details of FTIR Operation in AASHTO T 302-05

Since AASHTO T 302 is the most popular laboratory FTIR test for quantifying modifier contents, this section focuses on the details of this FTIR test. After that, considering some states preferring their own specifications, this section also compares AASHTO T 302 with some other states' revised specifications.

There are two methods of sample preparation in AASHTO T 302-05: solvent-diluted method and attenuated total reflectance (ATR) method. At first, both methods require asphalt binder to be heated and stirred to be homogeneous state (solid asphalt should be at less than 163˚C and emulsified asphalt should be at less than 82±1˚C). Then, for solvent-diluted method, the sample should be processed by the following steps: 1) placed in a glass vial and dried in a vacuum oven; 2) diluted and completely dissolved in the solvent under room temperature; 3) dropped on an infrared window by eyedropper and finally can be applied after complete evaporation of any residual solvent. For ATR method, the sample should be prepared in the following sequence: 1) poured on a piece of releasing paper and spread using a spatula; 2) cooled down and then directly affixed on the surface of the ATR crystal; 3) pressed to push out any bubbles on the interface between crystal and materials. It is worth pointing out that any residual solvent in solvent-diluted method or bubbles in ATR method can mislead final spectra (AASHTO, 2009). Moreover, tetrachloroethylene cannot be used as solvent in FTIR tests, because its absorption band is close to 966 cm^{-1} (Sun & Zhang, 2013).

The spectra can be captured on the window or crystal using solvent-diluted method or ATR method respectively. In these spectra analysis, the polymer modifier (SBR, SB, or SBS) can be identified on the peak at 965 cm^{-1} (A1). For the base asphalt binder, its peak value slightly varies based on specific sample preparation method. Using solvent-diluted method can capture relatively steady peak location at 1375 cm^{-1} (A2). However, since sample thickness can affect the spectrum captured from ATR method, the peak location is not necessarily fixed at 1375 cm^{-1}. After obtaining these peak values, the standard curve of absorbance ratio ($\frac{A1}{A2}$) with its corresponding polymer content percentage can be obtained and further used to quantify the polymer content, as shown in Figure 2-12 (b = 0.02, m = 0.045) (AASHTO, 2009). These peak locations have been verified in many previous studies since 1994 by Michigan Department of Transportation (Wei et al., 1994; Diefenderfer, 2006; Ma and Yuan, 2012; SHRP, 2012).

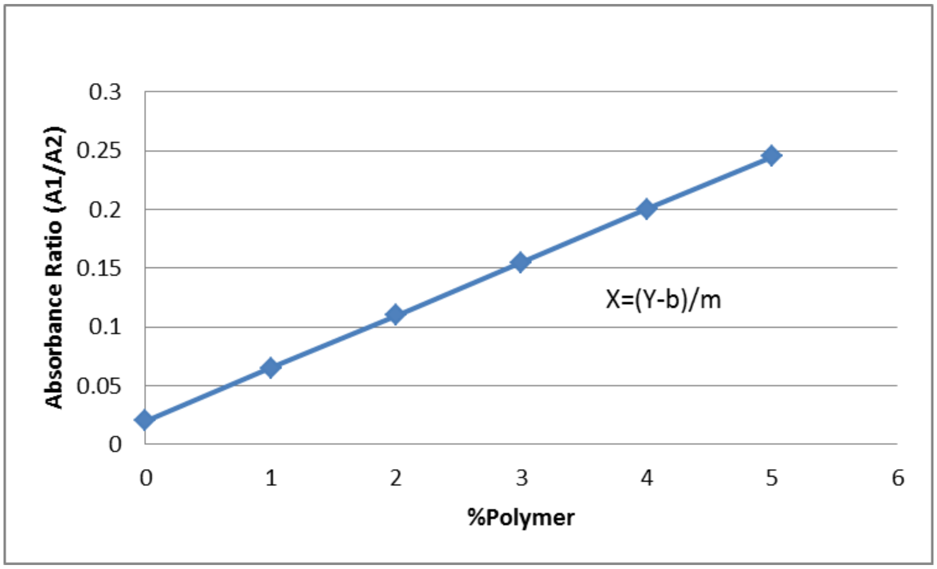


Figure 2-12 Calibration Curve of Polymer Content in AASHTO T 302-05 (AASHTO, 2009)

2.2.1.4 FTIR Test in Other Sources

In ALDOT-408, the polymers are prepared based on two states: liquid and solid. The sample preparation methods for these two states of polymers are both in accordance with the solvent-diluted method in AASHTO T 302-05. The only nuance between these two states is that liquid polymer additionally requests using eyedropper or pipette to add polymer to the binder. Compared to AASHTO T 302-05, there are the following main differences:

- The temperature required to heat asphalt binder until fluid is 182±2˚C in ALDOT-408, which is 19˚C higher than the value in AASHTO T 302-05.
- ALDOT-408 provides more details about FTIR test, such as using cell plate to load mixtures and allowing nitrogen purge system to evacuate residues.

- The binder peak in FTIR is located at 1370 cm^{-1}, which is also slightly different from that in AASHTO T 302-05.

Comparing Tex-533-C and AASHTO T 302-05, test methods and test parameters are almost the same. In Tex-533-C, more details of laboratory apparatus are introduced within test procedures. For ATR method, Tex-533-C requests prisms instead of just "crystal". For solvent-diluted method, Tex-533-C particularly uses salt plate with the infrared spectrophotometer (IR) and terms this method as salt plate method. Tex-533-C also provides the wave numbers of some other types of polymers: ethylene acrylic acid (EAA) peak is at 1700 cm^{-1} and ethylene vinyl acetate (EVA) peak is at 1735 cm^{-1}.

2.2.1.5 FTIR Test Equipment

One popular portable FTIR device is produced by Bruker Optics, as shown in Figure 2-13. The device dimension is 22×30×25 cm with 7 kg weighs. Its analyzed range is from 7500 cm^{-1} to 375 cm^{-1} with 0.01 cm^{-1}accuracy. This device can perform the FTIR test under 18 to 35 ºC temperature. Bruker Optics also provides convenient software for infrared spectroscopy analysis (SHRP, 2012).

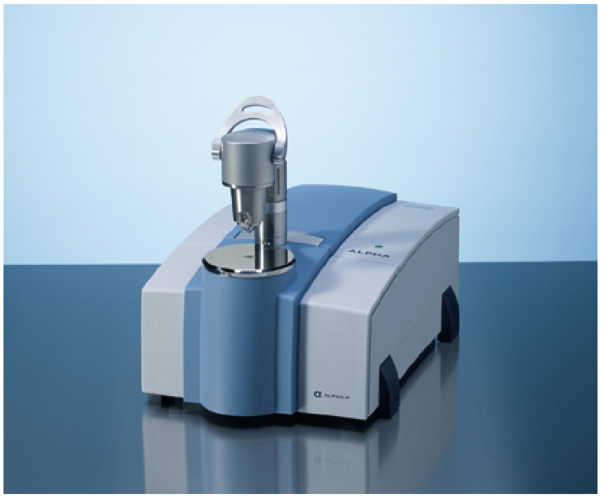


Figure 2-13 ALPHA ATR FTIR Portable Spectrometer

2.2.2 Raman Spectroscopy Test

2.2.2.1 Theory of Raman Spectroscopy Test

The experimental mechanism of Raman Spectroscopy (RS) is similar to FTIR: the molecular bond vibration with a specific frequency can be triggered by the energy from light. In this RS test, researchers use a laser beam to stimulate these different vibration modes and capture an experimental spectrum (intensity vs. frequency) to identify and quantify materials, especially for organic compounds (SHRP, 2012).

2.2.2.2 Background

Raman spectroscopy was named by the Indian scientist Raman.C.V who developed a narrow band photographic filter to generate monochromatic light using sunlight. This discovery also made him to win the Noble Prize in Physics in 1930. In the next few years, this technology was further developed to measure the frequency of molecular vibration (Wikipedia, 2014[c]).

In 1934, Hibben initially applied Raman effect to petroleum chemistry and discussed its present limitation, such as the complexity of examined system and difficulty of distinguishing Raman lines (Hibben, 1934). In his paper, he particularly stated that the Raman and Infrared (IR) spectroscopies might be supplementary, especially in the case of lighter atoms (Hibben, 1934). This Raman-IR supplementary application gradually became the mainstream of Raman application in the asphalt field.

However, up to the present, although Raman spectrum was fully developed and performed on molecular detection in 1990s (Edward et al., 2001; Naylor et al., 1995; Cooper et al., 1995; Cooper et al., 1996; Cooper et al., 1997; Cooper, 1999), still very few Raman spectroscopy tests were specifically performed in the asphalt field, except the Raman-IR supplementary application (Coelho et al., 2006; Wu et al., 2008; Yang et al., 2010). Most Raman spectrum studies concentrated on detecting aromatic structures in geological materials (Giuliani et al., 1996; Michaelian et al., 2001; Jehlicka et al., 2003; Jehlicka et al., 2006; Vandenabeele et al., 2007).

In 1996, Giuliani et al. applied first order Raman spectra to detect C-C vibrations within one of the bitumen bands, which were located at 1590 cm^{-1}. The main purpose for using Raman spectra in his study was to test the graphitic structure in bitumen through calculating the structure degree of structural ordering (Giuliani et al., 1996), based on area ratio on spectrum.

Similar study was conducted in 2003 by Jehlicka et al., with more concentrations on sedimentary and metamorphic rocks, which consist of natural carbonaceous materials (Jehlicka et al., 2003). In 2006, this group successfully observed different molecule components of one complex aromatic mineral using corresponding wavenumber regions on Raman spectroscopy, including 3000 cm^{-1}, 1650-1550 cm^{-1}, 1450-1000 cm^{-1}, 1000-600 cm^{-1}, and 600-150 cm^{-1} (Jehlicka et al., 2006).

In 2001, based on the Raman spectra's ability of sensitivity to aromatic components, Michaelian et al. applied Raman spectroscopy to detect the Syncrude sweet blend (SSB) from Athabasca bitumen. This study suggested that, before calculation of weight fractions, the fluorescence intensities of fractions should be very close, or would cause spectrum distortion (Michaelian et al., 2001).

In 2012, based on one Raman spectrum of SBS produced by SHRP, as shown in Figure 2-14, SHRP stated that Raman spectrum could identify the SBS presence. However, SHRP believed that its suitability for asphalt quantitative analysis should be evaluated in further study (SHRP, 2012).

In summary, Raman spectroscopy was invented before 1930s and developed to measure the frequency of molecular vibration in the next few years. In 1934, Hibben initially applied Raman effect to petroleum chemistry. However, in the next sixty years, this technology in the asphalt field seemed stagnant.

The Raman spectroscopy applications to pavement developed slowly, except the Raman-IR supplementary application. Currently, most Raman spectrum studies concentrated on detecting aromatic structures in geological materials, with using portable Raman spectrometer.

Theoretically, because of RS's similar features with FTIR's, RS should have potential to quantify the binder modifier content through its spectrum analysis.

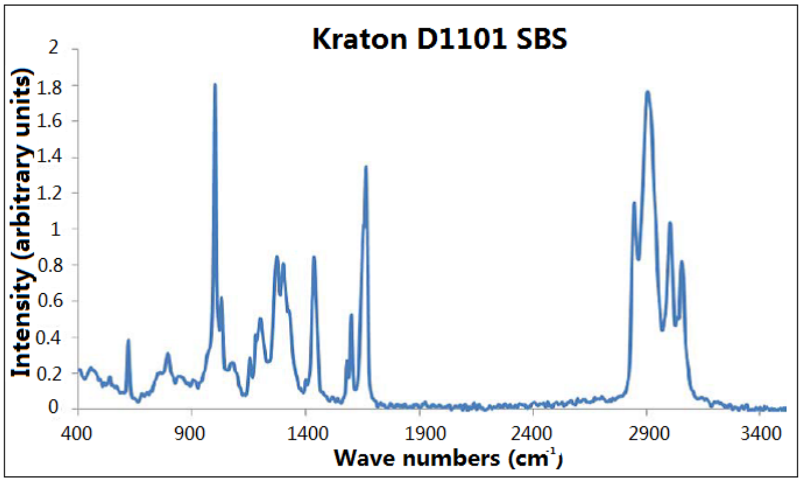


Figure 2-14 Kraton D1101 SBS Corrected Raman Spectrum (SHRP, 2012)

Since FTIR has already been developed to be an AASHTO standard on asphalt modifier quantification, understanding the difference between Raman spectrum and FTIR spectrum seems very necessary to develop Raman spectrum to be one similar standard in the future. Their main differences are summarized below:

- If the dipole moment is changed, the vibration should be IR-active; if the polarizability is changed, the vibration should be Raman-active. In other words, the symmetry of molecule might not be observed by IR spectrometer (Ferraro, 2003).
- The origins of IR and Raman spectra are different: "IR spectra originate in photons in the infrared region that are absorbed by transitions between two vibration levels of the molecule in the electronic ground state."; Raman spectra originate in the electronic polarization activated by ultraviolet, visible, and near-IR light (Nakamoto, 2009).
- Water can be used as solvent in Raman, but not in IR (Zhang & Cue, 2012).
- Raman requires little or even no sample preparation, which can be performed in any states. However, IR needs sample preparation (Socrates, 2004).

The above comparison between IR and Raman also shows what potential the Raman spectrometer has in the study of modified asphalts.

2.2.2.3 Details of Raman Spectrometer Operation

Considering the Raman spectrometer requires no sample preparation, and because of very few examples of Raman spectrometer application in modified asphalt detection, this section introduces one popular Raman spectrometer: Real-time analyzers' (RTA) portable Raman analyzer, as shown in Figure 2-15. This device is an advanced portable apparatus to capture the whole Raman spectrum from 3350 cm^{-1} to 150 cm^{-1}. The product's specification states that this device can analyze all solid or liquid within only around 10 sec, under 2 to 37 ºC. Moreover, this device eliminates the process of sample preparation, calibration and recalibration (SHRP, 2012).

Figure 2-15 RTA's Portable Raman Analyzer

2.2.3 Gel Permeation Chromatography (GPC)

2.2.3.1 Theory of GPC

The basic fractionation methods, which rely on solubility or absorptivity, cannot separate the asphaltic compounds because of their complex nature (Altgelt, 1965). This separation issue can be solved by GPC, since Gel can filter these asphaltic compounds through a column of highly cross-linked polystyrene gel based on its permeability. Specifically, large size molecules first pass through the interstitial volume of the column, and then small size molecules enter the gel to be size-separated (Maley, 1965). Thus, this separation procedure is also termed as gel filtration (Altgelt, 1965).

Because the modifier binder molecules are significantly larger than the asphalt molecules, the molecule size can be used to quantify polymer content mixed in asphalt (Wei et al., 1994). Since the molecular size can affect light permeation through absorbing light, GPC test gives researchers a pathway to measure the molecular size using water GPC apparatus for chromatography analysis.

Specifically, this test requests an ultraviolet (UV) device or evaporative light-scattering detector (ELSDs) to capture the various light absorptions, which are caused by adding elution reagent THF under 35ºC. The light absorption, which is exhibited as light intensities on chromatographic column, is changed with elution time. Then, the device can separately identify each compound based on these observed chromatographic columns with elution time (SHRP, 2012; Lee et al., 2008). Normally, the chromatogram profiles (intensity vs. elution time) of asphalt binder constituents can be identified into three significant different size levels: large, medium, and small (Wei et al., 1994). Typically, SBS belongs to the large material size, which is the first small part at earliest elution time in chromatography.

2.2.3.2 Background of GPC

GPC has a very long history since 1964, introduced by John Moore for initially capturing the molecular weight distribution of high polymers. He developed proper polystyrene gels to make molecular size fractionations within a wide range (Moore, 1964).

In 1965, for the first time, Altgelt applied GPC to asphaltenes, and found that the molecular weight distribution of the asphaltenes was very wide, from 700 g/mol to 4,000 g/mol, up to 40,000 g/mol (Altgelt, 1965). However, he felt GPC was not ideal process, because of the disturbances from interactions between gel, solute, and solvent. In the same year, Maley tested more types of polymers (polyethylene, polystyrene, polycarbonates, polypropylene, polybutylenes), asphalts, waxes, and resins, with different solvents (chlorinated hydrocarbons, carbon tetrachloride, toluene, benzene, ketones, etc.) using GPC. He also introduced the details of GPC test procedures, apparatus, operation temperature (less than 150°C), and suitable flow rate (1cc/min) (Maley, 1965). He also summarized the advantage and disadvantage of his original GPC test as follows:

- Advantage: (1) sample size can be small; (2) operation time is “rapidity”, around 1 hr per column system; (3) temperature and solvent are flexible; (4) test is reproducible (Maley, 1965).
- Limitation: (1) sample is limited by the column size; (2) operation temperature should be less than 150°C; (3) vacuum is required in the system (Maley, 1965).

In 1966, Moore and Hendrickson tested the relationship between molecular shape and elution, and found that the elution volume is a logarithmic function of the chain length of polymer molecule (Moore & Hendrickson, 1966). Based on this logarithmic function, Moore with two other researchers, Knight and Tung, developed the calculation function of molecular weight distribution from GPC by experiments (Moore et al., 1966). Meanwhile, one computer program for determination of molecular weight distribution from GPC was developed by the Chevron Research Company in California. This computer program successfully obtained the molecular weight curve from the raw data (elution volume and polymer concentration) from GPC test (Pickett et al., 1966).

In 1967, one research group from France initially introduced the “hydrodynamic volume” as the calibration parameter in GPC. Based on the Einstein viscosity law, they stated that GPC results should be contributed by the combination of molecular weight and viscosity (Grubsic et al., 1967). They collected the experimental data and plotted the calibration curve with these data, as shown in Figure 2-16. Since all experimental points fell on their calibration curve, Figure 2-16 confirmed that the retention in the chromatographic column was caused by viscosity (Grubsic et al., 1967). Thus, their GPC calibration should be universal for any polymer (Grubsic et al., 1967). As an improvement of this method, in 1970, Goedhart and Opschoor installed a capillary tube viscometer under the siphon of the GPC apparatus to directly measure each fraction’s viscosity (Goedhart and Opschoor, 1970).

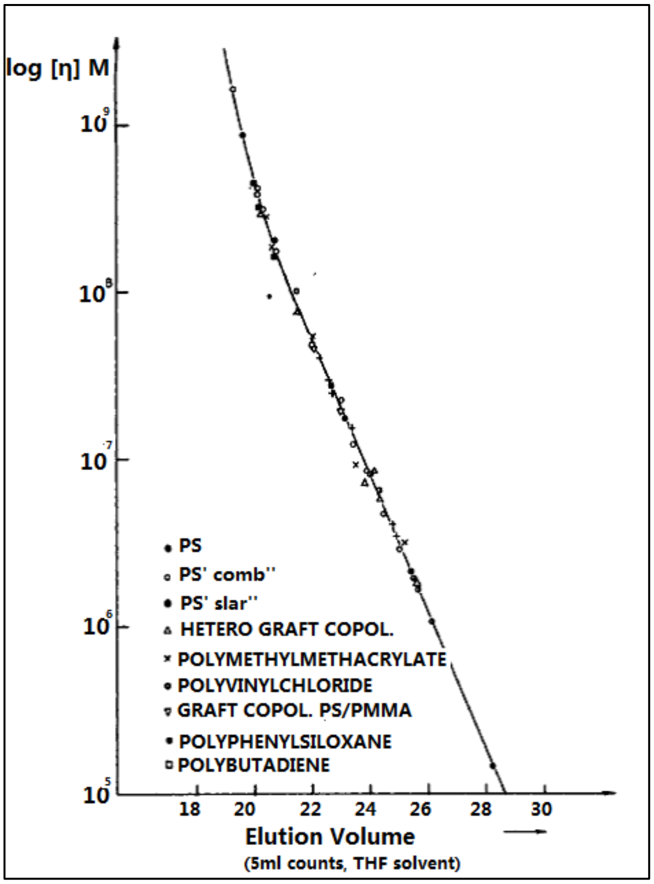


Figure 2-16 Elution Volume vs. Combination of Molecular Weight and Viscosity (Grubsic et al., 1967)

In 1974, for the calibration curve of "molecular weight" against "peak elution count" without considering viscosity, since the calibration curve of high molecular weight sample was nonlinear, the upper limitation of molecular weight (within linear part) in GPC was tested by Slagowski et al. They suggested that "the polystyrenes of molecular weight greater than 10^7 g/mol degrade under normal conditions" (Slagowski et al., 1974).

In 1991, one comprehensive literature review of "HP-GPC and Asphalt Characterization" was supported by the SHRP and conducted by University of California, Berkeley (Yapp et al., 1991). The main purpose of this report focused on the HP-GPC application for asphalt characterization and field performance. All the articles not related to field performance were not covered in their literature review.

In 1990s, many studies turned to focus on using HP-GPC to directly test asphalt characteristics, since many researchers realized that the asphalt property related to molecular sizes and molecular size distribution can be observed by HP-GPC. Most of them applied statistical analysis of physical test results with chromatograms. These articles were reviewed by McCann et al. in 2011. Since the purposes of these researches were not related to modifier quantification, this literature review does not cover the details of these literatures.

In 1993, Jennings et al. explored HP-GPC to study asphalt composition and their intermolecular interaction. Based on the observation of HP-GPC, they successfully classified these samples into four broad groups with different characteristics and observed their asphalt's properties (strength and elasticity). They also classified the molecules into three size levels based on the order of elution: large molecular size (LMS), medium molecular size (MMS), and small molecular size (SMS) (Jennings et al., 1993b).

In the same year, Kim and Burati conducted GPC to characterize aged asphalt cements (Kim & Burati, 1993). In the following years, this research group focused on the GPC application on asphalt property estimation: in 2006, they also estimated RAP's binder viscosity through GPC in 2006 (Kim et al., 2006); in 2008, they performed GPC to seek short-term aging characterization of asphalt binders with Superpave binder tests (Lee et al., 2008); in 2010, they tested the interaction effects of crumb rubber modified asphalt binder using GPC (Jeong et al., 2010).

Since 1995, many studies noticed that HP-GPC application to asphalt modified with crumb rubber tire (CRT) was disturbed by rubber's interaction with asphalt: when rubber swelled in the asphalt cement, a viscous gel was formed. This viscous gel could reduce the inter-particle distance between rubber particles and increase viscosity (Leite and Soares, 2007).

In 1997, Isacsson and Lu from Royal Institute of Technology studied the compatibility and storage stability of modified bitumens with SBS using GPC. Their study successfully identified the linear and branched SBS polymers by molecular weight (Isacsson & Lu, 1997).

In 1999, one research group from Saudi Arabia predicted asphalt rheological properties using HP-GPC. The samples in this study included 5, 10, and 15% crumb rubber (CR) and 3, 6, and 9% SBS. They conducted typical rheological tests and HP-GPC, respectively. Then, they built regression models of rheological properties using fractions from HP-GPC as independent variables. The statistically significant results showed that the prediction of asphalt rheological properties by HP-GPC was successful. They confirmed that HP-GPC could detect aging effect on the molecular size distribution of the asphalts (Wahhab et al., 1999).

In 2011, McCann et al. stated that GPC could detect the polymer presence in an asphalt binder because of the disparity in the molecular weight between polymer and asphalt binder. This study plotted several GPC results for eight different asphalt binders, which clearly captured modifier components.

In 2012, with much more precise apparatus, SHRP stated that there was an earlier SBS peak at elution time than that in asphalt binder. Based on a normalized chromatogram, SHRP also found that the ratios of SBS peak areas versus base binder peak areas have linear relationship with specific SBS content (SHRP, 2012), as shown in Figure 2-17 and Figure 2-18.

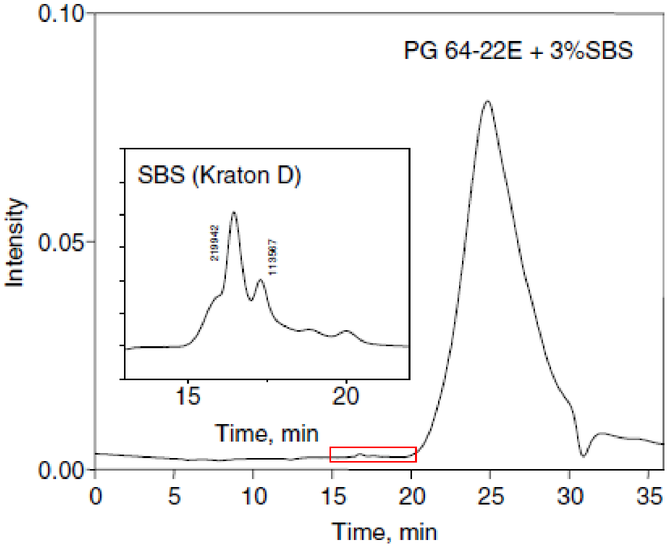


Figure 2-17 GPC Chromatogram of PG 64-22 Binder with 3% SBS (SHRP, 2012)

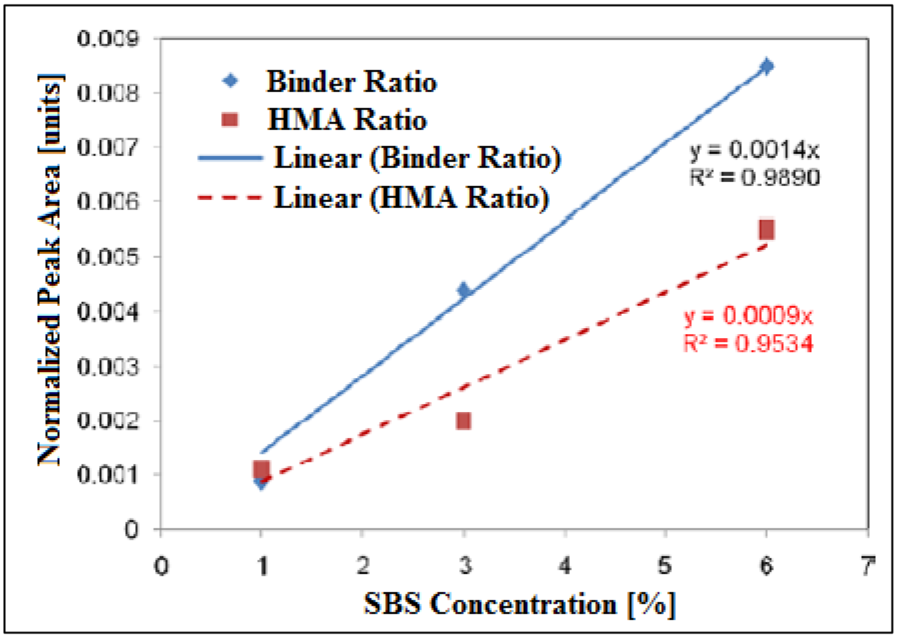


Figure 2-18 SBS Concentration vs. GPC Peak Area (SHRP, 2012)

In 2013, Louisiana materials laboratory developed a formal procedure of GPC to measure the percentage amounts of polymer modifiers. As a result, “an AASHTO standard test method for the quantification of polymer content in polymer modifier asphalt cements by GPC has been proposed” (Negulescu & Balamurugan, 2013).

Based on the above literatures, it is safe to say that GPC has a very long history since 1964, with a comprehensively developed theory. The entire mainstream of GPC development in the past fifty years might be divided into two stages.

The first stage was in the 1960s. GPC operation focused on capturing the molecular size distribution of high polymers, and later, with asphalt mixed. The main efforts focused on the elution selection, calibration method, and the effects of asphalt's viscosity property on GPC.

The second stage began in the 1990s, after the GPC technique and software were fully developed. After GPC could accurately capture the molecular size distribution of modified asphalts, with better understanding of the GPC calibration curves, researchers started to conduct GPC to capture asphalt behavior and pavement performance. GPC allowed researchers to directly study asphalt binders based on their molecular composition.

For the quantification of modifier content in asphalt binder, GPC could be a good approach, which actually has already been developed by Louisiana DOT in 2013. However, since this GPC standard in AASHTO has not been practically used in most DOTs, developing the details of GPC for modifier quantification is still necessary.

2.2.3.3 Details of GPC Operation

Since the GPC performed by Louisiana material laboratory has been proposed as one AASHTO standard test method, this section introduces the details of GPC operation mainly based on that report. Moreover, the information of GPC operation from other previous studies is also referred to for comparison.

Based on the proposed AASHTO standard test from Louisiana Department of Transportation and Development (LaDOTD), the required instruments of GPC system include the following parts: (1) a solvent reservoir to contain solvent; (2) a pumping system to provide constant flow rate solvent; (3) a sample injector which can control the sample quantity; (4) columns of required pore size; (5) detectors to measure the concentration of the molecules in the stream, including DRI detector and UV detector; and (6) a data processing system. The proposed AASHTO standard test suggests one advanced GPC system: EcoSEC high performance GPC system (HLC-8320GPC), which assembles all above required instruments, as shown in Figure 2-19 (Negulescu & Balamurugan, 2013). For GPC system selection, SHRP recommended in 2012 another GPC system called water GPC system, consisting of a PL-ELS100 ELSD and a Water 2487 dual wavelength absorbance UV(SHRP, 2012), as shown in Figure 2-20.

The proposed AASHTO standard test from LaDOTD prefers two reagents in GPC operation: tetrahydrofuran (THF) HPLC grade solvent and butylated hydroxytoluene (BHT) peroxide inhibitor. Specifically, BHT is used to prevent THF from forming peroxide in air.

Figure 2-19 EcoSEC High Performance GPC System (HLC-8320GPC) from LaDOTD Materials Laboratory (Negulescu & Balamurugan, 2013)

Figure 2-20 Water GPC System (SHRP, 2012)

Before GPC operation, asphalt sample should be dissolved in either 1% or 0.25% THF concentration. The 1% or 0.25% solution preparation includes following steps: 1) weight 100 mg asphalt (for 1% solution) or 25 mg asphalt (for 0.25% solution) into a 10 mL volumetric flask or a 20 mL scintillation vial; 2) add THF to 10 mL using burette, if vial is used; 3) keep overnight for the complete dissolution; 4) mix the contents again before filtration (Negulescu & Balamurugan, 2013).

For the solution filtration, there are three steps: 1) remove the plunger of the syringe and use pipette to add 2.3 mL of asphalt solution into the syringe; 2) plug the plunger back to the open syringe, and insert the filter outlet into an auto sampler vial; 3) push the plunger to collect the filtered solution in the vial (Negulescu & Balamurugan, 2013).

The proposed AASHTO standard test from LaDOTD specifically introduces the main procedures of using GPC system (HLC-8320GPC), which seems very convenient: the only things researchers should do is to press the power button, click on warm up screen, and click the instrument parameter from the operating menu with desired analysis parameters. The specific parameter settings recommended by LaDOTD are summarized in Table 2-1. After that, HLC-8320GPC can start to analyze the sample and only takes less than 60 minutes to complete (Negulescu & Balamurugan, 2013).

Table 2-1 Parameter Settings on HLC-8320 GPC System (Negulescu & Balamurugan, 2013)

Setting item	Desired parameter for GPC analysis
Solvent flow rate	0.35 mL/min
Reference flow ratio	equal
Column and pump oven temperature	40°C
RI detector	
Balance value	30,000 mV
Response	0.5 sec
UV detector	
Wavelength	254 nm
Balance value	30,000 nm
Response	0.5 sec

However, since the elution times and the chromatogram profiles are varied by many external factors, such as column packing, column length, and flow rate, the analysis parameter settings from other previous studies should also be discussed and considered. Thus, this study collected all relevant information from previous studies in Table 2-2. Based on Table 2-2, the range of each parameter setting can be concluded: 1) most materials of columns are styragel related; 2) flow rate is slightly varied from 0.9-2 mL/min; 3) most studies selected 24°C or 25°C as test temperature, which is promising to develop field GPC operation; 4) column sizes had a broad range from 100Å to 10000Å; 5) most sample concentrations are less than 1%.

One example of final chromatograms plotted by HLC-8320GPC is shown in Figure 2-21, in which y-axis is the RI response/relative amount and x-axis is the molecular weight or elution time. Polymers, asphaltenes, and maltenes can be clearly identified based on the molecular weight or elution time. Quantitative data can be calculated by the area under the curve using the instrument software (Negulescu & Balamurugan, 2013).

