Handheld FT-IR Spectrometer as a Quality Control Tool for Determination of SBS Content in Asphalt Binder and RAP Content in Plant Mixes

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Overall Layout of the Presentation

- ❑ Part I : Polymer Content Determination in Binder
- ❑ Part II : RAP Content in Plant Mixes
- ❑ Part III : Rejuvenator Identification and Quantification

Overall Layout of the Presentation

- **Part I : Polymer Content Determination in Binder**
- Part II : Quality Control of RAP Mixture
- Part III : Rejuvenator Identification and Quantification

Modification of Asphalt Binder

- ❑ Critical issue: Distress due to increased loads and high volumes of traffic
- ❑ Polymer modifications: enhance the performance

Modifier	Example
Elastomeric polymer	SBS (Styrene-Butadiene- Styrene) SBR (Styrene-Butadiene-Rubber) latex Crumb rubber and Elvaloy
Plastomeric polymer	EVA (Ethylene-Vinyl-Acetate)
Extenders	Sulfur, Otherhydrocarbon materials
Chemical	PPA

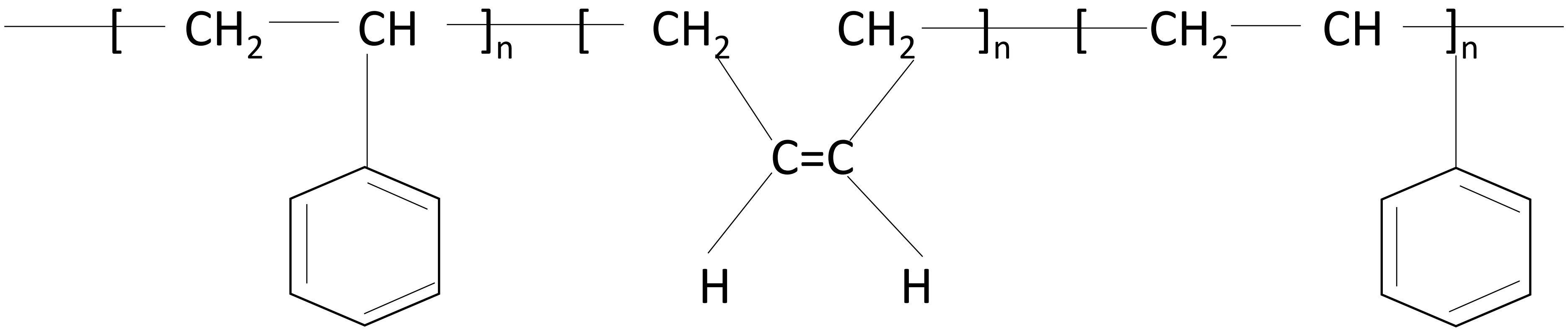
- ❑ SBS- mostly used polymer (more than 90%)

SBS polymer (powder)

SBS polymer (Pallet)

Benefits of SBS Polymer in Asphalt Binder

- Improvement due to SBS modification: physical and rheological properties of the base binder
  - ✓ Tri-block network increases the bonding strength of the base binder
  - ✓ Increases stability, elasticity and reduces stiffness of the binder compare to other modifiers
  - ✓ Shows the highest recovery on the strain in MSCR test
  - ✓ Reduces rutting and improves fatigue and thermal cracking resistance of the pavement



SBS polymer structure

Importance of Knowing SBS Content

- ❑ Challenges in quality control in SBS modified asphalt binder
  - ✓ Segregation
  - ✓ Thermal Decomposition
- ❑ Cross-linking agent and chemical modifiers are used by the manufacturer to achieve the higher performance grade because of
  - ✓ High cost of SBS polymer
  - ✓ High profit
- ❑ SBS is a better polymer
  - ✓ Adedeji et al., 1996 – transmission electron microscopy (TEM) – constitute a macro network at a low concentration
  - ✓ Wang et al., 2017 – Multiple stress creep recovery test – shows more elastic behavior
  - ✓ Singh and Kumar, 2019 – FT-IRS and Scanning electron microscopy (SEM) – improves aging resistance (compared to EVA)

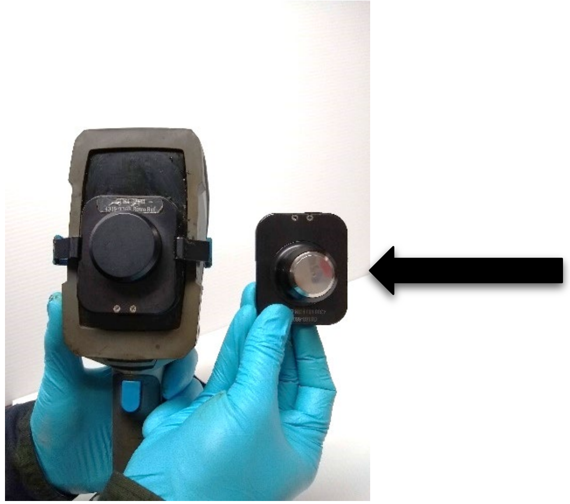
EVA: ethylene vinyl acetate

Why a Universal Equation is needed?

- ❑ A universal equation is needed to avoid developing a calibration curve in every project
- ❑ Because -
  - ✓ It's a time-consuming process and laborious
  - ✓ Manufacturer does not supply polymer because of propriety reasons. So, building a calibration curve is not feasible
  - ✓ Even if polymer is given, a calibration curve has to be developed project by project
  - ✓ Manufacturer does not specify the polymer content (%)

Fourier Transform Infrared Spectrometer (FT-IRS)

- FT-IRS –
  - ✓ A rapid, **field portable** and non-destructive technique
  - ✓ Requires minimal sample preparation and minimal training of operators
  - ✓ **Chemical analysis of asphalt binder** considering its simplicity in the sampling process and data interpretation proficiency



Diamond ATR sensor

- Diamond ATR sensor –
  - ✓ **Spectra remains unaffected** by the sample amount placed on the sensor
  - ✓ Has **corrosion and scratching resistivity** which makes it suitable for field measurement

Previous Literature on Polymer Content Determination

References	FT-IRS sensors	Index Used	Analysis Method	Comment	Quantify SBS in field
AASHTO T302	T	**965 cm^{-1}** and **1375 cm^{-1}**	**Ratio of peak**	Constructed a **Calibration** curve	NO
	ATR	**965 cm^{-1}**	**Peak area**		
Diefenderfer et al., 2006	-	**965** and **1375 cm^{-1}**	**peak ratio**	Constructed a **Calibration curve**	YES
Fernandez et al., 2006	T	**2820 to 2960 cm^{-1}**:	Peak area	Constructed a **Calibration** curve	NO
Hu et al., 2019	ATR	920 to 966 **cm^{-1}**	Peak area	Developed a quantification parameter	NO
Nasrazadani et al., 2010	T	**AASHTO T302** was followed	-	**Calibration curves** with R^2 = 0.9949	NO
	ATR	**AASHTO T302** was followed		**Calibration curves** with R^2 = 0.99	NO

T - Transmission

Development of A Universal Equation to Determine SBS Content

A study was performed to investigate the effects of **different base binders**, **different sources** of base binder, **different SBS** polymer types, and **cross-linking agent** on the SBS identifying functional groups,

And,

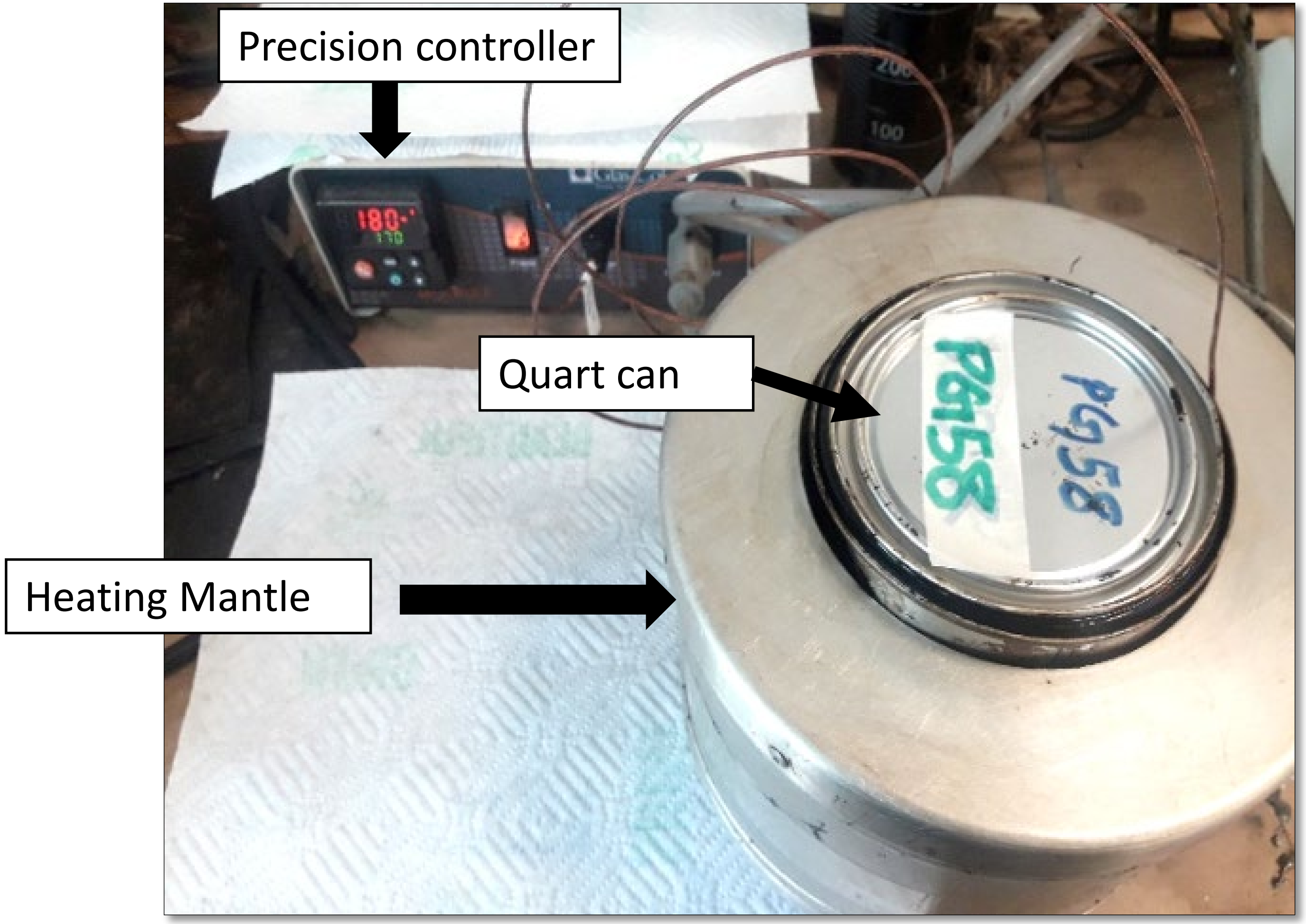
To develop a **universal equation** that can be used to successfully predict the SBS content (%) in the field.

Test Matrix for Developing Universal Equation for SBS Content Determination

Binder	Type of polymer	%SBS	Batch	Day	Sample tested in ATR-FTIR
PG52-34	**Radial**	**0%,1%, 2%, 3%, 4%**	1	1, 2, 3	**50, 25, 50**
PG58-28	Radial	0%, 1%, 2%, 3%, 4%	1	1, 2, 3, 4	**50, 50, 50, 50**
			2	1, 2, 3	**50, 50, 50**
PG64-22 (Source A-LA)	Radial	0%, 1%, 2%, 3%, 4%	1	1, 2, 3	**50, 50, 50**
			2	1, 2, 3	**50, 50, 50**
PG64-22 (Source B - NC)	Radial	0%, 1%, 2%, 3%, 4%	1	1, 2	**50, 50**
	Linear	0%,1%, 2%, 3%, 4%	1	1, 2	**50, 50**
	Diblock	0%, 1%, 2%, 3%, 4%	1	1, 2	**50, 50**
	Radial+ **0.5% Sulfur**	0%, 1%, 2%, 3%, 4%	1	1, 2	**50, 50**

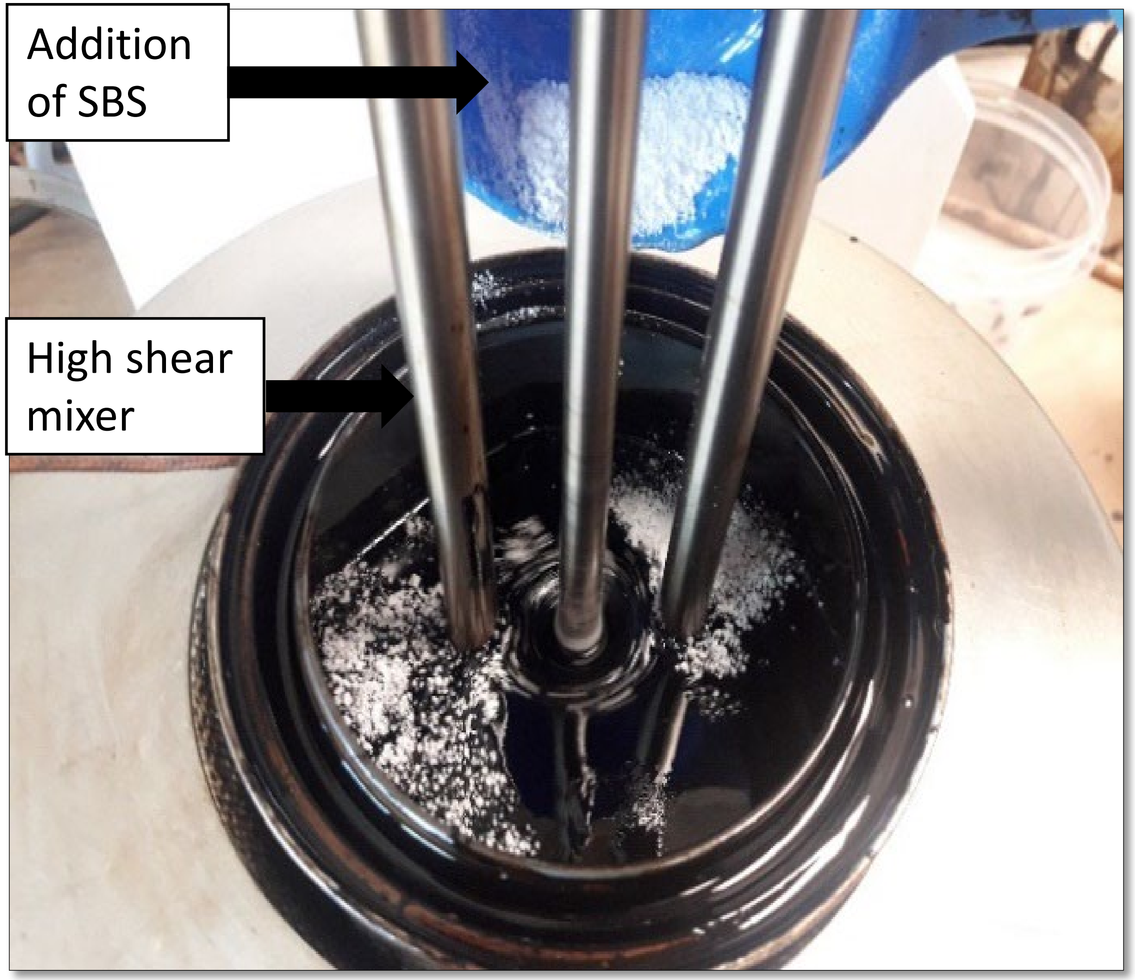
Sample Preparation

- ❑ **Heating binder** in a quart can using the **heating mantle**



Sample Preparation

- **Addition** of powdered **SBS** in the liquid asphalt binder



Sample Preparation

- **Mixing** of SBS with binder by **high shear mixture**
- Addition of SBS – within 30 minutes after starting the mixer
- Starting speed - **5000 rpm**
- After every 30 minutes, 8000 rpm for two minutes
- Total mixing time - **2.5 hours**
- Mixing temperature - **170℃**

Fourier Transform Infrared Spectrometer (FT-IRS)

Weight: > 4lbs.

13 inch

6 inch

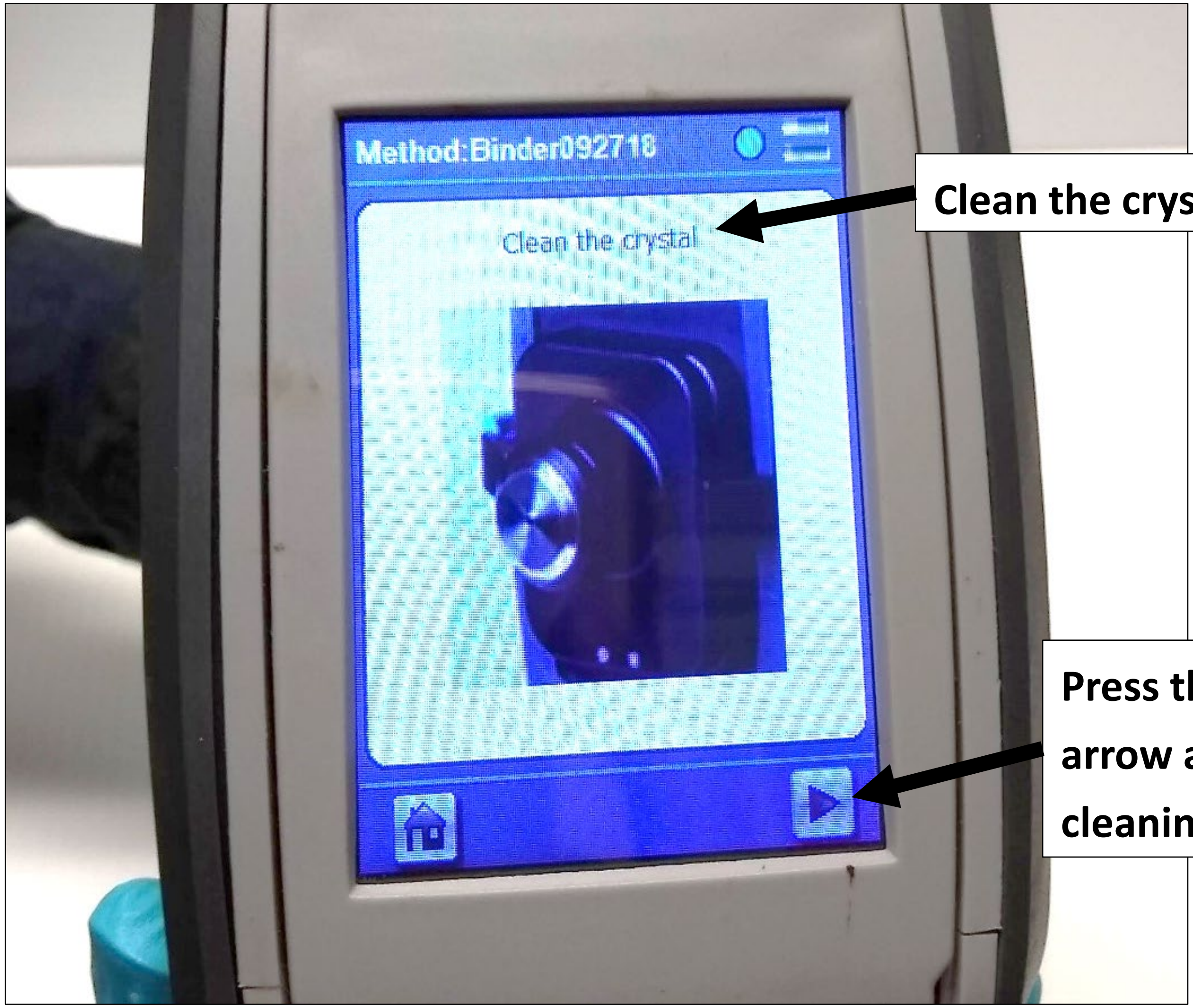
FT-IRS with ATR

Data Collection

- When the FT-IRS **power button** will be pressed, the system will show options
- **'Start'** will be pressed for further actions

Data Collection

- ❑ The system will show ‘**clean the crystal’**
- ❑ After cleaning the crystal, **right arrow** will be pressed

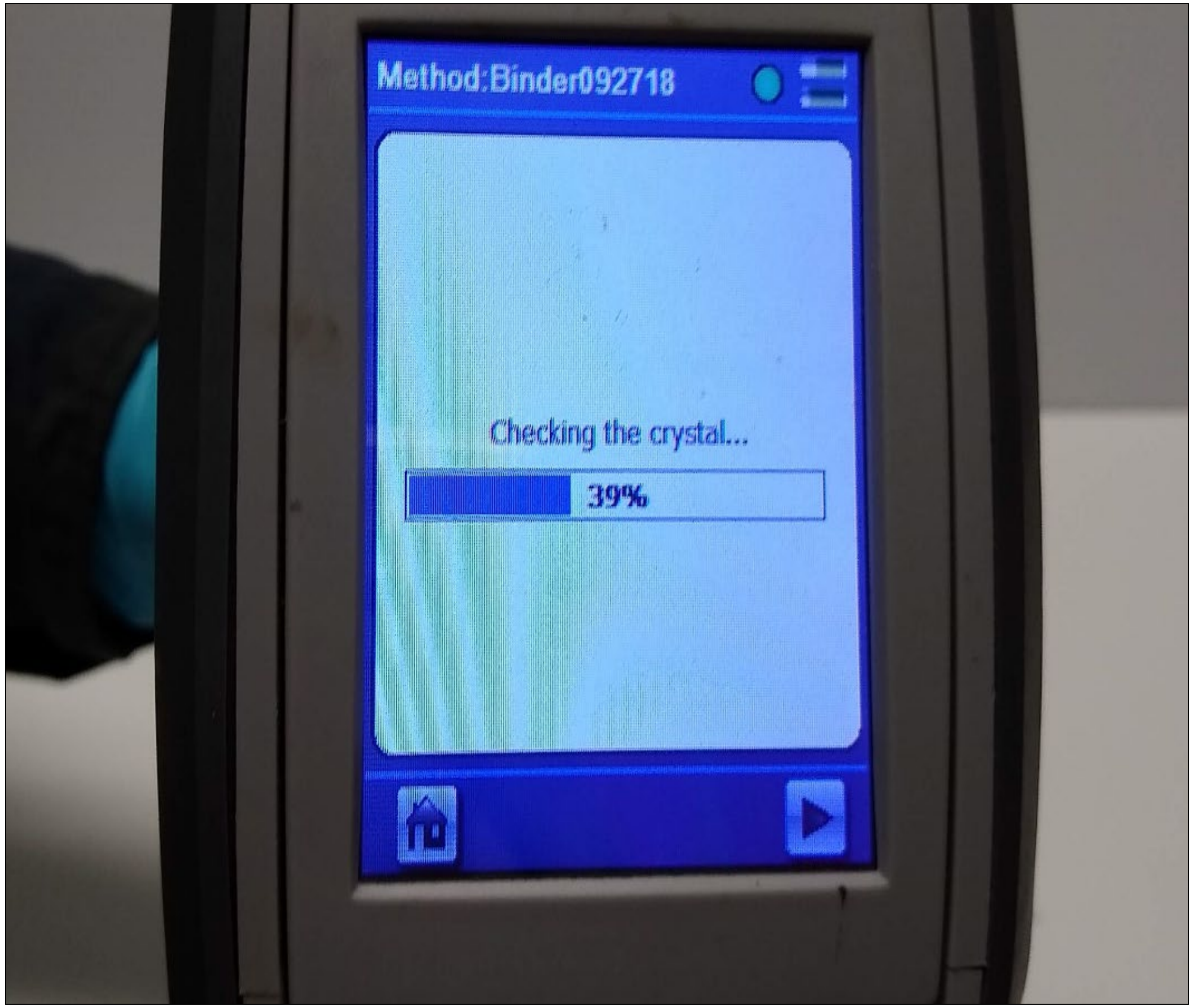


Data Collection

- ❑ Time required for cleaning the asphalt binder using paint thinner: **<1 min**
- ❑ Each time **the diamond sensor** will be **cleaned** with rubbing alcohol

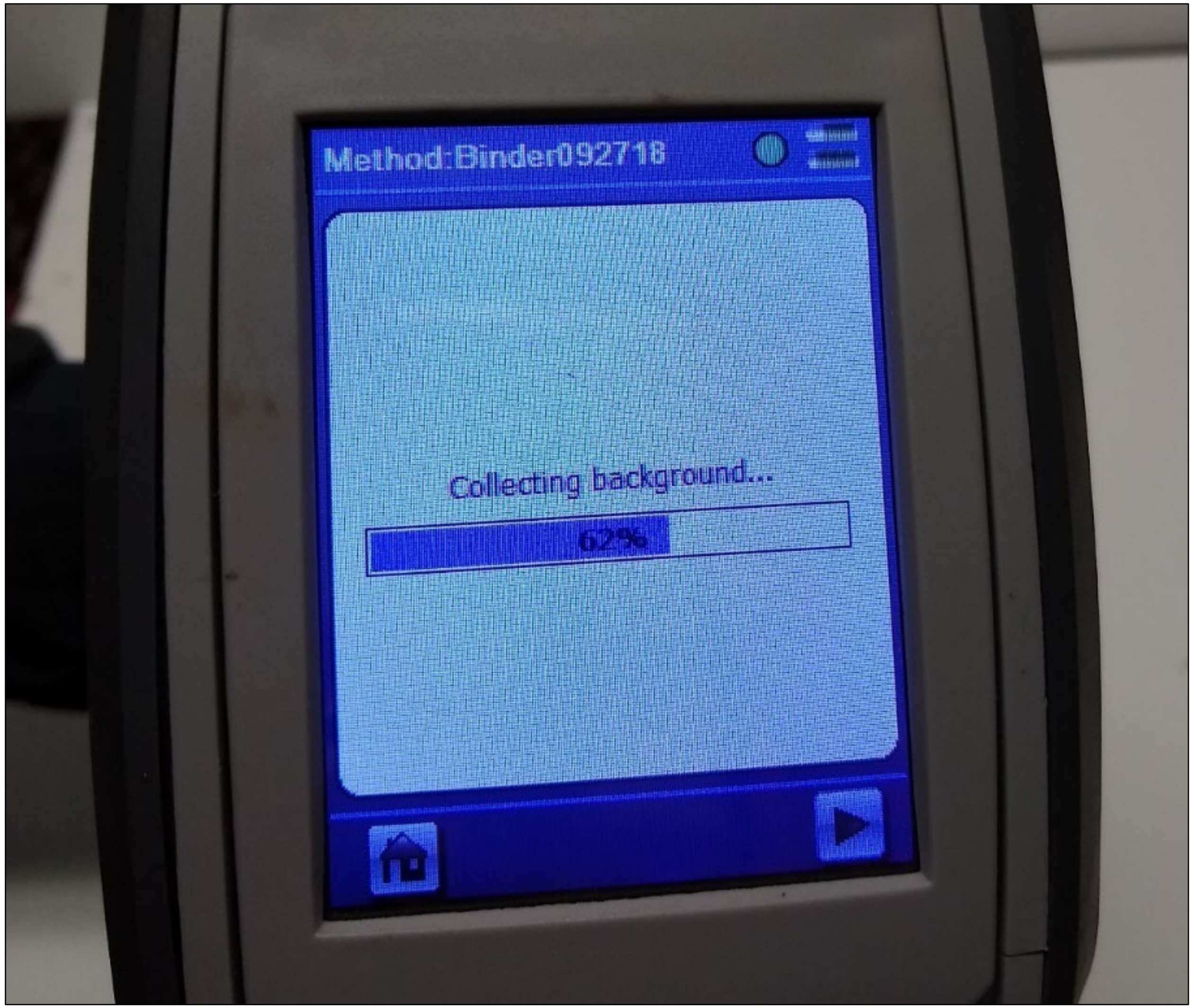
Data Collection

- The system will **check the crystal**



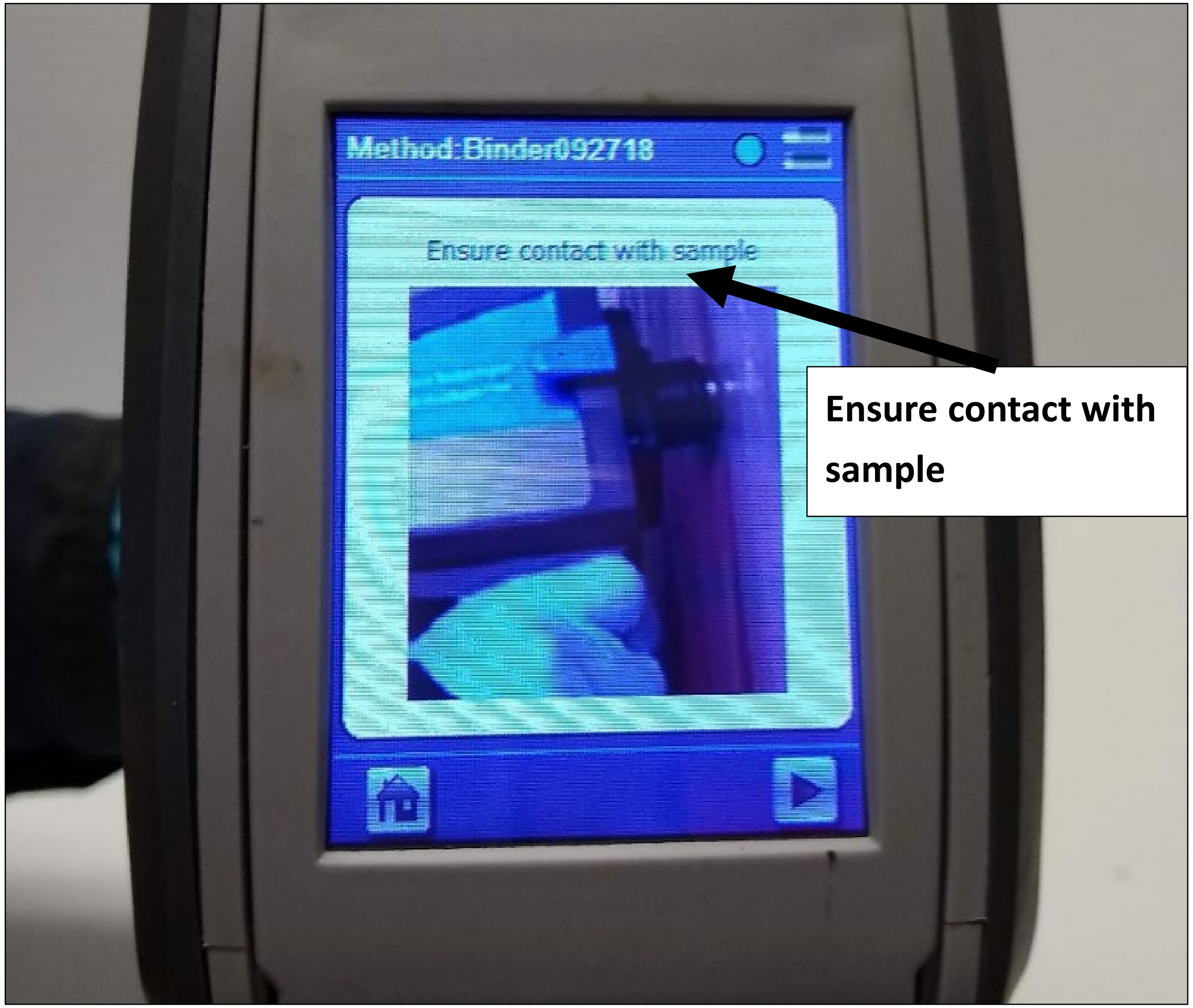
Data Collection

- The system will then **collect the background** spectra automatically
- Time required for this step: **<30 sec**



Data Collection

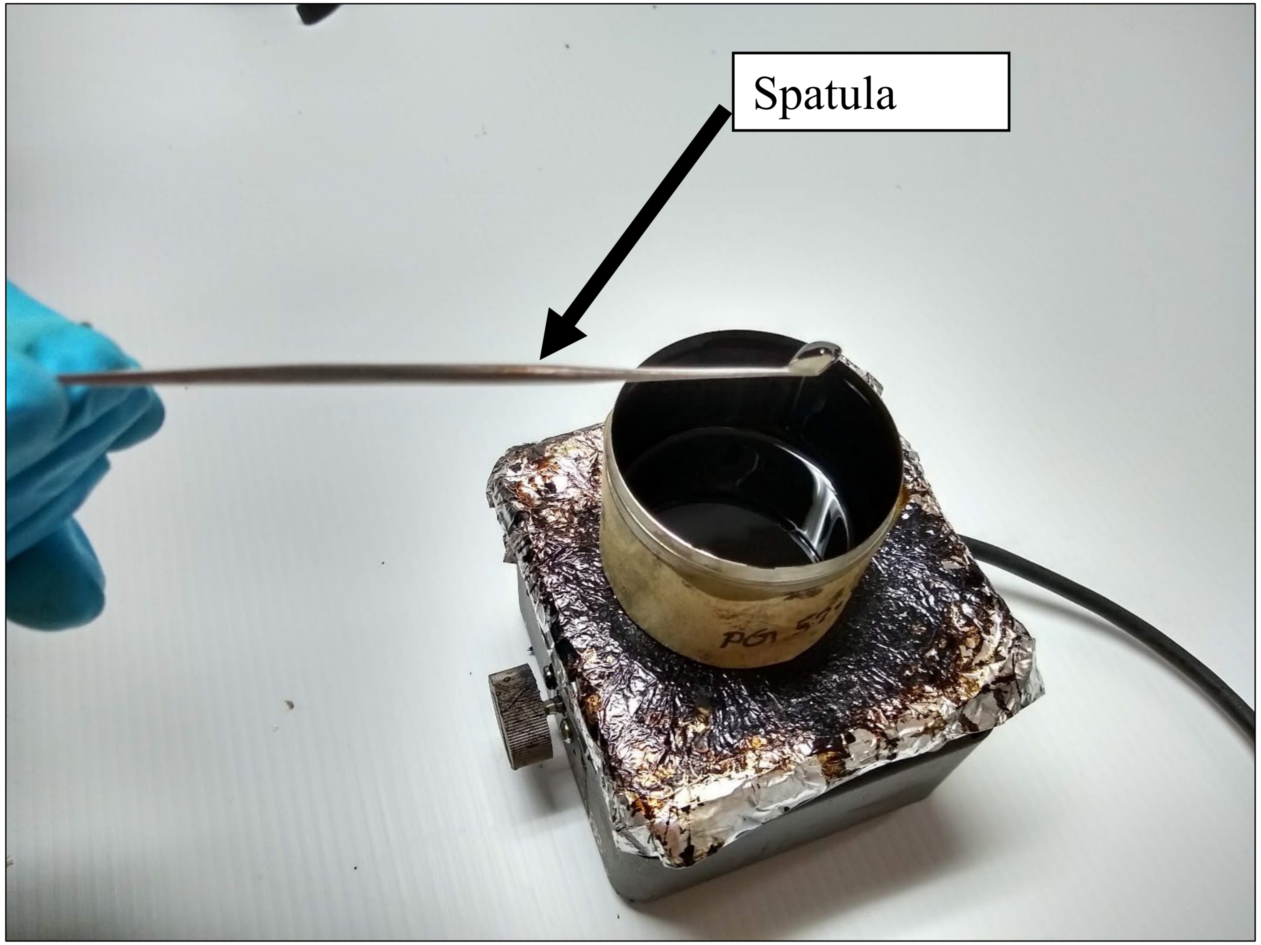
- **After** the collection of **background**, the software will **ask** for the sample



Ensure contact with sample

Data Collection

- **Collection** of SBS modified asphalt binder by **spatula**



Data Collection

- ❑ **Placement of sample** on the diamond ATR sensor of FT-IRS using spatula
- ❑ **Press** the arrow button
- ❑ Time required for this step: **<30 sec**

Data Collection

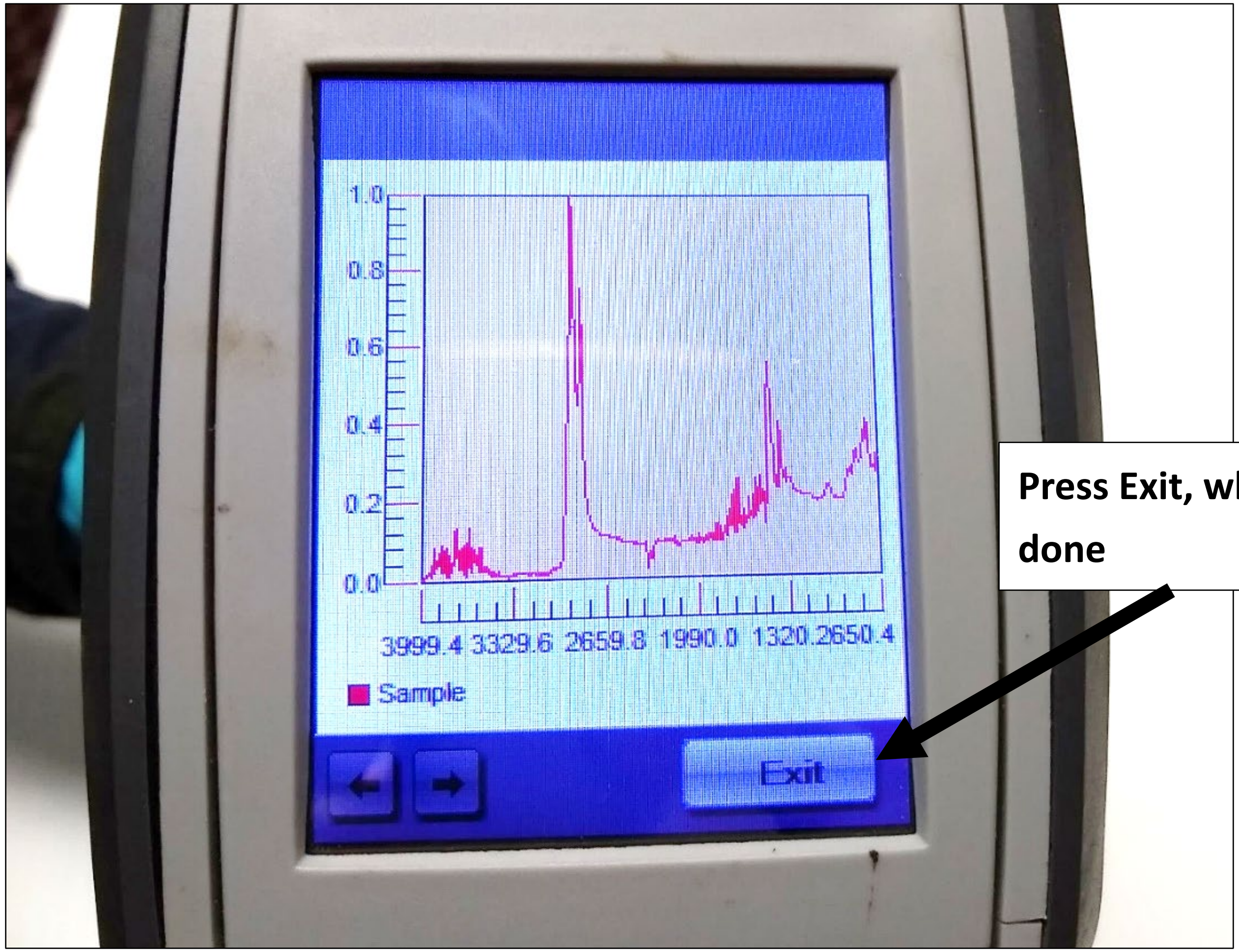
- If the contact is perfect, the **live signal strength** will show **above 0.10**
- Then the **equipment** will be **ready** to collect the spectra
- At this point, **sample name** should be inserted for future reference