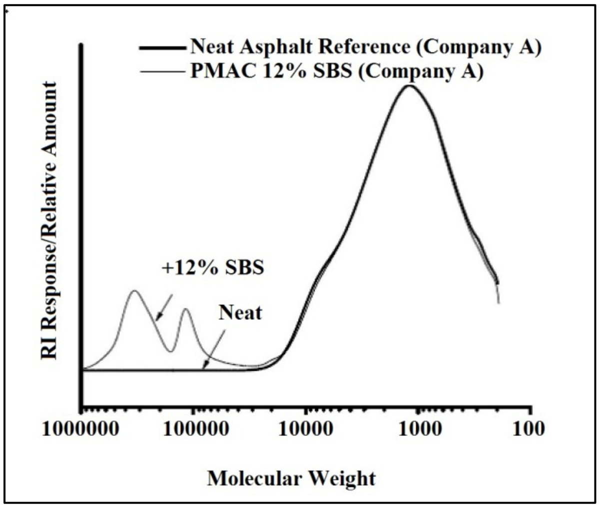


Figure 2-21 Superimposed GPC Traces of Neat Asphalt and of Its Derived PMAC (Negulescu and Balamurugan, 2013)

Table 2-2 Summary of Parameter Settings in Previous Studies

Researchers	Moore	Chollar et al.	Jennings et al.	Garrick & Wood	Kim & Burati
Year	1964	1985	1985	1986	1993
Column material	N/A	Styragel	Ultrastyragel	Styragel	Ultra-styragel
Sample Concentration	N/A	0.02	0.005	0.01	0.0025
Column size	N/A	3×500Å, 1,000Å, 100Å	2×500Å, 1,000Å	1,000Å, 3×500Å, 100,000Å, 1,000,000Å	2 × 500Å, 1,000Å
Solvent	N/A	THF	THF	THF	THF
Flow rate	1 mL/min	2 mL/min	0.9 mL/min	2 mL/min	1 mL/min
Temperature	N/A	25°C	25°C	25°C	25°C
Researchers	Jennings et al.	Isacsson & Lu	Wahhab et al.	McCann et al.	
Year	1993	1997	1999	2011	
Column material	Styrene-divinylbenzene	Ultrastyragel	Microstyragel	Phenogel	
Sample Concentration	0.1%, 0.3%, 0.5%, 0.7%	0.003	0.05	0.2% and 7%	
Column size	N/A	100Å, 3×500Å, 1,000Å, 10,000Å	10,000Å, 1,000Å, 500Å, 100Å	200 ~ 600,000 Daltons	
Solvent	THF	THF	THF	Isocratic solvent system	
Flow rate	0.9 mL/min	N/A	1 mL/min	1 mL/min	
Temperature	24°C	N/A	24°C	40°C	

2.2.4 Thermo-Gravimetric Analysis (TGA)

2.2.4.1 Theory of TGA

When temperature or time changes, because of the occurrence of decomposition, oxidation, or even volatility, the mass of specimen could lose or gain. Based on recording mass change within temperature domain, the components of some special materials can be studied and determined. This method is especially useful for polymeric material study (Wikipedia, 2013[d]).

2.2.4.2 Background

The first detailed introduction of the thermo-gravimetric analysis dates back to 1953 by Duval in the inorganic field (Duval, 1953). In 1961, Doyle initially applied TGA to estimate thermal stability of experimental polymers, and stated that TGA could be used to consistently compare polymers' chemical nature and decomposition mechanism. He also obtained the "integral procedural decomposition temperatures" of some polymers, such as polystyrene and silicone resin (Doyle, 1961[a]).

Considering that TGA could measure the change of residual weight fractions with temperature increasing, in the same year, Doyle derived one approximate equation of thermogram based on TGA's kinetic analysis ((Doyle, 1961[b]). In the next ten years, most TGA studies concentrated on exploring the equations to fit TGA experimental curves (weight loss vs. temperature) (Horowitz & Metzger, 1963; Broido, 1969). However, very few TGA studies were developed from polymer field to asphalt field from 1970s to 1990s, although TGA seems better than DSC for decomposition behavior determination (Wikipedia, 2014[d]).

In 2000s, numerous studies started to use TGA to investigate modified asphalts' thermal properties. However, most of them conducted TGA accompanying with other tests, such as FTIR and DSC (Picchioni et al., 2003; Zhang et al., 2008; Zhang et al., 2009; Yanan & Lan, 2011; Firoozifar et al., 2011; Ghavibazoo et al., 2013).

In 2007, Ahmedzade et al. performed TGA to capture the initial decomposition temperatures of three materials: AC-10, tall oil pitch (TOP), and SBS, as shown in Figure 2-22. Based on Figure 2-22, it is safe to say that SBS could be clearly detected from asphalt based on the decomposition temperature (Ahmedzade et al., 2007).

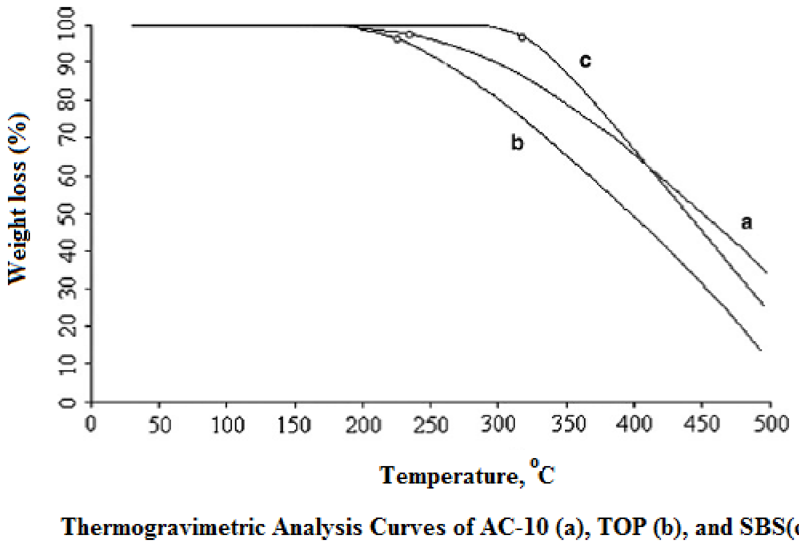


Figure 2-22 Thermo-gravimetric Analysis Curves of AC-10 (a), TOP (b), and SBS (c) (Ahmedzade et al., 2007)

In 2010, Xu and Huang combined FTIR and TGA techniques to study the combustion process of asphalt binder. Based on their FTIR-TGA method, they successfully divided the asphalt combustion process into three stages. They found that the main mass loss occurred in the 2nd stage, within temperature range from 405 to 490°C. The chemical reaction, such as thermal oxidative degradation, also could be observed very clearly from the TG-DTG curve, as shown in Figure 2-23 (note: FTIR measurements were performed with a DTGS detector) (Xu & Huang, 2010).

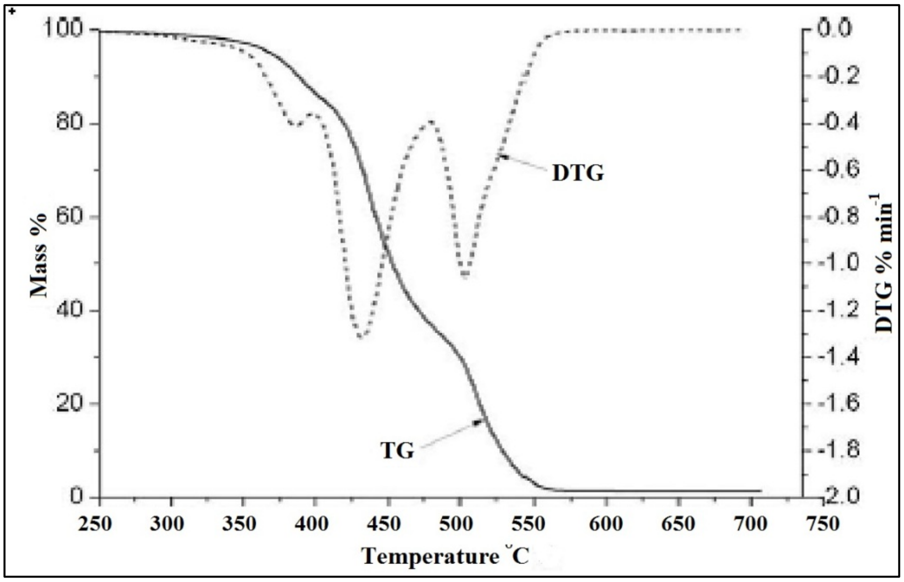


Figure 2-23 TG-DTG Curves of Asphalt Binder Combustion (Xu & Huang, 2010)

In 2013, Ghavibazoo et al. introduced an advanced TGA method: stepwise isothermal thermogravimetric (SITG) analysis. Through a programmed heating process, this advanced TGA technique could “prevent overlapping between decomposition temperature of different constitutes. (Ghavibazoo et al., 2013)” Thus, SITG probably could be developed to quantify the modifiers in asphalt binders.

Currently, most studies, which performed TGA to investigate modified asphalts’ thermal properties, were accompanied with other tests, such as FTIR and DSC. In other words, there was no independent TGA study directly related to modified asphalt quantification. However, considering the different decomposition temperatures between polymer and asphalt and the development of SITG technique, TGA still probably could be improved to quantify the modified asphalt in the future.

2.2.4.3 Details of TGA Operation

TGA test could be conducted very easily using TGA apparatus in a nitrogen environment: just place the testing samples in the TGA device and set the heating rate. When the temperature is increased, the percent of material loss (weight) can be measured and recorded by TGA device. Table 2-3 summarizes the TGA testing parameters from previous studies, with different thermo-balances.

Table 2-3 TGA Apparatus and Heating Rate Selection

Source	Apparatus	Heating rate
2003, Picchioni et al.	Mettler TC11 & Mettler M3	10ºC/min
2007, Ahmedzade et al.	TGA-50	10ºC/min
2008, Zhang et al.	TGA-APY-2P	40ºC/min
2011, Yanan et al.	PL-1500 TGA	10ºC/min
2012, Willis et al.	Perkin-Elmer TGA	10ºC/min
2013, Ghavibazoo et al.	Q500 TGA	20ºC/min

2.2.5 Differential Scanning Calorimetry (DSC)

2.2.5.1 Theory of DSC

DSC test is in the field of thermal analysis. Traditionally, DSC was performed to measure glass transition temperatures of asphalts (Wei et al., 1994). However, if adding polymers to asphalt, the range of blend's glass transition temperature oscillates between those of polymers and asphalts (Wei et al., 1994). Based on this phenomenon, researchers can use DSC test to capture the effect of polymer additive on the nature of transition. This potential effect might be referred to as quantitative analysis of the polymer presence. Moreover, many other thermal parameters, such as heat capacity, melting point, temperature of phase change, can be captured in DSC test and used to compare with known reference materials to determine material composition.

2.2.5.2 Background

Although DSC technique had already been developed in 1962 by Watson and O'Neill (Wikipedia, 2014[e]), the first application of DSC on asphalts was started by Noel and Corbett in 1970 for asphalts' thermal features (Noel and Corbett, 1970). In 1978, Huynh et al. studied the effect of molecular weight and composition on the asphalt's glass transition temperature using DSC, and found that the composition rather than molecular weight could affect asphalts' glass transition temperatures (Tg) (Huynh et al., 1978).

In 1985, Claudy et al. from France stated that DSC could evaluate the crystallized fractions in asphalt, and they further confirmed this theory through successfully quantifying the crystallization extent of the paving asphalt fractions in 1991 (Claudy et al., 1991). In the next year, this group achieved one breakthrough: they found that the molecular agglomerations of bitumens were at least partially caused by time-dependent shrinkage (Claudy et al., 1992). In other words, although the temperatures and other external factors were fixed, physical hardening in asphalt still would occur over time. This finding elevated the importance of thermal history to asphalt rheological behavior and made a large challenge for sample preparation on further experimental analysis: the thermal history of all samples should remain the same, or the comparison results would be oscillated and inaccurate. Considering this time-dependent feature of asphalt, one study conducted by Soenen et al. in 2006 demonstrated that the sample preparation and handling is important for the results of testing rheological properties of binders (Soenen et al., 2006).

As DSC became popular to measure the crystallized fractions and Tg of asphalts since 1990s, numerous studies turned to focus on the thermal properties of modified asphalts using DSC. In 1996, Adedeji et al. initially plotted the DSC thermographs of neat asphalt, neat SBS, and blends of asphalt and SBS with various proportions. Their results were shown in Figure 2-24, which illustrated that the contents of SBS could affect the heat flow in SBS modified asphalt. Although the purpose of this study was not to quantify the SBS content in modified asphalt, Figure 2-24 showed that DSC might be a potential method for SBS modifier quantification. The results were confirmed in similar studies conducted in the next few years (Saroop and Mathur, 1997; Canavate et al., 2000; Kamiya et al., 2001; Lepe et al., 2005; Navarro et al., 2005). The results from these previous studies are illustrated in Figure 2-25 and Figure 2-26. The curves in Figure 2-24 through Figure 2-26 show that the DSC thermographs vary with different contents of modifiers.

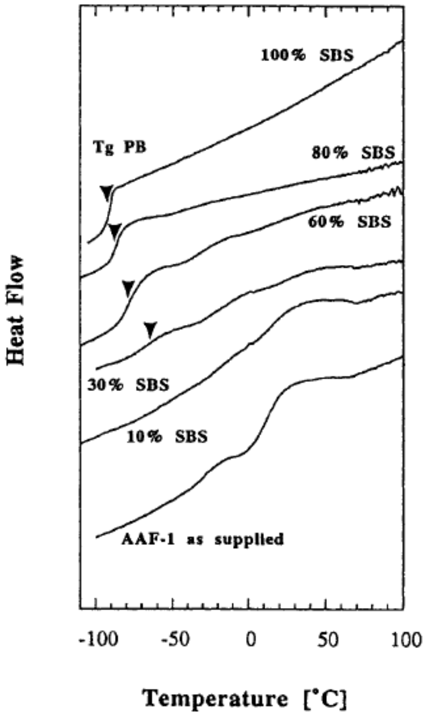


Figure 2-24 DSC Thermographs of Neat Asphalt, Neat SBS, and Asphalt / SBS Blends (Adedeji et al., 1996)

For the identification of modifier in asphalt binder, one typical study was conducted by Lucena et al. in 2004. They plotted a phase transition on SBS modifier using DSC and stated the glass transition temperature was around -30 ºC, as shown in Figure 2-27. They also practically quantified the crystallized fraction proportion based on the following equation:

$$\%F_c = \left(\Delta H_{obs} \times 100\right) / 200$$

where ΔH_{obs} is the observation value of enthalpy with paraffin dissolution in specimens.

In the 2000s, one advanced DSC method became popular in the field of analyzing modified asphalts: modulated differential scanning calorimetry (MDSC) (Gonzalez et al., 2002; Masson et al., 2002; Masson et al., 2005; Navarro et al., 2005; Sureshkumar et al., 2010). The function of MDSC was to deconvolute the original DSC signals from amorphous and ordered phases (Masson et al., 2005). Specifically, there were overlapping Tgs existing in SBS-bitumen blends observed from original DSC. Compared to DSC, based on converting to the specific heat capacity (cp) and its derivative (dcp/dT), MDSC could generate reversing and non-reversing heat flows to highlight the real Tg (Masson et al., 2002), as shown in Figure 2-28. This MDSC method was clearly described by Masson et al. in 2005 and was successfully used to define the composition of the phases in SBS-bitumen blends (Masson et al., 2005).

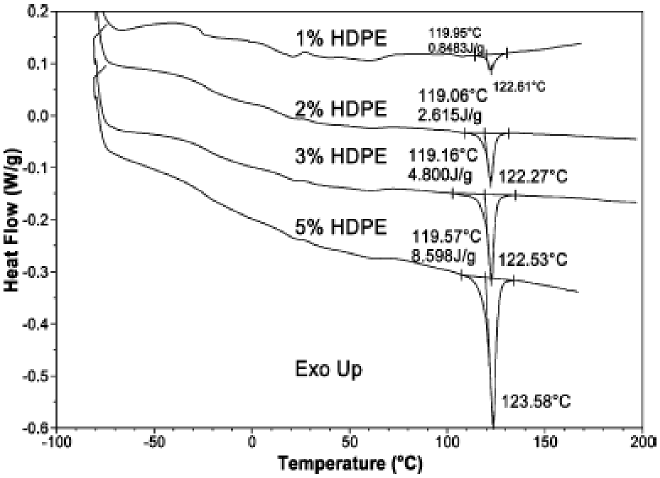


Figure 2-25 Differential Scanning Calorimetry (DSC) Thermograms of Different HDPE-modified Bitumens (Lepe et al., 2005)

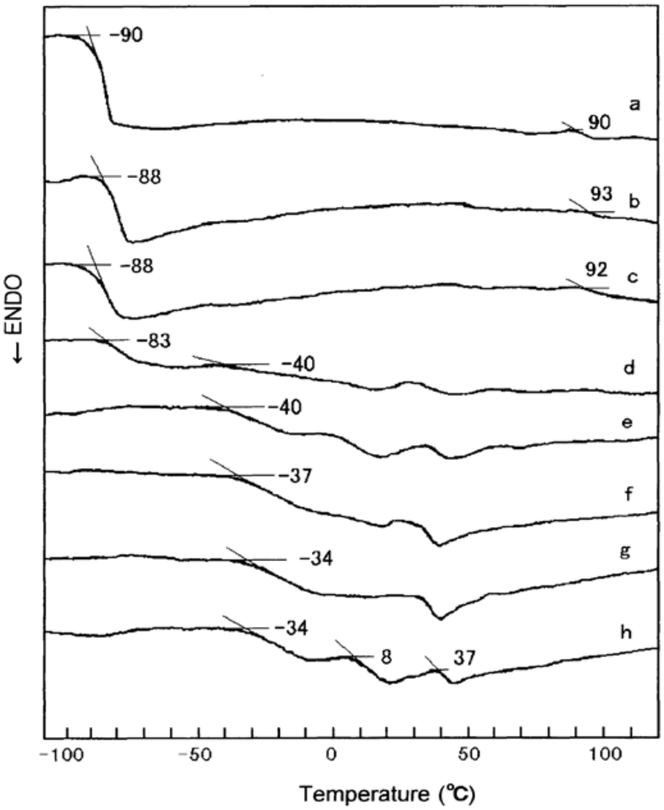


Figure 2-26 DSC Curves of Mixtures of SBS and Asphalt at Heating Rate of 10°C per minute (Kamiya et al., 2001)

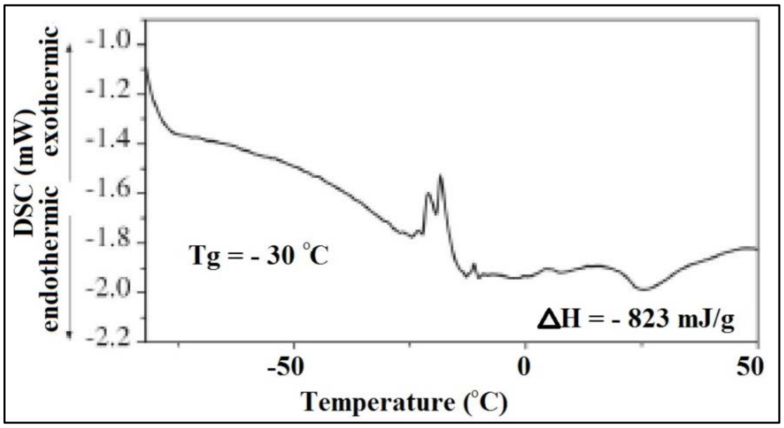


Figure 2-27 DSC Curve of CAPFLEX in an Inert Atmosphere (Lucena et al., 2004)

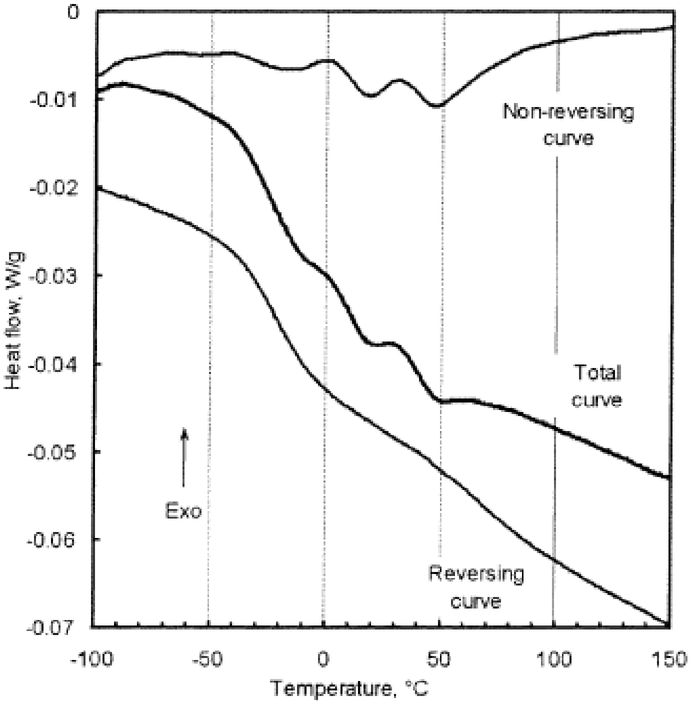


Figure 2-28 Total, Reversing, and Non-Reversing Heat-flow Curves for Bitumen (Masson et al., 2002)

Although DSC technique was introduced in 1960s, its application to asphalts was not fully developed until 1980s, as a tool to measure the crystallized fractions and transition temperature.

Accompanying with the popular application of modified asphalt, since 1990s, many studies turned attention to the thermal properties of modified asphalt binders using DSC. The results from previous studies could firmly show that DSC had utility to identify the modifier presence in asphalt binder. However, there is still no DSC-related study particularly concentrating on the quantification of modifier contents, but only for the crystallized fractions.

Based on the reviewed steps of DSC development, the obstacles of using DSC to quantify the modifier contents in asphalt binder could be summarized as follows:

- Strict sample preparation: DSC curves are time-dependent, which could be varied by different preparation and operation times.
- Unclear transition temperature: the Tgs of fractions in polymer and binder compounds overlap in DSC and could not be separated easily.
- Broad range of temperature: most DSC tests request the test temperature from -100ºC to 100ºC, which might not be convenient for field application.

Nevertheless, considering the high correlation between thermal properties of modifiers and their contents, if the above three obstacles could be overcome, DSC still has the potential for modifier quantification in asphalt binders.

2.2.5.3 Details of DSC Operation

There is no standard DSC test for the quantification of asphalt modifier content. Since most DSC tests were performed simply using different apparatus, this section summarizes the specific test parameters used in previous DSC applications, as shown in Table 2-4.

Table 2-4 DSC Apparatus with Different Test Parameters Used in Previous Studies

Source	DSC apparatus	Temperature range	Cooling rate	Heating rate
1992, Claudy et al.	Mettler TA 2000B	-100 - 100ºC	N/A	5ºC /min
1995, Daly et al.	SEIKO DSC 220C	-130 - 150ºC	5ºC /min	20ºC /min
1996, Adedeji et al.	Perkin-Elmer DSC 7	-170 - 150/200ºC	N/A	40ºC /min
2000, Canvate et al.	Mettler DSC 30	-120 - 100ºC	N/A	10ºC /min
2001, Kamiya et al.	Mac Science DSC3100	-110 - 120ºC	N/A	10ºC /min
2004, Lucena et al.	Shimadzu DSC-50	-80 - 200ºC	N/A	10ºC /min
2004, Silva et al.	TA 2010	from -100ºC	N/A	5ºC /min
2005, Abreu et al.	TA 2010	up to 200ºC	N/A	10ºC /min
2010, Sureshkumar et al.	DSC Q100	-120 - 150ºC	10ºC /min	4ºC /min
2010, Yeh et al.	PerkinElmer Pyris Diamond DSC	-55 - 200ºC	N/A	10ºC /min

Table 2-4 shows that most samples in DSC tests are heated from -125±45ºC to 150±50ºC. The high deviation of these test temperature ranges might be caused by different study samples or study purposes. For the heating rate selection, although thermal history of asphalt could affect DSC calibration, these previous studies did not use one unified heating rate, which might make these studies inconsistent. Table 2-4 also exhibits various DSC apparatus from 1992 to 2010: almost no study used the same DSC apparatus for the research of modified asphalt.

2.2.6 Nuclear Magnetic Resonance (NMR)

2.2.6.1 Theory of NMR

NMR test measures the difference between resonance frequencies of nucleus and a base, which is termed as the nucleus "chemical shift". Since each nucleus has its unique resonance frequency, this chemical shift can be adopted to identify the specific chemical elements (SHRP, 2012), using different NMR spectra, such as ^{1}H and ^{13}C. Thus, all chemical structures can be identified based on NMR spectra, as shown in Figure 2-29.

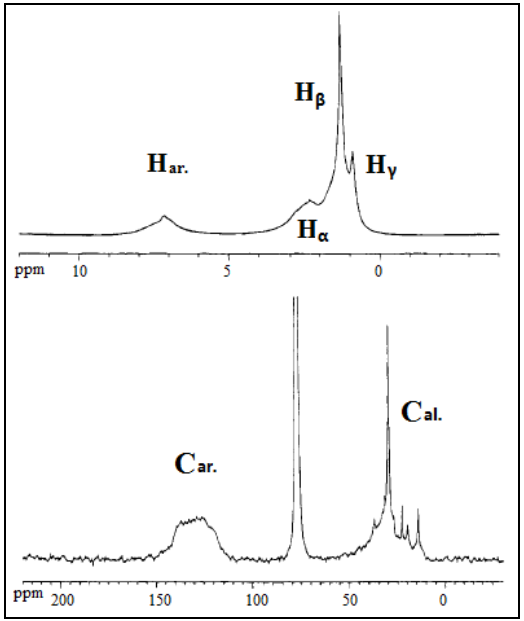


Figure 2-29 Typical ^{1}H (top) and ^{13}C (bottom) NMR Spectra of Asphaltenes for Which the Different Integration Domains are Shown (Calemma et al., 1995)

For clearly interpreting the meaning of NMR spectra, Figure 2-30 exhibits one example of NMR peaks and their corresponding meanings: both peaks at 2.1 ppm and 5.4 ppm in this NMR spectrum represent butadiene components, and one peak at 1.4 ppm shows terminal methyl of styrene (SHRP, 2012). Figure 2-30 was presented by SHRP in 2012 to show the potential function of NMR to quantify the amount of modifiers in asphalt binders.

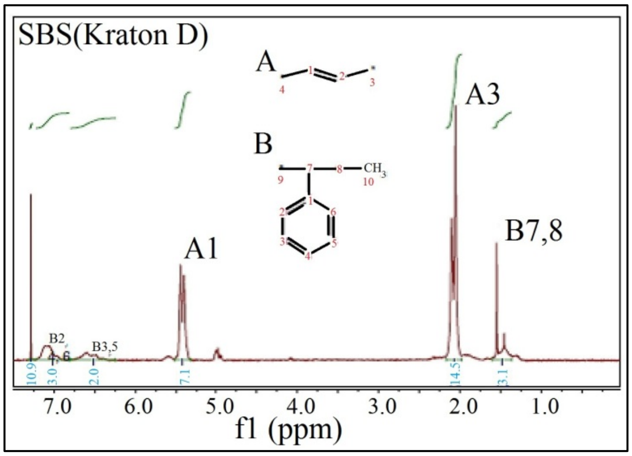


Figure 2-30 NMR Spectrum of Kraton D1101 SBS (SHRP, 2012)

2.2.6.2 Background

The concept of NMR was initially introduced by Rabi in 1938. Because of NMR, Rabi was awarded the Nobel Prize in physics in 1944 (Wikipedia, 2013[f]). After twenty years, NMR was developed to be applied to the field of asphalt.

In 1960, Brown and Ladner initially performed NMR to develop methods for calculating structure parameters (Brown & Ladner, 1960). In the next five years, high resolution NMR was developed and applied to structural investigations of coal tars (Ramsey et al., 1967).

In 1966, Wetmore et al. tested polymers of known asphalt compositions, using ultraviolet, infrared, and NMR. They stated that NMR could give more reliable structural parameters than the other two methods (Wetmore et al., 1966).

In 1967, Ferris et al. attempted to use NMR with other tests to detect aromatic structure in asphalt fractions, through calculating the relative areas of corresponding peaks in the NMR spectrum (Ferris et al., 1967). In the same year, Ramsey et al. confirmed that high resolution NMR could be used to get structural parameters of asphalt. They also measured the percentages of fractions in asphalt, including pentane, CCl_4, $CHCl_3$, CH_3OH, benzene, pyridine, and asphaltenes (Ramsey et al., 1967). The application of NMR to detect carbon, hydrogen, and nitrogen in asphalt became very popular in further studies (Enustun et al., 1990; Jennings et al., 1992; Calemma et al., 1995; Siddiqui & Ali, 1999; Ali & Siddiqui, 2001; Canto et al., 2006; Sanderson, 2010; Maife & Shaw, 2011; Yu et al., 2014). In the next year, Helm and Petersen applied NMR to obtain the carbon type distributions to study asphalt and its molecular distillation fractions (Helm & Petersen., 1968).

In 1972, based on structure parameters, Haley calculated the asphalt fractions' molecular weights using NMR, which was equivalent to the unit sheet weights obtained from molecular structural analysis. In 1978, his mathematical approach was modified by Klet et al. through bringing the structural parameters' values to the nearest integer, which made the approach simpler (Klet et al., 1978).

On another side, in the next few years, numerous NMR studies turned to focus on the identification and quantitative analysis of polymers (Axelson et al., 1978; McBrierty 1979).

In 1981, Bergmann and Gerberding studied the mobility of the rubbers' crosslink chains by NMR, including polystyrene (PS) and polybutadiene (PB). They found that, in SBS, the PB chains are partly immobile below 20°C and the PS chains are partly mobile above 60°C, which corresponds to the viscoelastic properties (Bergmann & Gerberding, 1981). Their finding argued that the rubber's relaxation time might be independent of its molecular weight (Bergmann & Gerberding, 1981).

In 1993, as NMR became a common analytical tool in the study of molecular structures of chemical compounds, one research funded by SHRP was conducted to elucidate chemical features of SHRP core asphalts using solution-state NMR. That study successfully measured the contents of aromatic carbon, aromatic hydrogen, and some functional groups, such as phenol and carboxylic acid (Jennings et al., 1993a). They found that each core asphalt had different local molecular mobility, which was also not easily quantified. However, they failed to relate the molecular structural features of asphalts' fractions with their mechanical properties (Jennings et al., 1993a).

In the following year, SHRP funded another project to use NMR to measure the amount of asphalt in asphalt-aggregate mixes. That program further developed a new NMR spectrometer to quantify the asphalt content in the 4-inch highway core in the field (Pearson, 1994). They also applied NMR to measure glass transition temperatures of asphalts and initially described how the aggregate affected these measurements (Pearson, 1994).

In 1996, Michon et al. applied Si-NMR to qualify and quantify the acidic fractions in bitumen to study bitumen aging, based on oxidation reactions (Michon et al., 1996). In 1997, this research group introduced a new set of average molecular parameters only based on ^{13}C NMR data and molecular weights (Michon et al., 1997).

In 1998, based on the signal remaining time observed from NMR image, Miknis and Michon introduced that NMR imaging could be used to study the interactions between crumb rubbers and asphalt, such as swelling by asphalt molecules and dissolution of rubber into asphalt (Miknis & Michon, 1998). In the same year, this research group captured another interesting finding: when they added titrant slowly into the iso-octane-asphalt-toluene, a special layer was generated at the solvent interface. Moreover, when the asphaltene content and the degree of aging increased, this layer became clearer. This phenomenon showed that NMR imaging probably could test asphalt compatibility in aged asphalts (Miknis et al., 1998). In 2005, this research group developed an interesting approach to measure the tensions on the asphalt's surface and interface using NMR imaging. They recorded the process of a water drop falling into asphalts during one week period, and then measured the water drop's contact angles to obtain surface tension (based on Young's equation or liquid lens equation) (Miknis et al., 2005).

In 2000s, as the technology of detecting ^{13}C and ^{1}H by NMR became very accurate, NMR was commonly applied as a tool to detect the chemical structures of rubbers and other polymers (Ali & Siddiqui, 2001; Canto et al., 2006; Sanderson, 2010; Maife & Shaw, 2011; Yu et al., 2014). However, there was still very few studies specifically concentrated on the quantification of asphalt modifier using NMR during 2000s.

In 2012, researchers in SHRP selected PG 64-22 binder with 1%, 3%, and 6% SBS contents and performed NMR to analyze the ratios of integration values of SBS butadiene protons versus those of virgin binder's aliphatic protons (SHRP, 2012). They found this NMR measured the correct SBS concentration, with less than 1% error. The results are shown in Table 2-5. Their report also stated that: "*although portable NMR devices were not available for evaluation in this study, it seems reasonable to assume that, in the future, NMR spectroscopy can be used in the field for both the qualitative and quantitative analysis of polymer modified binders and asphalt mixtures* (SHRP, 2012)."