Data Collection

- ❑ **Press** the trigger once, to **start** the data collection

Data Collection

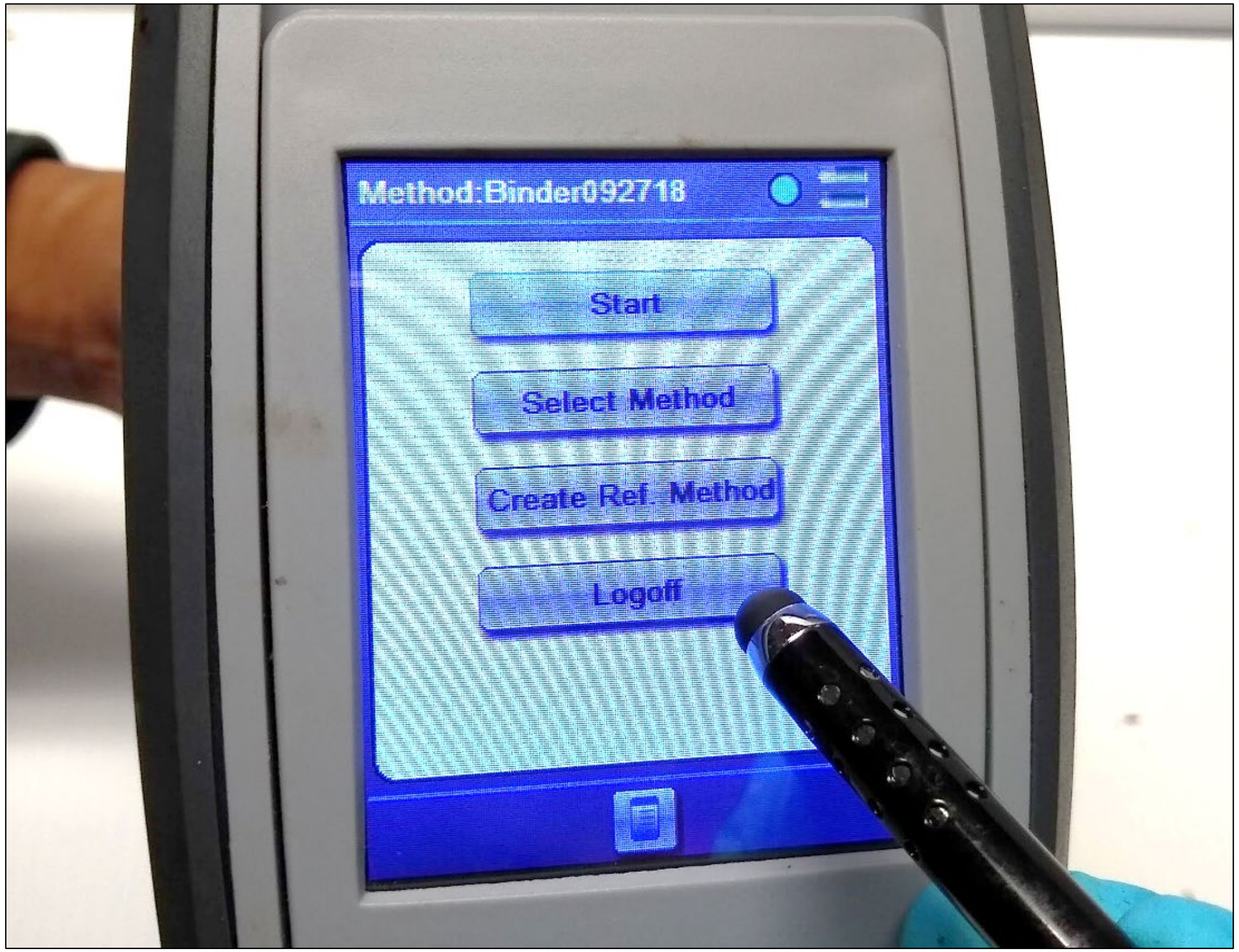
- The spectra will **appear** on the **screen**



Press Exit, when done

Data Collection

- ❑ **'Start'** to begin new sampling or **'Logoff'** if done



Sample Collection in Field

- **Collection** of hot sample from the asphalt tank

Sample Collection in Field

- ❑ **Storing** samples in gallon cans

Data Collection in Field

- ❑ **Placing** sample on ATR FT-IRS sensor by a spatula

Data Collection in Field

- ❑ Ensuring **good connection** between sensor and sample

Data Collection in Field

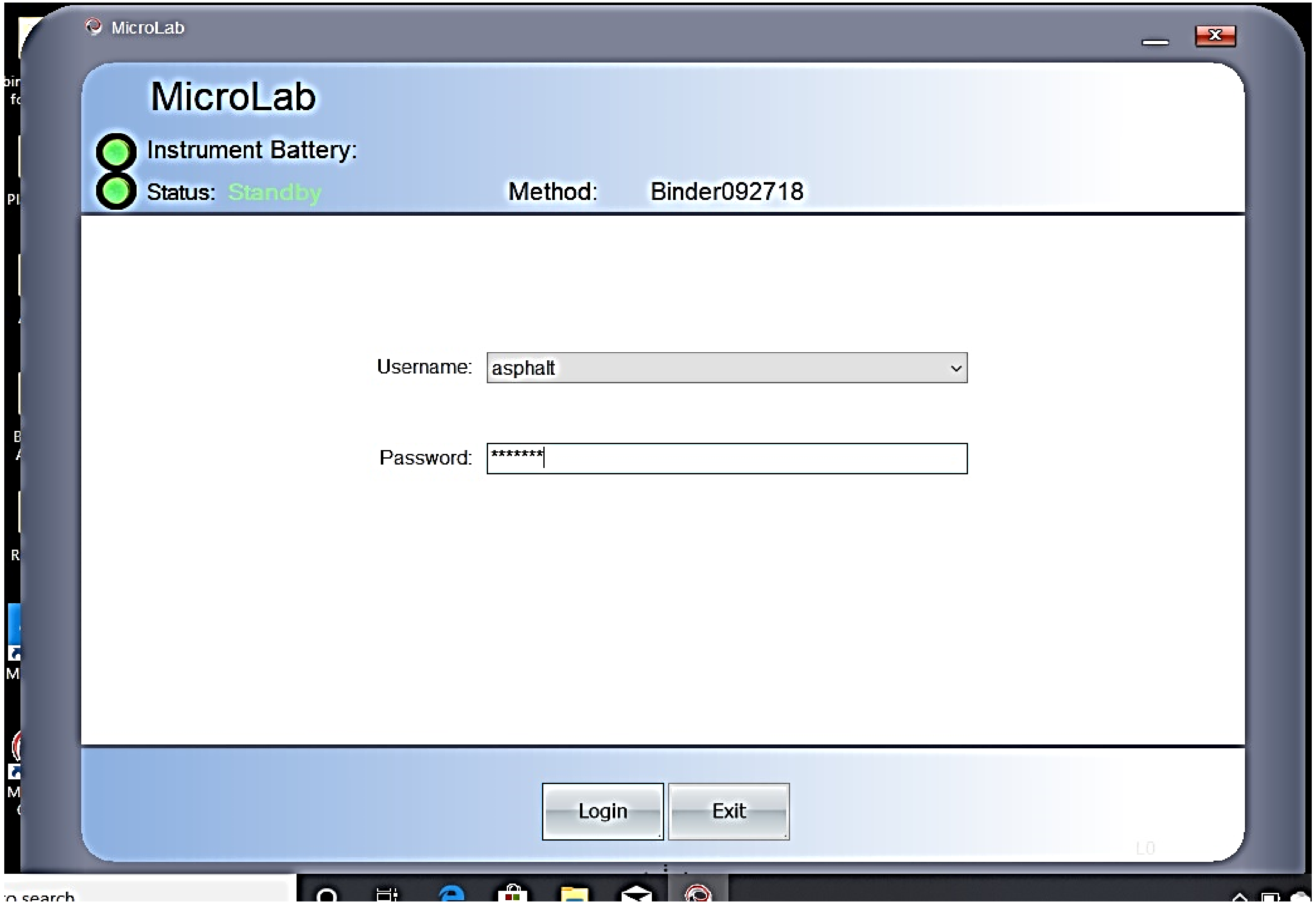
- ❑ Collection of **FT-IR spectra**

Data Collection in Field

- ❑ Repeating **same procedure** for other samples

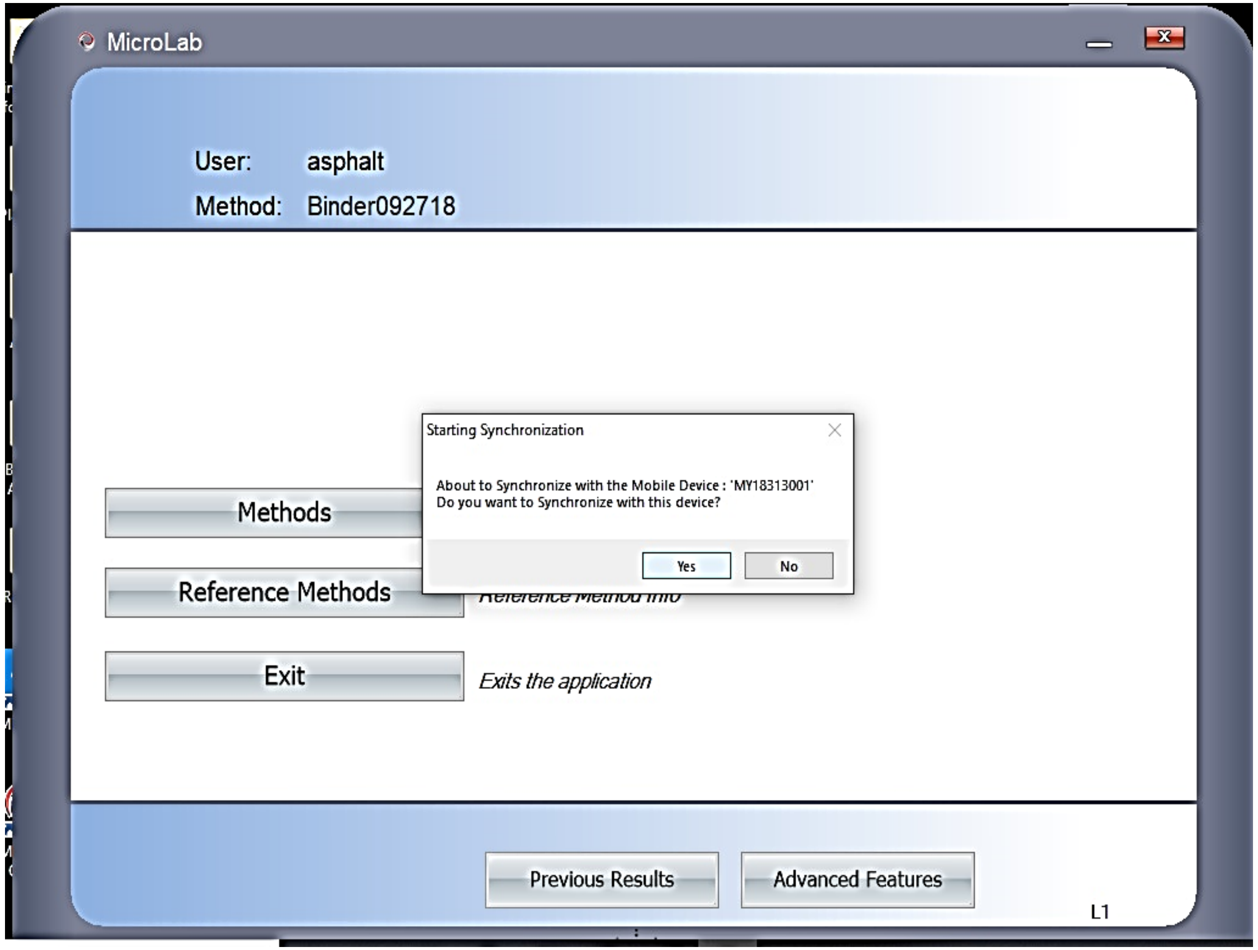
Data Analysis

- ❑ Open the **‘Microlab Lite’ icon** on the PC
- ❑ Insert the password and press **‘login’**



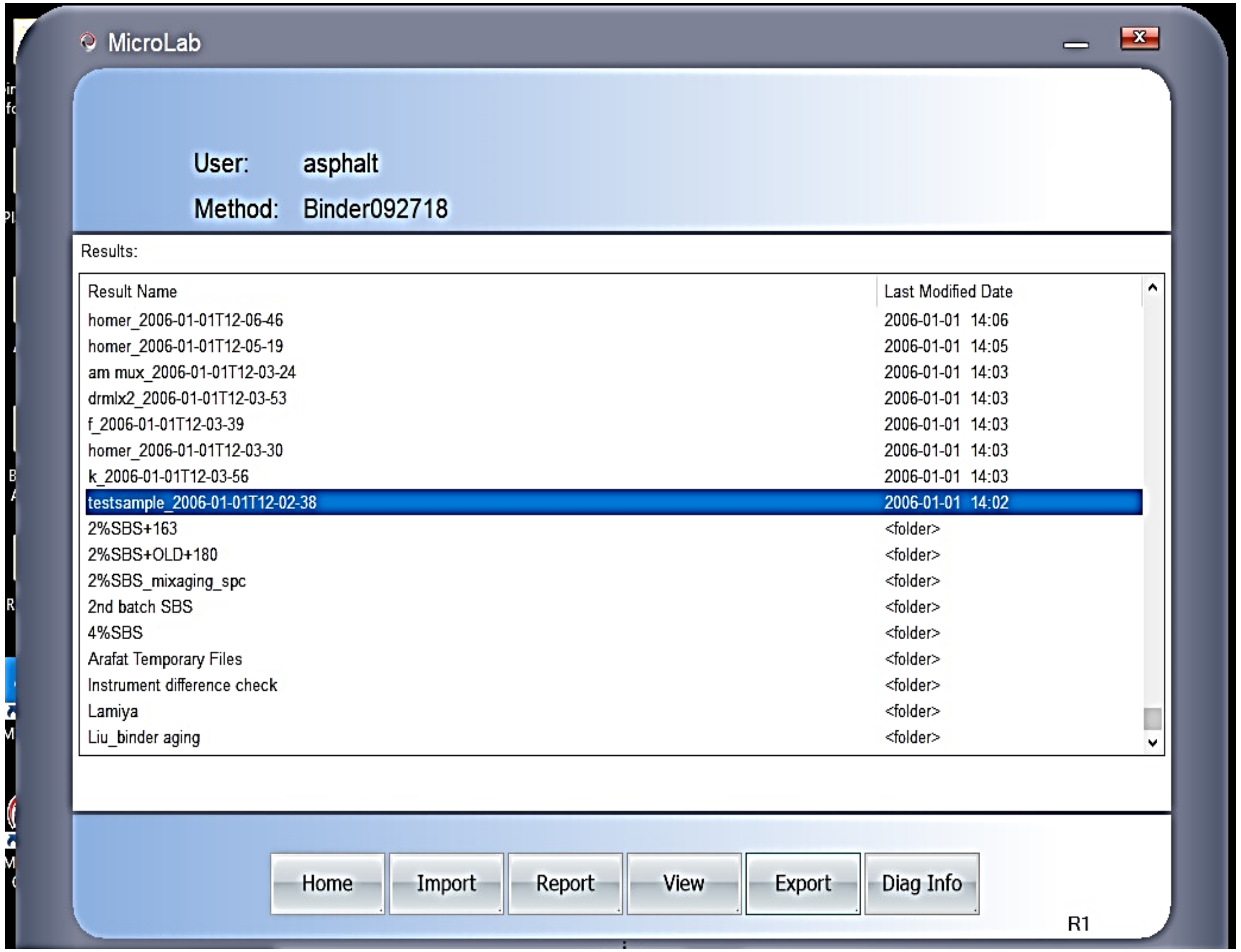
Data Analysis

- It will automatically ask to **synchronize** the data
- The **spectra saved** in the FT-IRS memory will be **transferred to the hard dive** of the PC
- Press **'yes'** wait till synchronization is done
- Press **'Previous Result'** to see the spectra data files



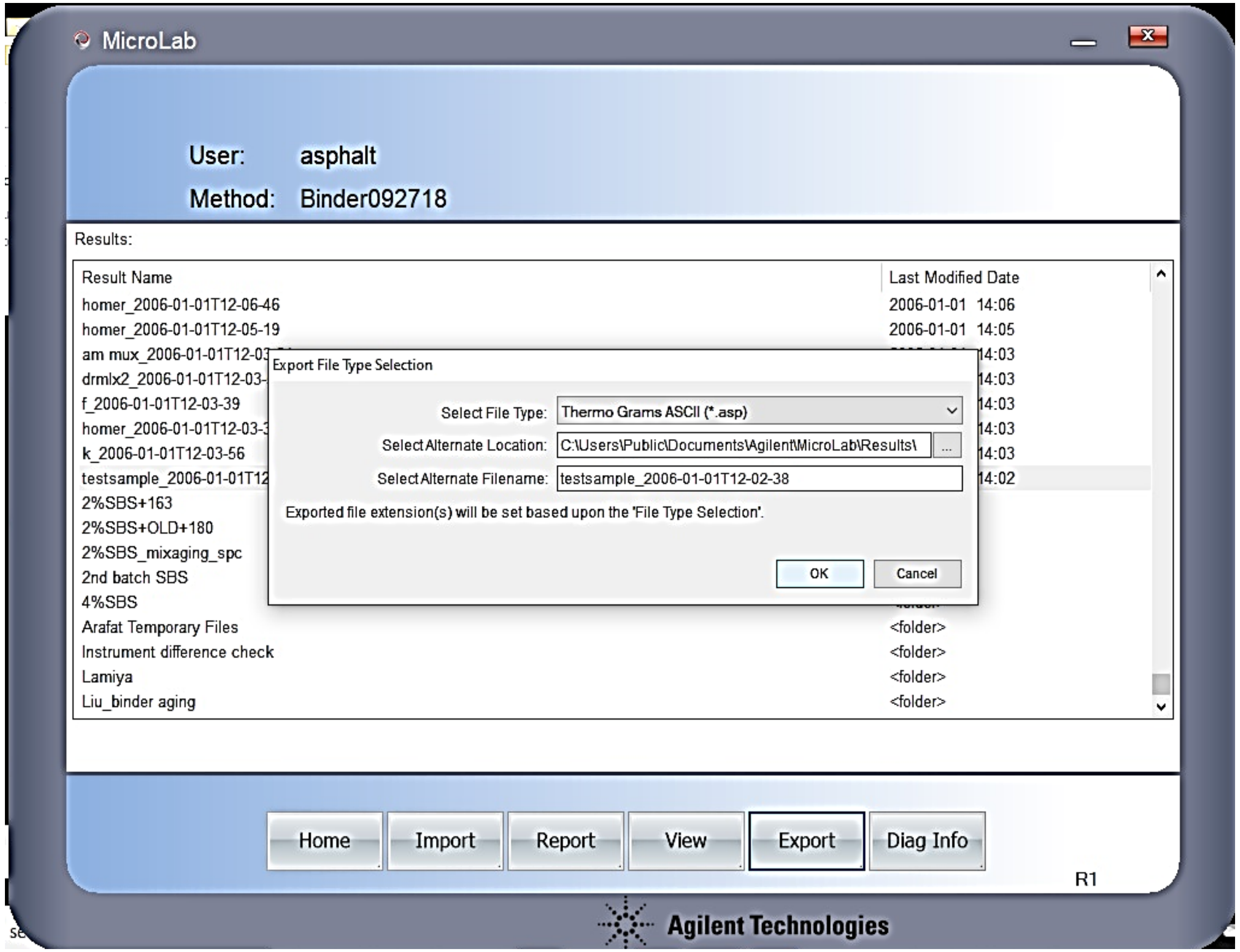
Data Analysis

- ❑ **Select** one file that need to be used for **analysis**



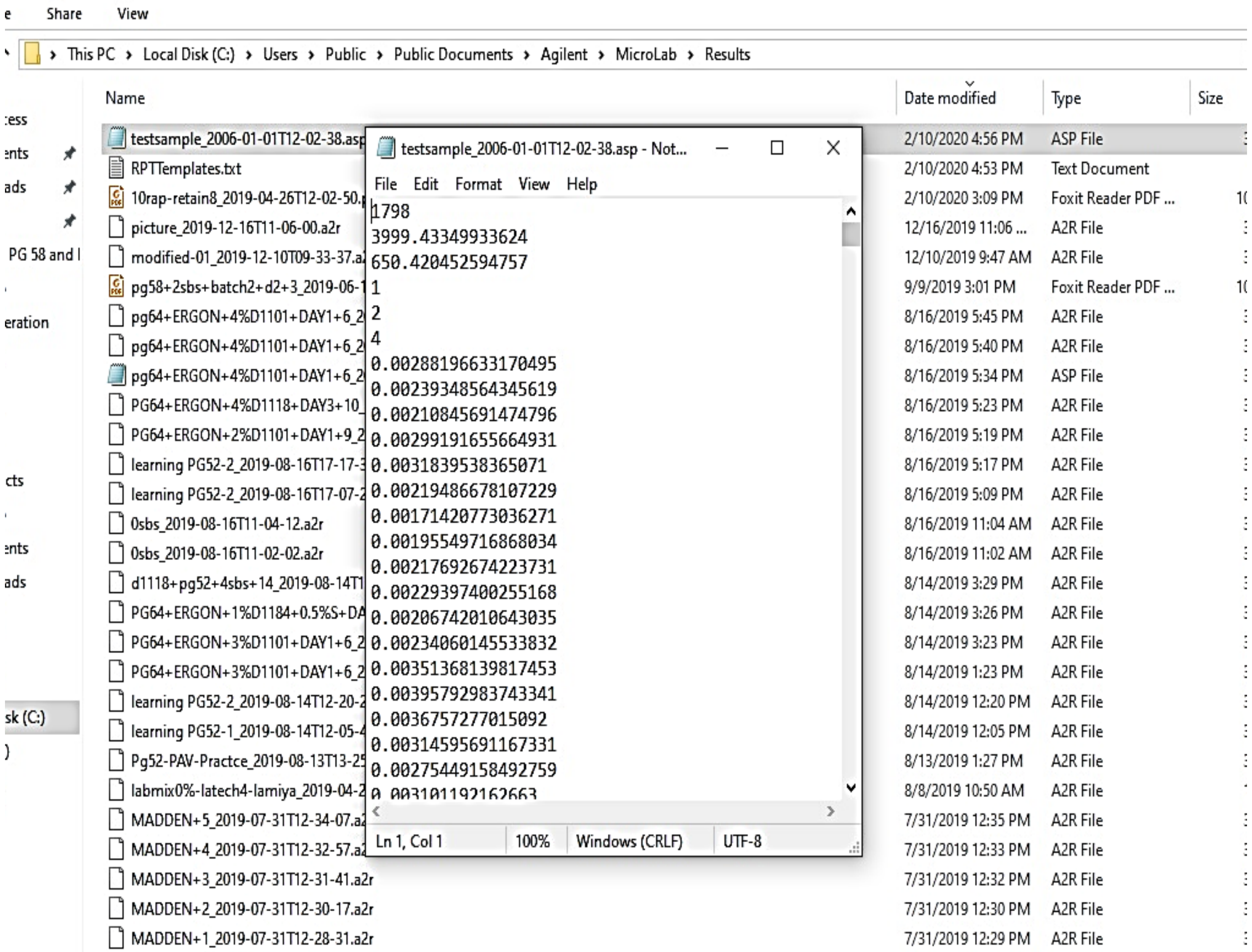
Data Analysis

- ❑ Press **'Export'** to convert it to text file



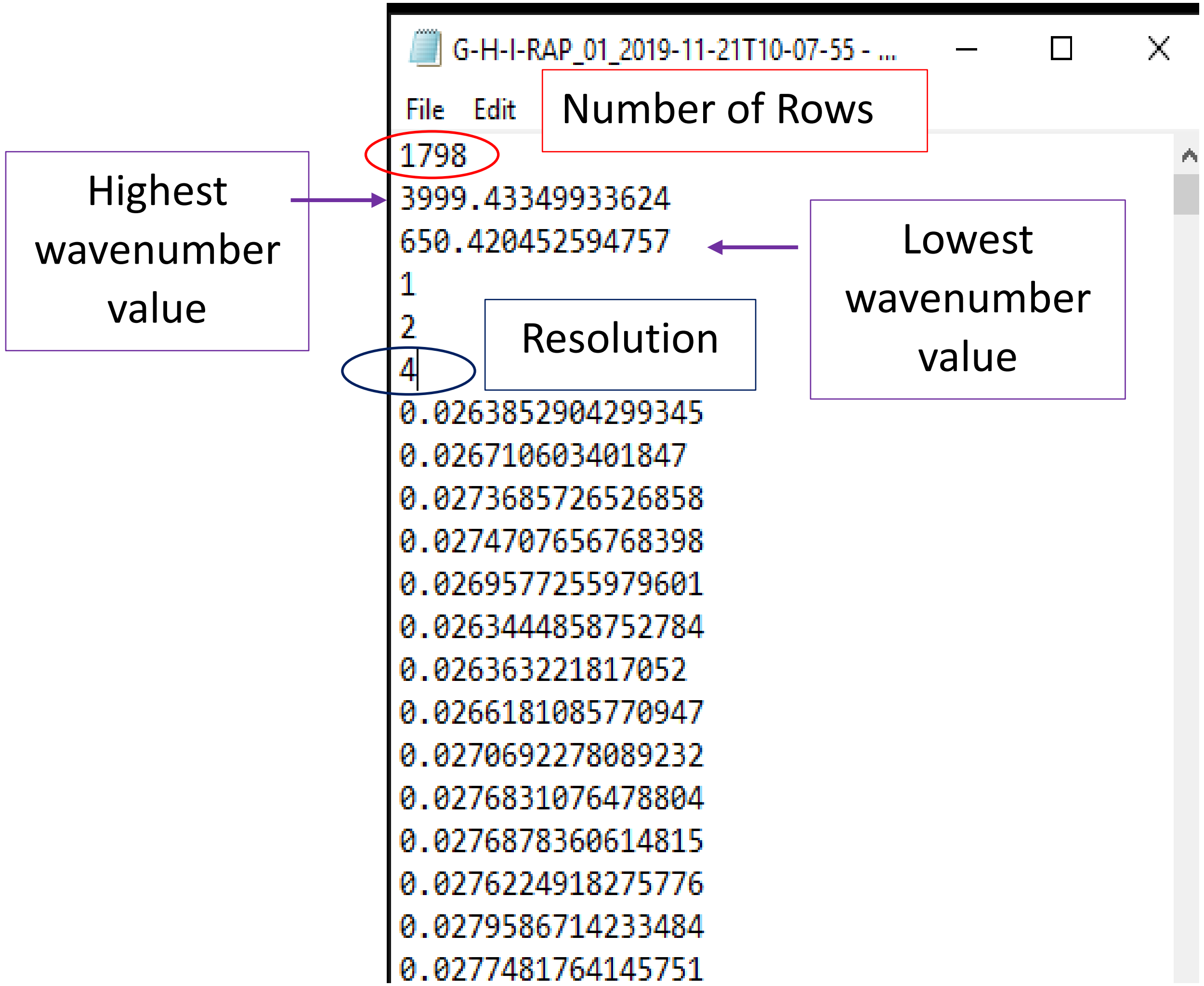
Data Analysis

- ❑ The **text file** will be saved in the **same directory**
- ❑ The data are **copied into the excel file** for further data **processing and analysis**



Data Analysis

- ❑ **Importing** the data file to excel



Data Analysis

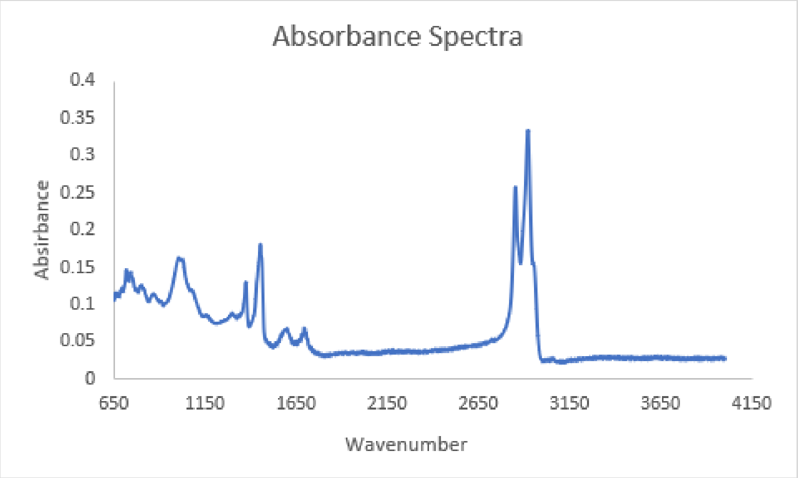
- Creating a column in Excel with the heading **'Wavenumber'**

  Value of first row of the data set = 3999.433
  Value of last row of the data set = 650.420
  Number of rows = 1798

  $$\text{Increment} = \frac{3999.433 - 650.420}{1798 - 1} = 1.8636$$

  The number of rows will vary if the scanning range or rate is changed. During the study, the resolution was kept fixed to 4cm-1
- Creating another column with heading **'Absorbance'**
- **Copying** the absorbance value directly from the **text file to exce**l
- **Plotting the scatter diagram** to check if there is any anomaly in the shape of the spectra

	A	B
1	**Wave Number**	**Absorbance**
2	3999.43	0.02638529
3	3997.57	0.026710603
4	3995.71	0.027368573
5	3993.84	0.027470766
6	3991.98	0.026957726
7	3990.12	0.026344486
8	3988.25	0.026363222
9	3986.39	0.026618109
10	3984.52	0.027069228
11	3982.66	0.027683108
12	3980.80	0.027687836
13	3978.93	0.027622492
14	3977.07	0.027958671
15	3975.21	0.027748176
16	3973.34	0.027220268
17	3971.48	0.027502487
18	3969.61	0.027937341
19	3967.75	0.027584303
1793	661.60	0.115602557
1794	659.74	0.113384027
1795	657.88	0.108820699
1796	656.01	0.105525139
1797	654.15	0.108125975
1798	652.28	0.111138329
1799	650.42	0.113612854
1800		



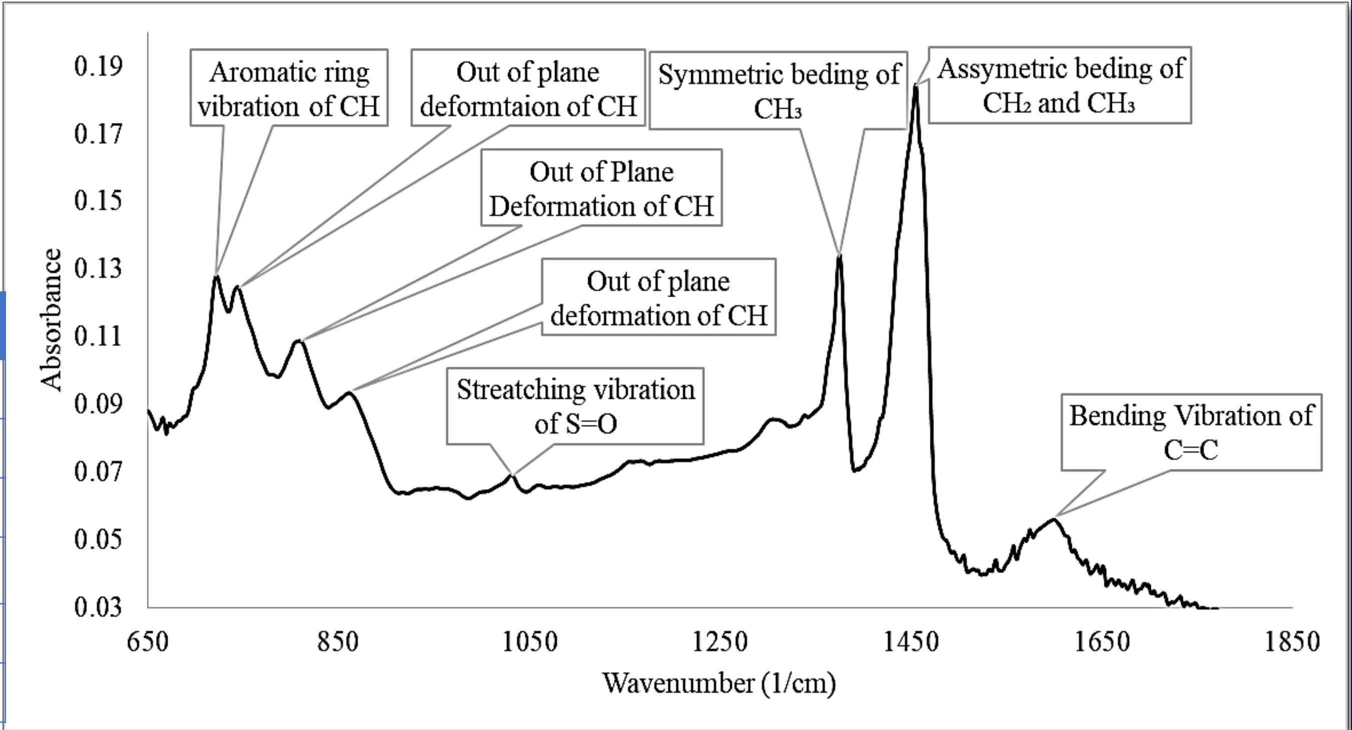
Data Analysis

- ❑ Two analysis method: **Qualitative** and **Quantitative**
- ❑ Qualitative analysis:
  - ✓SBS modified spectrum was superimposed on the unmodified spectrum
  - ✓**Characteristic functional group** due to modification was **identified**
- ❑ Quantitative analysis:
  - ✓To visualize the relationship between the absorbance intensity of the added functional group and the concentration of the modifier- **Regression analysis**
- ❑ The absorbance intensity in terms of **peak height or peak area** is directly **proportional** to the **concentration** (Beer's law)

Characteristics Functional Group

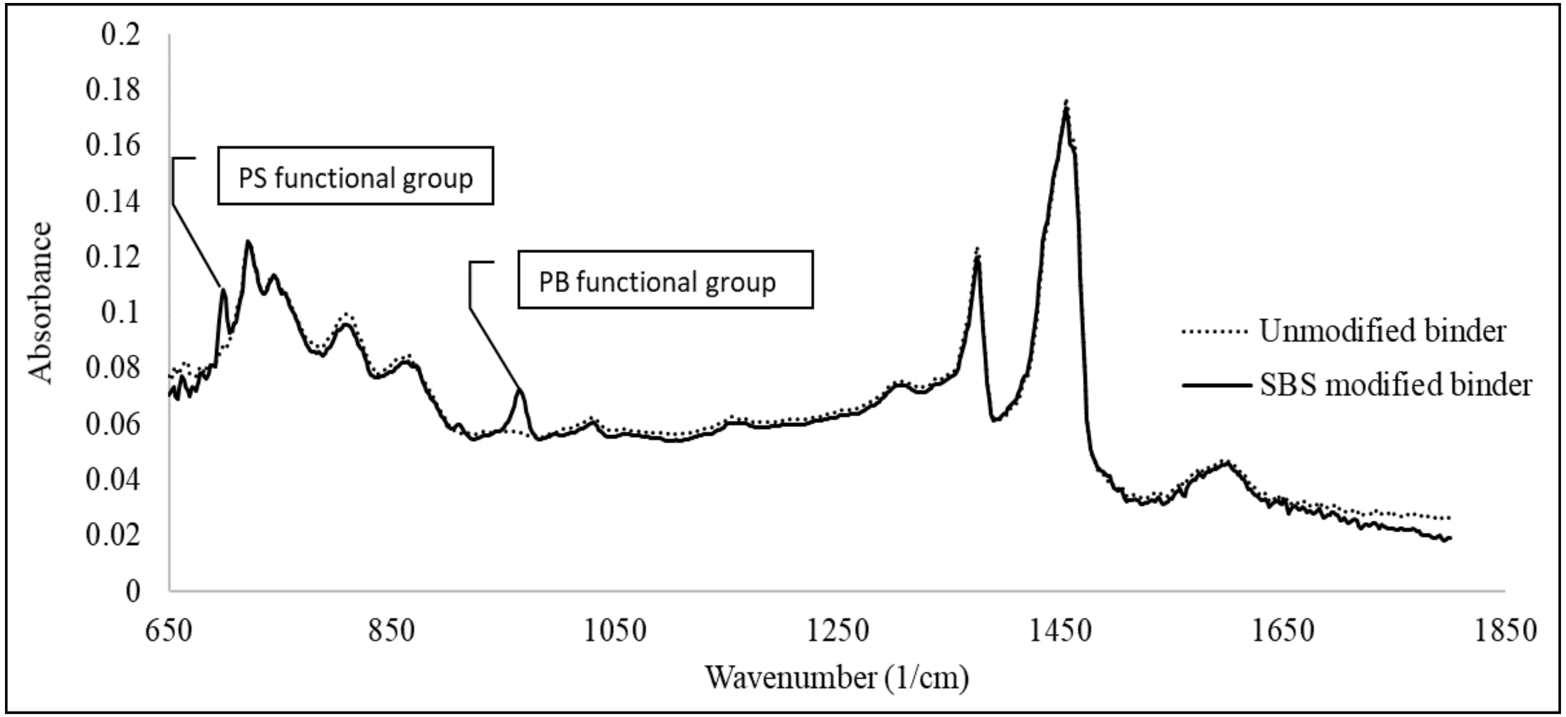
- Characteristic functional groups in **fingerprint region (650cm^{-1}- 1800cm^{-1})** of **unmodified asphalt binder**

Functional groups	Wave numbers (cm^{-1})
Bending vibration of **C=C**	**1600**
Asymmetric bending of **CH_2 and CH_3**	**1455**
Symmetric bending of **CH_3**	**1375**
Stretching vibration of **S=O**	**1030**
Out-of-plane deformation of **CH**	**870, 817 and 745**
Aromatic ring vibration of **CH**	**721**



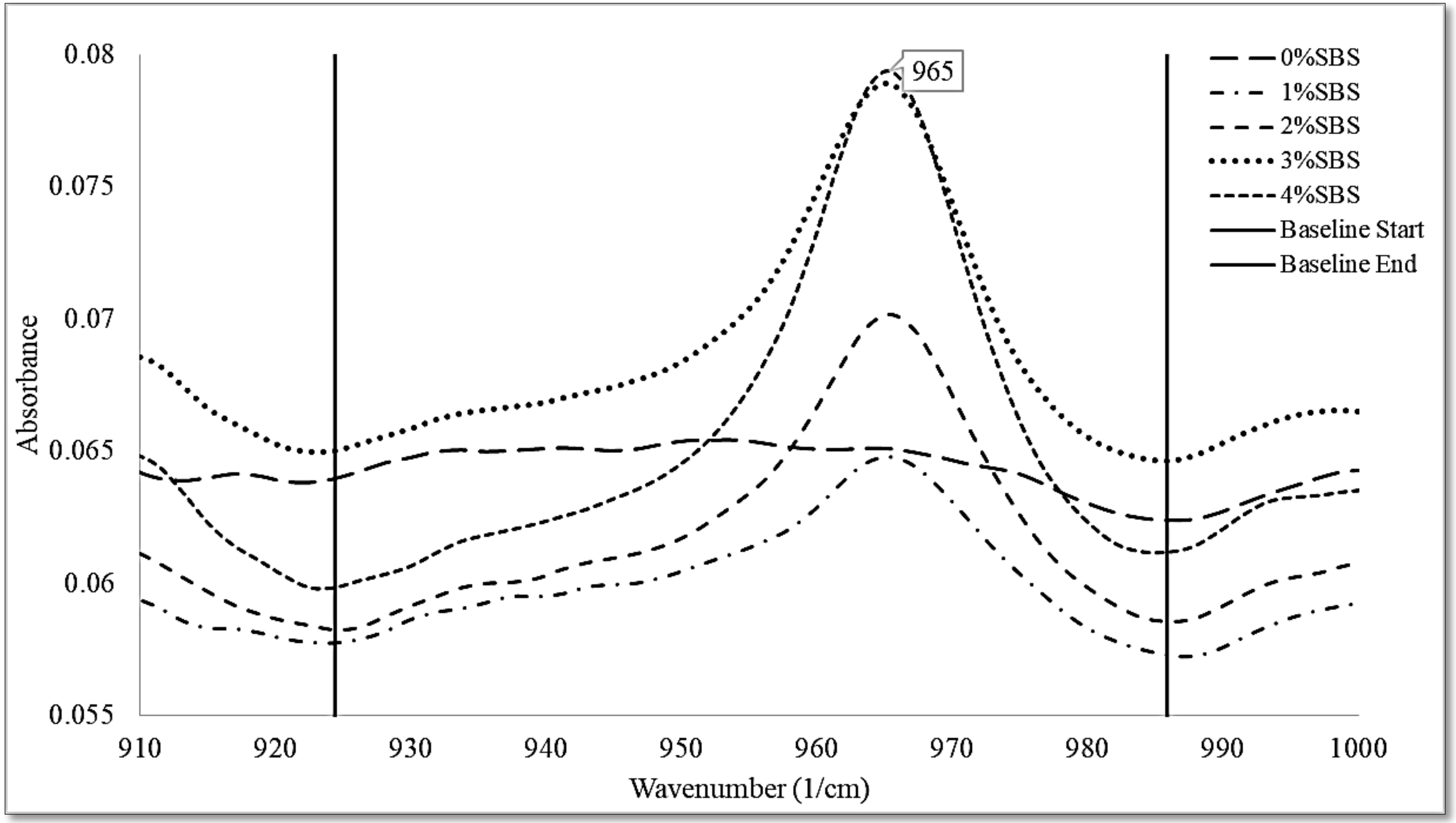
Characteristics Functional Group for SBS Modification