Table 2-5 SBS Concentration as Measured by NMR (SHRP, 2012)

SBS Content as Prepared in Laboratory (%)	Integration Ratio SBS-Binder	SBS Content as Measured by NMR (%)	Absolute Error (%)
1	1:67.5	1.48	0.48
3	1:34.9	2.87	-0.13
6	1:14.8	6.76	0.76

2.2.6.3 Details of NMR Operation

Since the concentrations of previous studies using NMR to detect the components of modified asphalts are various, the selections of NMR apparatus and its corresponding experimental parameters could be very different. Moreover, there is no standard test to quantify modifier contents in asphalts. Thus, this section only introduces two typical NMR tests which were performed in recent modified asphalt studies, as references.

In Ali & Siddiqui's report in 2001, the preparation of solution used in ^{13}C NMR spectra and ^{1}H NMR spectra, respectively, was described. For ^{13}C NMR spectra, 1 g of the asphalt should be dissolved in 2 ml of deuterated chloroform which was mixed with the relaxation agent: 10 mg ferric acetonyl acetonate, $Fe(acac)_3$. For ^{1}H NMR spectra, the formula is almost the same except that no relaxation agent is added. The report also described the experimental parameters in each NMR spectra, as summarized in Table 2-6. The apparatus selected in this study was a Varian XL-200 pulse Fourier transform (PFT) spectrometer (Ali & Siddiqui, 2001).

Table 2-6 Test Parameters Used in Ali & Siddiqui's Study in 2001 (Ali and Siddiqui, 2001)

Spectra	Sample tube	Spectrum width	Data point	Pulse width	Pulse delay	Number of transients
^{1}H	5 mm	2800 Hz	15680	3.5 ms	0	64
^{13}C	10 mm	10000 Hz	24000	12 ms	0	16000

In 2012, the final report of one SHRP project (S2-R06B-RR-1) also introduced the details of NMR tests, including the equipment setup and test sample preparation. Specifically, a Bruker DRX-400 NMR spectrometer was selected to perform NMR tests, as shown in Figure 2-31. This NMR spectrometer can shift time-domain and frequency-domain to analyze solutions and solids, respectively. This device provides several test environments: ^{1}H, ^{13}C, ^{31}PM, or ^{19}F. Similar to Ali & Siddiqui's work, d-chloroform was also selected as the lock solvent. The signals were collected by TopSpin software, and were analyzed by MestReNova software (SHRP, 2012).

Figure 2-31 Image of Bruker DRX-400 NMR System (SHRP, 2012)

However, since this apparatus only can analyze liquid state materials, similar to Ali & Siddiqui's work, the test sample should be prepared at following two simple steps: 1) use 2 mL 1wt% d-chloroform to dissolve modified asphalts; 2) transferred into NMR tube (SHRP, 2012).

For the settings of test parameters, previous literatures show that these settings strongly depend on the study purposes and NMR apparatus selections (Haley, 1972; Michon et al., 1996; Ali & Siddiqui, 2001; Canto et al., 2006; Kovalakova et al., 2013).

2.2.7 Summary of Non-Mechanical Tests

2.2.7.1 Test Developments

The development of non-mechanical tests for asphalt modifier quantification could be generally separated into four stages: 1) method invention; 2) application in the asphalt or polymer field; 3) attempts for detection and/or quantification of polymers; 4) standardization of test procedure. These four steps also can be used to weigh the extent of each relevant test's development.

Figure 2-32 mainly gives decision makers two ideas: "when did we start?" and "where have we reached?" The achieved steps of these six non-mechanical tests are expressed by the columns' colors: red column represents the tests already being standard; blue column represents the tests having high potential to be further developed; brown column represents the stagnant status of test at 2nd step. The columns' head and end also represent the tests' starting development time and the stagnant time, respectively. Figure 2-32 clearly shows that most tests were introduced around 1960s, except NMR and Raman spectroscopy. Moreover, most studies recently had "breakthroughs" around 2000s at fourth step or third step.

It is worth pointing out that the length of the column could not represent the exact time length for the development of each test. For example, Raman spectroscopy did not directly involve the modifier quantification in asphalt binders after 1934, until 2012 in SHRP study.

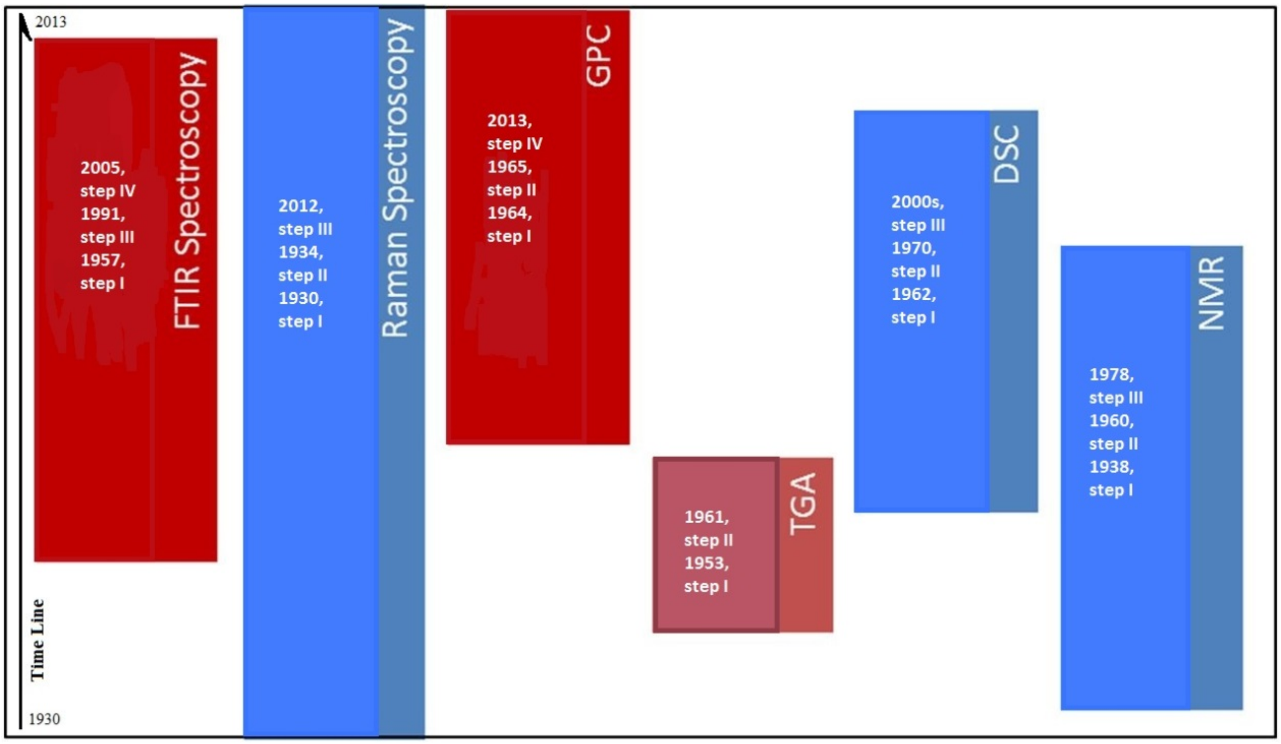


Figure 2-32 Development of Non-Mechanical Tests for Asphalt Modifier Quantification

For more clearly expressing "where have we reached?" the latest achievement of each test has been summarized in Table 2-7.

Table 2-7 Latest Achievement of Each Non-Mechanical Test

Tests	Latest Achievement
FTIR	Standard: AASHTO T 302-05
Raman	Identify the SBS presence
GPC	One proposed AASHTO standard test in 2013
TGA	Capture the decomposition temperatures of different constitutes
DSC	DSC thermographs vary with different contents of modifiers, shown by numerous studies in 2000s.
NMR	Successfully measure SBS contents within less than 1% error by SHRP.

Based on the latest achievement of each non-mechanical test, numerous topics of further potential study could be decided:

- Standard AASHTO T 302-05 is applied widely as a laboratory test. Simplification of the sample preparation process and development of standard curves for more asphalt sources are still needed to adapt the FTIR test from laboratory to field.
- Considering the similar functions of Raman and FTIR, since Raman requests less sample preparation, specifying one standard similar to AASHTO T 302-05 using Raman spectrometer seems promising and reasonable.

- For GPC, just like what Dr. Diefenderfer did after the year when AASHTO T 302-05 was published, future study can also focus on verifying the GPC test for modifier quantification, and may further develop it for field application.
- For DSC and TGA, they might be the toughest way, since no specific study directly focused on modifier quantification. However, based on their theories and backgrounds, these two tests could be initially developed to measure modifier contents in the laboratory.
- Since SHRP has successfully measured SBS contents using NMR, without developing any standard, NMR also provides a great opportunity to study on the quantification of modifier content. However, a portable NMR device needs to be developed for field use.

2.2.7.2 Test Gaps

Apparently, understanding "when did we start?" and "where have we reached?" are not enough for decision makers to figure out which tests have higher potential to be developed to reach the fourth step or to be enhanced at the fourth step. The more important information for decision makers are "what are the gaps we are facing?" and "how much cost we would pay?" Thus, as a summary of these six non-mechanical tests, the limitation and cost of each non-mechanical test are summarized below.

No matter which steps these non-mechanical tests reach, the limitations still exist in each test. Based on the background of each test development as mentioned in previous sections, the limitations could be summarized in Table 2-8. It can be seen that the main obstacle to the NMR test is lack of a portable NMR device. If a mobile laboratory is acceptable for field use, NMR test can be used for modifier detection and quantification in asphalt binders. TGA and DSC methods might be the most difficult to develop because of limited attempts and several difficult controlled experimental parameters. For Raman and GPC, both tests might meet some unpredicted measurement errors from asphaltenes' size and weight, which should be solved at the sampling preparation step. For FTIR, with the availability of portable FTIR test device, this test can be readily applied in the field, only under the condition that a standard curve needs to be developed for each source of asphalt.

Cost is another key aspect to consider in the further study. A comparison of the above-mentioned portable and mobile-laboratory-based tests is summarized in Table 2-9. Some information is missing due to the limited sources during the review. Generally, these devices have good accuracy, but most of them have high device costs.

2.3 Summary of Literature Review Findings

Since the mechanical properties of asphalt binders are significantly changed by SBS or GTR modifiers, many mechanical tests could detect the existence of modifiers based on the performance of asphalt binders. Previous studies on creep test, elastic recover test, flexural fatigue beam test, flow test, and binder fracture energy test have shown that several types of strain, creep stiffness, elastic recovery, viscosity, and fatigue life can be the indicators of modifier existence. However, because different modifiers might change binder performance to the same extent, very few tests can identify the specific modifier types. Currently, among these mechanical tests, elastic recovery test is the only one which has been included in AASHTO standards for modifier quantification, as presented in AASHTO T 301.

Table 2-8 Limitations of Each Non-Mechanical Test

	Tests		
	FTIR	Raman	GPC
Limitation	A reference binder is required for each source supplier	For large sample size, fluorescence might be generated by irradiation with 785-nm light.	Some asphaltenes' weights might be close to polymer.
		Expensive	Asphalt sample should be dissolved in THF, which requires long time for sample preparation.
			The operation time of GPC system is around 60 minutes, which is relatively long.
	Tests		
	TGA	DSC	NMR
Limitation	Very few attempts	Strict sample preparation: time-dependent	No portable NMR device is available
		Unclear transition temperature	
		Broad range of required temperature	

Table 2-9 Summary of Portable and Mobile-Laboratory Tests

Test	Easiness of Operation	Cost of Device ($)	Device Weight	Duration of measurement	Accuracy of Result
FTIR	Portable	25,000	7.3 kg	1 min	0.50%
RS	Portable	37,000	9 kg	1 min	2%
GPC	Mobile Laboratory	14,000	N/A	35min	N/A
DSC	Mobile Laboratory	N/A	24 kg	>1 min	N/A
TGA	Mobile Laboratory	N/A	23 kg	14-115 min	1 g

For non-mechanical tests, most were introduced around 1960s, and had breakthroughs in modifier detection and quantification around 2000s. Currently, the achievement of each technique for modifier detection and quantification has reached different levels. FTIR and GPC have been developed as AASHTO standards by Virginia DOT and Louisiana DOT respectively; Raman spectrometer can detect SBS presence; NMR measures SBS content successfully; DSC thermographs and contents of modifiers have significant relationship; TGA could capture the decomposition temperatures of different constitutes. Considering the current limitations of each test, NMR is limited due to the lack of portable NMR devices. TGA and DSC methods cannot be readily used for modifier detection and quantification due to limited research attempts and experimental parameters that are difficult to control. For Raman and GPC, both tests might meet some unpredicted measurement errors from asphaltenes’ size and weight, which need to be solved at the sampling preparation step. For the FTIR method, since portable FTIR test devices are already available, this test can be readily applied in the field, only under the condition that a standard curve needs to be developed for each source of asphalt.

CHAPTER 3 QUESTIONNAIRE SURVEY

3.1 Introduction of Questionnaire Survey

A survey questionnaire was designed and distributed to relevant national/international agencies/institutes to collect latest information on their practice/thoughts on SBS/GTR identification in asphalt binder. The respondents mainly involved three groups: state DOTs, asphalt research institutes, and Florida's asphalt binder producer industry. Specifically, State DOT personnel included pavement materials engineers, asphalt program managers, and bituminous laboratory supervisors; asphalt research institutes included the National Center for Asphalt Technology (NCAT), Western Research Institute (WRI), National Asphalt Pavement Association (NAPA), and the Association of Asphalt Paving Technologies (AAPT); asphalt binder producers involved in this questionnaire survey were primarily those who supply asphalt binders to Florida.

The numbers of respondents contacted and responses received are summarized in Table 3-1. It is worth pointing out that, since the respondents from one system (DOT, research institute, or asphalt industry) should provide similar answers, the unit of respondents counted in Table 3-1 is not individual person, but one state, institute, or company.

Table 3-1 Numbers of Respondents Contacted and Responses Received

Respondent Groups	Number of Respondents Contacted	Number of Total Responses Received
DOTs	33	21
Asphalt research institutes	4	3
Asphalt industries	4	1

3.2 Survey Design

The questionnaire included questions pertaining to the following aspects:

- Existence of a tool or test procedure for detecting/quantifying SBS/GTR in asphalt
- Current practice of quality control of modifier content in asphalt binders in the field
- Current research-based or practical efforts to develop/improve a test tool/procedure
- Other suggestions and comments useful to the investigators

Questions were varied based on the target survey group. Specifically, the following questions were designed to elicit the information of current practice of asphalt modifier identification and quantification from DOT staff:

- *In asphalt paving projects using binders modified with polymers (e.g., SBS) or ground tire rubber (GTR), do you verify the existence of polymer or rubber in asphalt binders during construction?*
- *Do you verify the content of polymer or rubber in asphalt binders during construction?*
- *If the answer to either of the above two questions is "yes", which approach is used to verify or quantify the existence of modifiers in modified asphalt binders?*
- *If a test procedure is adopted, what is the test method or test specification? Is the test conducted in the field or in a laboratory?*

- *Currently there are several types of tests proposed for detecting/quantifying modifiers based on different technologies, such as spectrum (FTIR, RS), chromatography (GPC, HPLC), thermo (DSC, TGA) , and "macro" vibration (NMR). Do you have any thought or opinion on a test that is available or has the potential to be developed for use in the field to detect and/or quantify modifiers in asphalt binders?*
- *Do you have any other comments on verifying/quantifying the existence of polymer or GTR modifiers in asphalt binders during construction?*

For research institutes and asphalt industry, the following questions were asked to gather the information of current research and developed tests on asphalt modifier identification and quantification:

- *For liquid asphalt binders modified with styrene butadiene styrene (SBS) or ground tire rubber (GTR), currently there are several types of tests proposed for detecting and /or quantifying modifiers based on different technologies, such as spectrum (FTIR, RS), chromatography (GPC, HPLC), thermo (DSC, TGA) , "macro" vibration (NMR), and mechanical properties (recovery, stiffness, elongation, etc). Are you familiar with any of these or other techniques that can detect and/or quantify the existence of the modifier (SBS or GTR) in the binders?*
- *If the answer to the first question is "Yes", what are your experience with the test(s) and your opinions of the test(s) (e.g., accuracy, efficiency, cost, and level of expertise required)? Do you think that a test or technique can be used, either directly or with minimal modification, in the field (i.e., the ideal field device should portable and the test procedure should be relatively quick and simple)?*
- *If the answer to the first question is "No", do you have any thoughts or ideas on ways to develop a method to detect/quantify modifiers in asphalt binders in the field?*

3.3 Survey Results

The specific answers from participating organizations are presented in Appendix A. Below is a summary of the responses.

3.3.1 Verification of Modifier Existence during Construction

Although SBS or GTR are widely used as binder modifiers in the U.S., verification of modifier existence during construction is not forcibly required by DOT specifications. The first task of the questionnaire survey is to investigate how commonly the verification of modifier existence is regulatorily required in the state DOTs. Based on the answers received from 21 states, a total of 11 states directly answered "yes"; 3 states did not directly say "yes" but mentioned that they performed tests to check the performance of modified binder; the rest of 7 states responded that no relevant test was performed during construction or they did not use GTR as binder modifier. Figure 3-1 clearly shows the percentage of each answer received in this survey, and illustrates that the verification of modifier existence has not been paid attention to by some states yet. It is also worth pointing out that some states do not select GTR as binder modifier, such as Alabama, Kansas, Mississippi, Oklahoma, and Virginia. Moreover, Oregon stated that the GTR is very limited in the state and is usually only utilized in some of chip seal work.

Furthermore, this questionnaire survey gathered some specific methods of verification of modifier existence from the respondents, which have already been found in previous literature review. Their answers are summarized as follows:

Georgia and Minnesota conducted dynamic shear rheometer (DSR) to limit maximum phase angle to verify the existence of polymer, which should be less than 75 degree. For rubber modified PG asphalt binder, Georgia and Minnesota add multiple stress creep & recovery (MSCR) test to check GTR existence in asphalt binder.

As previous literature review mentioned, the elastic recovery test (T301) is widely performed in many states to verify polymer existence in asphalt binder. In this questionnaire survey, six states, including Kansas, Kentucky, Louisiana, Nebraska, Oregon, and Virginia, mentioned that they perform the elastic recovery test. Take Oregon for instance, its DOT Standard Specifications for Asphalt Materials states that the PG 70-22ER grade shall have a minimum elastic recovery of 50% when tested according to AASHTO T 301. Nebraska DOT staff also stated that the elastic recovery test by AASHTO T301 should be for SBS, and the one by ASTM D 6084 should be for GTR since they have notable differences.

In summary, all responses on the verification of modifier existence in this questionnaire survey only involve three mechanical tests, including elastic recovery test AASHTO T301, MSCR, and basic DSR test. For these mechanical tests, one researcher from NCAT listed their pros and cons for asphalt modifier detection/quantification and their potential for field evaluation as follows:

> "*MSCR / phase angle*
>
> *Pros: 1) quick to run; 2) easy to analyze results; 3) can be run on samples already being tested for Performance Grade determination; 4) can be set up to run in a reasonably well equipped mix plant quality control lab (needs electricity and a good air compressor).*
>
> *Cons: 1) requires some technician training; 2) expensive to purchase the Dynamic Shear Rheometer (DSR) equipment; 3) can only identify the presence of a modifier; 4) can't quantify; 5) needs electricity and a good air compressor.*
>
> *Elastic recovery / ductility*
>
> *Pros: 1) inexpensive to set up; 2) simple to run; 3) easy to analyze; 4) minimal technician training.*
>
> *Cons: 1) time consuming; 2) requires a large laboratory footprint (not good for a tiny lab); 3) can only detect; 4) not quantify; 5) equipment is large and would not be considered portable; 6) requires electricity and water.*
>
> *Stiffness*
>
> *Stiffness alone is not a good indicator of modifier presence, type, or quantity."*

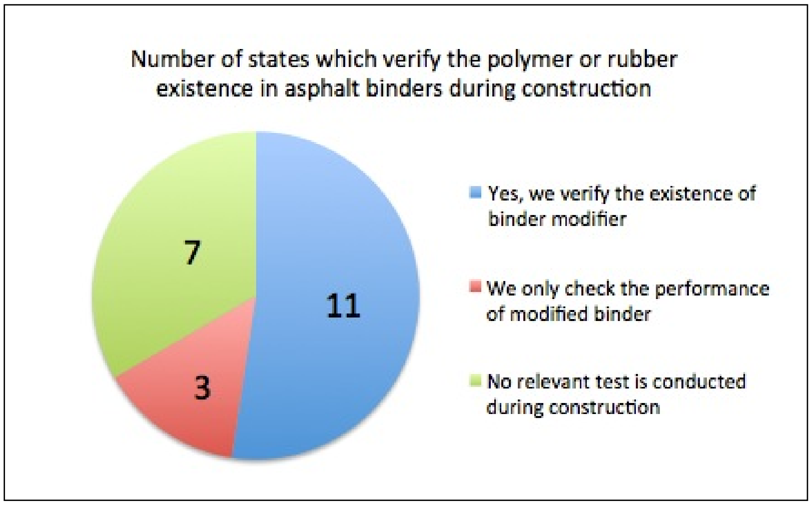


Figure 3-1 Number of States Which Verify the Modifier Existence in Binder during Construction

3.3.2 Quantification of Modifier Content during Construction

The second task in this survey was to seek some methods to quantify the modifiers in asphalt binders. Surprisingly, most states replied with the same answer: “We do not have specific test for polymer content.” This consensus answer directly showed the necessity of developing a convenient method for modifier quantification during construction.

3.3.2.1 Fourier Transform Infrared (FTIR) Spectroscopy Test

Some states mentioned FTIR test, but most of them did not perform FTIR test very often. In Alabama, quantifying the modifier content was a rare occurrence unless there was an issue with a project. FTIR test was contained in their test procedure 408 and only conducted in the laboratory. Georgia, Ohio, and Nebraska DOT staffs mentioned that the FTIR equipment was very expensive to maintain due to high repair cost. Mississippi and Nebraska DOT staffs stated that they had capability to perform the infrared spectroscopy test (FTIR), but no formal testing procedure was contained in their specifications.

For the FTIR test, Virginia conducted one project back in 2006, whose results tremendously induced the development of FTIR in the U.S. However, the respondents from Virginia DOT stated that using FTIR to qualify and quantify polymers was never adopted in Virginia: qualification was not particularly difficult but required a reference binder for each source supplier; quantification was tedious as, practically, they had to determine a reference curve for each binder supplier and polymer type to be able to calculate the sample content. Thus, the effort required to develop and maintain the necessary reference information for analysis was deemed impractical. As a consequence, they just continued to use the elastic recovery specification.

3.3.2.2 Gel Permeation Chromatography Test

In this questionnaire survey, only Louisiana and Virginia mentioned that gel permeation chromatography (GPC) test was already being used to successfully detect and even quantify the presence of SBS and GTR in asphalt binders, as described in the report FHWA/LA.13/505 (Negulescu and Balamurugan, 2013). According to the GPC research conducted at the LSU

Chemistry Laboratory and their research center (LTRC), Louisiana staffs believed that GPC was promising for polymer modifier quantification, and they will be working on the question of latex and GTR. However, they have not started the GPC required testing in the field yet. One Virginia DOT staff also does not think of GPC as being particularly portable for field detection, since GPC apparatus are bench top units, and are neither cheap nor particularly easy to use without training. Compared to FTIR test, although GPC deems more tedious, GPC does not require a reference curve for each binder supplier, which makes GPC more practical.

3.3.2.3 X-ray Fluorescence Spectrophotometer Test

In this questionnaire survey, Washington State mentioned X-ray fluorescence method which was not covered in previous literature review. They recently purchased an X-ray fluorescence spectrophotometer (WDXRF) and planned to use it to detect the presence of additives. However, they did not describe the details.

3.3.2.4 Other Mentioned Tests

NCAT responded that they have used a thermo-gravimetric analysis (TGA) test in some ways to try and quantify rubber content fairly well. WRI replied that they have developed a HPLC/SEC procedure for examining asphalts for FHWA (FHWA-RD-99-213) and have continued to conduct some studies since then. WRI also has extensive experience with FTIR, thermal analysis, including DSC and TGA, and with NMR measurement techniques.

3.4 Additional Suggestions

Currently, Louisiana DOT plans to use the loaded wheel tested and semi-circular bend for compliance testing in the case of a non-verifying GPC. The sample is the binder extracted from a core taken from the roadway for verification.

Washington DOT is planning to implement the MSCR including a percent recovery specification by 2016. MSCR test was also strongly suggested by Minnesota DOT staffs.

Some other professionals think that it is difficult to identify, particularly to quantify modifiers in asphalt binder. As said by one member from Western Research Institute:

> "*Quantification is always more difficult. There are many SBS formulations and many GTR sources and compositions. In addition, cross linking in GTR and to some extent in SBS materials limits their solubility in common solvents. This is a major limitation for GTR, but may not be as important for SBS. The development of a robust methodology or methodologies to identify and quantify SBS and GTR will require a large, diverse set of samples, and of course, access to the appropriate instruments*."

3.5 Summary of Questionnaire Survey Findings

Based on the questionnaire survey results, although SBS and GTR modifiers are widely used in the U.S., the verification of modifier existence has not been paid attention to by some states yet. Only three mechanical tests, including elastic recovery test (AASHTO T 301), MSCR, and basic DSR test, were mentioned by the respondents from DOTs to verify modifier existence in liquid asphalt binders. Currently, some states, such as Washington, Minnesota, and Georgia, are working on the development of MSCR test for modifier quantification.

For GTR, many states do not use GTR as binder modifier, such as Alabama, Kansas, Mississippi, Oklahoma, and Virginia. Moreover, because of the cross linking in GTR, the test methods and procedures for GTR are different from those for SBS. For example, the elastic recovery tests for SBS and for GTR have notable differences.

FTIR test is still impractical for modifier quantification in the field because FTIR equipment is very expensive to maintain due to high repair cost, and the test relies on a reference curve for each binder supplier to quantify the modifier content.

According to Louisiana and Virginia States, Gel Permeation Chromatography (GPC) test is already being used to successfully detect and even quantify the presence of SBS and GTR in asphalt binders. However, the GPC test is not portable for field use.

Generally, the rest of tests are not practically performed for modifier quantification in the field. "All of them would bring different pieces of the puzzle." as one respondent said.

3.6 Suggestions for Further Study

Based on the findings from literature review and questionnaire survey, currently there is no satisfactory test for field use to detect and/or quantify SBS or GTR modifiers in liquid asphalt binders. One method, the FTIR test, which is included in the AASHTO Standard Specifications as T 302-05, however, has been frequently applied in the laboratory. The reasons preventing it from being used in the field include non-portable and expensive equipment, complex sample preparation procedure, certain level of expertise required to run and analyze the test, and various reference curves required for different asphalt binders. Recent development in the FTIR testing, however, has cleared some of the obstacles. For example, handheld FTIR analyzers recently appearing on the market can run test on material samples in a quick and easy way, and are durable in field use. These new portable FTIR devices may be good candidates as field test tools for polymer modifier identification and quantification in asphalt binders. Their potentials, therefore, warrant further investigation.

CHAPTER 4 EXPERIMENTAL DESIGN OF LABORATORY STUDY

The objectives of the laboratory study include:

- to compare the results from portable FTIR devices with those from desktop FTIR devices
- to explore the relationship between portable FTIR results and polymer (SBS or GTR) contents and to develop prediction models using binder samples with known polymer contents
- to verify the prediction models with binder samples with unknown polymer contents
- to make recommendations for a potential field test device and procedure

The design of the experiments was described in this chapter.

4.1 Selection of Test Equipment

A survey of the portable FTIR devices available on the market showed that currently there are mainly three different brands:

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

Figure 4-1 shows the pictures of the three types of devices. Among the three, TruDefender FTX FTIR analyzer has the smallest volume and weight, so is most portable; the Alpha FTIR spectrometer needs to be connected to an external power supply and a laptop, so is least portable. In this study, one TruDefender FTX FTIR analyzer was loaned for a short period from Thermo Scientific and used in the investigators' laboratory. Binder samples were sent to Bruker Corporation for testing with the Alpha FTIR spectrometer. The ExoScan Series FTIR spectrometer was not included in the study due to the inability of the investigators to acquire the device.

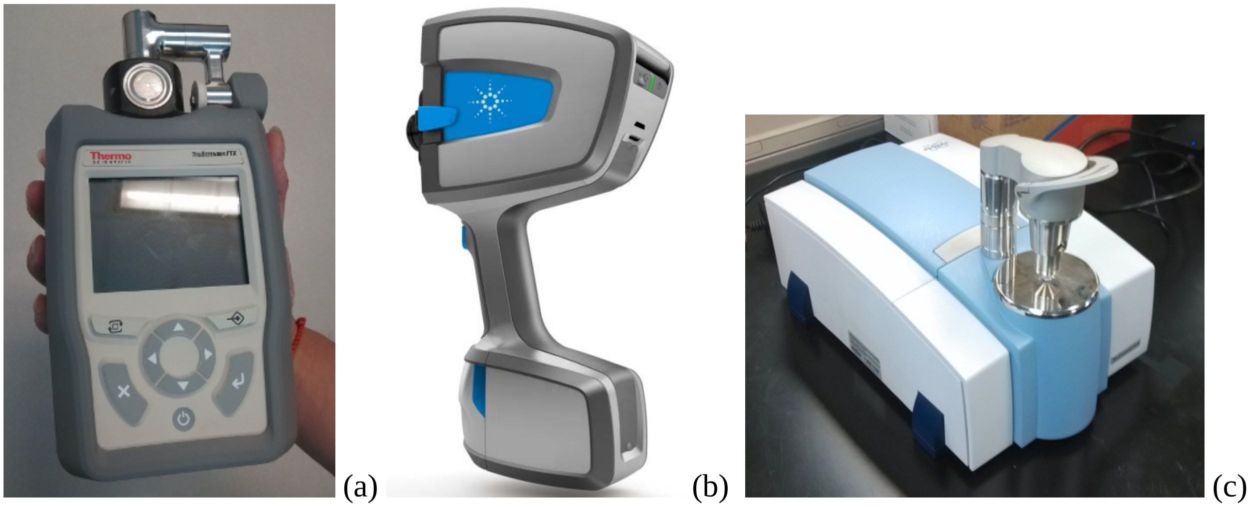


Figure 4-1 Portable FTIR Spectrometers: (a) TruDefender FTX; (b) ExoScan 4300; (c) Alpha FTIR

For comparison and cross validation of test results, a desktop FTIR device, Nicolet 6700 FTIR Spectrometer from Thermo Scientific, as shown in Figure 4-2 (a), was included in the study. Some binder samples were also sent to a Tampa asphalt company, Mariani Asphalt, for testing with another version of desktop FTIR device, Bruker Tensor II FTIR spectrometer, as shown in Figure 4-2 (b).

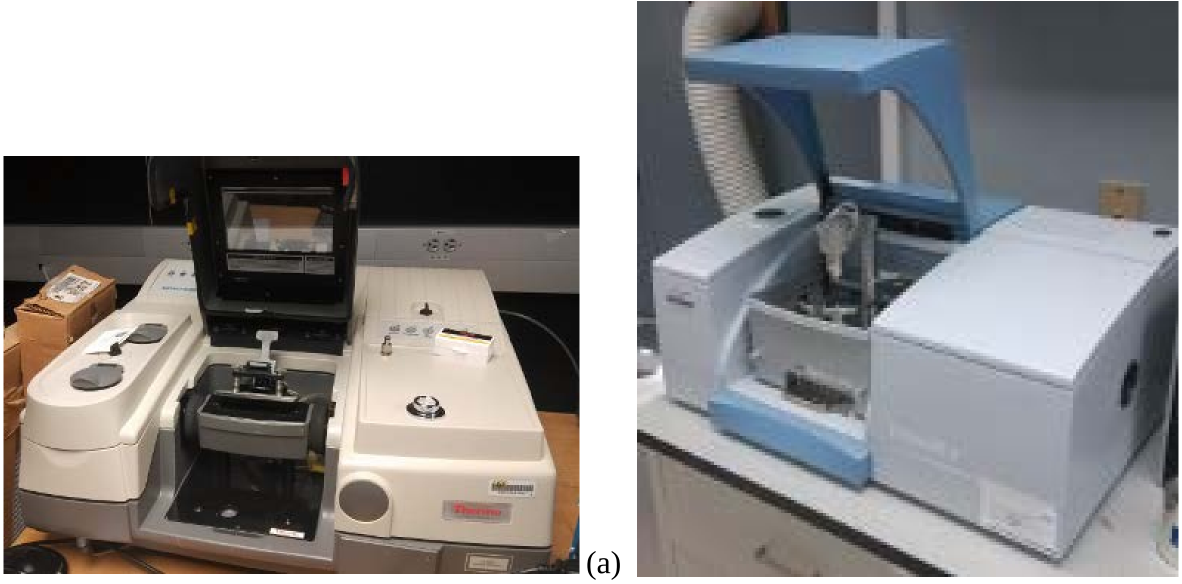

(a) (b)

Figure 4-2 Desktop FTIR Spectrometers: (a) Nicolet 6700; (b) Bruker Tensor II

For all the four FTIR spectrometers involved in the study, samples were tested using the attenuated total reflection (ATR) method. For the TruDefender FTX, Bruker Alpha, and Bruker Tensor II FTIR spectrometers, the crystal is solid diamond, which requires only a small amount of sample (around 2 mm in diameter and 1 mm in thickness) for testing and is easy to clean with solvents (e.g., mineral spirits and acetone). For the Nicolet 6700 FTIR spectrometer, the crystal is ZnSe, which requires a relatively large amount of samples (around 100 mm in length, 10 mm in width, and 1 mm in thickness), and so is more difficult to clean. General specifications of above mentioned FTIR spectrometers are summarized in Table 4-1.

Table 4-1 Specifications of FTIR Spectrometers

	TruDefender FTX	ExoScan 4300	Alpha FTIR	Nicolet 6700	Bruker Tensor II
Weight (lb.)	3.1	4.8	13.0	140.0	81.6
Size (inch)	8.9 × 4.5 × 2.1	N/A	8 × 11	25.5 × 27.5 × 12.5	26.2 × 17.1 × 11.1
Spectral Range (cm^{-1})	4,000 ~ 650	5000 ~ 650	7500 ~ 375	7800 ~ 350	7500 ~ 370
Spectral Resolution (cm^{-1})	4	4	2	0.1	1 ~ 0.5
Collection Optics	Solid Diamond Crystal ATR	Solid Diamond Crystal ATR	Solid Diamond Crystal ATR	ZnSe	Solid Diamond Crystal ATR or ZnSe (optional)

4.2 Material Selection and Sample Preparation

After discussion with FDOT State Materials Office, the following materials were selected for the study

- Two SBS modified binders with a range of known SBS contents
- Two GTR modified binders with a range of known GTR contents
- Components of the above two series of binders (i.e., SBS, GTR, and base asphalt)
- Several SBS or GTR modified binders used in field projects whose exact polymer contents are unknown, but the approximate content ranges are given
- Aggregates for preparing asphalt mixtures

The above materials were acquired from various sources and samples were prepared through procedures described in the following sections.

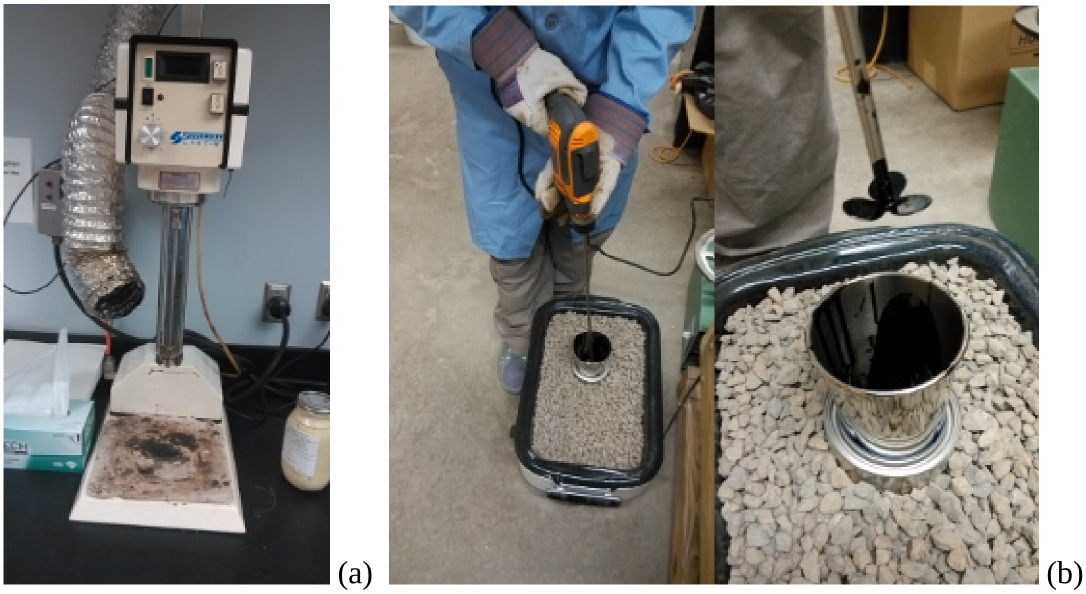
4.2.1 SBS Binders with Known SBS Contents

The two sets of SBS binder samples with known SBS contents were obtained from two different sources: Mariani Asphalt and Ergon Asphalt and Emulsions. Since the first set of samples was mixed by USF investigators and the second set of samples was prepared by Ergon, they are named as USF samples and Ergon samples respectively in this study.

For the USF samples, a PG 67-22 base asphalt and a 10% SBS binder were obtained from Mariani Asphalt. The 10% SBS binder was prepared by Mariani Asphalt in its laboratory using a Silverson L4RT high speed mixer, as illustrated in Figure 4-3(a). The 10% SBS binder was then diluted with the PG 67-22 base asphalt using an electric drill with a mixing head, as shown in Figure 4-3(b), to reach target SBS contents of 0, 1, 3, 5, 7, 9, and 10 percent (by mass of binder). The dilution procedure is summarized as follows.

1. Heat binders until fluid at 163°C (325°F) in a forced draft oven;
2. Weigh the calculated amounts of 10% SBS binder and base asphalt for each target SBS content, as shown in Table 4-2, into a steel cup;
3. Transfer the cup onto a hot plate at a temperature around 163°C (325°F);
4. Use the electric drill with a mixing head to mix the binder clockwise for about 3 minutes at a rotational speed of about 2400 RPM; then mix counterclockwise for about 3 minutes at the same rotational speed. Repeat this mixing pattern for four more times;
5. Repeat Steps 2 through 4 to produce the remaining SBS concentrations.

The Ergon samples were prepared with a PG 67-22 base asphalt and SBS at 0, 1, 2, 3, 4, 5, and 10 percent by mass of binder. In addition, a small quantity of SBS was provided by FDOT State Materials Office.



(a) (b)

Figure 4-3 Tools for Mixing SBS Binder: (a) Silverson L4RT High Speed Mixer; (b) Electric Drill with a Mixing Head from Grainger

Table 4-2 Masses for Preparing the USF SBS Binder Samples

SBS Content (%)	PG 67-22 (g)	10% SBS Binder (g)	Total mass (g)
0	70	0	70
1	63	7	70
3	49	21	70
5	35	35	70
7	21	49	70
9	7	63	70
10	0	70	70

4.2.2 GTR Binders with Known GTR Contents

The two sets of GTR modified binder samples with known GTR contents were prepared in the investigators' laboratory, using a PG 52-28 base asphalt (obtained from Mariani Asphalt) and GTR samples from two suppliers listed on the FDOT Qualified Product List for GTR. One GTR sample is MicroDyne 400-TR (40 mesh) from Lehigh Technologies Inc., and the other is Microgrind GTR (40 mesh) from Global Tire Recycling. The target GTR contents were chosen at 0, 5, 10, 15, 20, and 25 percent (by mass of binder) and the following procedure was followed for mixing:

1. Heat the asphalt sample until fluid at 177°C (350°F) in a forced draft oven;
2. Weigh the calculated amounts of asphalt and GTR powder for each target GTR content into a steel cup;
3. Transfer the cup onto a hot plate at a temperature around 170°C (338°F);
4. Use the electric drill with a mixing head to mix the binder clockwise for about 3 minutes at a rotational speed of about 2400 RPM; then mix counterclockwise at the same rotational speed for about 3 minutes. Repeat this mixing pattern for four more times;
5. Repeat Steps 2 through 4 to produce the remaining GTR concentrations.

4.2.3 Binder Samples with Unknown Polymer Contents

For verification purpose, a number of binder samples were also obtained from FDOT paving projects, for which the exact polymer contents were unknown but the approximate content ranges were given. These samples, as listed in Table 4-3, were directly supplied by FDOT State Materials Office.

4.2.4 Aggregate Samples for Preparing Asphalt Mixtures

Another intended objective of this research is to explore the possibility of directly using asphalt mixtures as samples in the FTIR measurement. To this end, three asphalt mixture samples were prepared in the laboratory using PG 76-22 (PMA), PG 76-22 (ARB), and PG 82-22 binders. Aggregate samples, including Martin Marietta granite (from Canada) and local sands, were obtained from five stockpiles of Tampa Pavement Constructors, Inc.. They were dried, sieved, and batched to reach a 12.5 nominal maximum aggregate size (NMAS) gradation for Superpave mix Type SP-12.5. Each of the three binders was then mixed with aggregates at a 5.8% binder content (by mass of mix). Both coarse and fine aggregate particles from mixtures, as illustrated in Figure 4-4, were tried as samples in the FTIR testing with the TruDefender FTX FTIR analyzer.

Figure 4-4 Asphalt Mixture Samples for FTIR Measurement

Table 4-3 SBS Binder Samples with Unknown Polymer Contents

Sample No.	Sample ID	Binder Grade	Sample No.	Sample ID	Binder Grade
1	FA	N/A	9	PolyHP	N/A
2	FB	PG52-28	10	15572	PG58-22
3	FC	PG67-22	11	15589	PG76-22
4	FD	PG76-22	12	15447	PG76-22
5	FE	PG76-22	13	15473	PG76-22
6	FF	N/A	14	15476	PG82-22
7	FG	PG76-22	15	15539	N/A
8	FH	N/A	16	15487	N/A

4.3 FTIR Test Procedures

The investigators conducted the FTIR tests with two FTIR spectrometers: Nicolet 6700 (desktop) and TruDefender FTX (handheld). Test procedures described in the equipment manuals were followed to run the tests.

4.3.1 Test with Nicolet 6700 Spectrometer

The desktop Nicolet 6700 spectrometer uses a ZnSe ATR crystal for holding samples, as shown in Figure 4-5. For this test, an asphalt binder sample in a tin can was first heated to liquid, and then poured onto a piece of wax paper to form a 100 mm by 10 mm strip. For each test, a background scan was first conducted with a clean crystal, which measures the absorbance spectrum of the crystal without sample. After that, the asphalt surface of a sample was affixed in direct contact with the top of the face of the ATR crystal. Finger pressure was applied to the wax paper to make sure asphalt is in complete contact with the crystal. The FTIR test was then run using 300 scans per test.

After each test, the ZnSe crystal was cleaned with hexane and acetone, as shown in Figure 4-5, and prepared for the next test.

Due to the lengthy periods of crystal cleaning, generally two duplicates were tested for each binder sample.

Figure 4-5 ZnSe Crystal for Nicolet 6700 FTIR Spectrometer

4.3.2 Test with TruDefender FTX FTIR Analyzer

The handheld TruDefender FTX spectrometer uses a diamond ATR crystal, which needs only a small amount of asphalt (about the size of a rice grain) for testing and is robust to cleaning. During the test, a background scan was first conducted when the crystal was clean. Then asphalt sample was put on the crystal, placed into complete contact with the crystal by an anvil, as shown in Figure 4-6. A scan was then performed on the asphalt sample. After each test, the crystal was cleaned with mineral spirits and acetone, and ready for the next test.

Generally at least three duplicates were tested for each binder sample. When high variability in test results was discovered for some samples, additional specimens were tested.

Figure 4-6 Anvil Handle on TruDefender FTX FTIR Spectrometer

4.4 TQ Analyst in Spectral Analysis Software

After each test, the resulting absorbance spectrum may be viewed in several spectral analysis software packages, such as OMNIC and OPUS. The spectral indicators of modifier contents then can be selected manually and analyzed to determine the linear relationship between modifier contents and spectral indicators.

In addition to building a simple linear regression model between modifier contents and spectral indicators, the spectral analysis software may be used to apply more complicated statistical models for data analysis, such as partial least squares (PLS), principal component regression (PCR), and stepwise multiple linear regression (SMLR). For example, these analysis models are included in the TQ Analyst program of OMNIC. Generally, these models can provide better fitting to calibration data than the simple linear regression model (Thermo, 2010) by incorporating more explanatory variables (i.e., more information from the absorbance spectra). However, they may not truly represent the underlying physical nature of the connection between spectral indicators and modifier contents, and so may not have better prediction power. Thus, both methods, including manually collecting spectral indicators for simple linear regression analysis and automatically selecting spectral regions for advanced modeling analysis, were implemented and compared with each other in this study.

4.5 Library Search in Portable FTIR Spectrometer

A library search function is integrated in the TruDefender FTX spectrometer, which compares the absorbance spectrum of tested material to those of known materials saved in the material database of the device and returns the name of a material with best match. There are over 10,000 materials in the TruDefender FTX database, and users may add to the library with new materials or build user-defined material library. The library search function potentially provides users a quick way to identify tested material. The efficiency of such functions, however, depends on the size of the material library, the similarity between absorbance spectra of various materials, and the accuracy of test results. The library search function was also explored in this study to determine polymer modifier presence and content. The details of library search procedures with their outputs are described in Section 5.4.

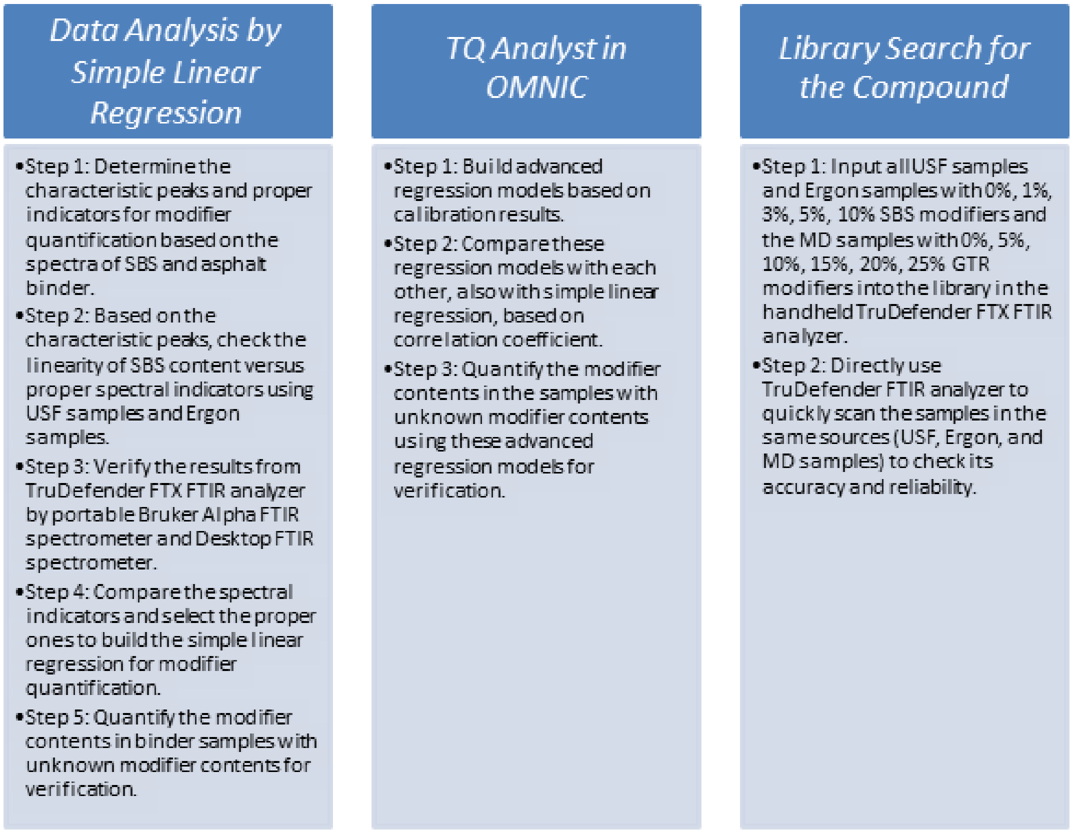
CHAPTER 5 RESULTS AND ANALYSIS

5.1 Data Analysis Procedures

To explore the best analysis method for polymer detection and quantification, the FTIR test data were analyzed in three ways.

- In the first approach, a first-order curve fit was performed to determine the linear relationship between polymer content and various absorbance spectrum features (i.e., certain characteristic peak height or area). This is the most common approach, which has been used in previous studies and specified in AASHTO T 302 (Wei et al., 1994; Curtis et al., 1995; Ling et al., 1997; Diefenderfer, 2006; SHRP, 2012).
- The second approach used more complicated statistical models for data fitting, such as partial least squares, principle component regression, and stepwise multiple linear regressions. These models are included in common spectral analysis software such as OMNIC.
- The third approach directly compared the scanned spectrum with a library of spectra of known materials, and identifies the material that has the best match. To this end, the absorbance spectra of a series of standard binders with polymer contents covering a sufficient range should be first generated and stored in the material library.

The specific steps of each way of data analysis are summarized in Figure 5-1. Results of all three approaches were used to predict the polymer contents of some binder samples from FDOT paving projects.



Data Analysis by Simple Linear Regression

- Step 1: Determine the characteristic peaks and proper indicators for modifier quantification based on the spectra of SBS and asphalt binder.
- Step 2: Based on the characteristic peaks, check the linearity of SBS content versus proper spectral indicators using USF samples and Ergon samples.
- Step 3: Verify the results from TruDefender FTX FTIR analyzer by portable Bruker Alpha FTIR spectrometer and Desktop FTIR spectrometer.
- Step 4: Compare the spectral indicators and select the proper ones to build the simple linear regression for modifier quantification.
- Step 5: Quantify the modifier contents in binder samples with unknown modifier contents for verification.

TQ Analyst in OMNIC

- Step 1: Build advanced regression models based on calibration results.
- Step 2: Compare these regression models with each other, also with simple linear regression, based on correlation coefficient.
- Step 3: Quantify the modifier contents in the samples with unknown modifier contents using these advanced regression models for verification.

Library Search for the Compound

- Step 1: Input all USF samples and Ergon samples with 0%, 1%, 3%, 5%, 10% SBS modifiers and the MD samples with 0%, 5%, 10%, 15%, 20%, 25% GTR modifiers into the library in the handheld TruDefender FTX FTIR analyzer.
- Step 2: Directly use TruDefender FTIR analyzer to quickly scan the samples in the same sources (USF, Ergon, and MD samples) to check its accuracy and reliability.

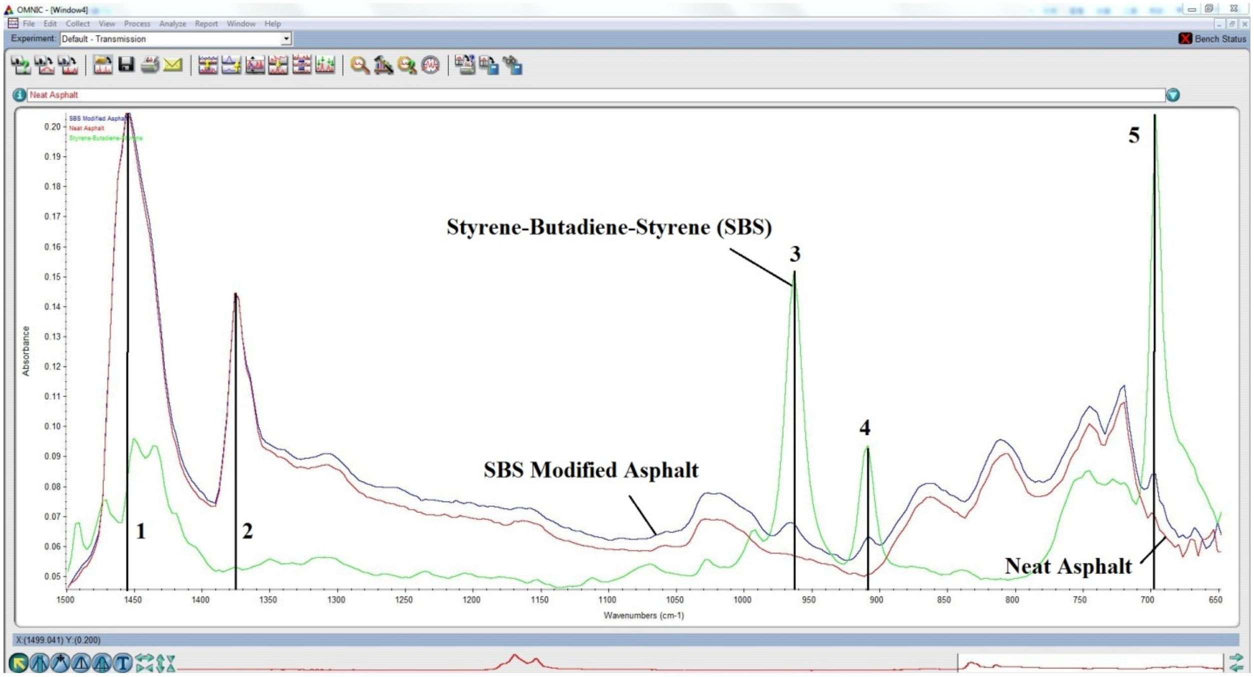
Figure 5-1 Three Ways of FTIR Data Analysis

5.2 Test Result Analysis Using Simple Linear Regression

5.2.1 Selection of Characteristic Peaks for SBS Quantification in Modified Asphalt

FTIR test collects an infrared absorption spectrum of a specimen. In the test, different atom or molecule structures absorb various amounts of energy displayed as characteristic peaks on an absorbance spectrum curve, which can be used to identify specimen’s specific ingredients. Thus, the SBS modified asphalt, which is the compound of SBS and neat asphalt, theoretically could be identified by certain characteristic peaks on absorbance spectra of both SBS and neat asphalt (Wei et al., 1994).

Figure 5-2 displays the FTIR absorbance spectra of SBS, neat asphalt, and SBS modified asphalt. It shows that the peak marked by 2 can represent the existence of neat asphalt, while the peaks marked by 3, 4 and 5 are unique for SBS. Once the neat asphalt is mixed with SBS, their characteristic peaks are combined to generate the spectrum of SBS modified asphalt.



Experiment: Default - Transmission

X:(1499.041) Y:(0.200)

Figure 5-2 FTIR Spectra of SBS, Neat Asphalt, and SBS Modified Asphalt

Since FTIR spectra generally contain multiple characteristic peaks, this study selected various peak variables and indicators, as summarized in Table 5-1, to decide the optimal indicator for asphalt modifier quantification. Generally the height or area of the selected peak increases with the increase of SBS content. For example, in Figure 5-3, which shows the FTIR spectra captured by the TruDefender FTX FTIR analyzer from a group of SBS binders, it is clear that the area of the peak at 966 cm^{-1} gradually increases with increasing SBS contents.

For the selected peak indicators, the following steps of analysis were performed:

1. Evaluate the linear relationship between SBS content and indicators using all test data;
2. Evaluate the linear relationship between SBS content and indicators using averaged test data;

3. Compare the test results from portable FTIR devices with those from desktop FTIR spectrometers to evaluate the performance of portable FTIR devices and their potential for field use;
4. Rank the goodness of fit of simple linear regression models for various indicators, and select the optimal indicator that can lead to best prediction of SBS content.

Table 5-1 Variable and Indicator Selections

Peak Variable	**ID**	**Comments**
Peak Area (1480~1420 cm^{-1})	PA1455	Represent asphalt content
Peak Area (1390~1350 cm^{-1})	PA1375	Represent asphalt content
Peak Area (980~930 cm^{-1})	PA966	Represent SBS polymer content
Peak Area (708~688 cm^{-1})	PA699	Represent SBS polymer content
Height (1455 cm^{-1})	H1455	Represent asphalt content
Height (1455 cm^{-1}, uncorrected)	H1455*	For scale adjustment of absorption
Height (1375 cm^{-1})	H1375	Represent asphalt content
Height (1375 cm^{-1}, uncorrected)	H1375*	For scale adjustment of absorption
Height (966 cm^{-1})	H966	Represent SBS polymer content
Height (699 cm^{-1})	H699	Represent SBS polymer content

Indicator	**Comments**
Ratio of PA966/PA1455	The SBS content might have linear relationship with the ratio of peaks at 966 cm^{-1} or 699 cm^{-1} and 1455 cm^{-1} or 1375 cm^{-1}, not only 966 cm^{-1} or 699 cm^{-1} itself.
Ratio of PA699/PA1455	
Ratio of PA966/PA1375	
Ratio of PA699/PA1375	
Ratio of PA966/H1455	
Ratio of PA966/H1375	
Ratio of H966/H1375	
Ratio of H699/H1375	
Ratio of H966/H1455	
Ratio of H699/H1455	
Ratio of PA966/H1455*	Peaks at 966 cm^{-1} or 699 cm^{-1} might sufficiently represent the content of SBS polymer. However, to eliminate the disturbance from slight changes of y scale (absorbance), these peaks are modified by dividing the relatively fixed height of peak at 1455 cm^{-1} or 1375 cm^{-1}.
Ratio of PA966/H1375*	
Ratio of H699/H1375*	
Ratio of H966/H1375*	
Ratio of H966/H1455*	
Ratio of H699/H1455*	
H966	Peaks at 966 cm^{-1} or 699 cm^{-1} might sufficiently represent the content of SBS polymer, without y scale correction.
H699	

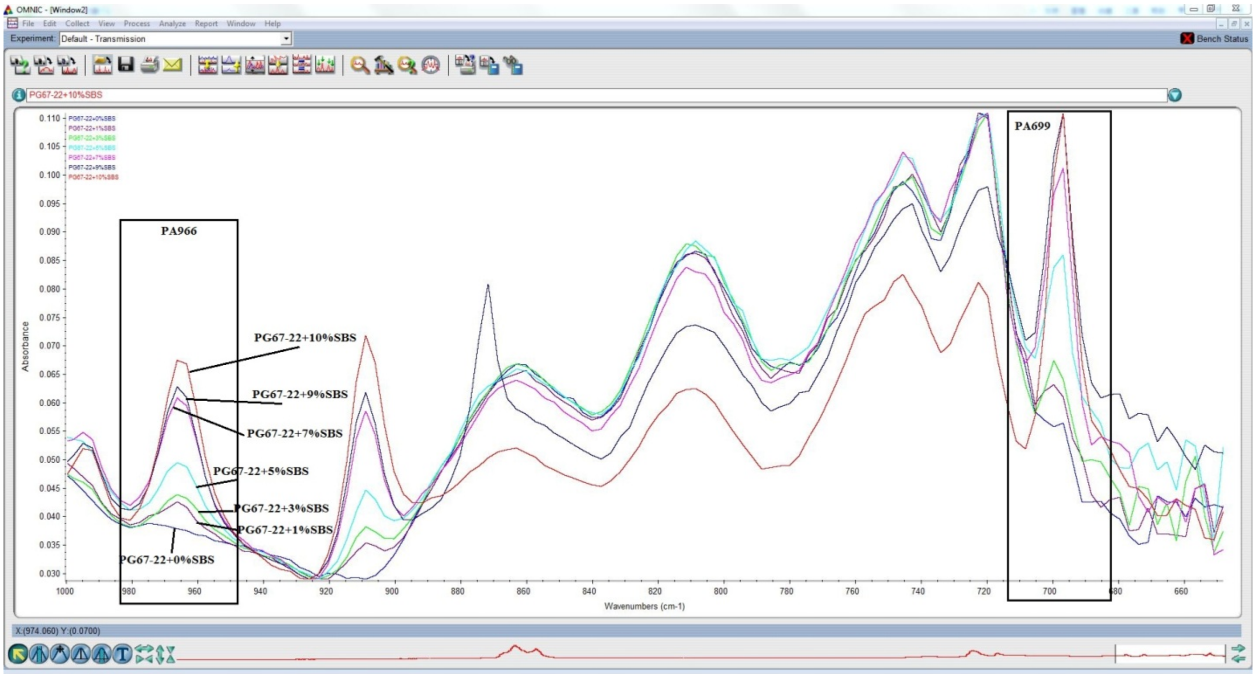

Experiment: Default - Transmission

Figure 5-3 Peak Height or Area as Indicator of SBS Content

5.2.2 Test Results of SBS Modified Asphalt Samples

The relationship between SBS content and each of the 18 indicators was first visually inspected using scatter plots. Figure 5-4 through Figure 5-6 show some typical plots. Other plots have similar patterns as those plots, so are not presented. As can be seen from Figure 5-4, higher SBS content generally increases the ratio of peak areas at 699 cm^{-1} and 1455 cm^{-1}. However, the variance of that ratio also increases with the SBS content, particularly when the SBS content exceeds 5 percent. To reduce estimation error in regression analysis, more replicates of samples were tested for binders with high SBS contents. For example, at least 9 samples were measured for the binder with 10 percent SBS.

Although the data patterns in all the plots seem similar, there are some distinctions. For example, Figure 5-4 and Figure 5-5 show that the ratio of peak areas at 966 cm^{-1} and 1455 cm^{-1} is a better indicator than the ratio of peak areas at 699 cm^{-1} and 1455 cm^{-1}, because its sample variance is smaller, particularly for samples with SBS contents less than 5 percent. Thus, it is necessary to select an indicator that can minimize the prediction error of an estimated simple linear regression model. Ranking of the indicators is discussed in Section 5.2.4, and summarized in Table 5-2.

To better examine the relationship visually, the average values of each indicator were plotted against SBS contents, as illustrated in Figure 5-7 through Figure 5-9. These figures more clearly exhibit the relationship between indicators and SBS content, and emphasize the importance of indicator selection. For example, for the Ergon samples, the indicator PA966/PA1455 (Figure 5-7) has a better linear relationship with SBS content than the indicator PA699/PA1455 (Figure 5-8). For the USF samples, Figure 5-9 shows that the H699 indicator has a good linear relationship with SBS content.