- **Modification** of base binders with **SBS** copolymers: two additional groups
- Out-of-plane (wagging) vibrations of the CH groups at **965 cm^{-1}** which is accountable for **polybutadiene** block
- Out-of-plane bending of the CH groups in the aromatic ring at **699 cm^{-1}** for **polystyrene** block



Effect of SBS Content (%) on FT-IR spectra

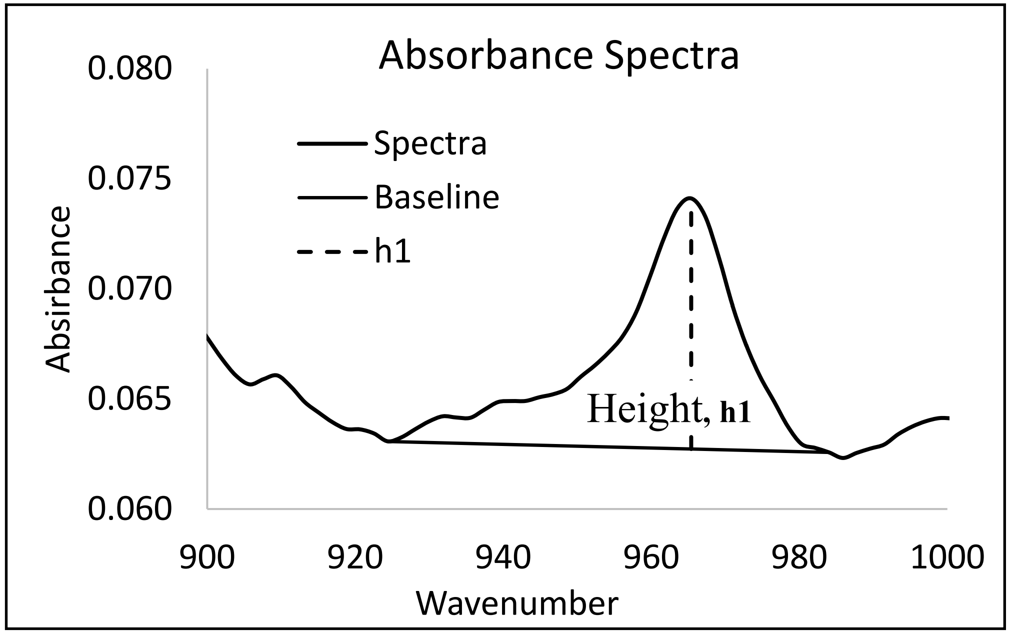
- Increasing pattern in absorbance intensity of the FT-IR spectra at wavenumber **965 cm^{-1}** due to the addition of **different percentage of SBS** in asphalt binder
- **Negligible peak height and area** in unmodified samples **(0% SBS)**: due to the **scattering** effect of the **IR beam** and no **pretreatment** of the raw spectra



Effect of SBS addition in different percentages in asphalt binder at wavenumber 965cm^{-1}

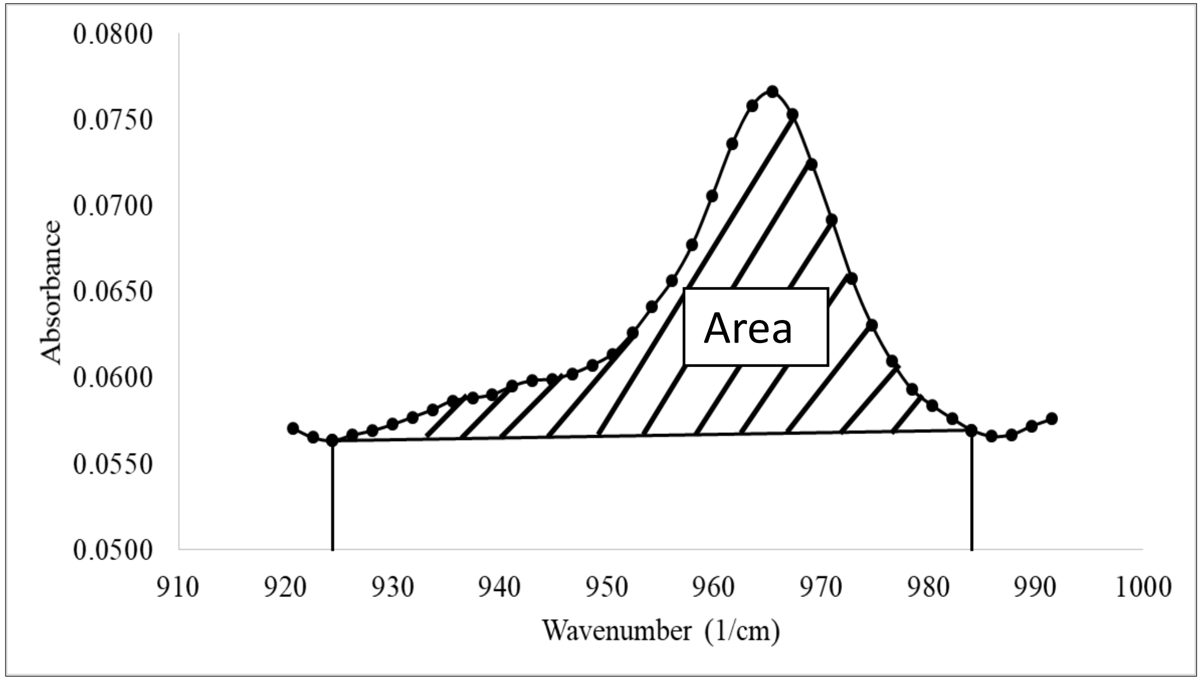
SBS Quantification: Peak Height Method

- ❑ Absorbance intensity of the characteristic functional group - quantified by **peak height and area** method
  - ✓ To find the appropriate method which would provide repeatable measurements
  - ✓ **Peak height and area** method : they have ability to eliminate noise and baseline shift effects
- ❑ Height of the functional group - by drawing a **baseline** considering the **two lowest points (924 and 984 cm^{-1})** on both side of the characteristic functional group **(965 cm^{-1})**
- ❑ **Peak height –** difference between the peak point and the baseline



SBS Quantification: Peak Area Method

- The absorbance area - **trapezoidal rule method**
- The baseline can be drawn following the similar process as the peak height method
- After drawing the baseline, the **area under the baseline** is subtracted from the **total area under the peak**



Data Analysis in Excel File

- **Calculation of peak height and area** at wavenumber 965 cm^{-1}: screenshot of the excel file

Wavenumber	Absorbance	Baseline Value	Height Under Curve	Area Segment	Positive Area
984.02	0.057851	0.057851	0.000000		
982.15	0.058208	0.057864	0.000343	0.00032	0.00032
980.29	0.058761	0.057878	0.000884	0.00114	0.00114
978.43	0.059689	0.057891	0.001799	0.00250	0.00250
976.56	0.061067	0.057904	0.003164	0.00462	0.00462
974.70	0.062930	0.057917	0.005014	0.00762	0.00762
972.84	0.065287	0.057930	0.007357	0.01153	0.01153
970.97	0.068303	0.057943	0.010360	0.01651	0.01651
969.11	0.071567	0.057956	0.013611	0.02234	0.02234
967.24	0.074276	0.057969	0.016307	0.02788	0.02788
965.38	0.075556	0.057982	0.017573	0.03157	0.03157
963.52	0.074998	0.057995	0.017003	0.03222	0.03222
961.65	0.072919	0.058008	0.014911	0.02974	0.02974
959.79	0.070237	0.058022	0.012215	0.02528	0.02528
957.93	0.067784	0.058035	0.009749	0.02047	0.02047
956.06	0.065896	0.058048	0.007848	0.01640	0.01640
954.20	0.064531	0.058061	0.006470	0.01334	0.01334
952.33	0.063513	0.058074	0.005439	0.01110	0.01110
950.47	0.062750	0.058087	0.004663	0.00941	0.00941
948.61	0.062076	0.058100	0.003976	0.00805	0.00805
946.74	0.061486	0.058113	0.003372	0.00685	0.00685
944.88	0.061134	0.058126	0.003008	0.00595	0.00595
943.02	0.060918	0.058139	0.002779	0.00539	0.00539
941.15	0.060670	0.058153	0.002518	0.00494	0.00494
939.29	0.060318	0.058166	0.002152	0.00435	0.00435
937.43	0.060079	0.058179	0.001900	0.00378	0.00378
935.56	0.059978	0.058192	0.001786	0.00344	0.00344
933.70	0.059912	0.058205	0.001707	0.00326	0.00326
931.83	0.059583	0.058218	0.001365	0.00286	0.00286
929.97	0.059198	0.058231	0.000967	0.00217	0.00217
928.11	0.058750	0.058244	0.000506	0.00137	0.00137
926.24	0.058364	0.058257	0.000107	0.00057	0.00057
924.38	0.058270	0.058270	0.000000	0.00010	0.00010

Calculation for Baseline

	Wavenumber	Absorbance
Peak at	965.38	0.0756
Valley at Right	984.02	0.0579
Valley at Left	924.38	0.0583

Calculation for Peak Height

Slope of the Baseline	m=	-0.0000070
Intercept of the Baseline	c=	0.0648
Wavenumber at Peak at x1	x1=	965.38
y-value on the Baseline, at x1	y1=	0.0580
y-value on the spectra, at x1	y2=	0.0756
Peak height, at x1	h1=	0.0176

Area under the curve above baseline

Area under the curve above baseline	A1=	0.3370

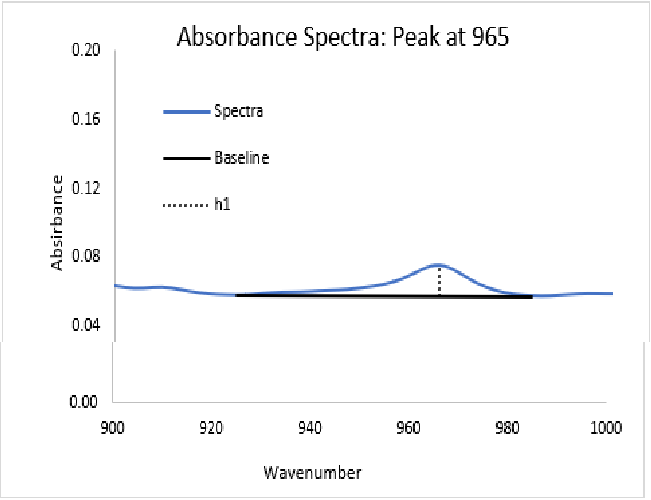


Chart Area

Data Analysis in Excel File

Calculation for Baseline

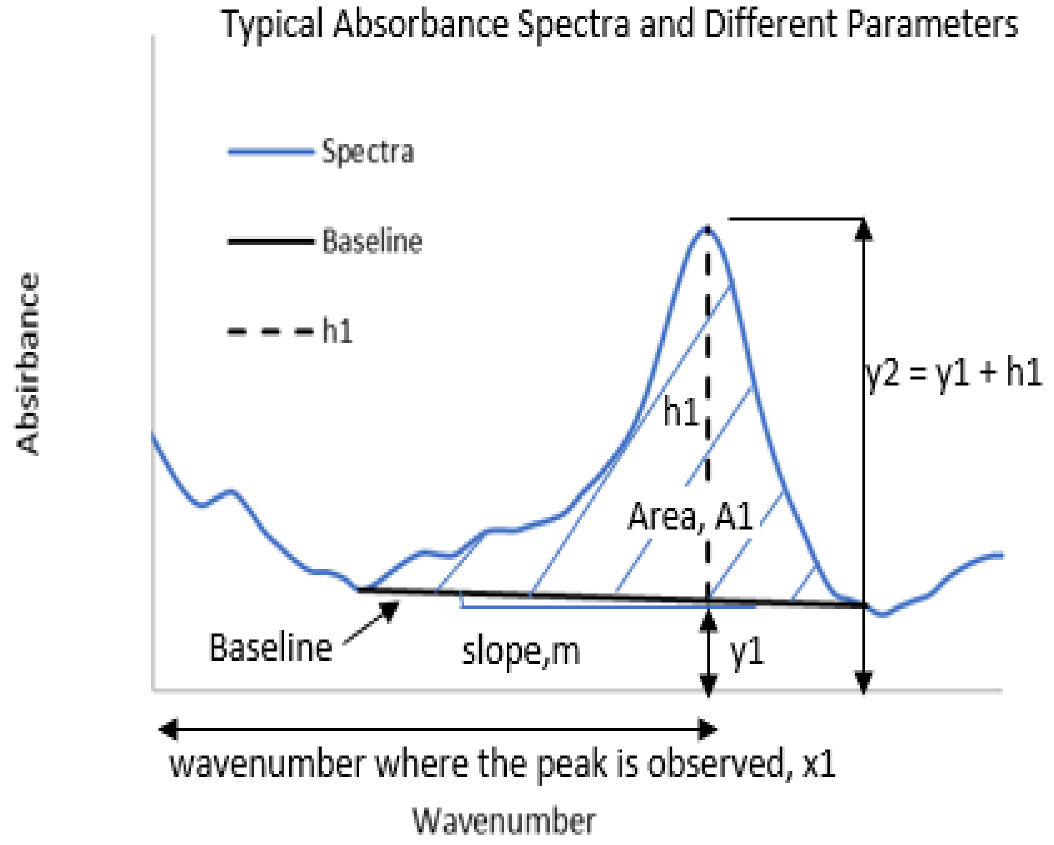
	Wavenumber	Absorbance
Peak at	965.38	0.0756
Valley at Right	984.02	0.0579
Valley at Left	924.38	0.0583

Calculation for Peak Height

Slope of the Baseline	m=	-0.0000070
Intercept of the Baseline	c=	0.0648
Wavenumber at Peak at x1	x1=	965.38
y-value on the Baseline, at x1	y1=	0.0580
y-value on the spectra, at x1	y2=	0.0756
Peak height, at x1	h1=	0.0176