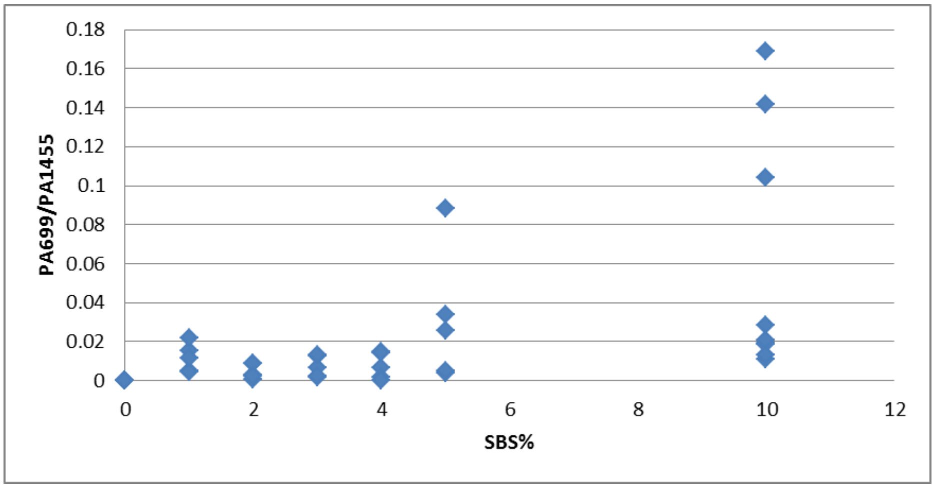


Figure 5-4 Scatter Plot of PA699/PA1455 vs. SBS Content from Ergon Samples

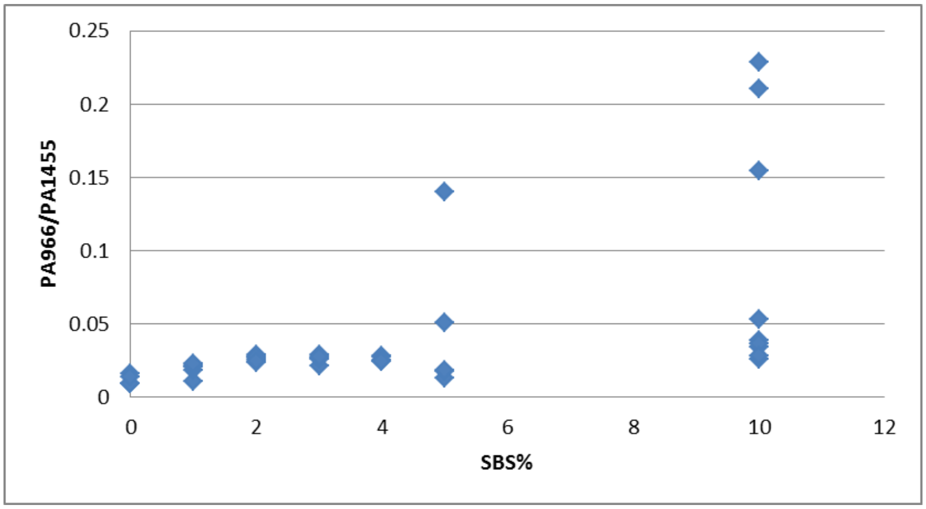


Figure 5-5 Scatter Plot of PA966/PA1455 vs. SBS Content from Ergon Samples

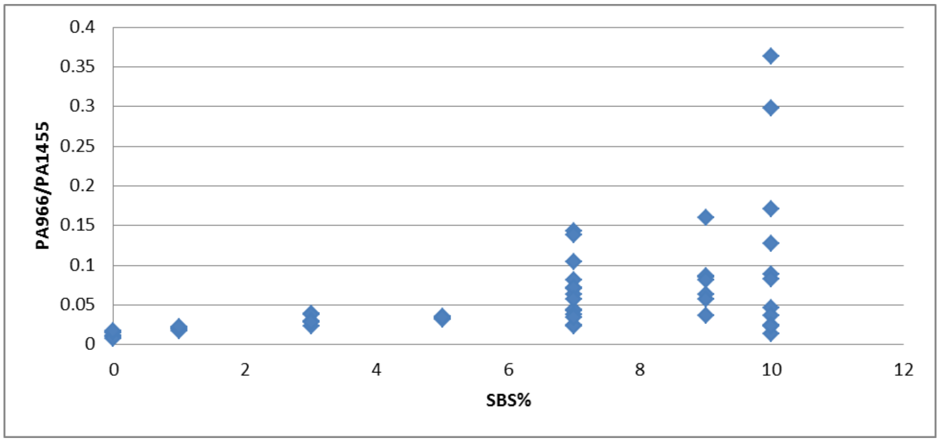


Figure 5-6 Scatter Plot of PA966/PA1455 vs. SBS Content from USF Samples

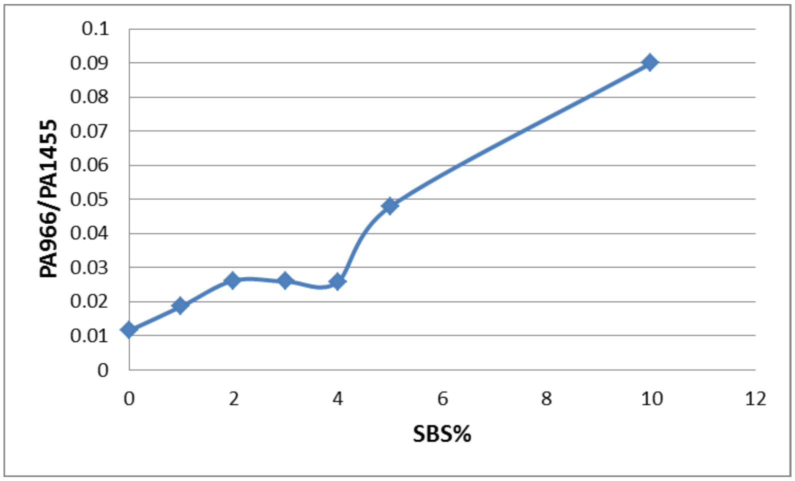


Figure 5-7 Average Value of PA966/PA1455 vs. SBS Content from Ergon Samples

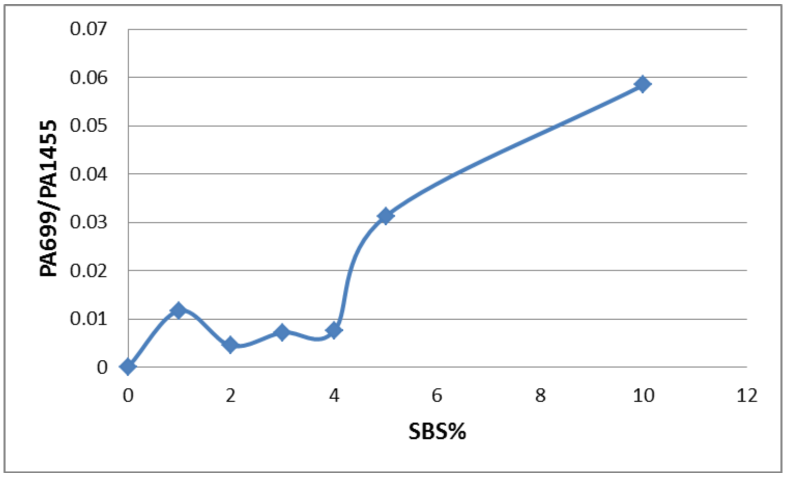


Figure 5-8 Average Value of PA699/PA1455 vs. SBS Content from Ergon Samples

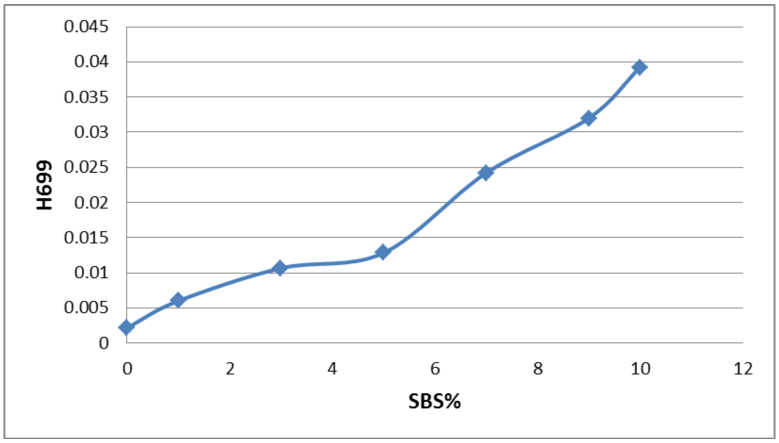


Figure 5-9 Average Value of H699 vs. SBS Content from USF Samples

5.2.3 Comparison of Results from Various FTIR Spectrometers

Before continuing with further data analysis, the test results from the handheld TruDefender FTX FTIR analyzer were compared with the results from the desktop Nicolet 6700 FTIR spectrometer and the portable Bruker Alpha FTIR spectrometer, to examine the accuracy of these devices and the quality of the binder samples.

5.2.3.1 Comparison of Results from Desktop and Handheld FTIR Spectrometers

Currently, mainly desktop FTIR spectrometers are used in research and practice for quantifying polymer content in asphalt binders. The FTIR test procedure specified in AASHTO T 302-05 also seems to be based on desktop FTIR spectrometers. Whether or not the use of a portable FTIR spectrometer would lead to less accurate or more noisy data remains a question. This study intended to use the Nicolet 6700 FTIR spectrometer, which is well calibrated and maintained, to provide reference data for the portable FTIR spectrometer for comparison. For the other desktop analyzer (the Bruker Tensor II) that was initially included in the study, due to limited access of investigators to it, it was later excluded from the test plan.

As introduced previously, the Nicolet 6700 FTIR spectrometer has a sample measurement area much larger than the TruDefender FTX FTIR analyzer. Moreover, its number of scans per test is almost nine times more than that of the TruDefender FTX FTIR analyzer. Variance in test results from replicate samples, therefore, is smaller for the Nicolet 6700 FTIR spectrometer. Thus, only two replicate samples at each SBS content were tested by the Nicolet 6700 FTIR spectrometer.

Figure 5-10 and Figure 5-11 compare the absorbance spectra of the same binder sample (USF 4% SBS binder) measured by the desktop (Nicolet) and handheld (TruDefender) spectrometers, respectively. It can be seen that the two absorbance spectra are very similar in terms of shape and characteristic peak locations. Note that absorbance (y scale) does not have a unit so its value has only relative meaning. The two spectra do not have to perfectly match each other. This comparison indicates that the handheld FTIR spectrometer can produce results compatible with those of the desktop FTIR spectrometer.

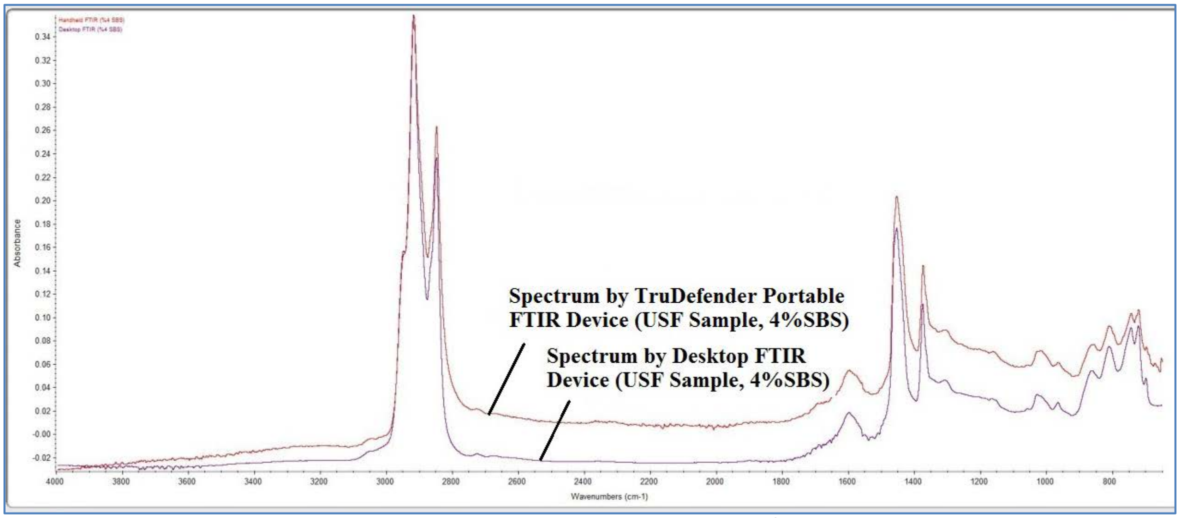


Figure 5-10 Comparison between Spectra (4000 - 650 cm^{-1}) from Handheld and Desktop FTIR Spectrometers

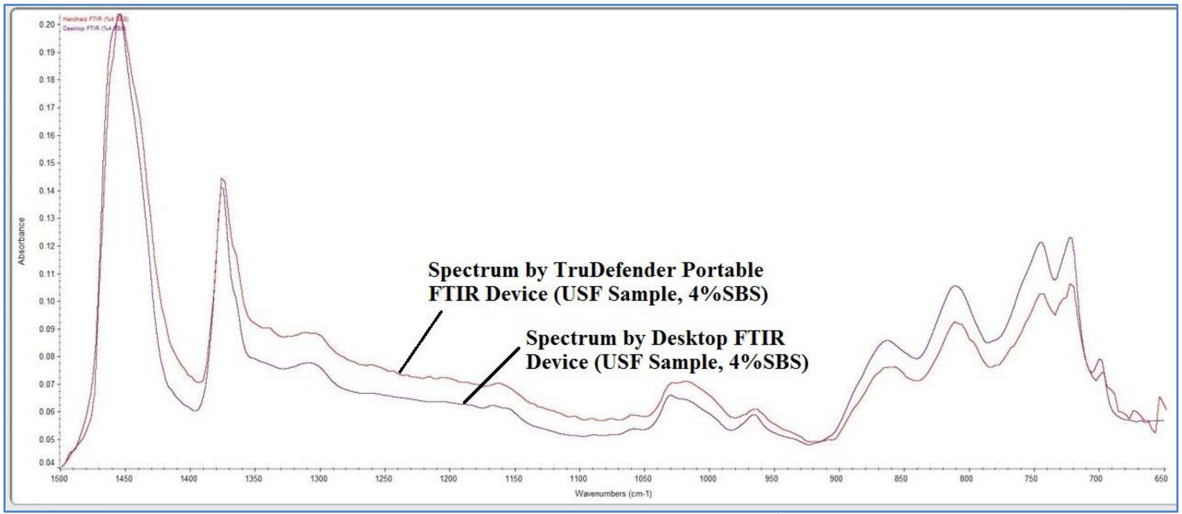


Figure 5-11 Comparison between Spectra (1500 - 650 cm^{-1}) from Handheld and Desktop FTIR Spectrometers

The relationships between indicators and SBS content are also compared for the handheld and desktop FTIR spectrometers. Comparison based on the Ergon samples is illustrated in Figure 5-12 and Figure 5-13, which use H966/H1455 and H966/H1375 as indicators, respectively. Comparison based on the USF samples is illustrated in Figure 5-14 and Figure 5-15, which use PA966/PA1455 and PA966/PA1375 as indicators, respectively. In all the figures the error bar represents one standard error of the handheld FTIR test data.

As can be seen from Figure 5-12 and Figure 5-13, results from the handheld and the desktop FTIR spectrometers match well with each other for Ergon binder samples with SBS content less than 5 percent. Changing the indicator may slightly affect the goodness of match. For Ergon binder samples with 5 or 10 percent SBS, the desktop FTIR spectrometer produced lower values of the indicators.

For the USF samples, good match in results between the handheld and the desktop FTIR spectrometers is also observed (Figure 5-14 and Figure 5-15). It can be seen that for USF binder samples with 10 percent SBS, the desktop FTIR spectrometer produced lower values of the indicators.

The consistency in test results from the handheld and the desktop FTIR spectrometers indicates the following facts:

- In terms of quantifying SBS content in asphalt binders, particularly for binders with less than 5 percent SBS, the handheld FTIR spectrometer may provide results of similar accuracy to those of the desktop FTIR spectrometer.
- SBS is uniformly distributed in each of the asphalt binders, at least for Ergon binders with SBS content less than 5 percent and for USF binders with SBS content less than 10 percent, since different samples were tested in the handheld and the desktop FTIR spectrometers.

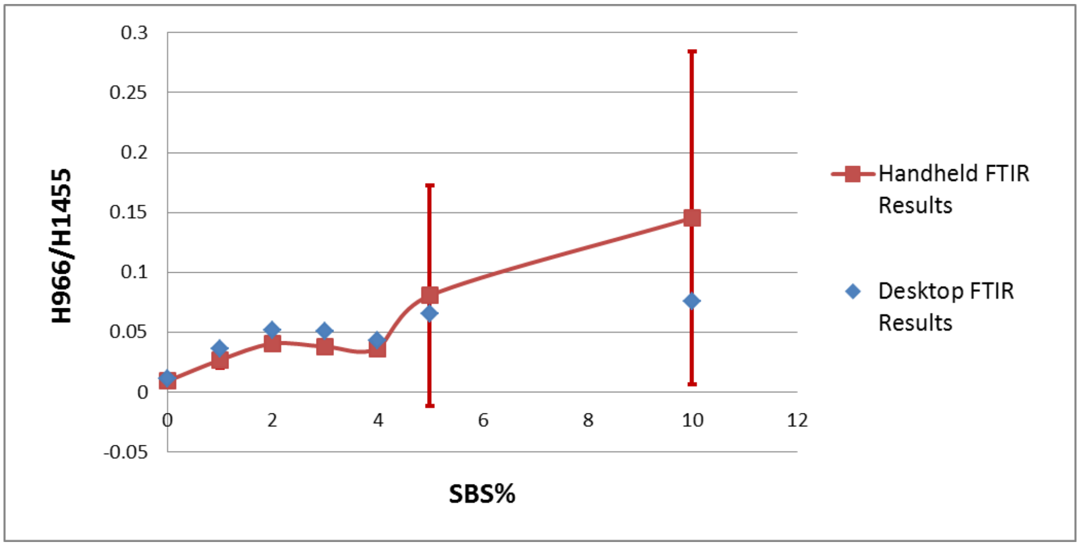


Figure 5-12 H966/H1455 vs. SBS Content in Ergon Samples Using Handheld and Desktop FTIR Spectrometers

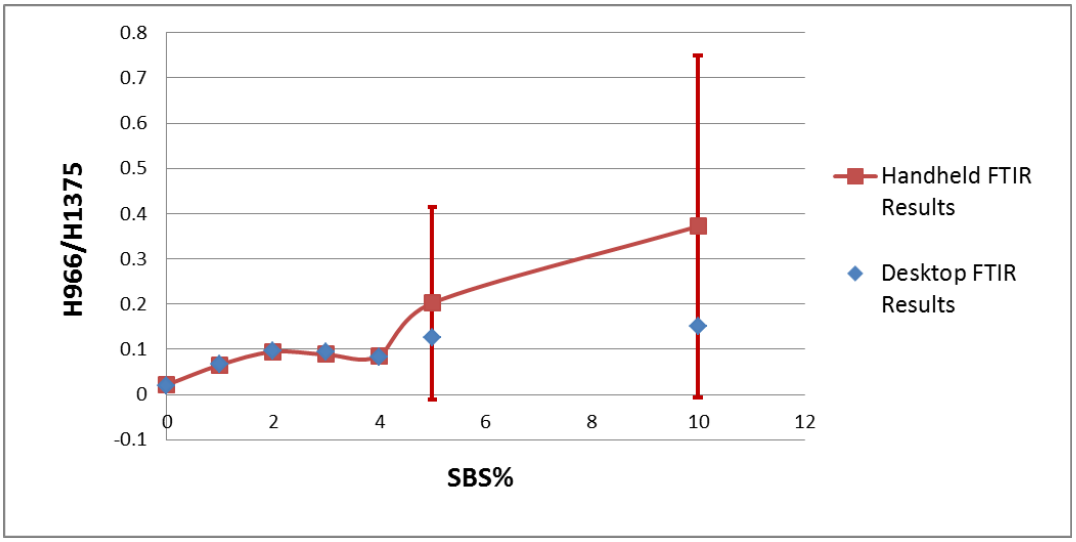


Figure 5-13 H966/H1375 vs. SBS Content in Ergon Samples Using Handheld and Desktop FTIR Spectrometers

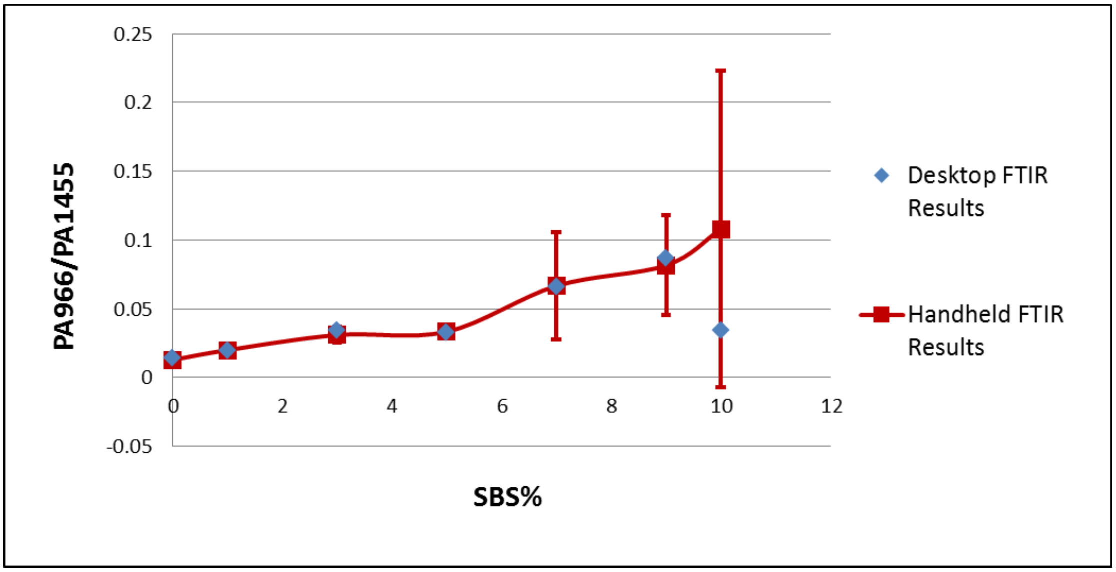


Figure 5-14 PA966/PA1455 vs. SBS Content in USF Samples Using Handheld and Desktop FTIR Spectrometers

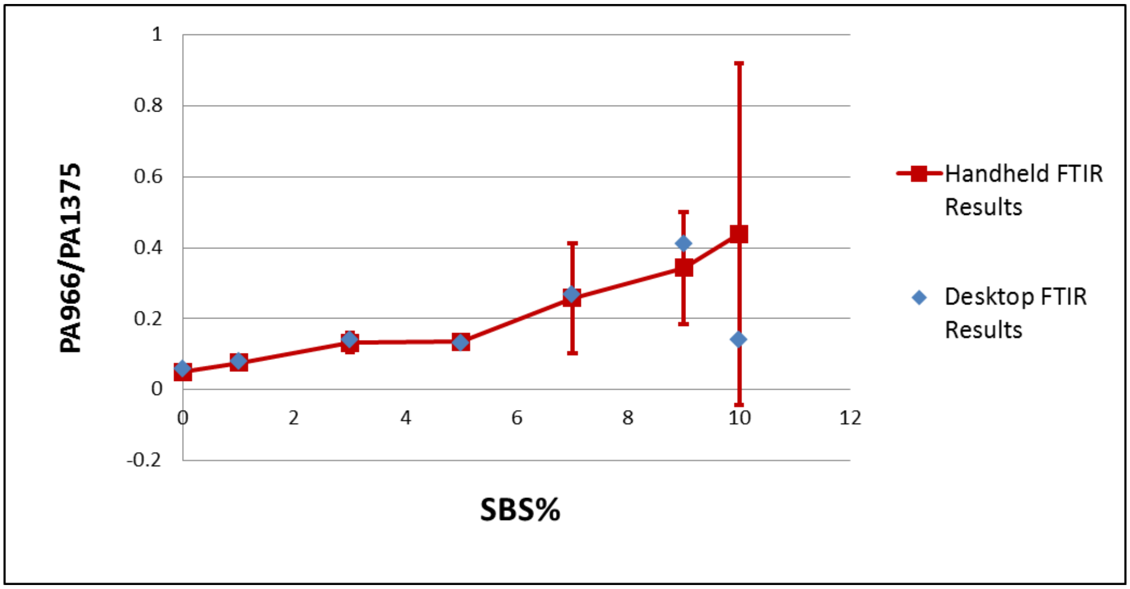


Figure 5-15 PA966/PA1375 vs. SBS Content in USF Samples Using Handheld and Desktop FTIR Spectrometers

5.2.3.2 Comparison of Results from the Bruker and the TruDefender Portable FTIR Spectrometers

As discussed in Section 4.1, the Bruker Alpha FTIR spectrometer is less portable than the TruDefender FTX FTIR analyzer. Both spectrometers, however, use diamond crystal requiring the same amount of test sample, and follow similar test procedures. Since different samples of each asphalt binder were tested by the two spectrometers, comparison of results from the two spectrometers can also attest the uniformity of SBS distribution in each binder.

Figure 5-16 gives a first glimpse of the spectra of one binder from these two portable spectrometers, along with that from the desktop Nicolet 6700 FTIR spectrometer. It can be seen that the two portable FTIR spectrometers produce very similar test results.

Figure 5-17 presents the comparison based on the USF samples, using PA966/PA1455 as the indicator. As can be seen, results from the two portable spectrometers match well with each other, particularly for binder samples with SBS content less than 10 percent. Higher variance in the Bruker data is also observed at higher SBS contents, which is consistent with the TruDefender data. These findings suggest that the USF binder samples prepared using the dilution procedure (described in Section 4.2.1) are uniform in terms of SBS distribution.

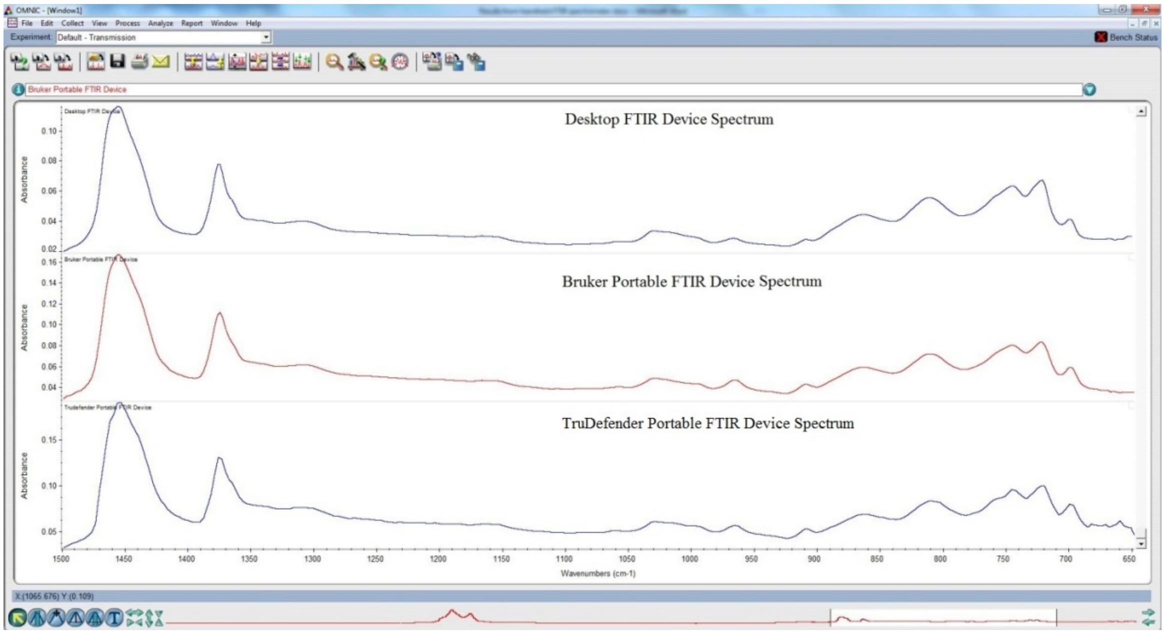


Figure 5-16 Comparison of Spectra of USF Sample with 10% SBS from Two Portable FTIR and One Desktop Spectrometers

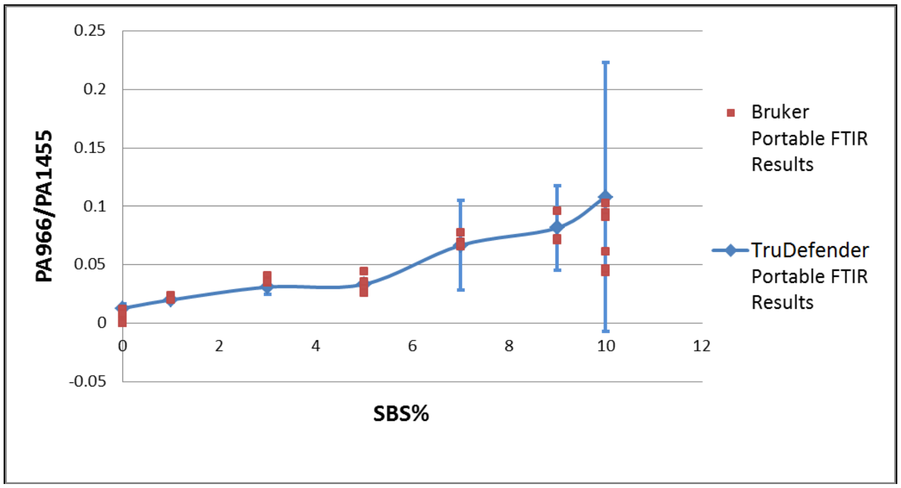


Figure 5-17 Results from Bruker and TruDefender Portable FTIR Spectrometers Based on USF Samples

5.2.4 Ranking of Various Spectrum Indicators

Since the absorbance spectra measured by the TruDefender FTX FTIR analyzer are similar to those measured by the desktop Nicolet 6700 FTIR spectrometer and the portable Bruker Alpha FTIR spectrometer, they were used for further analysis to rank the 18 indicators (listed in Table 5-1) based on the linearity of relationship between them and SBS content. The results are summarized in Table 5-2, in which the linearity of relationship is represented by R-square (R^2) from simple linear regression analysis of SBS content versus each indicator.

Data measured from USF samples and Ergon samples were analyzed separately. Moreover, the linear regression analysis was performed separately on average test data (i.e., average indicator value at each SBS content) and on all test data (i.e., all indicator values from replicates at each SBS content). As can be seen, the R-square values from analysis on all test data are significantly smaller than those from analysis on average test data. This is due to the variability of test results within replicates, particularly from binder samples with high SBS contents.

Based on the R-squares from analysis on average data, it can be seen that H966 has R-squares similar to those of PA966/H1455 but higher than those of other indicators. This indicates that the peak height at 966 cm^{-1} itself can be used to quantify SBS content using the handheld TruDefender FTX FTIR analyzer, without considering scale correction. For the 699 cm^{-1} peak height, R-squares are high for the USF samples, but relatively lower for the Ergon sample, so the H699 indicator is slightly inferior to the H966 indicator.

Using PA966/H1455 and H966 as the proper indicators, their linear relationships with SBS contents are fitted with simple linear regression models on the USF and Ergon samples separately, as shown in Figure 5-18 through Figure 5-21, and presented below.

For USF samples (PG 67-22 + SBS):
PA966/H1455 as indicator: $y = -0.8487 + 3.8124x$ ($R^2=0.935$) (1)
H966 as indicator: $y = -0.2273+454.5455x$ ($R^2=0.936$) (2)

For Ergon samples (PG 52-28 + SBS):
PA966/H1455 as indicator: $y = -0.9794+4.5872x$ ($R^2=0.943$) (3)
H966 as indicator: $y = -0.5263+526.3158x$ ($R^2=0.936$) (4)

In the above equations, y is SBS content (%), and x is the indicator. Note that these model estimations are based on the measurements from the TruDefender FTX FTIR analyzer. It can be seen that for different asphalt sources the estimated parameter values of the linear functions are also different, suggesting that different prediction models for SBS content may need to be developed for different sources of asphalt.

With knowledge of measurement variance of indicators, the minimum number of test repetitions to reach a required level of prediction error in SBS content may be estimated from the above equations. Using Equation (2) for example, the standard error of predicted SBS content can be expressed as

Table 5-2 R-squares For Various Indicators and Data Process Methods

R-square Based on Average Test Data						
	PA966/PA1455	PA699/PA1455	PA966/PA1375	PA699/PA1375	PA966/H1455	PA966/H1455*
USF	0.911	0.943	0.915	0.94	0.922	0.866
Ergon	0.93	0.834	0.917	0.836	0.932	0.933
Ave.	0.9205	0.8885	0.916	0.888	0.927	0.8995
Rank	3	13	6	14	1	10
	PA966/H1375	PA966/H1375*	H966/H1375*	H699/H1375*	H699/H1375	H966/H1375
USF	0.915	0.827	0.817	0.856	0.932	0.907
Ergon	0.922	0.92	0.918	0.874	0.853	0.914
Ave.	0.9185	0.8735	0.8675	0.865	0.8925	0.9105
Rank	5	16	17	18	11	7
	H966/H1455*	H966/H1455	H699/H1455*	H699/H1455	H966	H699
USF	0.859	0.915	0.897	0.941	0.924	0.95
Ergon	0.926	0.923	0.873	0.86	0.923	0.854
Ave.	0.8925	0.919	0.885	0.9005	0.9235	0.902
Rank	11	4	15	9	2	8
R-square Based on All Test Data						
	PA966/PA1455	PA699/PA1455	PA966/PA1375	PA699/PA1375	PA966/H1455	PA966/H1455*
USF	0.291	0.296	0.297	0.298	0.293	0.283
Ergon	0.237	0.253	0.23	0.243	0.248	0.214
Ave.	0.264	0.2745	0.2635	0.2705	0.2705	0.2485
Rank	7	2	9	4	4	14
	PA966/H1375	PA966/H13758*	H966/H1375*	H699/H1375*	H699/H1375	H966/H1375
USF	0.284	0.267	0.274	0.261	0.271	0.289
Ergon	0.235	0.183	0.172	0.188	0.238	0.217
Ave.	0.2595	0.225	0.223	0.2245	0.2545	0.253
Rank	10	16	18	17	11	12
	H966/H1455*	H966/H1455	H699/H1455*	H699/H1455	H966	H699
USF	0.291	0.299	0.277	0.281	0.301	0.28
Ergon	0.199	0.229	0.221	0.253	0.247	0.275
Ave.	0.245	0.264	0.249	0.267	0.274	0.2775
Rank	15	7	13	6	3	1

$$e = 454.5455\sqrt{\frac{Var(x)}{n}} \tag{5}$$

in which *e* is the standard error of predicted SBS content; *Var(x)* is the variance of H966 measurements; and *n* is the number of test repetitions. The measurement variances of H966 based on USF samples are shown in Table 5-3. Using these data for Equation (5), it can be shown that for binders with SBS contents less than or equal to 5 percent, three test replicates may lead to a standard error in prediction less than 0.5 percent; while for binders with 7 or 9 percent, at least 20 test replicates are required to reach a 1 percent standard error in prediction.