Area under the curve above baseline

Area under the curve above baseline	A1=	0.3370

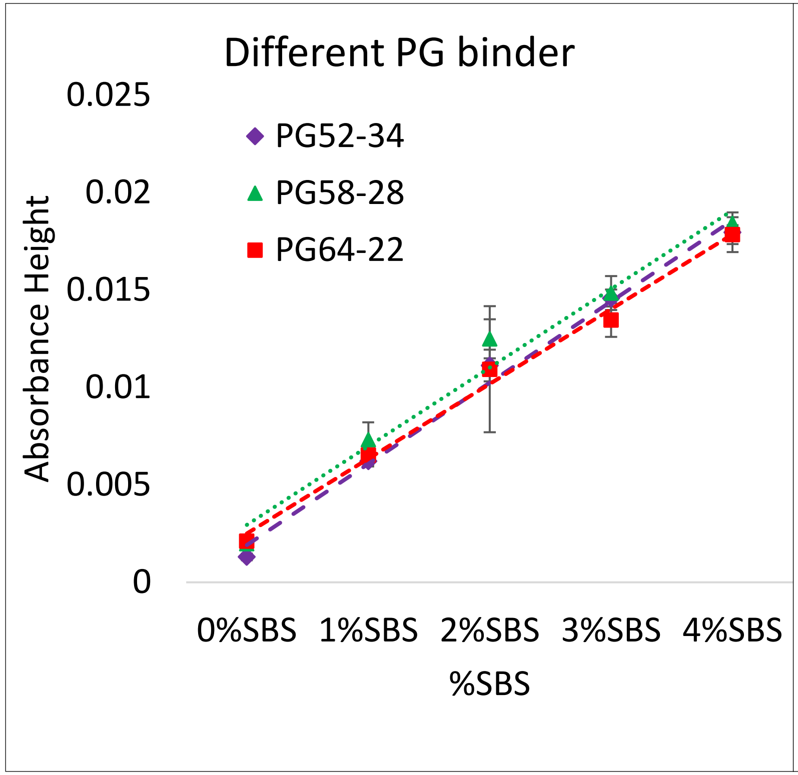


Linear Relation: Different Scenario

PG 52-34: $R^2 = 0.991$

PG 58-28: $R^2 = 0.978$

PG 64-22: $R^2 = 0.993$

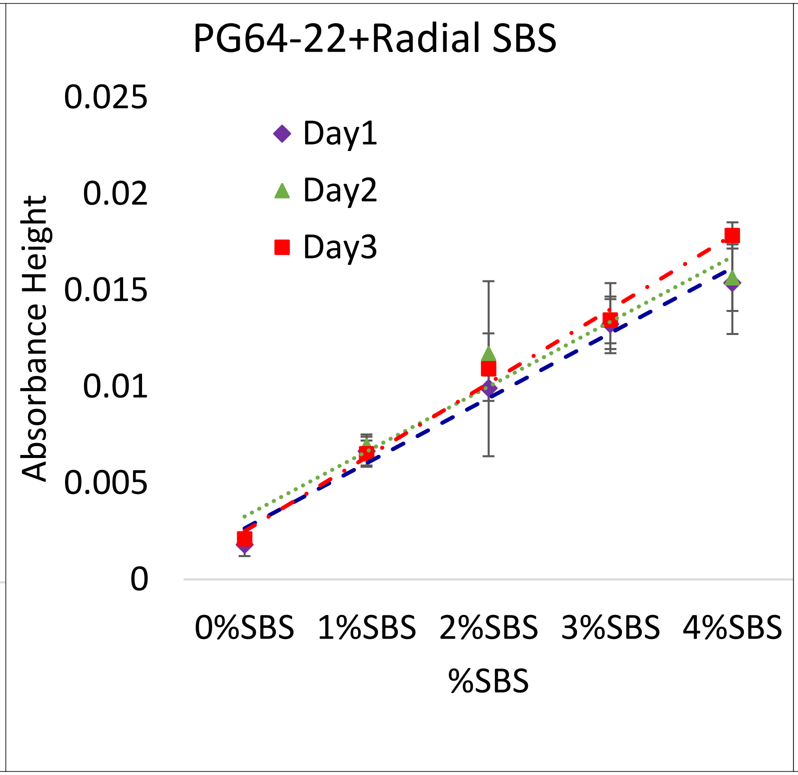


Different types of PG binder

Day 1: $R^2 = 0.981$

Day 2: $R^2 = 0.953$

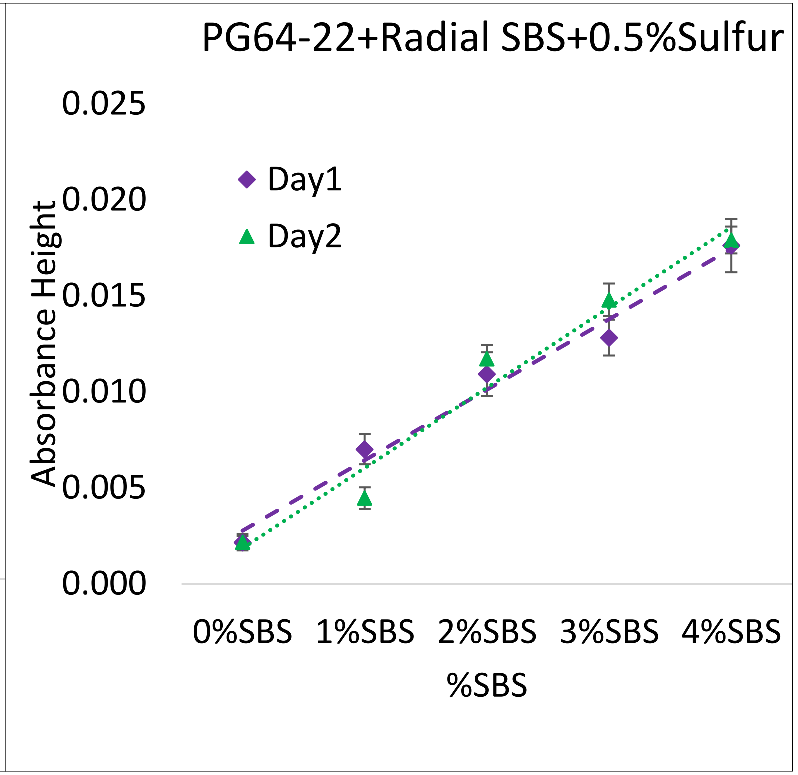
Day 3 : $R^2 = 0.993$



Data collection in different days for same binder

Day 1: $R^2 = 0.983$

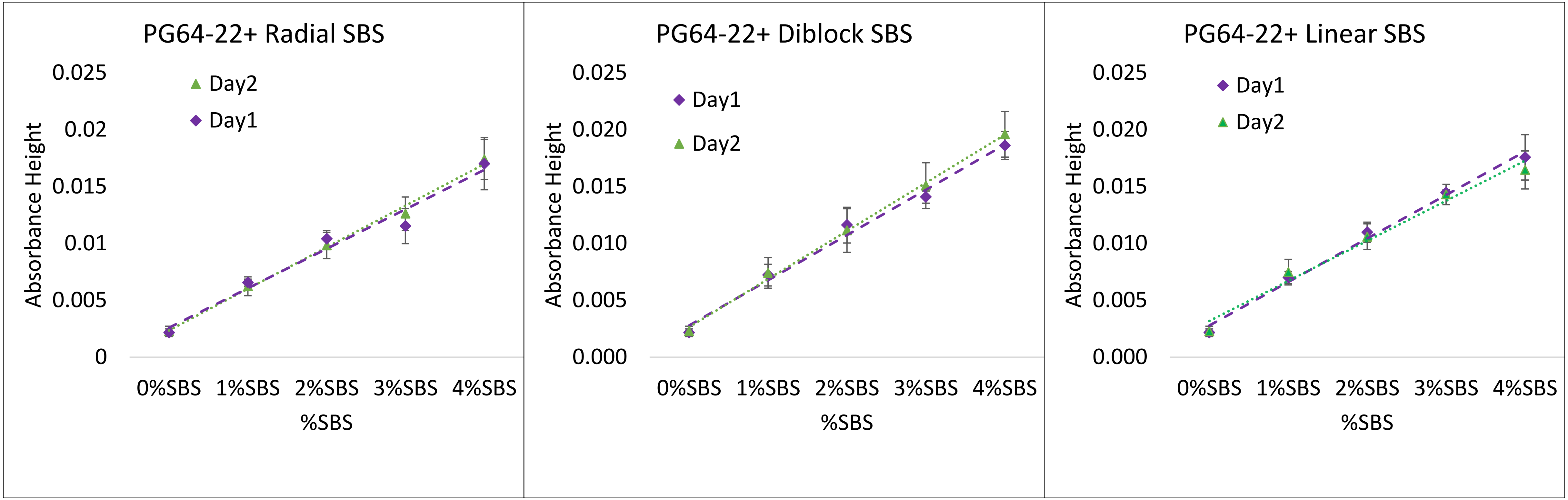
Day 2: $R^2 = 0.969$



Addition of cross-linking agent (sulfur) with SBS modified PG 64-22 binder

Linear Relation: Different Types of SBS Polymer

PG64-22+ Radial SBS	PG64-22+ Diblock SBS	PG64-22+ Linear SBS
Day 1: $R^2 = 0.971$	Day 1: $R^2 = 0.989$	Day 1: $R^2 = 0.992$
Day 2: $R^2 = 0.994$	Day 2: $R^2 = 0.997$	Day 2: $R^2 = 0.979$



Correlation of SBS Content (%) with Absorbance Height

Total 24 Linear Equation

Type of Sample	Linear Equation	R^2	Type of Sample	Equation	R^2
PG52-34+**Radial SBS**+B1+D1	y =0.0041x-0.0032	**0.99**	PG64-22+Radial SBS+S1+B1+D3	y = 0.0036x-0.002	**0.94**
PG52-34+Radial SBS+B1+D2	y =0.0034x-0.0014	**0.97**	PG64-22+Radial SBS+S1+B2+D1	y = 0.0034x-0.0007	**0.98**
PG52-34+Radial SBS+B1+D3	y =0.0042x-0.0023	**0.99**	PG64-22+Radial SBS+S1+B2+D2	y =0.0034x-0.0001	**0.95**
PG58-28+Radial SBS+S1+B1+D1	y =0.0031x-0.0002	**0.95**	PG64-22+Radial SBS+S1+B2+D3	y =0.0038x-0.0013	**0.99**
PG58-28+Radial SBS+S1+B1+D2	y =0.0035x-0.0005	**0.97**	**PG64-22**+Radial SBS+**S2**+B1+D1	y =0.0035x-0.0009	**0.97**
PG58-28+Radial SBS+S1+B1+D3	y =0.0052x-0.0036	**0.95**	PG64-22+Radial SBS+S2+B1+D2	y =0.0037x-0.0013	**0.99**
PG58-28+Radial SBS+S1+B1+D4	y =0.0040x-0.0011	**0.98**	PG64-22+**Linear SBS**+S2+B1+D1	y = 0.0038x-0.001	**0.99**
PG58-28+Radial SBS+S1+B2+D1	y =0.0030x-0.0004	**0.94**	PG64-22+Linear SBS+S2+B1+D2	y =0.0035x-0.0003	**0.98**
PG58-28+Radial SBS+S1+B2+D2	y =0.0043x-0.0023	**0.96**	PG64-22+**Diblock SBS**+S2+B1+D1	y =0.004x-0.0012	**0.99**
PG58-28+Radial SBS+S1+B2+D3	y =0.0038x-0.0016	**0.97**	PG64-22+Diblock SBS+S2+B1+D2	y =0.0042x-0.0016	**1.00**
PG64-22+Radial SBS+**S1**+B1+D1	y =0.0036x-0.0007	**0.96**	PG64-22+Radial SBS+ **0.5% sulfur** +S2+B1+D1	y =0.0037x-0.0009	**0.98**
PG64-22+Radial SBS+S1+B1+D2	y =0.0038x-0.0017	**0.94**	PG64-22+Radial SBS+0.5% sulfur +S2+B1+D2	y =0.0042x-0.0023	**0.97**

Universal Equation (Combining 24 Cases)

With outlier:

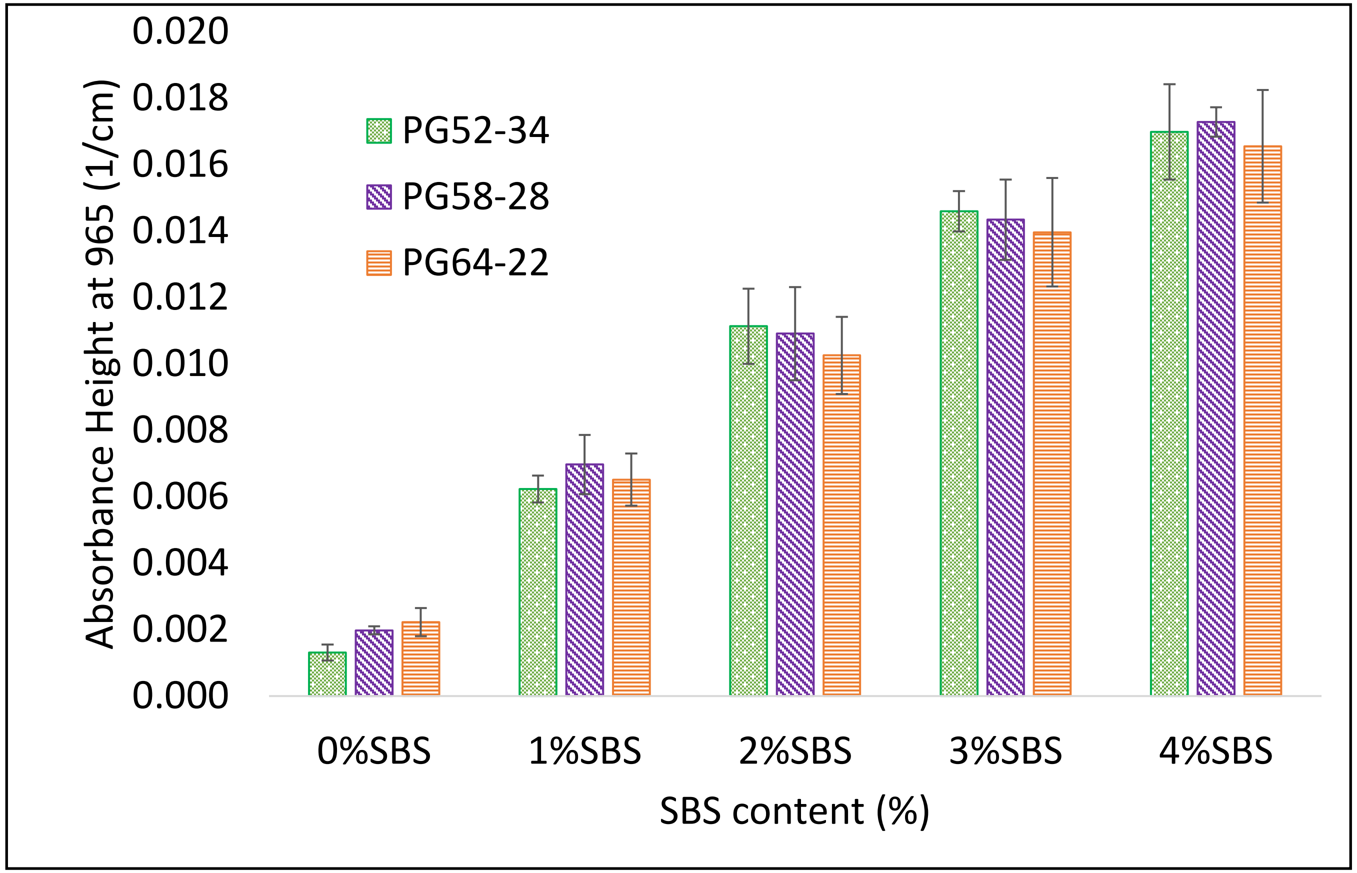
Peak height at 965 cm^{-1}= 0.003814***SBS concentration**+0.002419

Without outlier:

Peak height at 965 cm^{-1}= 0.003809***SBS concentration**+0.002413

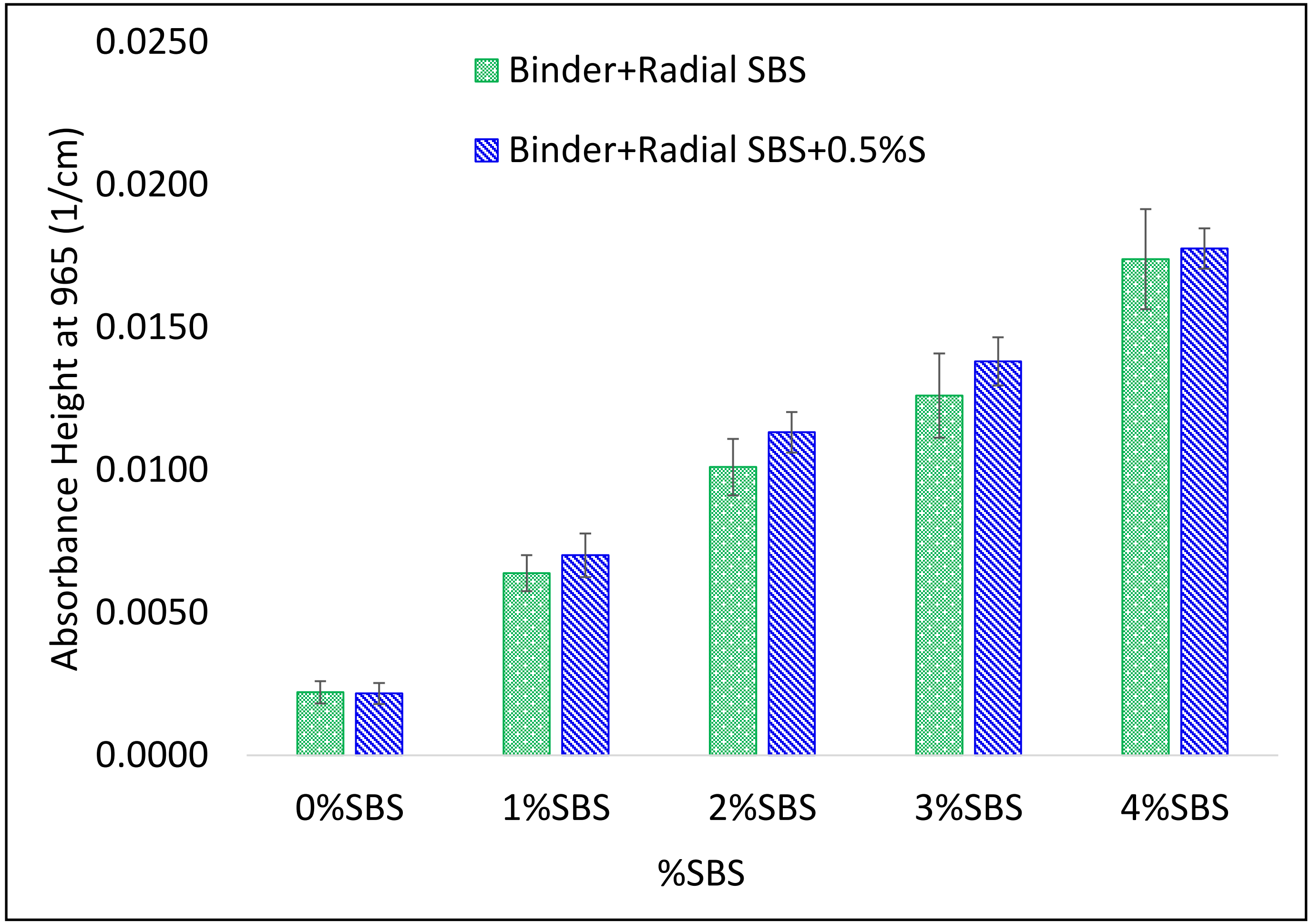
Effect of Different PG Binder

- ❑Physical properties depend on the binder's performance grade
- ❑**Significant difference** in peak height was **not** observed



Effect of Cross-Linking Agent (Sulfur)

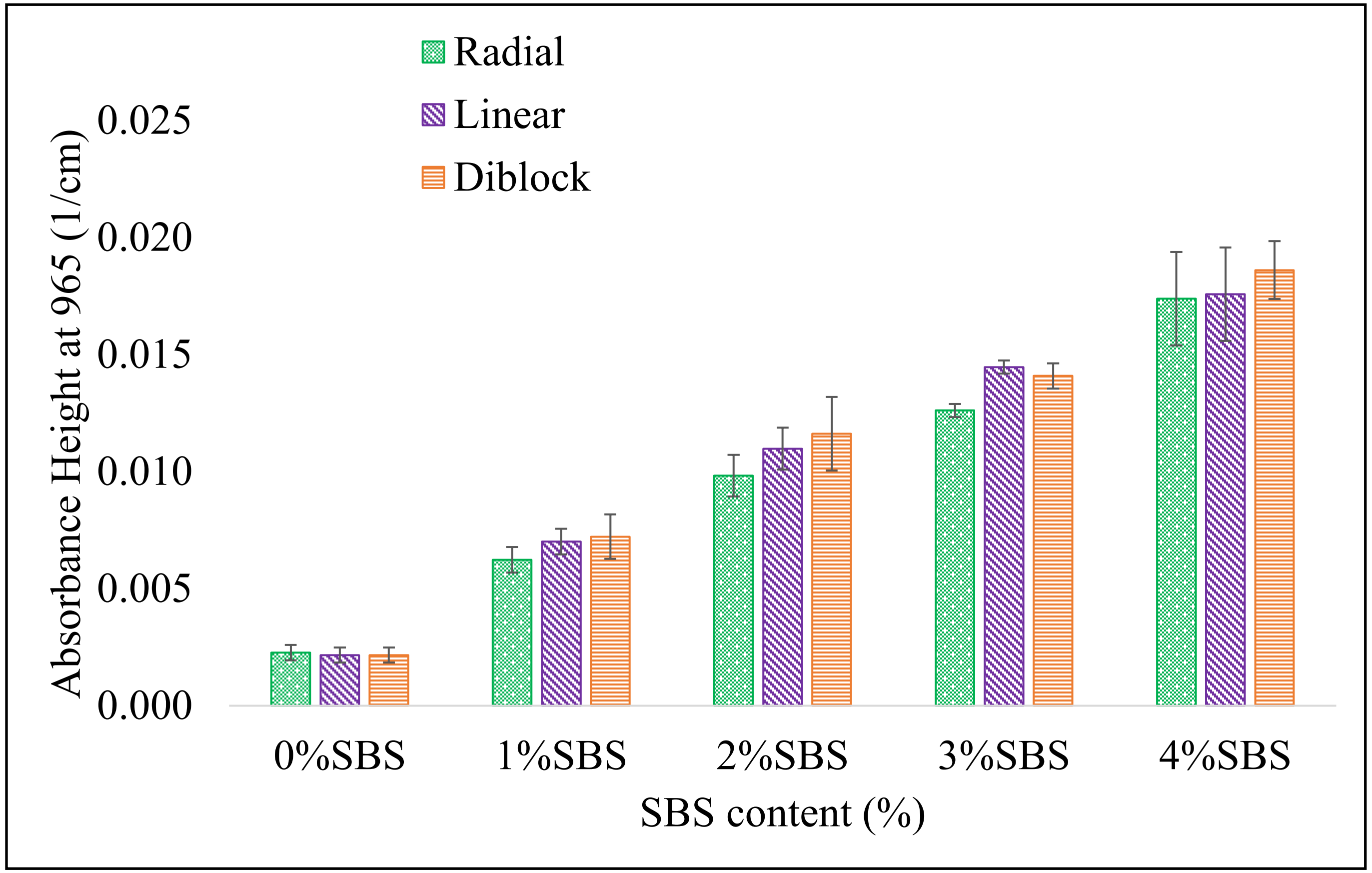
- ❑**Sulfur** was added as cross-linking agent
- ❑Improves the **storage stability** of SBS modified asphalt binder
- ❑Does not add any new functional group
- ❑**Does not affect** the peak height and shape **at 965 cm^{-1}** wavenumber



Effect of Different SBS polymer structure

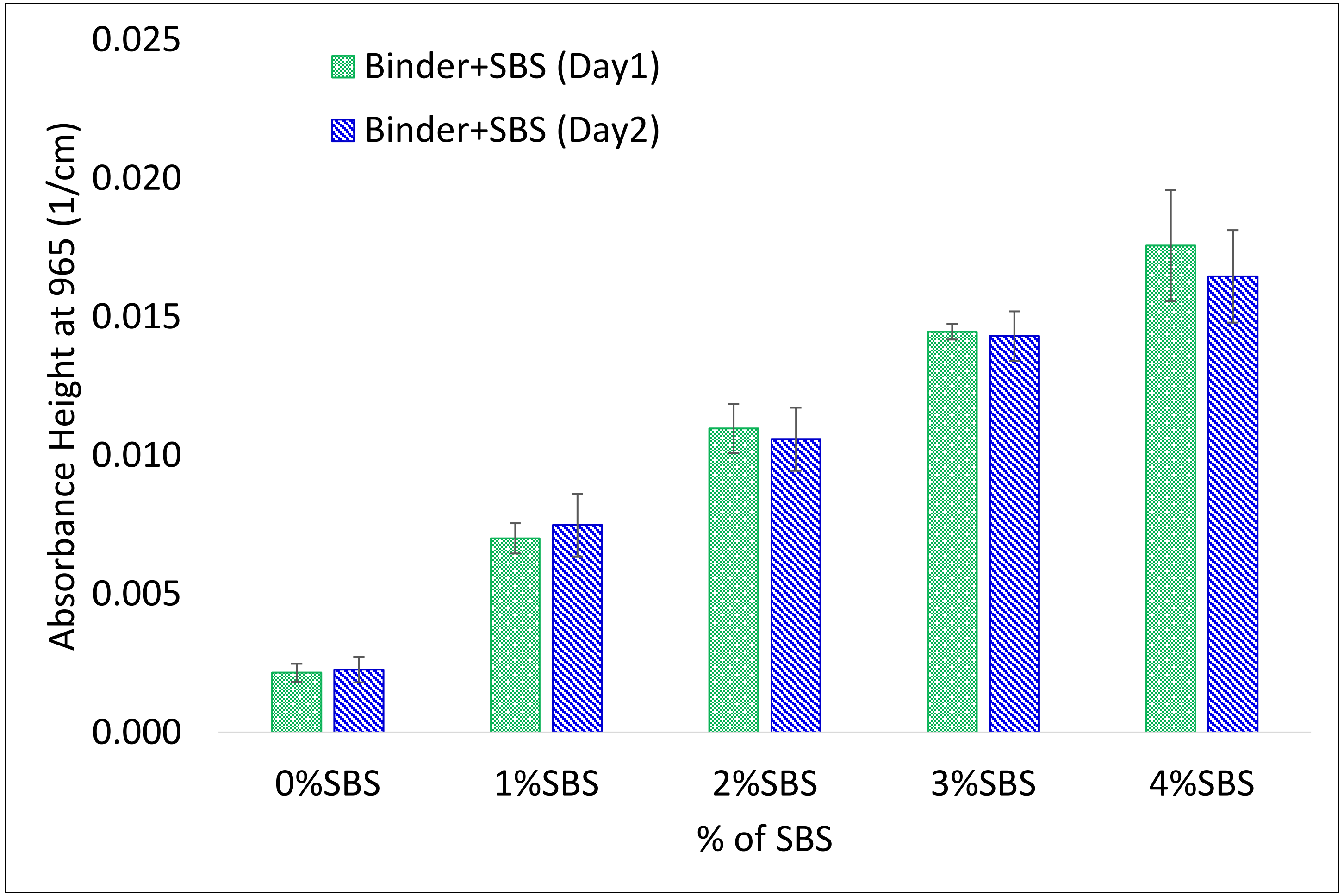
- ❑ 3 types of SBS polymer **(Radial, Linear and Diblock)** was added
- ❑ **No difference** was observed in the absorbance height

SBS polymer type	S/B Ratio
Radial	31/69
Linear	31/69
Diblock	33/67



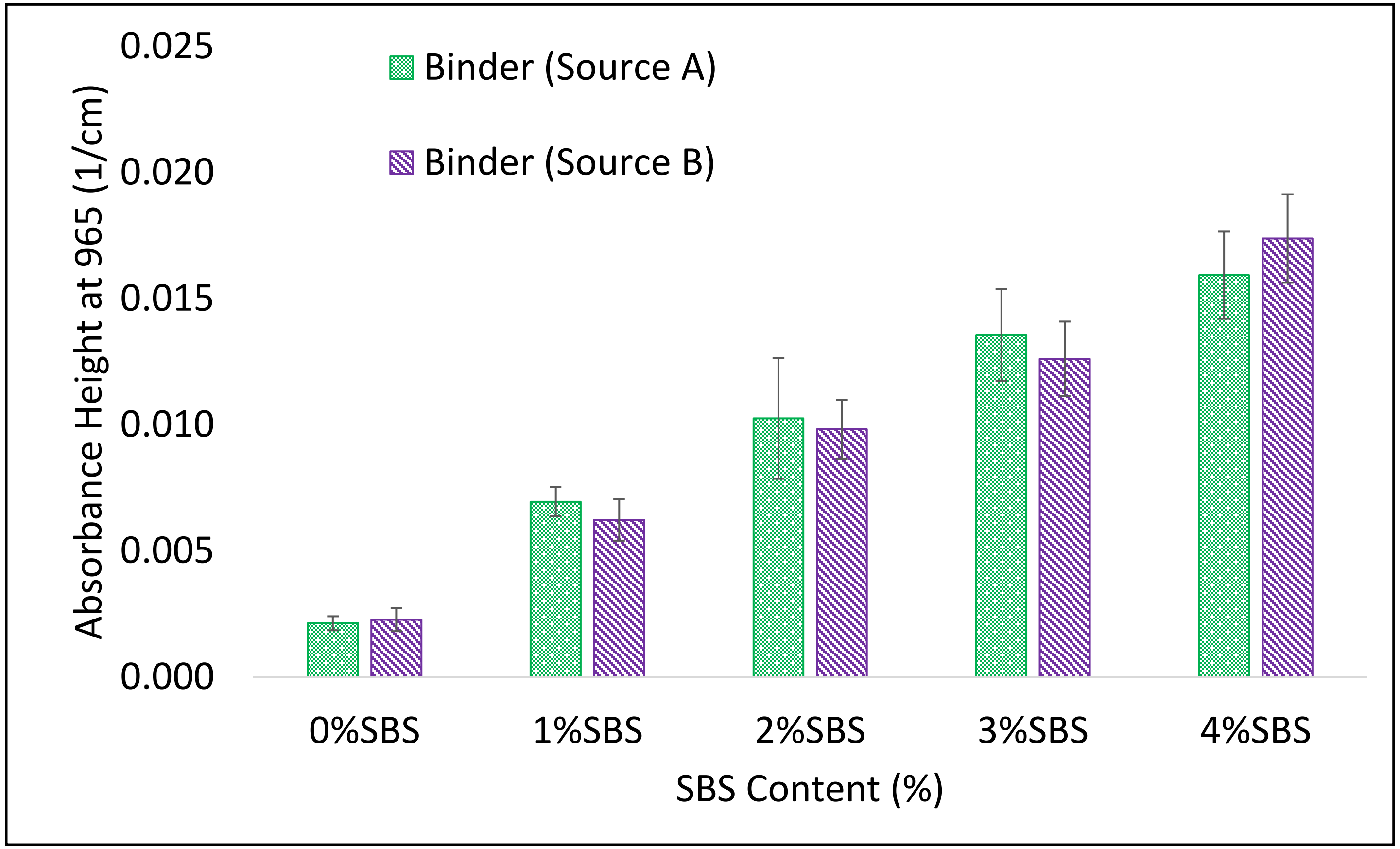
Effect of Data Collection in Different Days

- The **same** SBS modified PG binder was used for FT-IRS data collection on **two different days**



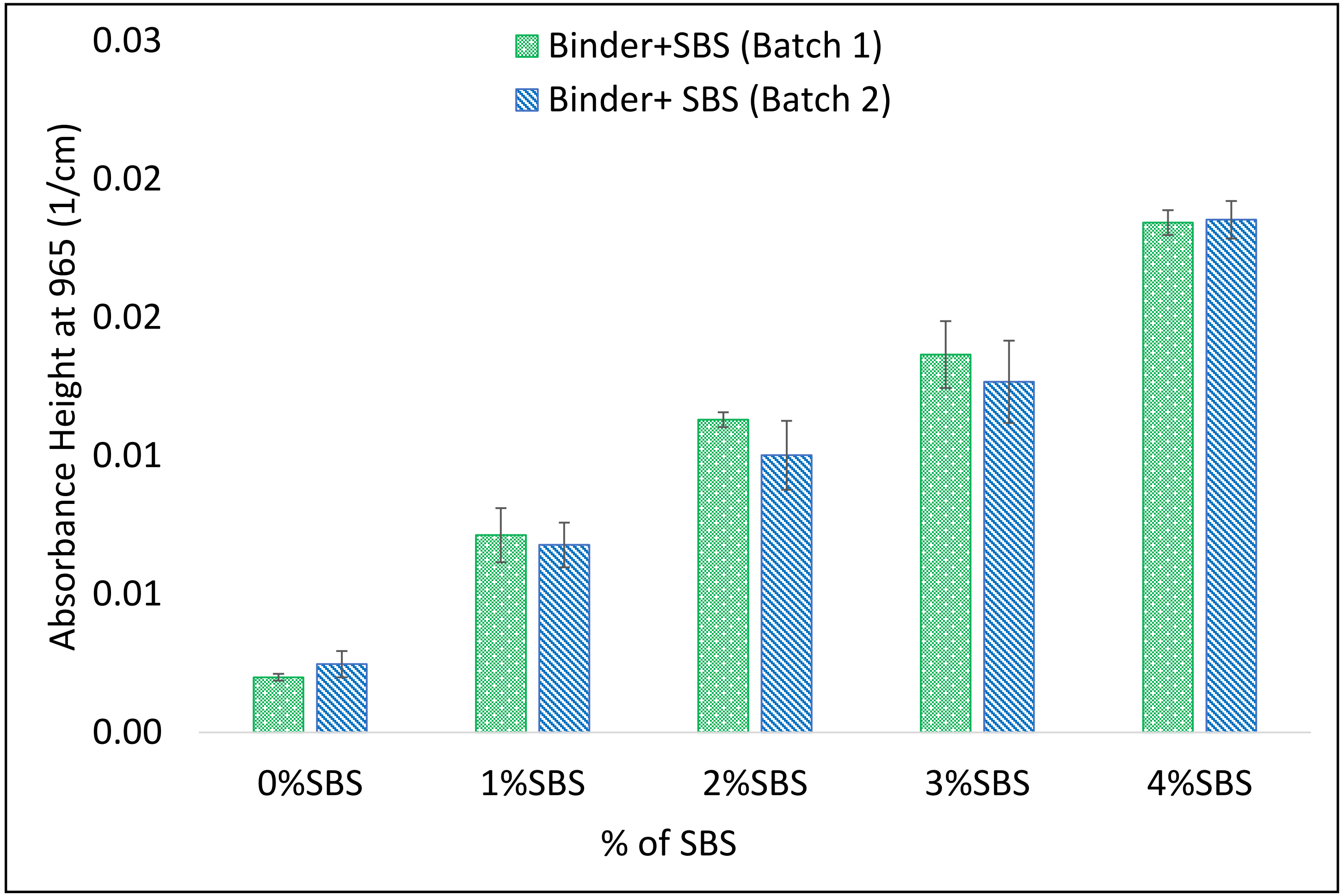
Effect of PG Binder from Different Sources

- PG64-22 binder was collected from two different sources (**LA** and **NC**) and mixed with same SBS polymer
- **Binder sources** did not **affect** the peak height and peak shape at 965cm^{-1}



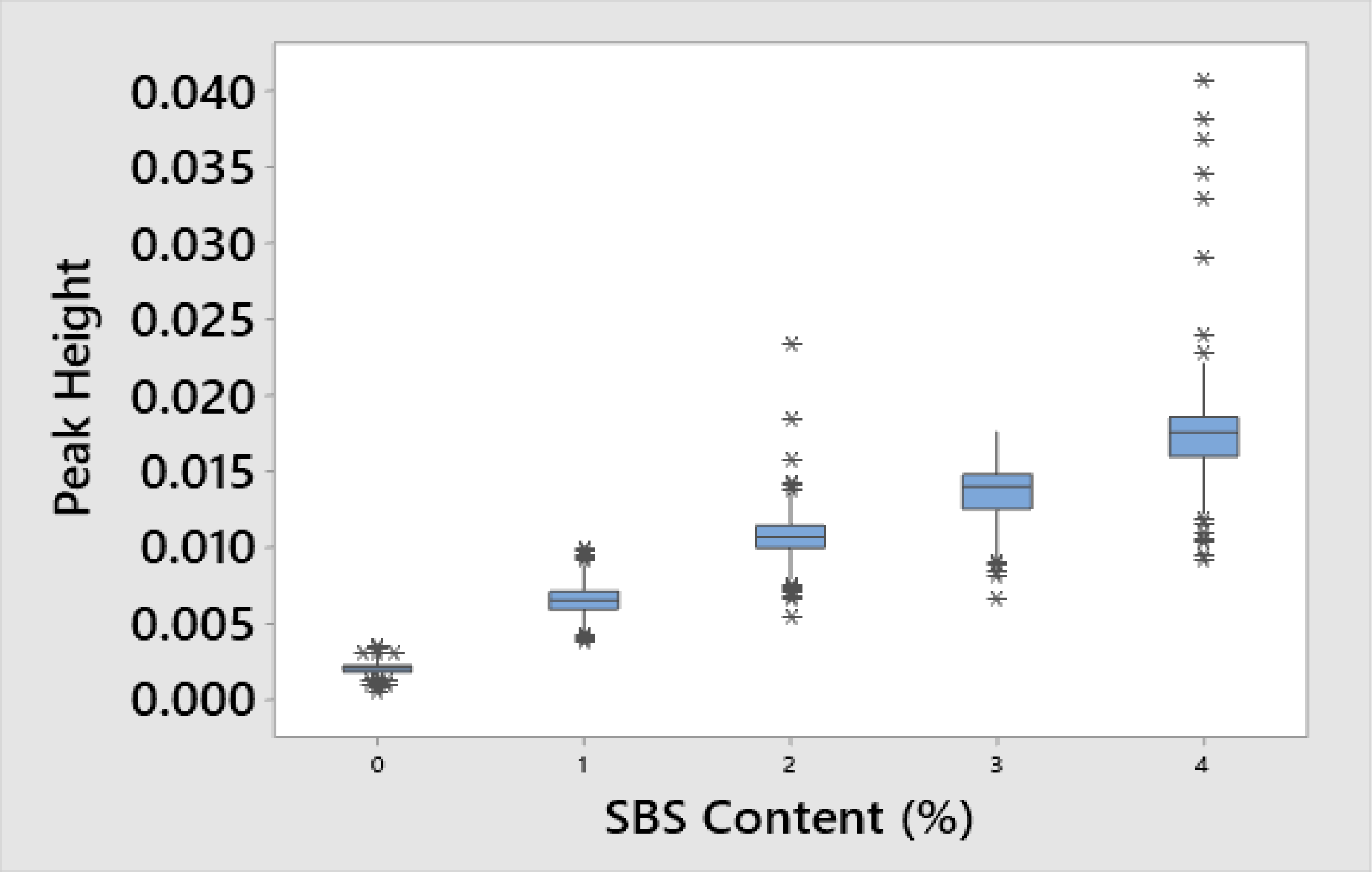
Effect of SBS Mixing in Two Different Batches

- ❑**Radial SBS** was mixed with PG 64-22 binder in two different time exactly following the same mixing procedure



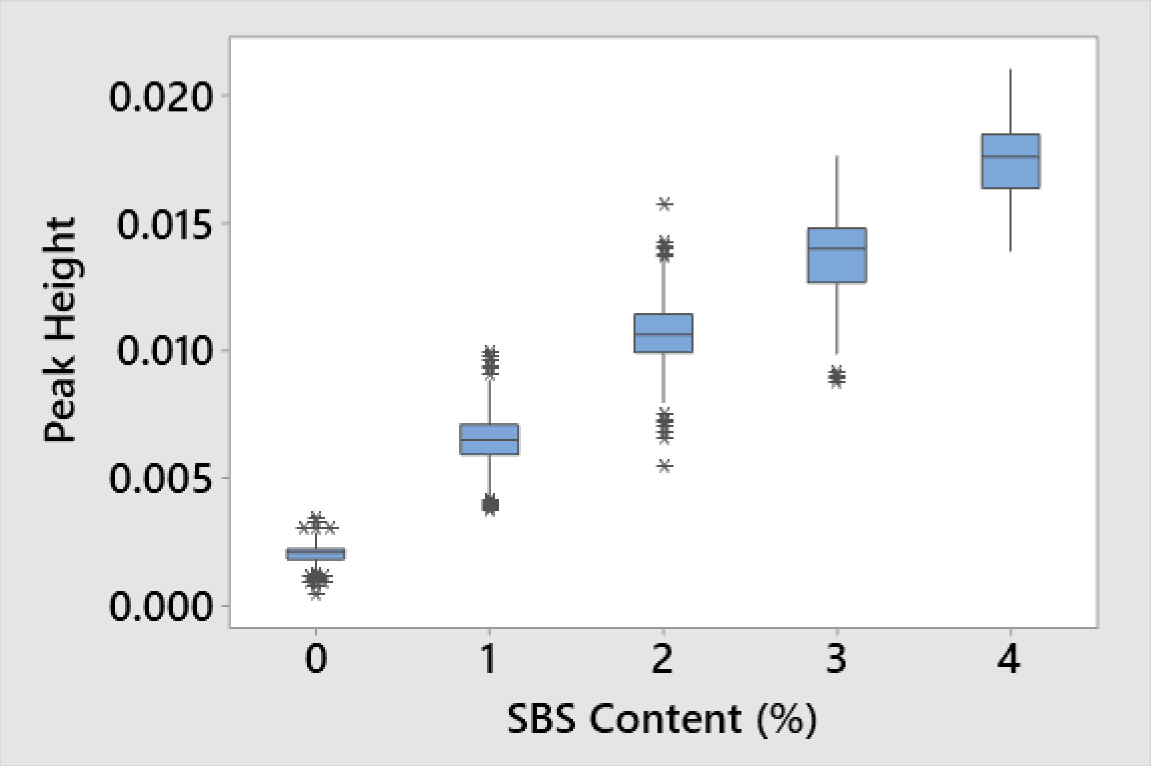
Correlation among SBS Concentration: W Outliers

- ❑A total of **1175** data points obtained from **24 different cases** for peak height measurements
- ❑Correlation with outlier: **0.93**



Correlation among SBS Concentration: W/O Outliers

- **2% and 4%** SBS data points contained some **outlier** values in the analysis methods
- To remove the outliers, **Cook's distance** algorithm was applied
- Among **1175 data** points, **39 data** points- **Outlier**
- After deleting these points, correlation of the regression model among variables increased significantly
- Correlation W/O outlier: **0.97**



Cross-validation of the Predictive Model

Parameters of regression model	With outlier		Without outlier	
	Intercept	Concentration	Intercept	Concentration
Coefficients	**0.002419**	**0.003814**	**0.002413**	**0.003809**
St. error	1.084×10^{-4}	4.427×10^{-5}	7.13×10^{-5}	2.99×10^{-5}
t- value	22.30	86.16	33.84	127.51
Pr (>|t|)	$<2 \times 10^{-16}$	$<2 \times 10^{-16}$	$<2 \times 10^{-16}$	$<2 \times 10^{-16}$
RSE	0.002146		0.001403	
Multiple R^2	0.8636		0.9348	
Adjusted R^2	0.8634		0.9347	
F-statistics	7424		1.63×10^{4}	
P-value (<0.05)	$<2.2 \times 10^{-16}$		$<2.2 \times 10^{-16}$	

Variability Evaluation

- With same operator:
  - ✓Same sample was being used for taking **FT-IRS** data for **several times**
- Different operator:
  - ✓Different operators (**A, B, C, D**) collected FT-IRS data for the same sample