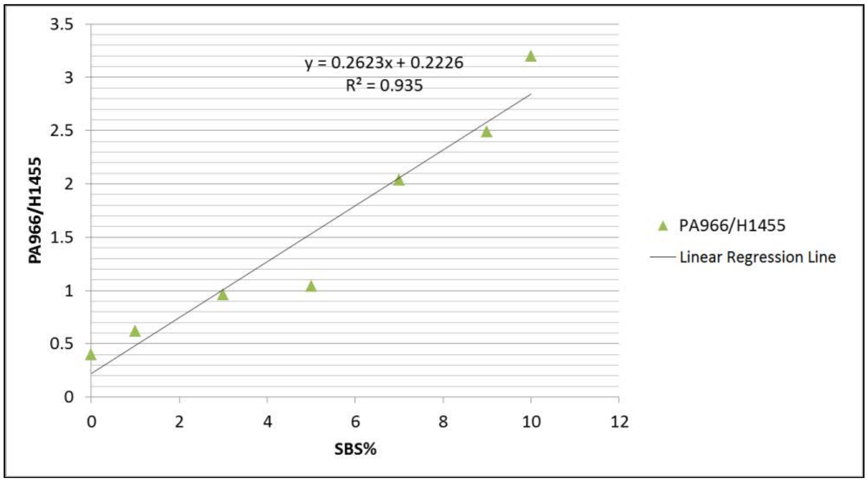


Figure 5-18 PA966/H1455 vs. SBS Content (USF Samples)

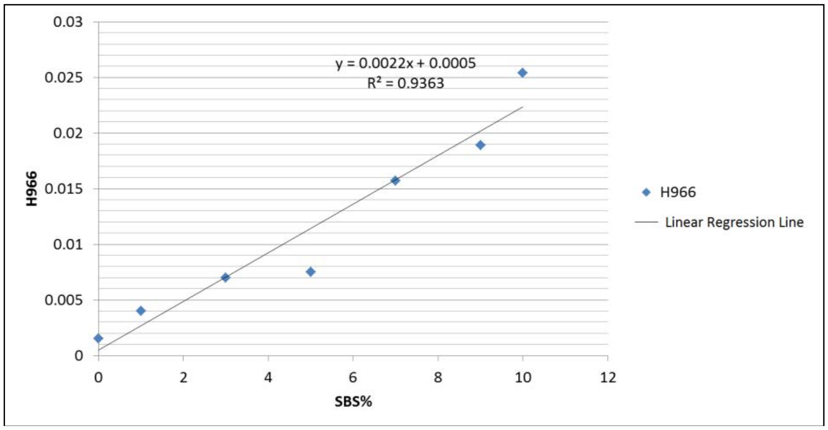


Figure 5-19 H966 vs. SBS Content (USF Samples)

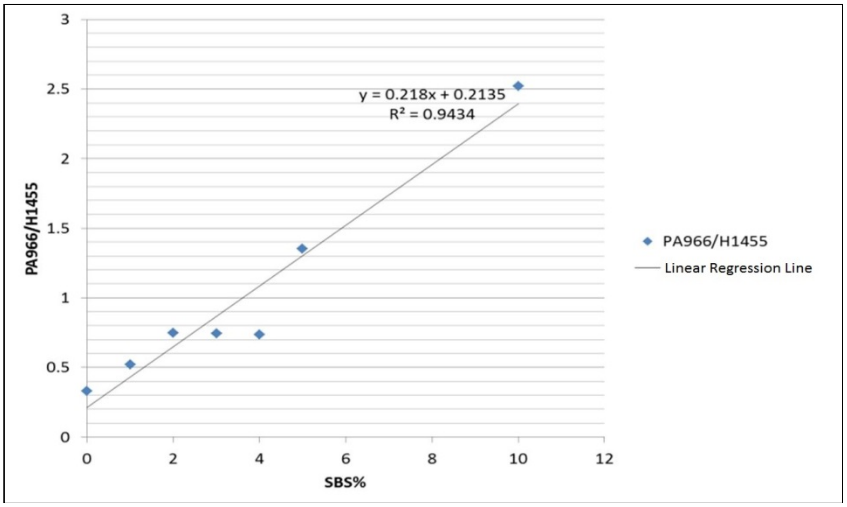


Figure 5-20 PA966/H1455 vs. SBS Content (Ergon Samples)

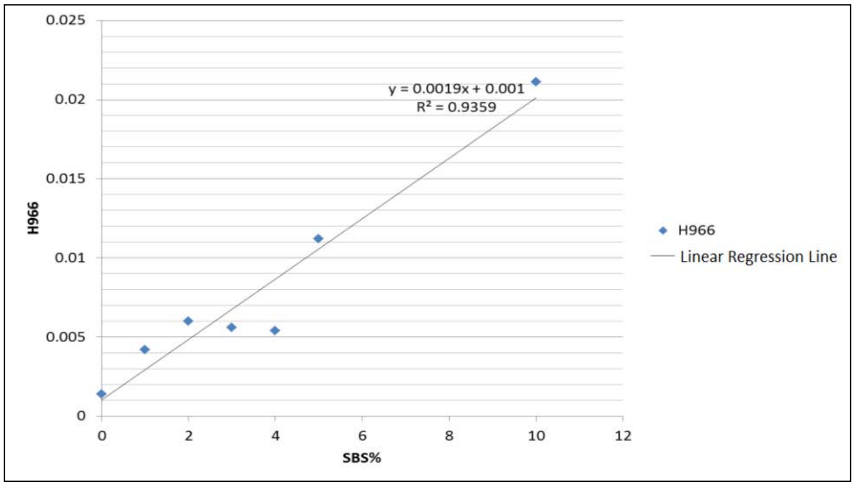


Figure 5-21 H966 vs. SBS Content (Ergon Samples)

Table 5-3 Measurement Variance of H966 from USF Samples

SBS Content (%)	Measurement Variance of H966 (10^{-6})
0	0.3
1	0.0
3	1.6
5	0.7
7	101.8
9	103.6
10	736.8

5.2.5 Verification Using Binder Samples with Unknown Polymer Contents

To verify the prediction models developed in the previous section, binder samples with unknown polymer contents were measured by the TruDefender FTX FTIR analyzer, and their measurements were used as inputs to the prediction models to estimate the SBS contents. It has to be kept in mind that these binder samples are of asphalt sources different from the USF or Ergon samples, so extra prediction errors may be introduced due to this discrepancy.

The prior information of these binder samples, including their PG grades and possible SBS and GTR contents, is shown in Table 5-4. Without loss of generality, the linear functions developed from USF samples (Equations 1 and 2) were used to estimate their SBS contents, with the prediction results summarized in Table 5-4.

If one percent difference from the possible SBS content ranges is deemed acceptable, the prediction results are highlighted in green and red colors, with green representing acceptable estimations while red representing unacceptable estimations. As can be seen, among the 16 binder samples, the linear functions developed from USF samples produced unacceptable prediction results for 6 of them, which are mainly PG 76-22 and PG 82-22 binder samples. This observation is also displayed in Figure 5-22. 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. Thus, it is necessary to develop specific prediction models for each source of asphalt binder.

Table 5-4 Estimated SBS Contents in Binder Samples with Unknown Polymer Contents

Sample ID	Binder Grade	Possible SBS%	Possible GTR%	PA966/ H1455	H966	Estimated SBS% by PA966/ H1455	Estimated SBS% by H966	Comment
FA	N/A	0	0	0	0	0	0	Recycled Asphalt with Oxidation
FB	PG 52-28	0	0	0.415	0.001	0.734	0.227	Asphalt Flux
FC	PG 67-22	0	0	0.368	0.001	0.554	0.227	From Refinery
FD	PG 76-22	2	0	1.843	0.012	6.178	5.227	
FE	PG 76-22	1~2	7	0.413	0.001	0.726	0.227	
FF	N/A	0	0	0	0.006	0	2.500	Fog seal; polymer emulsion residual
FG	PG 76-22	7~8	0	1.884	0.015	6.334	6.591	
FH	N/A	0	12	0.470	0.002	0.943	0.682	
PolyHP	N/A	7~8	0	2.338	0.018	8.065	7.955	
15572	PG 58-22	0	0	0.435	0.001	0.810	0.227	
15589	PG 76-22	1~4	0	2.204	0.016	7.554	7.045	
15447	PG 76-22	0	7	1.478	0.011	4.786	4.773	
15473	PG 76-22	0	0	1.515	0.01	4.927	4.318	
15476	PG 82-22	3~6	0	2.255	0.016	7.748	7.045	
15539	N/A	0	5	0.414	0.001	0.730	0.227	
15487	N/A	0	12	0.212	0.001	0	0.227	

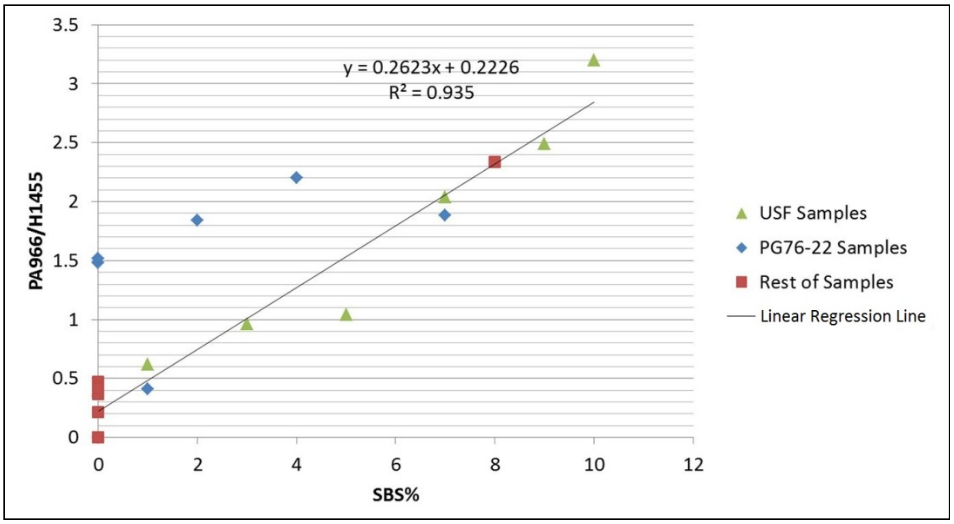


Figure 5-22 SBS Quantification Results of Binder Samples with Unknown Polymer Contents

5.2.6 Test Results of GTR Modified Asphalt Samples

Different from the SBS spectrum, ground tire rubber (GTR) spectrum has no significant characteristic peaks, as shown in Figure 5-23. Its relatively plain shape obstructs the GTR quantification via FTIR devices. There is, however, one general feature in the absorbance spectrum for GTR samples containing carbon. Since carbon can absorb light throughout the entire infrared region and because, with the ATR method, light penetrates to a relatively large depth in the long wavelength region, the baseline of the entire absorbance spectrum would tilt up to the right end, and the tilting angle increases with the carbon content (Shimadzu, 2015). Based on this phenomenon, the tilting angle of the spectrum baseline may be used as an indicator for quantification of GTR in asphalt binders.

In this study, two sets of GTR modified binder samples were prepared in the laboratory with known GTR contents: one using MicroDyne 400-TR sample from Lehigh Technologies Inc., and the other using Microgrind GTR sample from Global Tire Recycling.

For the first set of binder samples (named as MD samples), their absorbance spectra measured by the TruDefender FTX FTIR analyzer are shown in Figure 5-24. As can be seen, the slope of tilted baseline increases with the GTR content in the binder samples. To measure the slope, the spectrum segment between 1093 cm^{-1} and 1268 cm^{-1} was chosen to fit a straight line, due to its relatively smooth shape. The slopes of the fitted lines are shown in Figure 5-25. For comparison, results from the desktop Nicolet 6700 FTIR spectrometer are also shown in the figure. As can be seen, similar to the finding from SBS modified binders, the handheld and the desktop FTIR spectrometers give very close results. Moreover, Figure 5-25 shows that the relationship between GTR content and the slope can be potentially fitted by a quadratic curve.

For the second set of GTR binder samples (i.e., GTR from Global Tire Recycling), however, the tilted baseline was not observed and there is no significant difference among the spectra, as shown in Figure 5-26. This is likely caused by difference in the GTR powder samples. As shown in Figure 5-27, FTIR measurements of the two types of GTR samples revealed a significant difference in the shapes of the spectra in the region 1200 cm^{-1} to 1000 cm^{-1}. It seems like the characteristic peak at 1050 cm^{-1} in the MicroDyne tire rubber spectrum is the cause of observing different baseline slopes in the spectra of the first set of binder samples. Whether or not other sources of GTR will have spectrum features similar to those of the MicroDyne GTR is unknown. More GTR samples from other sources, therefore, need to be evaluated to draw conclusions on the applicability of using a spectrum's tilting angle to quantify GTR content.

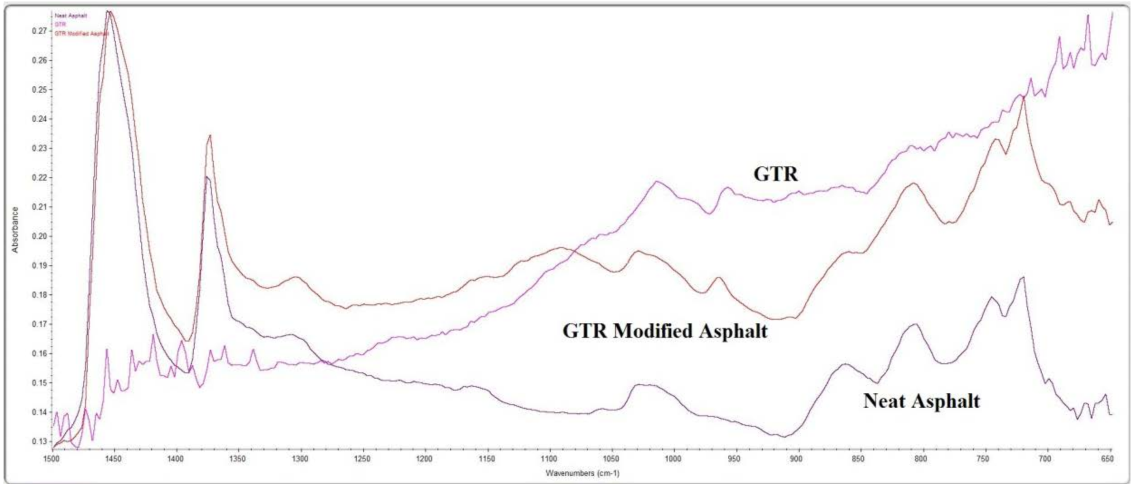


Figure 5-23 FTIR Spectra of GTR, Neat Asphalt, and GTR-Modified Asphalt

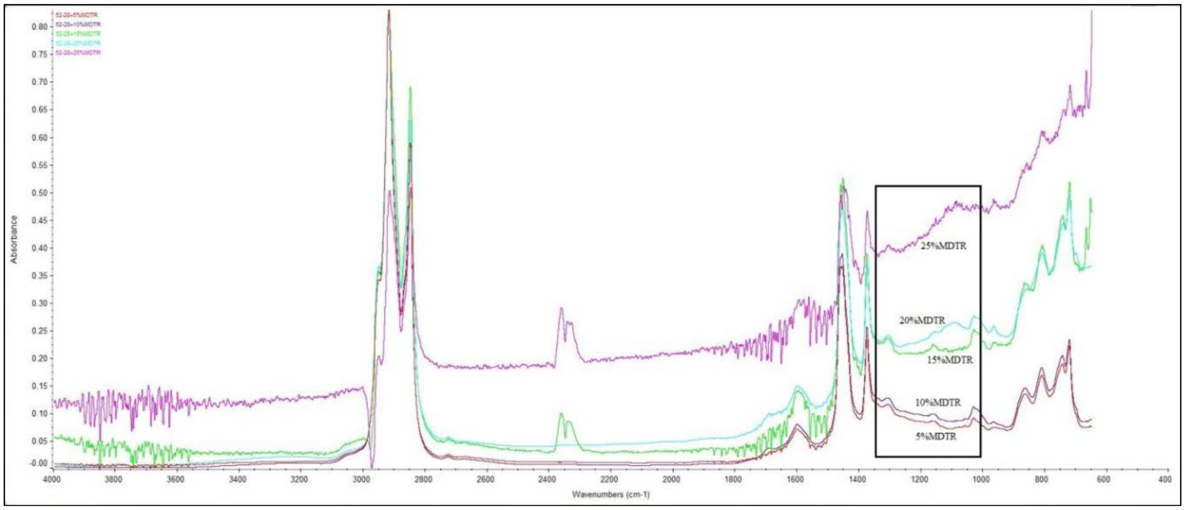


Figure 5-24 Spectra of Binders with Different MD GTR Contents

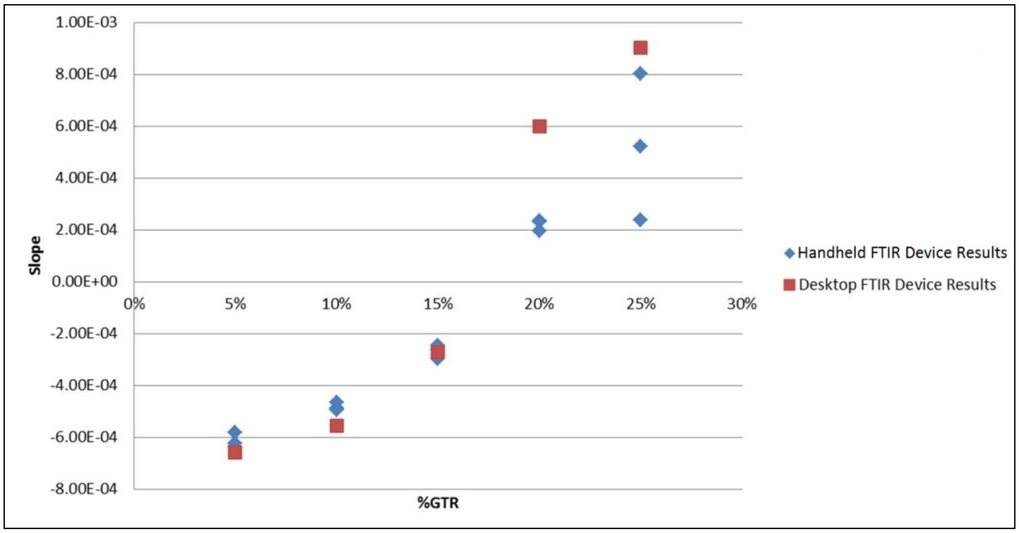


Figure 5-25 GTR Content in MD Samples vs. Slope of Spectrum Baseline

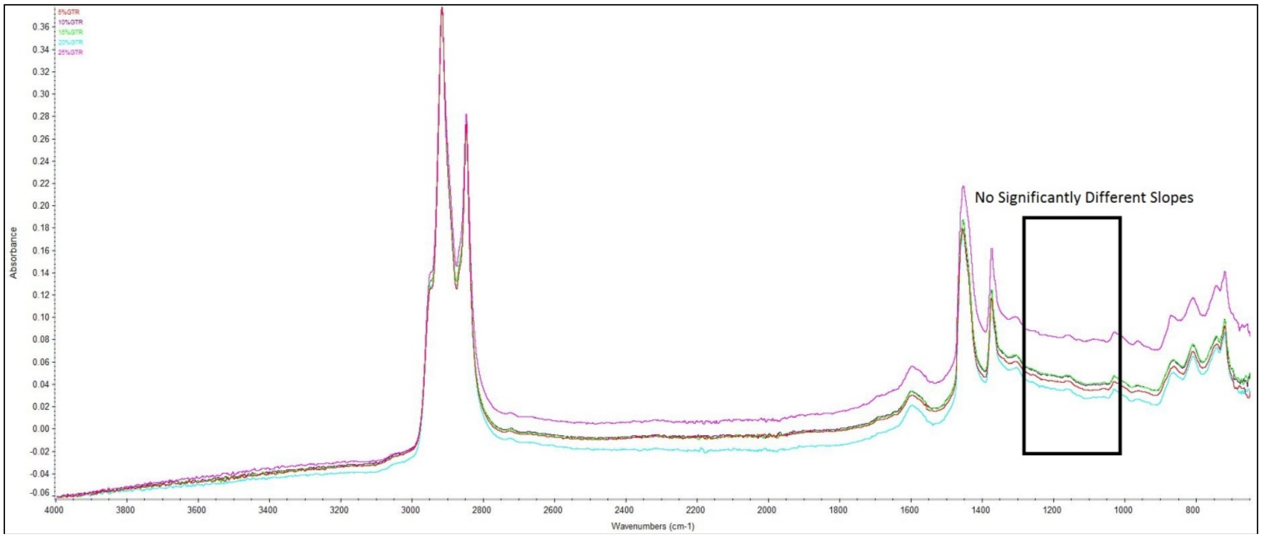


Figure 5-26 Spectra of Binders with GTR from Global Tire Recycling

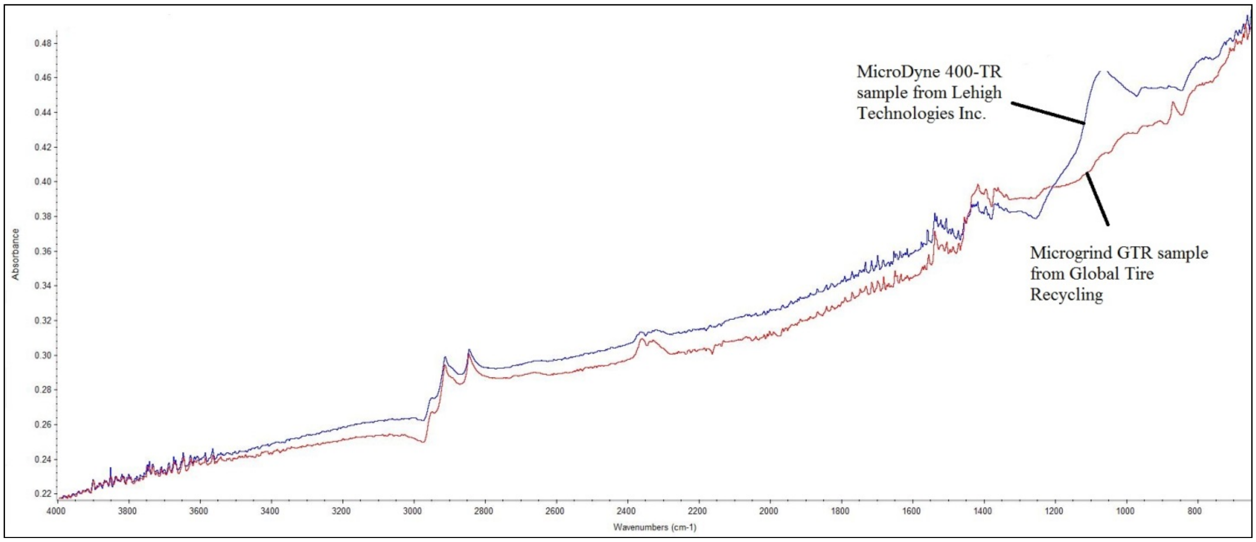


Figure 5-27 Spectra of Two Ground Tire Rubbers

5.2.7 Possibility of Using Mixture Samples in FTIR Test

Instead of scanning asphalt binder samples, asphalt mixtures samples containing aggregates were attempted in the TruDefender FTX FTIR analyzer testing. Both coarse aggregate particles coated with asphalt film and asphalt mastic particles were tried. Unfortunately, in multiple trials with three asphalt mixtures, the scanning process was all stagnant and failed to produce successful results, likely due to insufficient asphalt film thickness or incomplete contact between aggregates and diamond crystal. Thus, it is infeasible to run the FTIR test directly on mixture samples.

5.3 Test Result Analysis Using TQ Analyst in OMNIC

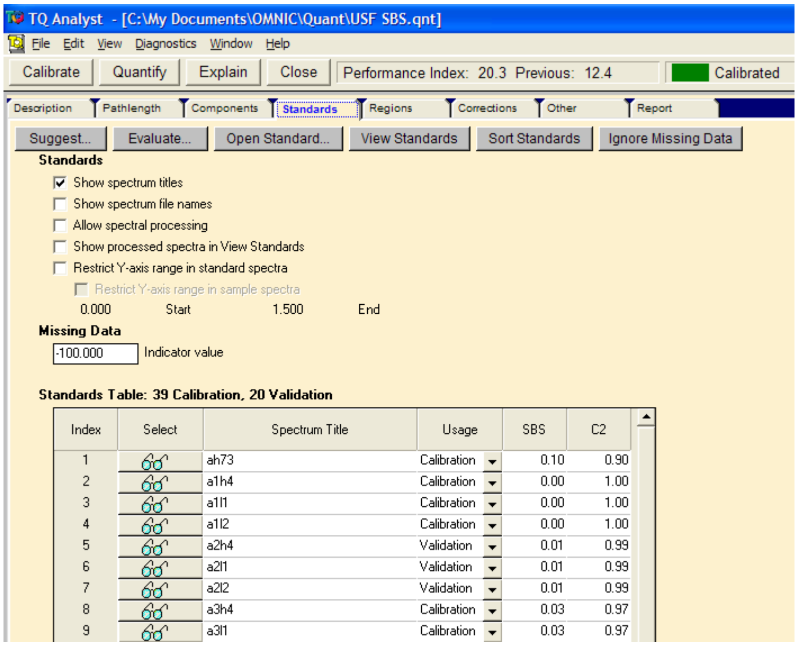
Common FTIR analysis software, such as OMNIC and OPUS, incorporates functions for material content prediction, which are generally based on advanced statistical models. In this section, the TQ analyst in OMNIC was tried for data analysis. Three procedures, based on partial least squares (PLS), principal component regression (PCR), and stepwise multiple linear regression (SMLR) analysis, were followed and compared.

5.3.1 Partial Least Squares

In the field of spectral analysis, partial least squares (PLS) is one of the most powerful regression models for measuring the amount of each component in the complex spectrum, although the sample size is limited and the peaks severely overlap (Haaland and Thomas, 1988; Tobias, 2003; Cong et al., 2013). Differing from standard regression methods, PLS projects both X and Y data to a new dimension, which is termed as bilinear model. Instead of using all manifest factors, PLS introduces latent factors to connect both spaces and indirectly explains dependent variables Y by independent variables X.

In TQ analyst, PLS method allows user to quantify at most fifty components in each specimen through setting several spectrum regions. For the sample size of PLS, termed as “standard” in TQ analyst, this program requests the user to calibrate at least three standards for each component and recommends at least one validation standard. All calibrated spectra are inputs with their corresponding contents of SBS and neat asphalt to generate the database for PLS statistical analysis, as shown in Figure 5-28.

Since the intensities of spectrum peaks vary with sample thickness and composition, TQ analyst requires users to set pathlength for the quantitative purpose. Since the handheld TruDefender FTIR analyzer controls sample thickness properly, pathlength type was set as “constant” in this case.



Performance Index: 20.3 Previous: 12.4

Standards

☑ Show spectrum titles
☐ Show spectrum file names
☐ Allow spectral processing
☐ Show processed spectra in View Standards
☐ Restrict Y-axis range in standard spectra
☐ Restrict Y-axis range in sample spectra
0.000 Start 1.500 End

Missing Data

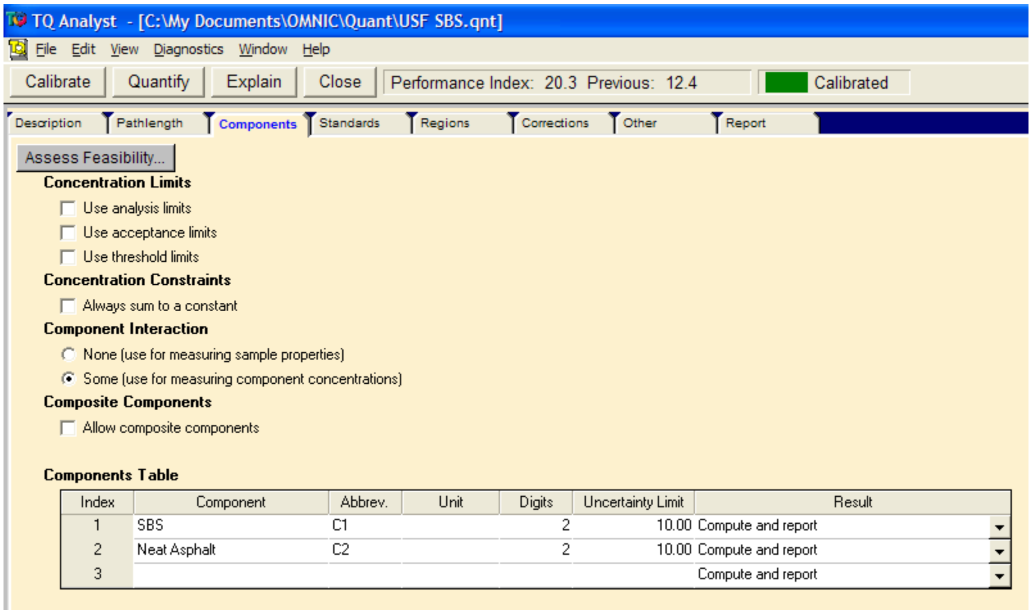
-100.000 Indicator value

Standards Table: 39 Calibration, 20 Validation

Index	Select	Spectrum Title	Usage	SBS	C2
1		ah73	Calibration	0.10	0.90
2		a1h4	Calibration	0.00	1.00
3		a1l1	Calibration	0.00	1.00
4		a1l2	Calibration	0.00	1.00
5		a2h4	Validation	0.01	0.99
6		a2l1	Validation	0.01	0.99
7		a2l2	Validation	0.01	0.99
8		a3h4	Calibration	0.03	0.97
9		a3l1	Calibration	0.03	0.97

Figure 5-28 Standards: Calibration Input as Database

The dependent variables in PLS in this study include two components: pure SBS and neat asphalt. The component interaction is also considered to measure the component concentrations, as shown in Figure 5-29. For the independent variables, several spectrum regions are automatically selected in TQ analyst, via comparing samples' spectra to pick the significant characteristic peaks. The region type, location, and baseline type also can be manually adjusted. In this case, for the USF samples, five spectral ranges with baselines were picked as shown in Figure 5-30.



Performance Index: 20.3 Previous: 12.4

🟩 Calibrated

Concentration Limits

☐ Use analysis limits
☐ Use acceptance limits
☐ Use threshold limits

Concentration Constraints

☐ Always sum to a constant

Component Interaction

○ None (use for measuring sample properties)
● Some (use for measuring component concentrations)

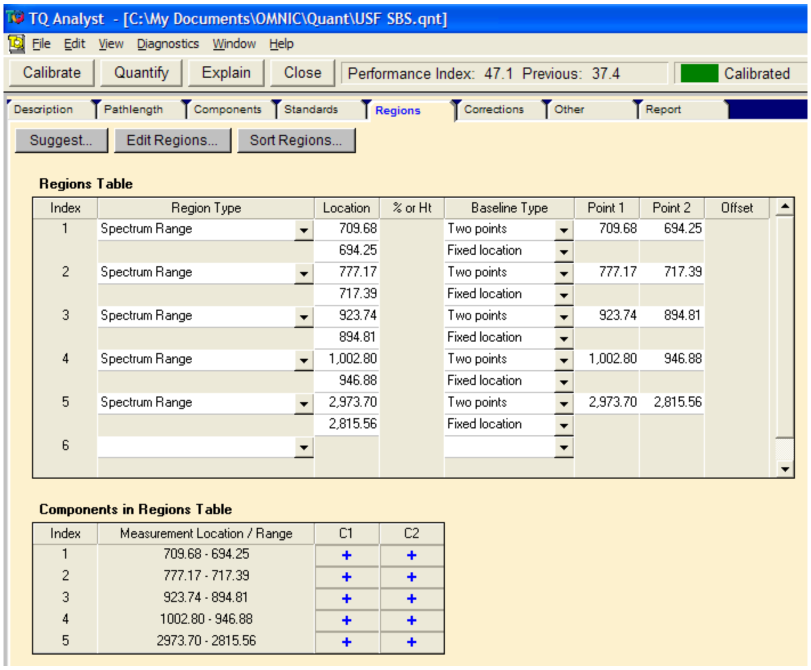
Composite Components

☐ Allow composite components

Components Table

Index	Component	Abbrev.	Unit	Digits	Uncertainty Limit	Result
1	SBS	C1		2	10.00	Compute and report
2	Neat Asphalt	C2		2	10.00	Compute and report
3						Compute and report

Figure 5-29 Components: Dependent Variable Definition



Performance Index: 47.1 Previous: 37.4

🟩 Calibrated

Regions Table

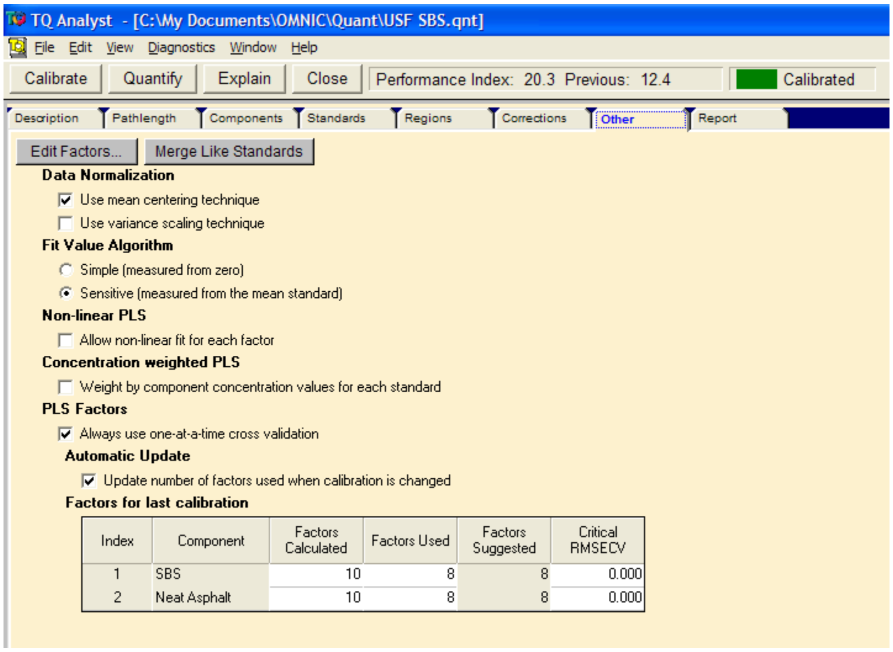
Index	Region Type	Location	% or Ht	Baseline Type	Point 1	Point 2	Offset
1	Spectrum Range	709.68		Two points	709.68	694.25	
		694.25		Fixed location			
2	Spectrum Range	777.17		Two points	777.17	717.39	
		717.39		Fixed location			
3	Spectrum Range	923.74		Two points	923.74	894.81	
		894.81		Fixed location			
4	Spectrum Range	1,002.80		Two points	1,002.80	946.88	
		946.88		Fixed location			
5	Spectrum Range	2,973.70		Two points	2,973.70	2,815.56	
		2,815.56		Fixed location			
6							

Components in Regions Table

Index	Measurement Location / Range	C1	C2
1	709.68 - 694.25	+	+
2	777.17 - 717.39	+	+
3	923.74 - 894.81	+	+
4	1002.80 - 946.88	+	+
5	2973.70 - 2815.56	+	+

Figure 5-30 Regions: Independent Variable Definition

TQ analyst also allows user to set the data normalization techniques and to pick the fit value algorithms, and provides user options for non-linear fit, weighted PLS method, and correction standards, as shown in Figure 5-31. Through several trials to reach the maximum correction coefficient, this study selected mean centering technique with sensitive fit value algorithm, and did not use weighted PLS or non-linear PLS. To best fit the calculated versus actual values, the "third order" correction curve plot was also applied, which increased the correction coefficient from 0.967 to 0.969 as the final result.



Performance Index: 20.3 Previous: 12.4

🟩 Calibrated

Data Normalization

☑ Use mean centering technique

☐ Use variance scaling technique

Fit Value Algorithm

○ Simple (measured from zero)

● Sensitive (measured from the mean standard)

Non-linear PLS

☐ Allow non-linear fit for each factor

Concentration weighted PLS

☐ Weight by component concentration values for each standard

PLS Factors

☑ Always use one-at-a-time cross validation

Automatic Update

☑ Update number of factors used when calibration is changed

Factors for last calibration

Index	Component	Factors Calculated	Factors Used	Factors Suggested	Critical RMSECV
1	SBS	10	8	8	0.000
2	Neat Asphalt	10	8	8	0.000

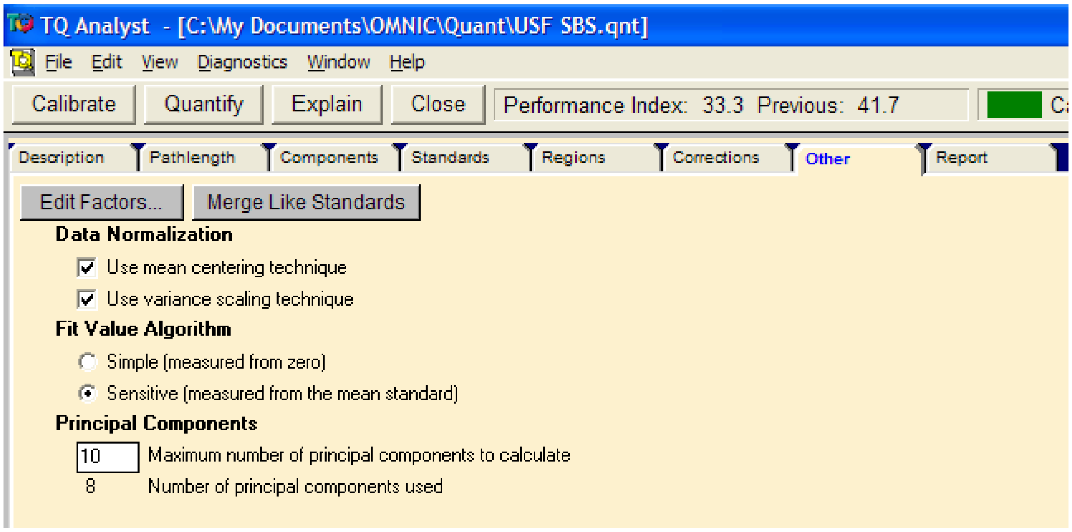
Figure 5-31 Other: Setting of Advanced PLS

5.3.2 Principal Component Regression

Principal component regression (PCR) is another useful regression method for spectral analysis, since it could filter the highly correlated regions in spectrum. Specifically, through orthogonal transformation, a set of highly correlated variables are converted to a set of linearly uncorrelated values. This set of values is termed as principal component. The higher variance represents higher level of principal component, and the lower variance shows the "component" which could be filtered out. After obtaining all principal components, PCR estimates the dependent variables by these principal components via standard linear regression model (Bair et al., 2006; Wikipedia, 2015).

PCR algorithm requires more factors to describe the variation in the spectral data than the PLS does. Moreover, compared with the PLS method, all components should be observed in each spectral region using PCR method, or the PLS method is better.

In TQ analyst, differing from PLS, PCR does not contain non-linear or weighted fit function, as shown in Figure 5-32.



Data Normalization

☑ Use mean centering technique

☑ Use variance scaling technique

Fit Value Algorithm

○ Simple (measured from zero)

● Sensitive (measured from the mean standard)

Principal Components

10 Maximum number of principal components to calculate

8 Number of principal components used

Figure 5-32 Other: Extra Setting of PCR

5.3.3 Stepwise Multiple Linear Regression

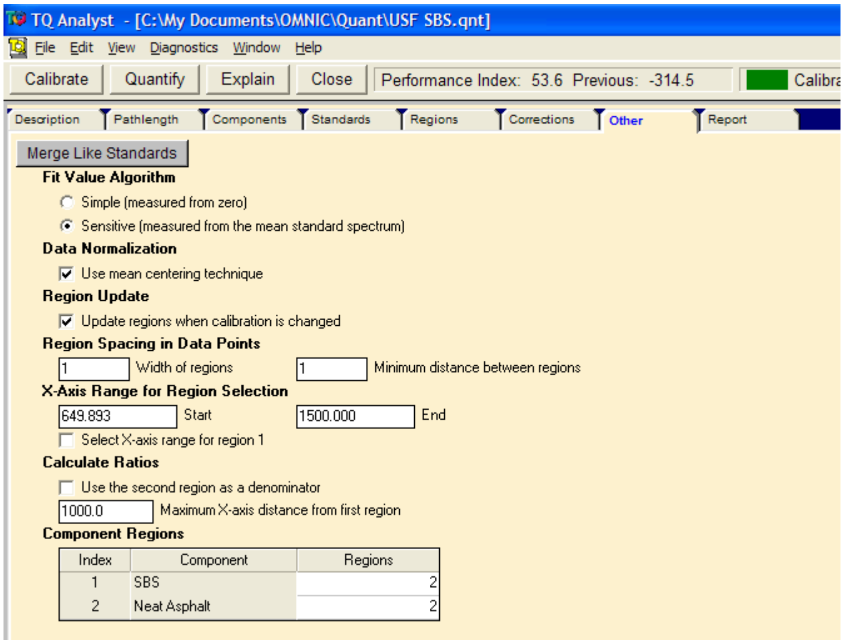
In TQ analyst, the Stepwise Multiple Linear Regression (SMLR) is defined as a function of the absorbance at various frequencies to express the concentration, which is the opposite of the classical least squares technique. As one of the common stepwise regression methods, TQ analyst orderly selects regions (frequencies) for each component until each component automatically matches one proper region.

Given the weakness of correctly matching the spectral regions with their corresponding components via SMLR, the additional regions may mismatch the correct components and further degrade the percision of SMLR estimation. Thus, SMLR requires proper region selections with very few spectral overlaps to explain the content of each component in the specimen. For the setting of SMLR in TQ analyst, instead of manually selecting individual region, only the range of all region selections is required to be set. In this case, the selected wavelength is located within 650 to 1500 cm^{-1}. The rest of setting option are the same as those in the PLS method.

5.3.4 Regression Method Comparison

For illustrating and comparing the accuracies of these regression methods, Figure 5-34 plots the calculated versus actual values using different regression methods. Based on the correction coefficients, PLS is the most proper regression method to explain the SBS contents in modified asphalt by the spectral indicators in this study. Moreover, PLS, PCR, and SMLR all have significantly better estimation performance than the classical least squares (CLS).

It is worth pointing out that the TQ analyst software automatically alters some calibration standards to be verification standards, if the number of standards is sufficient for regression. In this case, the USF samples with 1% and 7% SBS were regarded as verification data. In next section, since 16 extra samples were input as verification standards, all USF samples were set as calibration standards. Thus, the correction coefficients displayed in the figures in section 5.3.4 and 5.3.5 are slightly different.



Performance Index: 53.6 Previous: -314.5

Fit Value Algorithm

○ Simple (measured from zero)

● Sensitive (measured from the mean standard spectrum)

Data Normalization

☑ Use mean centering technique

Region Update

☑ Update regions when calibration is changed

Region Spacing in Data Points

1 Width of regions

1 Minimum distance between regions

X-Axis Range for Region Selection

649.893 Start

1500.000 End

☐ Select X-axis range for region 1

Calculate Ratios

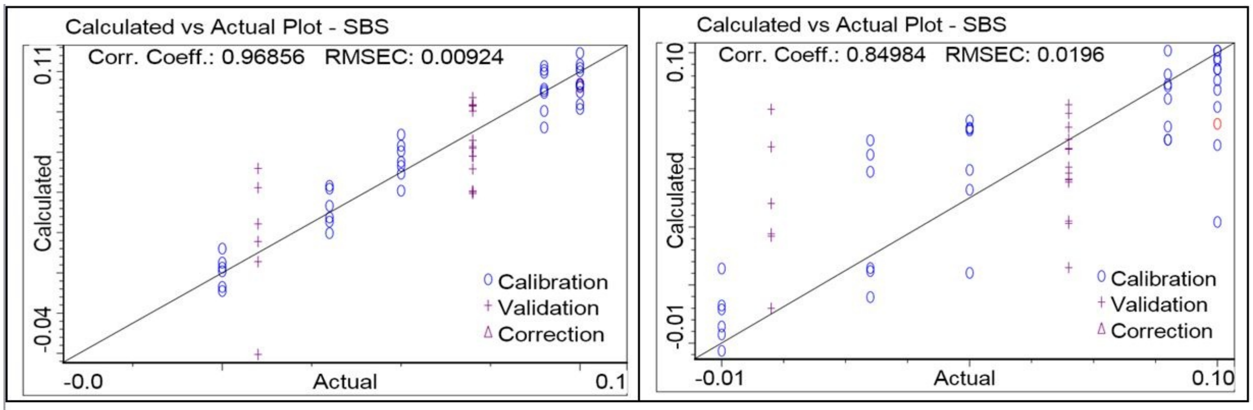
☐ Use the second region as a denominator

1000.0 Maximum X-axis distance from first region

Component Regions

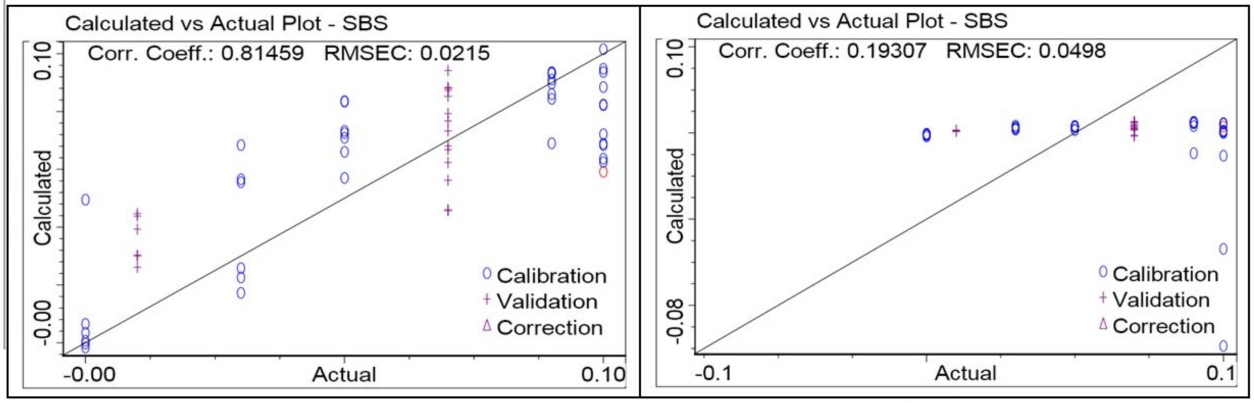
Index	Component	Regions
1	SBS	2
2	Neat Asphalt	2

Figure 5-33 Other: Extra Setting of SMLR



Partial Least Squares

Principal Component Regression



Stepwise Multiple Linear Regression

Classical Least Squares

Figure 5-34 Results Comparison between Regression Methods in TQ Analyst

5.3.5 Verification in TQ Analyst

Although the PLS explains the SBS contents with the highest correction coefficient, it does not mean that this PLS can best estimate SBS content in any asphalt binder. This section selected several samples from other sources to verify the accuracies of these advanced regression models.

After the standards for calibration were input into these regression models, the spectra of 16 samples from other sources (as listed in Table 5-4) with their average possible SBS contents were also input as the standards for verification. As results, TQ analyst output the difference between calculated contents and actual contents, as shown in Figure 5-35 through Figure 5-37. These figures indicate that the measurement performance of PCR in this case is significantly better than those of PLS and SMLR, although the correction coefficient in PLS is the highest. For PLS and SMLR, the large differences between calculated and actual values show their unacceptable inaccuracies.

Comparing Figure 5-22 with Figure 5-36, however, the advantage of PCR is not significant. Thus, it is sufficient to use the simple linear relationship between peak height at 966 cm^{-1} and SBS content to quantify SBS content, while using the more advanced statistical models is not necessary, although they could fit the calibration curve better.

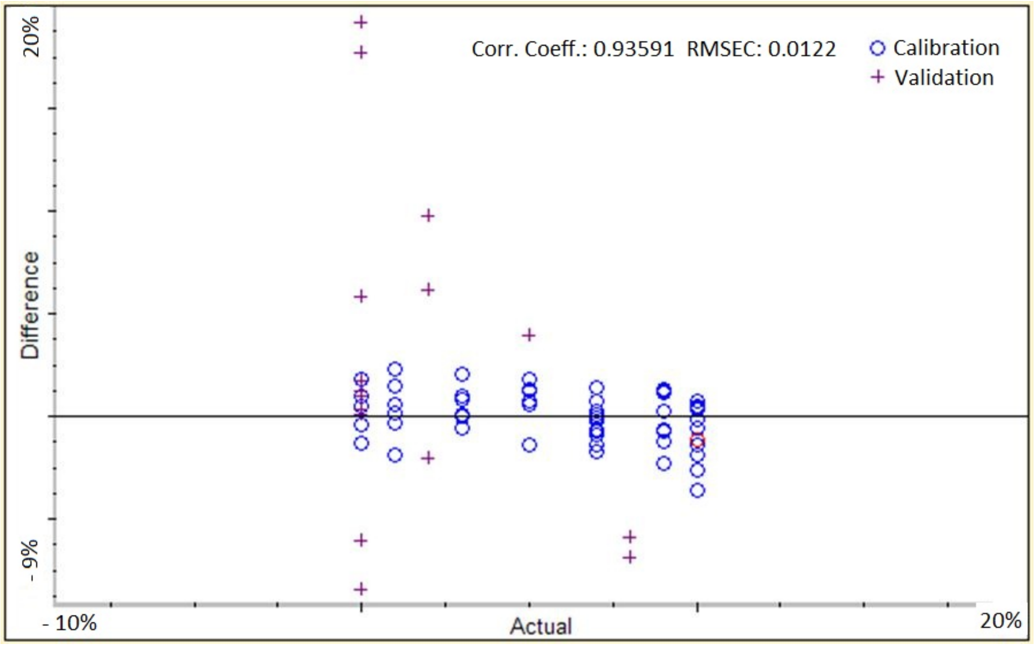


Figure 5-35 Difference between Actual and Calculated Values Using PLS

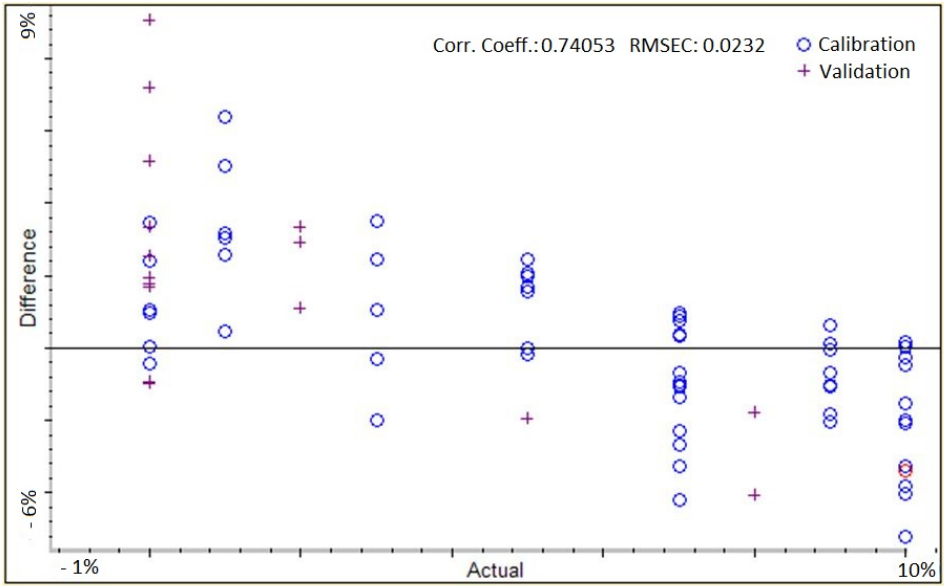


Figure 5-36 Difference between Actual and Calculated Values Using PCR

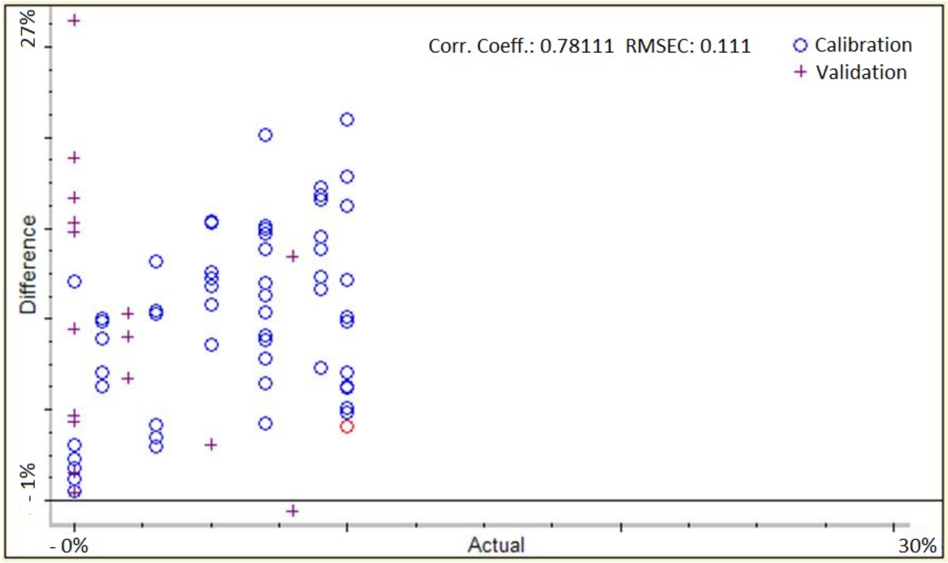


Figure 5-37 Difference between Actual and Calculated Values Using SMLR

5.4 Binder Identification through Library Search in TruDefender FTX FTIR Analyzer

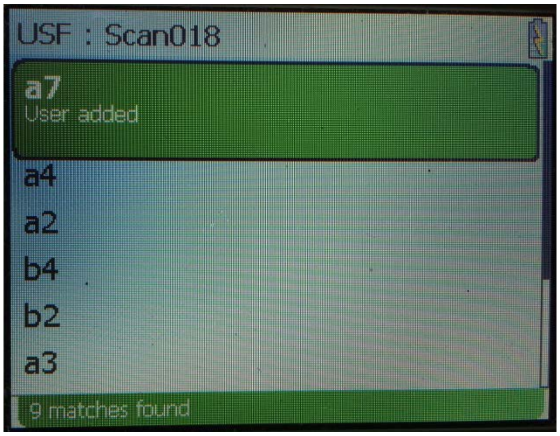
Instead of quantifying polymer content via calibration curves developed from regression models, another potentially efficient method is to use library search in portable FTIR devices in the field to quickly identify the binder type and therefore the polymer content. The idea is to first save the spectra of a set of standard binders with a range of known polymer contents into the material library of a FTIR device, then during field use, the FTIR device scans the unknown sample, compares its spectrum to the material library, and returns the name of the material that has the most similar spectrum. The material name can then tell the polymer content of the unknown sample. This method relies not on any individual region of the measured spectrum, but on the shape of the entire spectrum. Although the idea is plausible, it might not work in some situations due to the following potential reasons:

1) If change in spectrum shape due to change in polymer content is insignificant or comparable to measurement errors, the FTIR device might not be able to detect it and so may return wrong material names;
2) Some non-characteristic peaks might be more prominent than the characteristic peaks for polymer or asphalt and so may dominate the outcome of the matching algorithm of a FTIR device, which would also lead to mismatched results. For example, if a binder sample is oxidized, although its characteristic peaks for SBS match those of the corresponding standard binder in the library, the FTIR device might detect changes in the peaks for oxidized molecule more sensitively than change in the SBS peaks and return wrong results.
3) If the material library contains several different materials that have spectra similar to that of the test sample, the FTIR device might not be able to identify the correct material.

The influence of the third potential reason may be minimized by reducing the size of the material library. The TruDefender FTX FTIR analyzer contains a comprehensive library of thousands of chemicals, but it also allows users to limit their search to a user-defined library.

This section evaluated the effectiveness of the library search function by using a small-sized material library. First, the USF and Ergon SBS binder samples with 0, 1, 3, 5, and 10 percent SBS and the MD GTR binder samples with 0, 5, 10, 15, 20, and 25 percent GTR were scanned and saved into a user-defined material library of the TruDefender FTX FTIR Analyzer. Then, some extra binder samples were scanned to check whether the FTIR device can correctly identify them in the library. For example, as shown in Figure 5-38, after scanning a test sample, the FTIR analyzer returned the best matched material in the library: a7 (which in this example represents the USF sample with 10 percent SBS). Figure 5-39 shows the spectra of the same material, one (USF: Scan018) created during the test scanning and the other (a7) created during the library scanning. Note that the library spectrum is smoother than the test spectrum. This is because the library scanning has higher resolutions and takes longer time than the test scanning.

The specific trials and their results are summarized in Table 5-5. Each sample was scanned and detected twice. The results show that only the USF sample of neat asphalt and the Ergon sample with 4 percent SBS were not correctly identified. Specifically, for the neat asphalt in USF sample, the handheld FTIR analyzer incorrectly identified it as the neat asphalt from Ergon at one time. For the Ergon sample with 4 percent SBS, both matching results were wrong. Based on these findings, it is safe to say that, if a set of standard binder samples covering a possible range of polymer contents are pre-scanned into a small material library, there is a high chance that the handheld FTIR analyzer can correctly identify the type of binder of a test sample from the library, and therefore its polymer content.


USF : Scan018

a7
User added

a4
a2
b4
b2
a3

9 matches found

Figure 5-38 Best Matched Spectrum in the Library Displayed on the Screen of Handheld TruDefender FTIR Analyzer

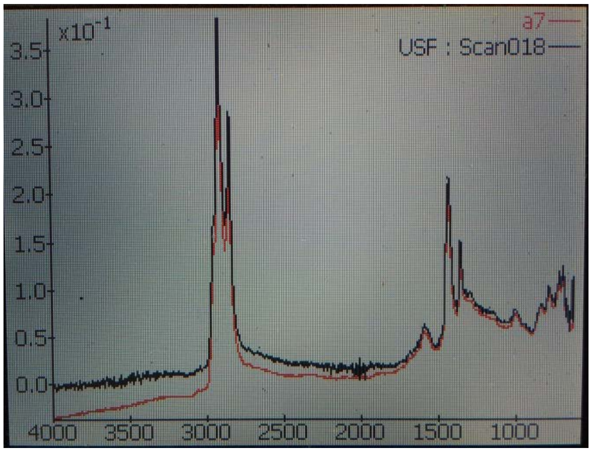


Figure 5-39 Comparison between the Spectra from Scanned Sample and Library Sample

Table 5-5 Accuracy of Library Search in Handheld TruDefender FTIR Analyzer

Tested Sample	Pass 1	Pass 2
USF Sample (0% SBS)	Yes	No
USF Sample (1% SBS)	Yes	Yes
USF Sample (3% SBS)	Yes	Yes
USF Sample (5% SBS)	Yes	Yes
USF Sample (10% SBS)	Yes	Yes
Ergon Sample (1% SBS)	Yes	Yes
Ergon Sample (3% SBS)	Yes	Yes
Ergon Sample (4% SBS)	No	No
Ergon Sample (10% SBS)	Yes	Yes
MD Sample (0% GTR)	Yes	Yes
MD Sample (10% GTR)	Yes	Yes
MD Sample (15% GTR)	Yes	Yes

CHAPTER 6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

This study first conducted a comprehensive literature review and a nationwide questionnaire survey on the state of the art and state of the practice of tests related to modifier detection and/or quantification in asphalt binders. A number of potential tests were identified and analyzed, and the Fourier transform infrared spectrometer (FTIR) test was selected for further evaluation.

In the evaluation, two sets of SBS binders and two sets of GTR binders were prepared in the laboratory and tested by the portable FTIR devices to provide standard information, for either developing prediction models or building material library. Several binder samples from real paving projects were used to verify the effectiveness of the prediction models or the library. After data analysis, the following conclusions were obtained:

1. The two portable FTIR spectrometers (TruDefender FTX and Bruker Alpha) included in this study can give absorbance spectrum measurements similar to those from a desktop FTIR spectrometer, and are easier to operate than the desktop device.
2. For SBS modified binders, the portable FTIR spectrometers can detect a generally linear increase in height or area of characteristic peak at 966 cm^{-1} or 699 cm^{-1} of the absorbance spectrum when the SBS content increases. The peak height at 966 cm^{-1} can be used as a good indicator in the standard curve, which is a simple linear regression model, to calculate SBS content. Parameters of the standard curve, however, vary with the source of asphalt. Therefore, for SBS binders with different base asphalt, different standard curves need to be generated and used. Moreover, variance of indicator values increases significantly at high SBS contents, particularly when the SBS content is over 5 percent (by mass of binder). Thus, the estimation error of SBS content may be unacceptably large for binder samples containing more than 5 percent SBS if the number of test replicates is not increased.
3. For SBS modified binders, more complicated statistical models for data analysis, such as partial least square regression (PLS), principle component regression (PCR), and stepwise multiple linear regression (SMLR), can make a standard curve to fit data better than a simple linear regression model. However, compared with a simple linear regression model, they provide no significant advantage in determining SBS content of asphalt binders from other sources.
4. For GTR modified binders, the existence of carbon in GTR may cause the spectrum baseline to tilt up to the right end. For the two sets of GTR binder samples prepared in this study, one set showed good correlation between GTR content and spectrum slope in the region of 1093 cm^{-1} to 1268 cm^{-1}, while the other did not. The effectiveness of using spectrum baseline slope for GTR quantification still needs further verification.
5. The library search function of the TruDefender FTX FTIR analyzer may be used to quickly identify a test sample. Once the absorbance spectra of a set of standard binders with a range of polymer contents are saved into the material library of the TruDefender FTX FTIR analyzer, there is a high chance that the analyzer can correctly identify a test sample by comparing its spectrum with those in the library.

6.2 Recommendations

This study showed that portable FTIR devices could produce test results very similar to those from a desktop FTIR spectrometer. The AASHTO standard test method for polymer content quantification, AASHTO T 302, may be implemented with a portable FTIR device, such as the TruDefender FTX FTIR analyzer or the Bruker Alpha FTIR spectrometer. Unlike the Bruker Alpha FTIR spectrometer, the TruDefender FTX FTIR analyzer does not need to be connected to an external power supply or a laptop computer during testing, so it is more portable and robust for field use. Testing with both FTIR devices is easy and quick. Only a small amount of binder at room temperature is needed for scanning its spectrum, and it generally takes less than 5 minutes to run a background scan, scan a binder sample, and clean the diamond crystal.

6.2.1 Recommendations on Preliminary Implementation

Based on the findings from a limited number of binders involved in this study, it is recommended that portable FTIR test devices, particularly the TruDefender FTX FTIR analyzer, may be used preliminarily in the field to estimate polymer contents in modified binders. The FTIR test, however, can only be performed on binder samples, not on loose mix samples or on compacted pavements.

The calculation of polymer content from FTIR measurements is generally based on a standard curve. The input to the standard curve is either the height or area of certain characteristic peak on the sample spectrum. For this reason, the measurements from portable FTIR devices cannot directly give the polymer content, but have to be viewed and measured in certain FTIR software installed on a computer. For the TruDefender FTX FTIR analyzer, measurements can be transferred to a computer wirelessly or through an SD card. For the Bruker Alpha FTIR spectrometer, since it is connected to a laptop during testing, measurements can be directly viewed on the computer. For this “standard curve” approach, the following recommendations are provided:

- A standard curve needs to be previously calibrated by measurements from a set of binder samples with known polymer contents and with the same base asphalt as that in the test sample (i.e., calibration binders). For samples with different base asphalt, different standard curves need to be used. Care needs to be taken in preparing the calibration binders to make sure that the actual polymer contents match the claimed values.
- Using a straight line (i.e., a simple linear regression model) as the standard curve is generally sufficient. More complicated statistical models, which are included in common FTIR software, may also be used to reach a better fitting to the calibration data.
- For SBS modified binders, high variance in the input to the standard curve would be expected when the SBS content is higher than 5 percent by mass of binder. Therefore, for binder samples with high SBS contents, it is recommended that either the FTIR test not be run on them, or the number of test repetitions be significantly increased (e.g., 20 test replications may reduce the prediction error of SBS content within 1% for binders with 7 or 9 percent SBS). For binder samples with SBS contents lower than 5 percent, a test repetition number of three can lead to a standard error less than 0.5% in the predicted SBS content.
- For GTR modified binders, no firm conclusion can be made now regarding the effectiveness of the FTIR test to quantify GTR content. Further study is needed to include more GTR samples from various sources.

The library search function of the TruDefender FTX FTIR analyzer may be used in conjunction with the "standard curve" approach to give a quick estimation of polymer content in the field. To this end, the absorbance spectra of the set of calibration binders shall be saved into a user defined library that is separated from other material libraries, and the search function shall be confined within this library.

6.2.2 Recommendations on Future Study and Evaluation

Due to limitations on resources (e.g., the availability of a portable FTIR device) and time, this study only included two sets of SBS binders and two sets of GTR binders for calibration purpose. For the two sets of SBS binders, one set was prepared by diluting a 10 percent SBS binder sample provided by an asphalt supplier and the other set was provided by another asphalt supplier. The investigators had no full control over the quality of the samples, so were not completely sure about whether the actual SBS contents in samples truly equal their labelled values. Therefore, it is difficult to explain the local nonlinearity observed in the standard curves. It is recommended that a follow-up study be conducted prior to or along with the preliminary implementation, with the following suggestions:

- A portable FTIR device, such as the TruDefender FTX FTIR analyzer, 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. Binders with both SBS and GTR polymer modifiers may also be included to examine the potential interaction between the two modifiers. 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.
- GTR samples of the same grade but from various suppliers should be included in the study to further evaluate the potential of using spectrum baseline slope to quantify GTR content.
- To use the "standard curve" approach to calculate polymer content, users need to have a certain level of training on how to use the FTIR software to identify the characteristic peak and measure its height or area. The easiness of such software operation by field engineers needs to be evaluated.
- The effectiveness of the library search function of the portable FTIR device needs to be further evaluated by incorporating more sets of calibration binders. For each set of calibration binders, the minimum increment of polymer content which can be detected by the FTIR device shall be established. More spectra from various binders may be saved into the same library to examine how well the FTIR device can distinguish a particular binder from a larger binder pool.

In late 2014, a new method based on electrochemical analysis (ECA) appeared in the Chinese literature. The method can measure SBS content to a precision of ±0.1%, and is easy to perform with developed test equipment. It has been successfully applied in over 20 paving projects. A brief introduction of this method is included in Appendix B. This method was not evaluated in this study due to its late appearance. It is recommended that it be looked into in future studies.

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APPENDIX A: SURVEY RESPONSES

A. Responses from Departments of Transportation in the U.S.

Question 1: In asphalt paving projects using binders modified with polymers (e.g., SBS) or ground tire rubber (GTR), do you verify the existence of polymer or rubber in asphalt binders during construction?

State DOT	Response No.	Answers
ALDOT	1	Yes. During construction of a project, samples of the PGAB will be taken from the contractors tank before mixing. (This all refers to SBS, we do not currently have a GTR spec)
AZDOT	1	Yes
	2	No
AHDOT	1	No
ConnDOT	1	No
FDOT	1	No
	2	The binder program system checks and balances are performed during construction through sampling during projects, but is not considered project verification. The results of these samples are typically not tied to any responsibility of the contractor or the binder producer. The sampling frequency of these samples are very low, but do allow us to monitor the program and follow-up with the binder producers with issues. The project personnel do have the right to sample binder if there is a suspicion of the incorrect binder being supplied, i.e. a neat binder in lieu of a polymer binder or a highly diluted modified binder.
GDOT	1	Yes, for polymer modified PG asphalt binder, we use DSR to limit maximum Phase Angle <75 degrees, to verify the existence of polymer. For rubber modified PG asphalt binder, we perform Multiple Stress Creep & Recovery (MSCR) test with DSR to report Jnr 3.2.
Iowa DOT	1	No
KSDOT	1	We don't test specifically for the existence of polymers but do perform verification testing on construction samples that includes elastic recovery which we feel ensures the presence of polymer. We do not allow GTR.
	2	Yes (SBS)
KTC	1	Samples of binder are taken during production of the mix. We currently use the elastic recovery test (T301) to help determine polymer existence
LA DOTD	1	We verify the grade of asphalt specified/allowed. We currently specify a PG plus PG76-22M which requires force ductility ratio and elastic recovery; and are moving towards MP-19 testing. We allow PG82-22RM in lieu of PG76-22M (this is PG plus elastic recovery.) Specs are online part X.
	2	No
	3	Yes
Minnesota DOT	1	Not during construction, we verify polymer content via phase angle and now recently with the MSCR test in the lab.
	2	No
Mississippi DOT	1	No (FYI – currently no GTR modified binders are being used in MS, so no need to verify/quantify existence at this point.)

State DOT	**Response No.**	**Answers**
Nebraska DOT	1	If the Contractor elects to use a PG Binder that has been modified with GTR, they can do so as per our spec's, but they need to let us know because the Elastic Recovery test we specify is by AASHTO if SBS, and by ASTM (which has notable differences) if GTR is the modifier.
NH DOT	1	Yes. We test binder from every project. The exception is AR binder, which is currently blended at the mix supplier plant. Observational verification takes place, as well as volumetrics.
Ohio DOT	1	We take a minimum of one project liquid asphalt sample to confirm properties.
	2	Yes
OKCDOT	1	No. GTR is not used in Oklahoma other than in an AC 20-5TR.
ODOT	1	OR DOT only test for modifiers is done on PGXX-XX ER specified binders. In other words OR DOT has a PG(+) spec for a PG70-22 ER below is the specification language: Performance Graded Binders with "ER" designation: ,The PG grade with the additional designation of "ER" (for example, PG70-28ER) per the project schedule of items shall meet the following limit when tested according to AASHTO T 301 "Standard Method of Test for Elastic Recovery Test of Asphalt Materials by Means of a Ductilometer": % Elastic Recovery – 50 minimum The samples will be conditioned per AASHTO T 240 "Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin Film Oven Test) prior to testing per AASHTO T 301. The specified temperature for section 3.3 of the AASHTO T 301 procedure shall be 77°F
	2	Oregon DOT does use polymer modified asphalts for our 'ER' spec. The GTR asphalt use is very limited in the state and is usually only utilized in some of your chip seal work. QC collects one set of samples per 1000 tons of HMAC and submits it to ODOT's Central Lab for testing per the below specification (1 in 5 sets are tested unless an issue is found): Use PG 70-22 asphalt cement for base course mixes and PG 70-22ER only for wearing course mix. In addition to the requirements in the ODOT Standard Specifications for Asphalt Materials, PG 70-22ER grade shall have a minimum Elastic Recovery of 50% when tested according to AASHTO T 301 "Standard Method of Test for Elastic Recovery Test of Asphalt Materials by Means of a Ductilometer". Test samples shall be conditioned per AASHTO T 240 "Standard Method of Test for Effect of Heat and Air on a Moving Film of Asphalt (Rolling Thin Film Oven Test) prior to testing per AASHTO T 301. The specified temperature for section 3.3 of the AASHTO T 301 procedure shall be 77°F.
RIDOT	1	Yes
TxDOT	1	No

State DOT	Response No.	Answers
WSDOT	1	We don't specify how we want our suppliers to formulate their binders, or the amount of polymer required. We do run AASHTO T-301, Elastic Recovery, on grades PG64-28, PG70-22, PG70-28, and PG76-28. We feel this ensures that we are receiving a binder with elastomeric response in the applications where we need it.
	2	Yes
	3	Yes
VDOT	1	VDOT specifies that polymer modified binders must meet an Elastic Recovery requirement in addition to the any Performance Grades specified, which currently consist of the PG 76-22 and the PG 70-28 binders. At this time we do not use ground tire rubber as a modifier in our Asphalt Program. VDOT then uses a program level approach to verify the material at the shipping location and the HMA plant meets that specification, we will sample primarily at the PG terminal on a monthly basis and during production from the HMA producer's holding tanks on a more limited basis. This program level approach is a combination of Approved Supplier List, monitored QC and QA program and material specification. The full program is detailed in our Manual of Instructions at the following link: http://www.virginiadot.org/business/resources/Materials/bu-mat-MOI-II.pdf. Section 204.05 covers our acceptance and assurance plan for PG Binders.
	2	Yes

Question 2: Do you verify the content of polymer or rubber in asphalt binders during construction?

State DOT	Response No.	Answers
ALDOT	1	No. We verify the existence, but do not quantify it for every project. If there is an issue with a project or if it is requested, we might go back and quantify the modifier, but this is a rare occurrence.
AZDOT	1	Through certification
	2	No
AHDOT	1	No
ConnDOT	1	No
FDOT	1	No
	2	No
GDOT	1	No verification is done during construction except for DSR phase angle that is reported on a start-up sample for the polymer modified asphalt binder, PG76-22. For rubber modified asphalt, we do audit on purchase invoice of the total quantity of rubber materials for the project to estimate the percentage of rubber content used in binder/mix.
IowaDOT	1	No
KSDOT	1	No, as long as they meet our elastic recovery test we do not verify the content.
	2	No
KTC	1	We do not verify a minimum polymer content (% polymer).

State DOT	**Response No.**	**Answers**
LA DOTD	1	We do not require a min. or max. content of polymer or CRM. We do run GPC; gelled permeation chromatography, for information and can measure the quantity of SBS modifier from roadway or neat asphalt sample. This process is not suitable for CRM, however in primary filtration of elution, we can see that CRM is present and can weigh the filter residue to compare related amounts.
	2	No
	3	Yes
Minnesota DOT	1	No
	2	No
Mississippi DOT	1	No (MS DOT does check rheological properties and viscosity during construction and requirements for non-modified and modified binders are set accordingly.)
Nebraska DOT	1	No, not specifically. But to us, if the content is insufficient, the material will not pass M320 specifications. As our quality assurance process, we only care that the material passes, not what the actual content of the polymer is.
NH DOT	1	We do not specifically test for polymer content. We perform the MSCR TP 70 test.
Ohio DOT	1	If you mean type and/or % no. We do verify an elastic recovery value which validates the presence of polymer and minimum amount.
	2	No
OKCDOT	1	No.
ODOT	1	No
	2	ER spec only at this point.
RIDOT	1	Yes
TxDOT	1	No
WSDOT	1	No. Our T-301 specification is 60% minimum at 25 C.
	2	No
	3	No
VDOT	1	At this time we have not adopted any method to quantify or verify the content of SBS in the binders used on VDOT projects.
	2	No

Question 3: If the answer to either of the above two questions is "yes", which approach is used to verify or quantify the existence of modifiers in modified asphalt binders?

State DOT	**Response No.**	**Answers**
ALDOT	1	We perform an FTIR scan on all modified asphalt samples, as well as normal PG plus testing.
AZDOT	1	Binders must pass the following lab tests (In addition to AASHTO M320): solubility, softening point, elastic recovery, resilience and phase angle. These tests are used in acceptance testing of the binder during construction to indicate the presence of modifiers.

State DOT	Response No.	Answers
AZDOT	2	Respondent skipped this question
AHDOT	1	Respondent skipped this question
ConnDOT	1	Respondent skipped this question
FDOT	1	Respondent skipped this question
	2	We currently use Phase angle and MSCR %Recovery as our PG Plus tests to verify the elastic property of the binder. If needed, we will use FTIR to quantify the amount of SBS polymer, no method is used currently for the quantification of GTR.
GDOT	1	DSR phase angle, invoice auditing/ MSCR with Jnr 3.2.
IowaDOT	1	Respondent skipped this question
KSDOT	1	Respondent skipped this question
	2	Binder is sampled in the field and tested.
KTC	1	Elastic recovery test (T301).
LA DOTD	1	See AASHTO procedures for GPC.
	2	Respondent skipped this question
	3	We are currently implementing methods using Gel Permeation Chromatography (GPC) to both verify and quantify non-GTR polymers.
Minnesota DOT	1	Respondent skipped this question
	2	Respondent skipped this question
Mississippi DOT	1	MS DOT has capability to perform infrared spectroscopy (FTIR). Its use is not adopted into formal testing procedures at this point.
Nebraska DOT	1	As mentioned above, we do not quantify. But our verification process is to test the binder to ensure that it meets the minimum specification requirements of AASHTO M320. We also specify that for grades with a temperature spread greater than 92, that a SB/SBS or GTR modifier be present. Also, we feel the Elastic Recovery test, which we run on all modified binders, is the watermark test for verifying SB/SBS or GTR modification, whereas a DSR, can be "fooled."
NH DOT	1	AR is tested for AC content through ignition and can be back calculated.
Ohio DOT	1	PG grade and elastic recovery. Phase angle is also considered.
	2	We pull samples at the asphalt mix plant and test them at our central lab, which may be 2 weeks after sampling. We use the phase angle on the original DSR and if needed the elastic recovery on rolling thin film oven (RTFO) aged samples. The contractor also pulls mix samples at the plant and tests. They should know if the mix does or doesn't have polymer in it.
OKCDOT	1	Respondent skipped this question
ODOT	1	Respondent skipped this question
	2	ER spec only at this point.
RIDOT	1	MSCR (AASHTO TP-70, MP-19)
TxDOT	1	Respondent skipped this question
WSDOT	1	Respondent skipped this question
	2	Currently we test our modified PGAB for elastic recovery using AASHTO T 301.
	3	Testing of elastic recovery in accordance with AASHTO T 301

State DOT	Response No.	Answer
VDOT	1	The Elastic Recovery test is used to set a minimum performance standard and does a good job of verifying a polymer loading, however we do not have a method to quantify the loading.
	2	Elastic Recovery

Question 4: If a test procedure is adopted, what is the test method or test specification? Is the test conducted in the field or in a laboratory?

State DOT	Response No.	Answers
ALDOT	1	The test method currently in use for the FTIR scan is ALDOT test procedure 408, and it is conducted in the laboratory.
AZDOT	1	Typically AASHTO. Tests are conducted in the laboratory.
	2	Respondent skipped this question
AHDOT	1	Respondent skipped this question
ConnDOT	1	In Connecticut, we use AASHTO R49 3.1.4 to verify that the unmodified binders (source samples) are conventional unmodified. Binders that fail these criteria are no considered conventional unmodified.
FDOT	1	Respondent skipped this question
	2	The test method is what this project is supposed to propose a work plan for validation on. The test would be performed wherever it is recommended for best results from the research. The assumption is that the “field” in this question is at the roadway during construction and the “laboratory” is in lab at the contractor’s plant.
GDOT	1	AASHTO T315 & AASHTO TP70
IowaDOT	1	Respondent skipped this question
KSDOT	1	Our verification testing is performed on field samples in our Central Laboratory.
	2	See attached. Testing is performed in the lab.
KTC	1	The elastic recovery test (T301) is conducted in the laboratory from field samples.
LA DOTD	1	Respondent skipped this question
	2	In the field and in a laboratory
	3	In a laboratory
Minnesota DOT	1	Since the required grade is specified beforehand, we would verify the existence of polymer via phase angle and now using the MSCR test.
	2	Respondent skipped this question
Mississippi DOT	1	AASHTO T-302
Nebraska DOT	1	As mentioned above, a verifier to us is the Elastic Recovery test, which is run in a laboratory. Since we do not quantify the amount of polymer, no other test is necessary to us.
NH DOT	1	AASHTO T 308 is performed in the field for AR mixes.

State DOT	Response No.	Answers
Ohio DOT	1	Conducted in the lab. ER is from ASTM D 6084, 10 cm @ 77˚F, hold 5 min. before cut, on rolling thin-film oven (RTFO) aged samples.
	2	In a laboratory
OKCDOT	1	Respondent skipped this question
ODOT	1	Respondent skipped this question
	2	See #1 above.
RIDOT	1	In a laboratory
TxDOT	1	Respondent skipped this question
WSDOT	1	See above. The testing is performed at the State Materials Laboratory
	2	The ER specification is 60% minimum. We perform this test at our state materials laboratory.
	3	In a laboratory
VDOT	1	The following is from our Road and Bridge Specification outlining the testing required of polymer modified binders: 1. Type E asphalt mixtures shall consist of mixes incorporating a neat asphalt material with polymer modification complying with the requirements of PG 76-22 and have a rolling thin film oven test residue elastic recovery at 77 degrees F of a minimum of 70 percent when tested in accordance with ASTM D 6084 procedure A. E-designated mixtures shall not contain more than 15 percent reclaimed asphalt pavement (RAP) material.
	2	In a laboratory

Question 5: Currently there are several types of tests proposed for detecting/quantifying modifiers based on different technologies, such as spectrum (FTIR, RS), chromatography (GPC, HPLC), thermo (DSC, TGA) , and "macro" vibration (NMR). Do you have any thought or opinion on a test that is available or has the potential to be developed for use in the field to detect and/or quantify modifiers in asphalt binders?

State DOT	Response No.	Answers
ALDOT	1	No
AZDOT	1	We are in the early stages of looking into the possibility of these technologies.
	2	Respondent skipped this question
AHDOT	1	Respondent skipped this question
ConnDOT	1	Respondent skipped this question
FDOT	1	Respondent skipped this question
	2	I have read papers on most of these tests in the respect to detecting/quantifying modifiers. The issue becomes the "difficulty" in performing and / or interpreting the results of these tests. I like the concepts of using some of these techniques and theories, but the application would have to be user friendly to an inspector in the field or a District Office, none of which these techniques are as they stand currently. Time (the test should be relatively quick, possibly portable), sample prep (easily done at a plant or a district lab), and interpretation (the result should be 2 values: modifier and quantity) are the three key aspects to consider.

State DOT	Response No.	Answers
GDOT	1	We once tried FTIR to determine the SBR content for polymer modified emulsion asphalt, and found the equipment is very expensive to maintain due to high repair cost.
IowaDOT	1	Respondent skipped this question
KSDOT	1	Respondent skipped this question
	2	No
KTC	1	No
LA DOTD	1	Respondent skipped this question
	2	GPC
	3	GPC research conducted at the LSU Chemistry Lab and our research center (LTRC) indicates GPC is promising for polymer modifier quantification. We will be working on the question of latex and GTR.
Minnesota DOT	1	No opinion thus far as I'm not familiar with these tests being used in this particular application; however, they must be accurate AND fast in order to be useful. The MSCR is such a test for determining the presence of polymer (but not type) and already uses equipment readily available in most asphalt labs.
	2	No Opinion
Mississippi DOT	1	No experience with field testing methods to detect/quantify modifiers in binder.
Nebraska DOT	1	If we were concerned in quantifying the amount of polymer or rubber, I feel FTIR is adequate. We have an FTIR in our building (a different laboratory than mine) and we are well versed in its operation. Other DOT's may have one as well. Something to use in the field, no matter which analytical instrument option you choose, may prove to be cost prohibitive to most organizations. Most, like us, may not put enough importance on needing to know the exact amount of modifier.
NH DOT	1	No opinion.
Ohio DOT	1	I have little knowledge on this.
	2	Only familiar with FTIR and it would be expensive to run. You would need to know the molecular structure of the polymer used.
OKCDOT	1	No. We have looked at FTIR but it does not quantify polymer content.
ODOT	1	No
	2	Respondent skipped this question
RIDOT	1	An accurate test that is not difficult or extremely time consuming to perform in the field would be very useful.
TxDOT	1	I have seen a few of these; we generally have the instrumental capability, but there would need to be some very careful standardization if this will affect payment or acceptance of a material on a project.
WSDOT	1	No. Our Department has historically specified end product specifications and not formulation specifications. We do not have any of the equipment listed above. We are always interested in new test procedures that ensure we are receiving quality materials. At this point, we are not interested in a test that can take place in the field. We don't have the resources/personnel to perform binder testing away from the central laboratory.

State DOT	Response No.	Answers
WSDOT	2	We recently purchased a X-Ray Fluorescence Spectrophotometer (WDXRF) and have been considering it is use to detect the presence of additives in our PGAB.
	3	Only to say that whatever is considered needs to be as simplistic and accurate as possible, otherwise it will result in another research tool.
VDOT	1	GPC is already being used to successfully detect and even quantify the presence of SBS in asphalt binders (LTRC report FHWA/LA.13/505). It can also be used to detect the presence of other macromolecules such as crumb rubber, although it is my understanding that dissolving the rubber can be somewhat tedious. HPLC can also be used, but the molecular weight distribution is usually in reverse. Most current work is being done with GPC or an HPLC that is modified using GPC columns in lieu of HPLC columns. FTIR can be used to detect polymer modifiers in binders, however there is generally an overlap of the bands between the binder and the polymer. Thus, a reference binder (no modification) would likely be necessary to tell whether or not there is a polymer present. FTIR can be used to quantify polymer content as well, however it is a tedious process that applies Beer's law must be used. When only comparing GPC and FTIR the GPC is clearly the easier choice for both detection and quantification. Back in 2006, VCTIR completed a study to look at using FTIR to qualify and quantify polymers in PMBs, primarily as an alternative to elastic recovery. The results indicated that it could be done, however those methods were never adopted. Qualification wasn't particularly difficult but required a reference binder for each source supplier. Quantification was tedious, as practically, we had to determine a reference curve for each binder supplier and polymer type to be able to calculate the sample content. Using FTIR wasn't the problem; the effort required to develop and maintain the necessary reference info for analysis was deemed impractical and we continued to use the elastic recovery specification that was in place. Moving to where we are today – Research Council does own a handheld FTIR unit that can be used to help determine additive presence. However, as before, we do need a reference samples and calibration curves for the results to be meaningful. But this technology also has potential for other applications, so agencies would be more likely to justify its cost. I don't think of GPC as being particularly portable for field detection – they are benchtop units, and are neither cheap nor particularly easy to use without training. I know that DSC, TGA, and NMR have been used to study different characteristics of binder (including polymer modified binder), however I don't know that they have been used to evaluate polymer/rubber presence and/or content. While DSC, TGA, and NMR all offer good fundamental information, it seems that GPC and FTIR would be the most likely methods to be adopted in the field due to their ability to be applied to a number of problems in asphalt paving beyond studying polymer modified binders (e.g. oxidation characteristics, forensic analysis, etc.).
	2	No

Question 6: Do you have any other comments on verifying/quantifying the existence of polymer or GTR modifiers in asphalt binders during construction?

State DOT	Response No.	Answers
ALDOT	1	No
AZDOT	1	None at this time.
	2	Respondent skipped this question
AHDOT	1	Respondent skipped this question
ConnDOT	1	No
FDOT	1	Want to be simple enough and take a little time with a valuable information
	2	I would like to see the Binder QC/QA Test being developed by Raj Dongre be reviewed during this project as well.
GDOT	1	No
IowaDOT	1	There is a need for such a test. It is preferable to use equipment already in use by DOTs such as FTIR.
KSDOT	1	The movement is to go to performance specifications, so as long as they meet these performance specifications I don't see the need for a specific test verifying/quantifying the existence of polymers.
	2	No
KTC	1	No
LA DOTD	1	Refer to ltrc.lsu.edu website. Or contact Dr. Ioan Negulescu and Dr. William Daly with LSU for more information on this. They have done much work for LTRC (LADOTD's research arm) on this issue and I would expect you to have already read some of their reports prior to contacting them.
	2	We have not started the required testing in the field. But currently we have GPC on trial in the lab.
	3	Currently, our procedure will be to "screen" an extracted binder from a core taken from the roadway for verification. We plan to use the loaded wheel tested and semi-circular bend for compliance testing in the case of a non-verifying GPC.
Minnesota DOT	1	No
	2	MSCR
Mississippi DOT	1	Respondent skipped this question
Nebraska DOT	1	When we adopt the MSCR test by Dynamic Shear Rheometer, which will be within a year, we will be using that test to verify proper polymer modification. We will then drop elastic recovery. Dynamic Shear Rheometers are already in place in organizations that test PG Binder, and so additional equipment such as FTIR, GPC etc. will not be necessary.
NH DOT	1	
Ohio DOT	1	The test would have to be very accurate and repeatable if it were to be used as art of the contract and penalties were to be assessed.
	2	Easier to pull a binder sample at the plant. There would be some delays, but a lot of contractors in Ohio have their own binder labs and can run a check with a DSR. Only issues we have are in-line injection of latex polymers (SBR) at the plant with sampling issues. Good luck!

State DOT	**Response No.**	**Answers**
OKCDOT	1	There are no easy solutions for a quick field verification. We typically only perform elastic recovery (ASTM D 6084) for the refinery bimonthly samples PG 70-28 OK and PG 76-28 OK. We are doing the MSCR % recovery (AASHTO TP 70) tests this year for both the qualifying samples and the periodic field checks. Our specifications for MSCR recovery are more strict than the plot in AASHTO TP 70. Our partial MSCR implementation specifications are in: http://www.okladot.state.ok.us/c_manuals/specprov2009/oe_sp_2009-708-28.pdf
ODOT	1	No
	2	Respondent skipped this question
RIDOT	1	Same comment from question 5 above.
TxDOT	1	I don't really want to be in the business of specifying the binder composition, so I don't really have a big priority of verifying it.
WSDOT	1	We have interest in verifying the elastomeric response of binders being used in our state, but not necessarily the formulation, type, or amount.
	2	No
	3	WSDOT is planning on implementing the MSCR including a percent recovery specification by 2016.
VDOT	1	Respondent skipped this question
	2	No

B. Responses from Asphalt Research Institutes and Binder Producer

Question1: For liquid asphalt binders modified with styrene butadiene styrene (SBS) or ground tire rubber (GTR), currently there are several types of tests proposed for detecting and /or quantifying modifiers based on different technologies, such as spectrum (FTIR, RS), chromatography (GPC, HPLC), thermo (DSC, TGA) , "macro" vibration (NMR), and mechanical properties (recovery, stiffness, elongation, etc). Are you familiar with any of these or other techniques that can detect and/or quantify the existence of the modifier (SBS or GTR) in the binders?

Institute/ Producer	Response No.	Answers
National Center for Asphalt Technology	1	Some what
	2	Yes, I am familiar with most of the test methods that you mention. Here at NCAT we only do the mechanical property methods (Multiple Stress Creep and Recovery (MSCR), phase angle, elastic recovery, stiffness, ductility, etc). I am also familiar with the FTIR, GPC, and DSC methods, we just do not have the capability to run them here.
Western Research Institute	1	We are familiar with techniques that may be applied to detect SBS, GTR and other modifiers in binders. Quantification is always more difficult. There are many SBS formulations and many GTR sources and compositions. In addition, cross linking in GTR and to some extent in SBS materials limits their solubility in common solvents. This is a major limitation for GTR, but may not be as important for SBS. The development of a robust methodology or methodologies to identify and quantify SBS and GTR will require a large, diverse set of samples, and of course, access to the appropriate instruments.
National Asphalt Pavement Association	1	Respondent skipped this question
Bituminous Technologies	1	I think that would be a very helpful tool to have especially in the case of forensic investigations. I have some limited experience with FTIR results. Testing was performed on extracted asphalt from core samples in the lab. We were able to detect SBS polymer vs a sample with no polymer, but detecting quantities was not reliable. I am not sure how to go about detecting in the field.

Question 2: If the answer to the first question is "Yes", what are your experience with the test(s) and your opinions of the test(s) (e.g., accuracy, efficiency, cost, level of expertise required)? Do you think that a test or technique can be used, either directly or with minimal modification, in the field (i.e., the ideal field device should portable and the test procedure should be relatively quick and simple)

Institute/ Producer	Response No.	Answers
National Center for Asphalt Technology	1	TGA. We have used TGA in some ways to try and quantify rubber content. It works fairly well.
	2	We run the mechanical property tests for asphalt binders on a regular basis. I've listed the main procedures and their pros and cons for asphalt modifier detection / quantification and their potential for field evaluation below: MSCR / phase angle Pros: quick to run, easy to analyze results, can be run on samples already being tested for Performance Grade determination, can be set up to run in a reasonably well equipped mix plant quality control lab (needs electricity and a good air compressor). Cons: requires some technician training, expensive to purchase the Dynamic Shear Rheometer (DSR) equipment, can only identify the presence of a modifier, can't quantify, needs electricity and a good air compressor. Elastic recovery / ductility Pros: inexpensive to set up, simple to run, easy to analyze, minimal technician training. Cons: time consuming, requires a large laboratory footprint (not good for a tiny lab), can only detect, not quantify, equipment is large and would not be considered portable, requires electricity and water. Stiffness Stiffness alone isn't a good indicator of modifier presence, type, or quantity. FTIR / GPC / DSC I have no experience running these so I can't give you an opinion on their ease of use. The equipment is expensive and will require a trained technician to run. Dr. William Daly at LSU and Stacy Diefenderfer at the Virginia DOT have both reported success with these test methods for determining polymer and GTR content. If you haven't done so already you may want to consider contacting them for their opinions.
Western Research Institute	1	I am sure you are aware that there is an AASHTO procedure for measuring polymer content (AASHTO T302, Polymer Content of Polymer-Modified Emulsions and Asphalt Binders, that uses Fourier transform infrared (FTIR) spectroscopy), and that there are many articles discussing the use of GPC, SEC, and HPLC/SEC to determine the presence of polymers.WRI developed a HPLC/SEC procedure for examining asphalts for FHWA (FHWA-RD-99-213) and has continued to conduct some studies since then. WRI also has extensive experience with FTIR, thermal analysis, including DSC and TGA, and with NMR measurement techniques. All of them would bring different pieces of the puzzle.

Institute/ Producer	Response No.	Answers
National Asphalt Pavement Association	1	I'm aware of some of these test methods, but am not intimate with them myself. I have led research related to the mechanical properties of binders.
Bituminous Technologies	1	Most of my experience is on the mechanical properties. All of these done of course by coring the pavement and bringing to the lab. Destructive testing. Coring, extracting and recovering asphalt, then testing. I do not believe coring has much effect on the binder. Extracting and recovering exposes the asphalt to solvent and heat, so this can be undesirable. Unfortunately that is the best way to go about these things currently.

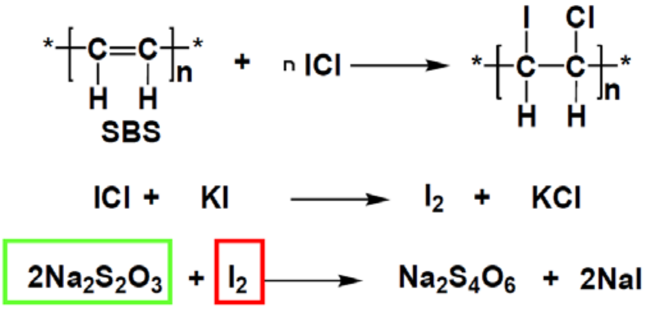
Question 3: If the answer to the first question is "No", do you have any thoughts or ideas on ways to develop a method to detect/quantify modifiers in asphalt binders in the field?

Institute/ Producer	Response No.	Answers
National Center for Asphalt Technology	1	Respondent skipped this question
	2	Respondent skipped this question
Western Research Institute	1	Respondent skipped this question
National Asphalt Pavement Association	1	I would suggest reaching out to the Asphalt Institute, NCAT and FHWA's Binder ETG through John Bukowski.
Bituminous Technologies	1	I really do not have any suggestions for field testing, that is a tricky one. I hope you make progress with this, good luck.

APPENDIX B: ELECTROCHEMICAL ANALYSIS (ECA)

Theory of ECA

Iodine monochloride (ICl), which is the main component of Wijs solution, has an addition reaction with the carbon-carbon double bonds in SBS. ECA quantifies the SBS content in modified asphalt binders based on the consumption of Wijs solution, following the chemical reactions shown below.



$$*\!-\!\left[\mathrm{CH{=}CH}\right]_n\!-\!* \;(\text{SBS}) + n\,\mathrm{ICl} \longrightarrow *\!-\!\left[\mathrm{CHI{-}CHCl}\right]_n\!-\!* \qquad (1)$$

$$\mathrm{ICl} + \mathrm{KI} \longrightarrow \mathrm{I_2} + \mathrm{KCl} \qquad (2)$$

$$\boxed{2\mathrm{Na_2S_2O_3}} + \boxed{\mathrm{I_2}} \longrightarrow \mathrm{Na_2S_4O_6} + 2\mathrm{NaI} \qquad (3)$$

Titration is completed when there is an abrupt change in the slope of the electric potential versus sodium thiosulfate ($Na_2S_2O_3$) curve.

Background

This method was developed by Central South University in China in late 2014, funded by Department of Communications of Hunan Province. An ECA analyzer has been developed, which integrates functions of automatic measurement (titration, cleaning, analysis, and result report) and system database management. It has a measurement precision of ±0.1% SBS content, and has been successfully applied in over 20 paving projects. Figure 1 shows the solution preparation system, and Figure 2 shows the ECA analyzer.

Details of ECA Operation

The test procedure of ECA includes the following steps:

1. Sampling of asphalt binder
2. Dissolving of asphalt binder sample in chloroform ($CHCL_3$) in an ultrasonic cleaner
3. Addition reaction with Wijs solution in a water bath. This reaction takes about one hour at 50°C with the use of catalyst.
4. Titration analysis
5. Calculation of SBS content

For each type of base asphalt, a standard curve needs to be first developed based on a set of SBS binders with known SBS contents (1, 2, 3, 4, and 5%). The procedure to develop a standard curve is

1. Prepare a set of standard binder samples with SBS contents of 1, 2, 3, 4, and 5%
2. For each standard binder sample, dissolve 2 g into 75 ml chloroform ($CHCL_3$)
3. Add 20 ml Wijs solution and 10 ml catalyst, keep in a 50°C water bath for 1 hour
4. Add 10 ml 100g/L potassium iodide (KI) solution to allow reaction for 3 minutes
5. Titrate with sodium thiosulfate ($Na_2S_2O_3$) until there is an abrupt change in the slope of the electric potential versus sodium thiosulfate curve.

Research shows that this method can be applied to various types of SBS modifiers. Dissolution enhancers (e.g., furfural extract oil and aromatic oil), stabilizers, and nano-montmorillonite do not have significant effects on the test results.

Figure B-1 Solution Preparation System

Figure B-2 ECA Analyzer

Reference

Liu, C.Z. *Research on the detection method and packaged technology of SBS content in modified asphalt*. Central South University, October 12, 2014.