Prediction of SBS (%) in Laboratory Prepared Samples

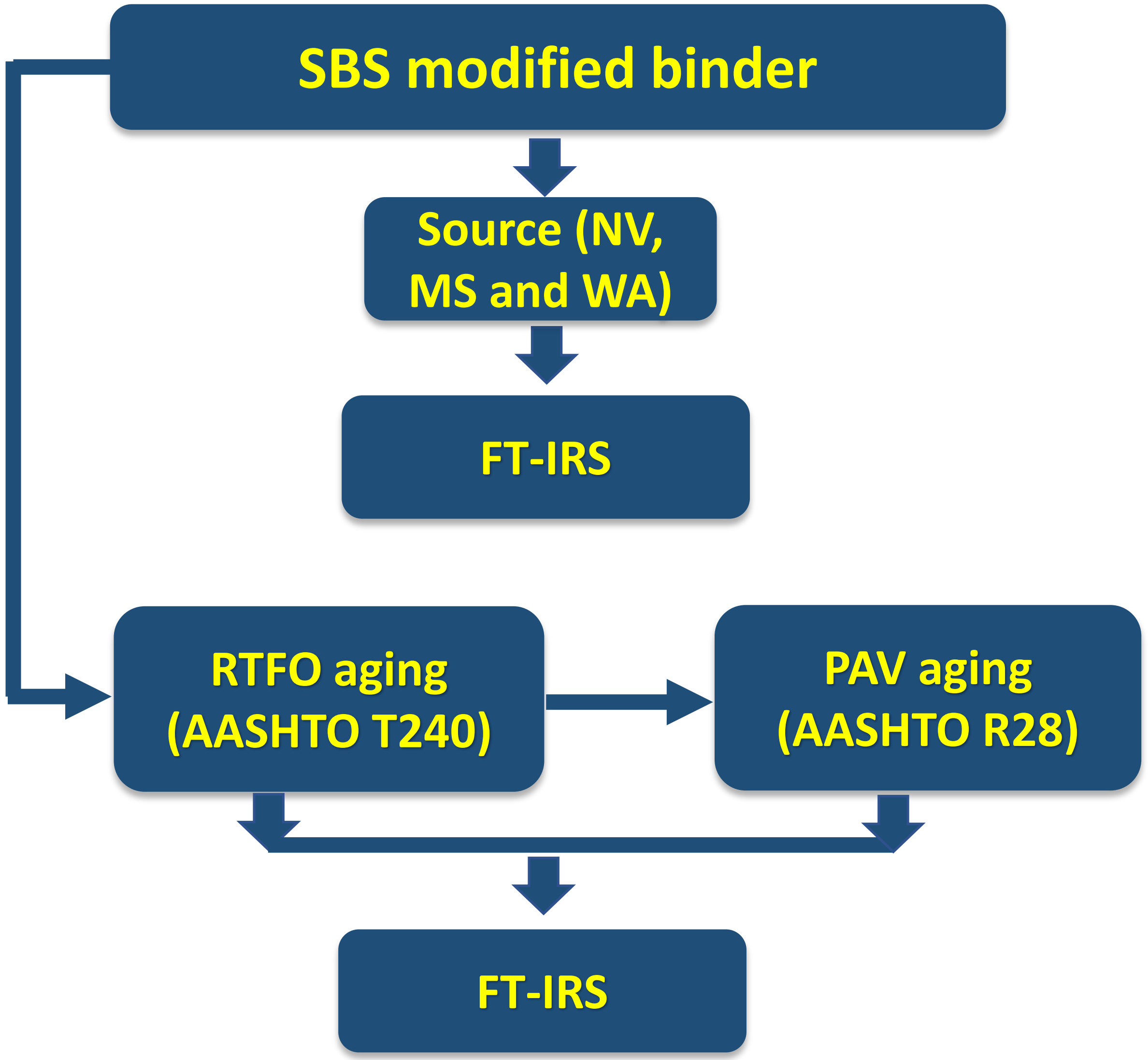
Sample ID	1	2	3	4	5	6	7
Sample used in regression analysis	Yes	Yes	No	No	No	No	No
Operator	**A**	**B**	**A**	**A**	**B**	**C**	**D**
Avg. height	0.018	0.014	0.017	0.017	0.015	0.011	0.011
Predicted SBS (%)	**4.2**	**3.0**	**3.9**	**4.0**	**3.4**	**2.2**	**2.2**
SD	0.197	0.115	0.301	0.077	0.295	0.001	0.001
CV	4.745	3.856	7.814	1.940	8.802	6.918	6.787
CI	0.141	0.082	0.215	0.055	0.211	0.001	0.001
95% CI Upper	4.3	3.1	4.1	4.0	3.6	2.3	2.0
95% CI Lower	4.0	2.9	3.6	3.9	3.1	2.3	2.0
Actual SBS (%)	**4**	**3**	**4**	**4**	**3.5**	**2**	**2**
% error $\left\|\frac{Actual-Predicted}{Actual}\right\| * 100$	**5**	**0**	**2.5**	**0**	**2.9**	**10**	**10**

Field implementation

Field demo	Source	Operator	Avg. height from FT-IRS	Predicted SBS (%)	SD	CV	CI	95%CI Upper	95%CI Lower	Actual SBS (%)
1	**D&J plant**	**A**	0.007	1.1	0.1	5.1	0.042	1.2	1.1	unknown
2	D&J plant	A	0.009	1.8	0.2	11.2	0.142	1.9	1.6	unknown
3	D&J plant	**B**	0.011	**2.2**	0.2	9.0	0.140	2.3	2.0	**1%-3%**
4	D&J plant	A	0.010	**2.1**	0.1	7.1	0.107	2.2	2.0	**1.5%-3%**
5	**AR**	C	0.010	**1.9**	0.2	7.8	0.140	2.0	1.7	**2%**
6	AR	A	0.011	**2.1**	0.1	2.8	0.042	2.2	2.1	**2%**
7	**NV**	**C**	0.015	**3.2**	0.15	9.95	0.13	3.2	3.2	**3% or less**
8	NV	C	0.018	**4.2**	0.03	1.37	0.02	4.2	4.2	**More than 3%**

Test Matrix for the Evaluation of SBS Degradation

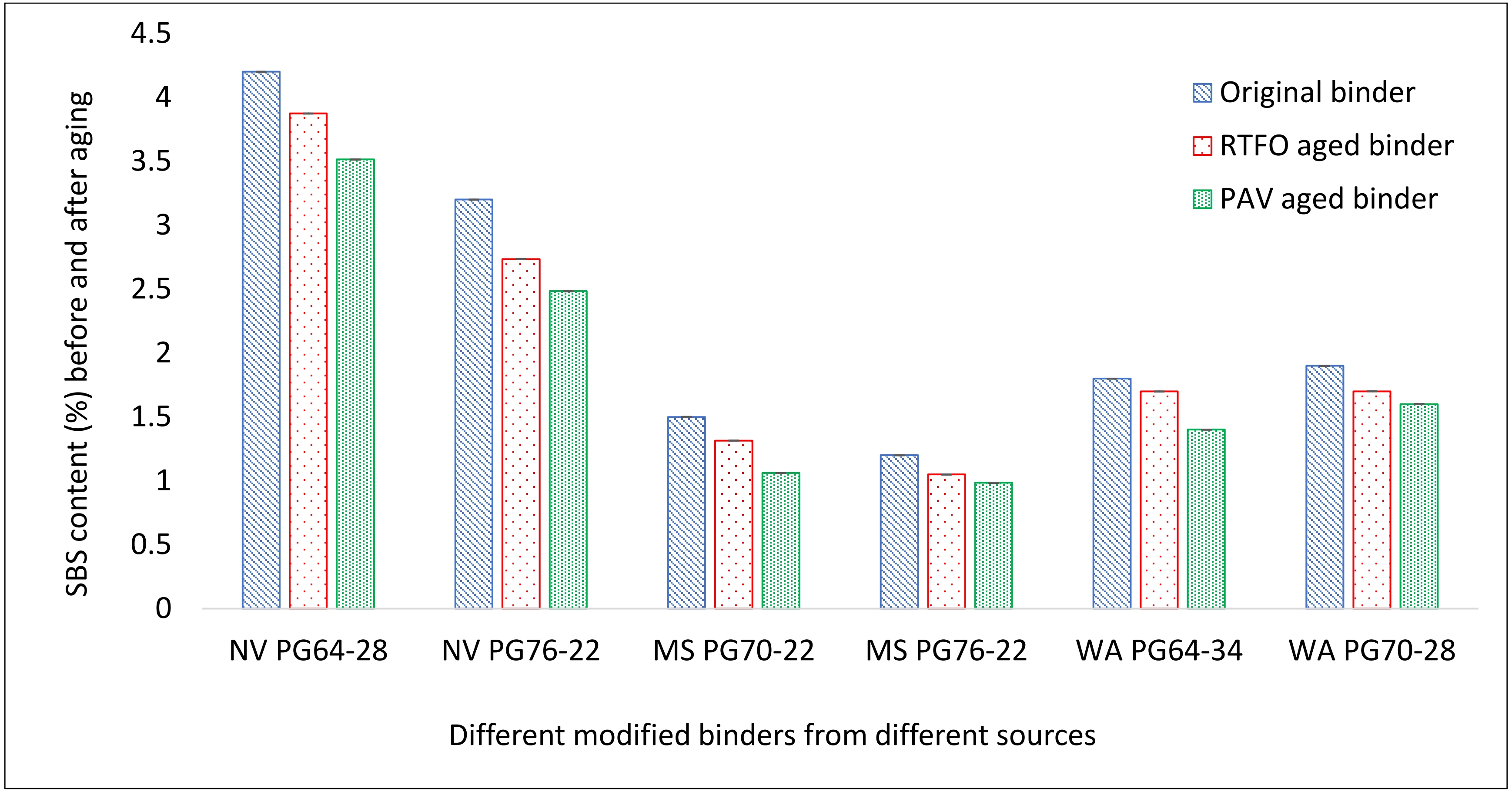
- ❑ **Six** SBS modified asphalt binders namely **PG 64-28, PG 64-34, PG 70-22, PG 70-28 and PG 76-22 (2)** were used for the evaluation of SBS degradation due to aging



Prediction of SBS content (%) before and after aging

- **Equation** used for the evaluation of degradation of SBS content (%) after RTFO and PAV aging

Peak height at 965 cm^{-1} = 0.003809*SBS concentration+0.002413



Reduction in SBS content (%) after RTFO and PAV aging

Binder	Source	Binder condition	SBS content (%)	% reduction after aging	SD	CV	CI	95% upper CI	95% lower CI
PG 64-28	**NV**	Original	4.2		0.0003	**1.37**	0.02	4.2	4.2
		RTFO aged	3.9	**7.46**	0.0008	**4.48**	0.06	3.9	3.9
		PAV aged	3.5	**16.06**	0.0005	**3.15**	0.04	3.5	3.5
PG 76-22	**NV**	Original	3.2		0.0015	**9.95**	0.13	3.2	3.2
		RTFO aged	2.7	**14.46**	0.0009	**7.01**	0.11	2.7	2.7
		PAV aged	2.5	**22.33**	0.0007	**6.26**	0.09	2.5	2.5
PG 70-22	**MS**	Original	1.5		0.000	**5.99**	0.04	1.5	1.5
		RTFO aged	1.3	**13.19**	0.000	**4.32**	0.02	1.3	1.3
		PAV aged	1.1	**29.91**	0.000	**6.35**	0.03	1.1	1.1
PG 76-22	**MS**	Original	1.2		0.0003	**3.83**	0.02	1.2	1.2
		RTFO aged	1.1	**8.88**	0.0003	**5.36**	0.03	1.1	1.0
		PAV aged	1.0	**14.59**	0.0004	**7.26**	0.04	1.0	1.0
PG 64-34	**WA**	Original	1.8		0.000	**4.253**	0.05	1.8	1.8
		RTFO aged	1.7	**5.56**	0.000	**2.019**	0.02	1.7	1.7
		PAV aged	1.5	**16.67**	0.000	**2.735**	0.08	1.5	1.5
PG 70-28	**WA**	Original	1.9		0.000	**3.313**	0.03	1.9	1.9
		RTFO aged	1.7	**10.53**	0.001	**3.867**	0.11	1.7	1.7
		PAV aged	1.6	**15.79**	0.000	**5.703**	0.06	1.6	1.6

NV: Nevada, MS: Mississippi, WA: Washington

Conclusion : Polymer Content Determination

- ❑ **SBS quantification at 965 cm^{-1}** was unaffected by the variation in base binder **performance grades and sources**, SBS polymer structures (**linear, radial, and diblock**) and presence of cross-linking agent (**sulfur**)
- ❑ A universal equation for SBS content (%) prediction was developed from peak height measurement (**R^2 = 0.97**)
- ❑ Percent error for predicting SBS concentration (%) in laboratory prepared samples and in field measurement was ranged from **0%-5%** and **5%** respectively
- ❑ The total process for sample collection and data processing for SBS content (%) prediction in each field demonstration required **30 minutes (10 samples)** by the handheld FT-IRS

Overall Layout of the Presentation

- ❑ Part I : Polymer Content Determination in Binder
- ❑ **Part II : Quality Control of RAP Mixture**
- ❑ Part III : Rejuvenator Identification and Quantification

Use of RAP in HMA

Use of RAP

- RAP : Most recycled materials - almost 99%
- Economic savings and Environmental benefit
- Use of >30% is allowed
- Average RAP use 10% to 20%

Challenges

- Highly Aged Asphalt
- Different sources: Higher variability
- Lack of proper characterization of RAP
- Unknown degree of blending
- Increased quality control Effort

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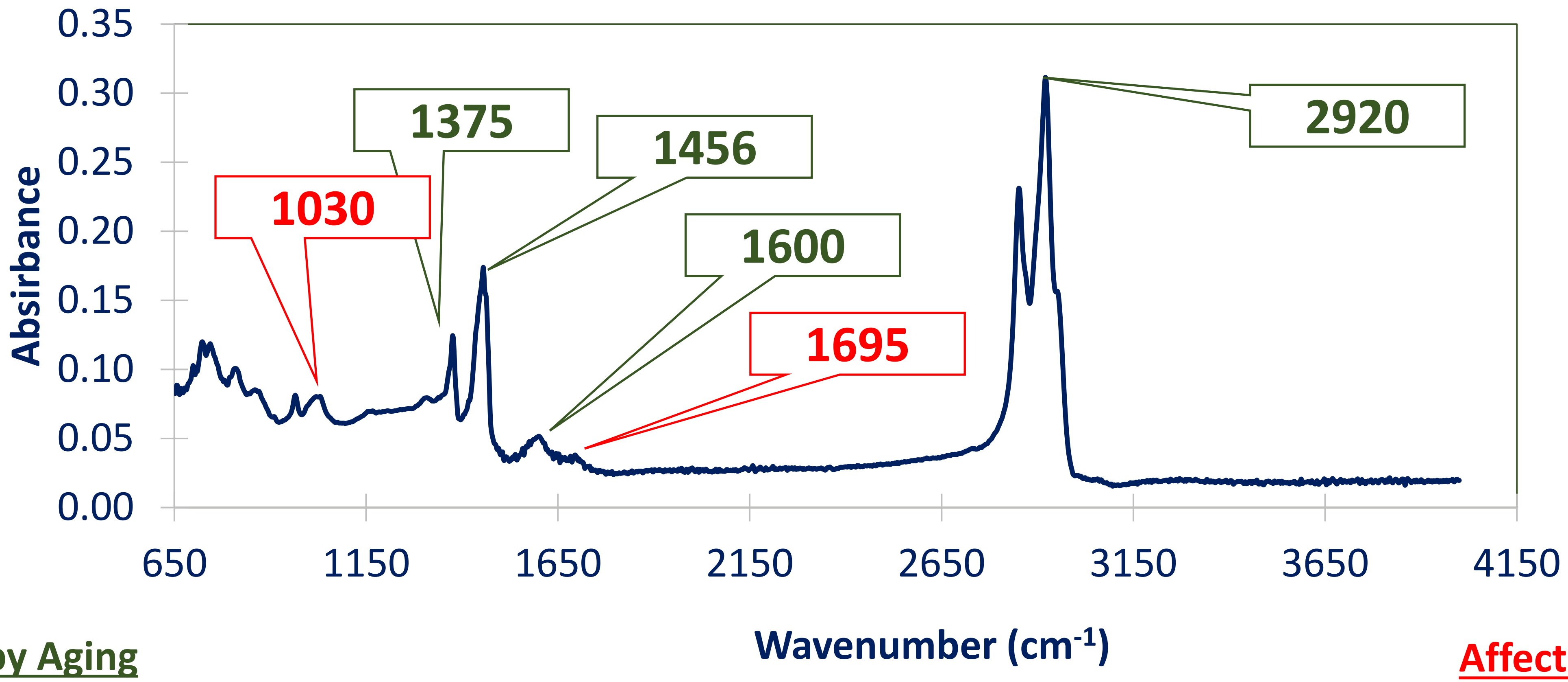
- Different sources: Higher variability
- Lack of proper characterization of RAP
- Unknown degree of blending
- Increased quality control Effort

Potential of FT-IR

Monitoring mix aging → **Assurance of Quality**

Absorption Spectra of Aged Asphalt



Unaffected by Aging

Vibration Type	Functional Group	Wavenumbers (cm^{-1})
Bending vibration	**C=C**	**1600**
Asymmetric bending	**CH_2 and CH_3**	**1455**
Symmetric bending	**CH_3**	**1375**
asymmetric stretching	**CH_2**	**2920**

Affected by Aging

Vibration Type	Functional Group	Wavenumbers (cm^{-1})
Stretching	**S=O**	**1030**
Stretching	**C=O**	**1695**

Research Need

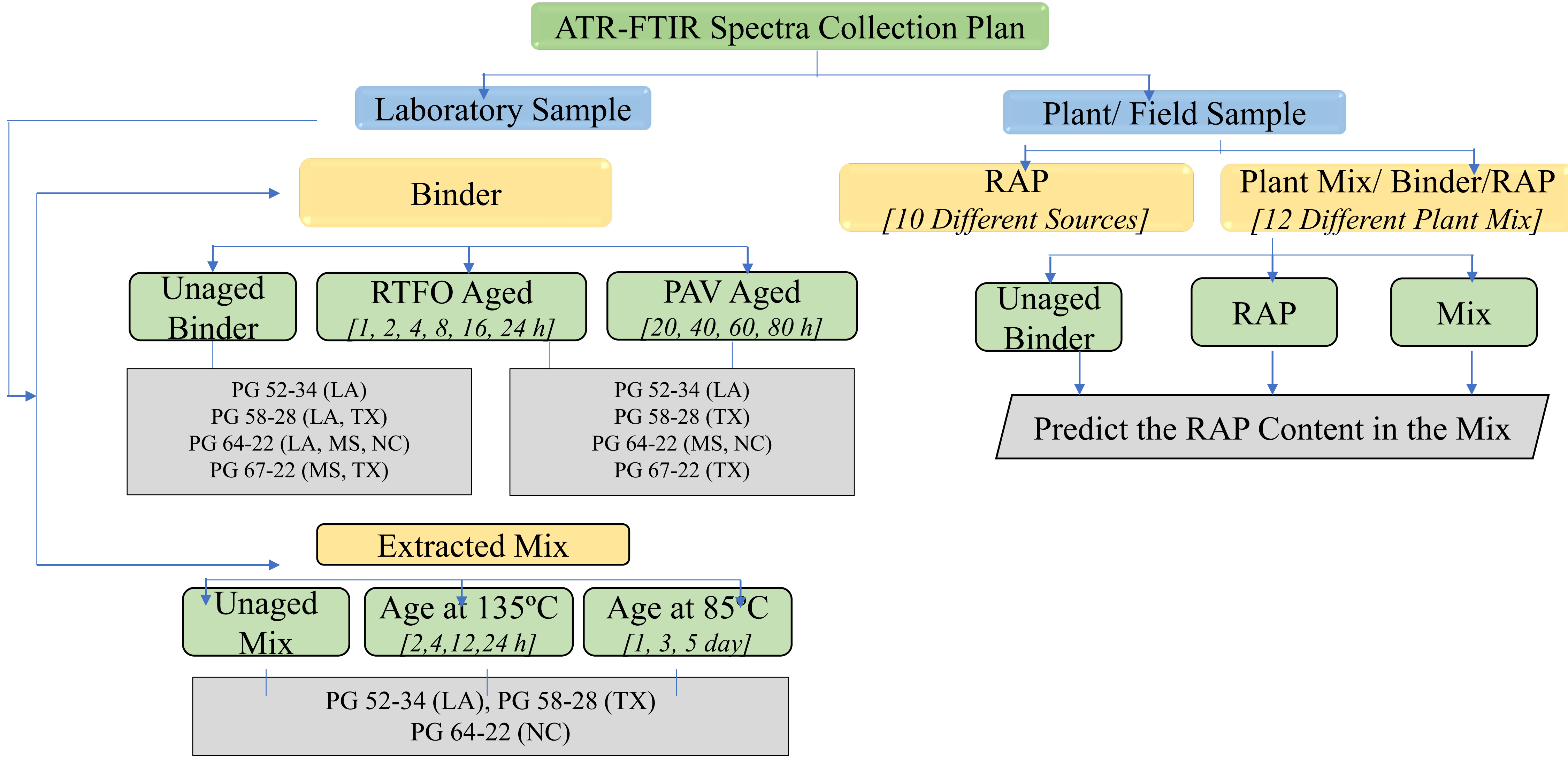
- FT-IR has been used as supporting tools
- Binder aging was investigated
- Very few studies were performed on mix aging
- Carbonyl and Sulfoxide concentrations increase with aging:
    - which one is suitable for both binder and mix?
- Oxidation state and aging of RAP were not addressed

Research Goal

Objectives

- Quantifying the laboratory aging of the binder and mix using ATR-FTIR
- Selection of a suitable index to quantify the binder and mix aging
- Development of a quick extraction process that can be easily implemented in the plant/ field
- **Determine the RAP content in the plant mix**

Experimental Plan



Laboratory Binder Aging

Rolling Thin Film Oven (RTFO)

Temperature: 163 ^{o}C
Duration: 2, 4, 12, 24 hours

Pressure Aging Vessel (PAV)

Temperature: 100 ^{o}C Pressure: 2.1 MPa
Duration: 20, 40, 60, 80 hours

Binder Used for Aging: PG 52-34 (LA); PG 58-28 (TX), PG 64-22 (MS, NC); PG 67-22 (TX)

Laboratory Mix Aging

Forced Draft Oven

Shorter Duration Aging

Temperature: 135 ^{o}C
Duration: 2, 4, 12, 24 hours

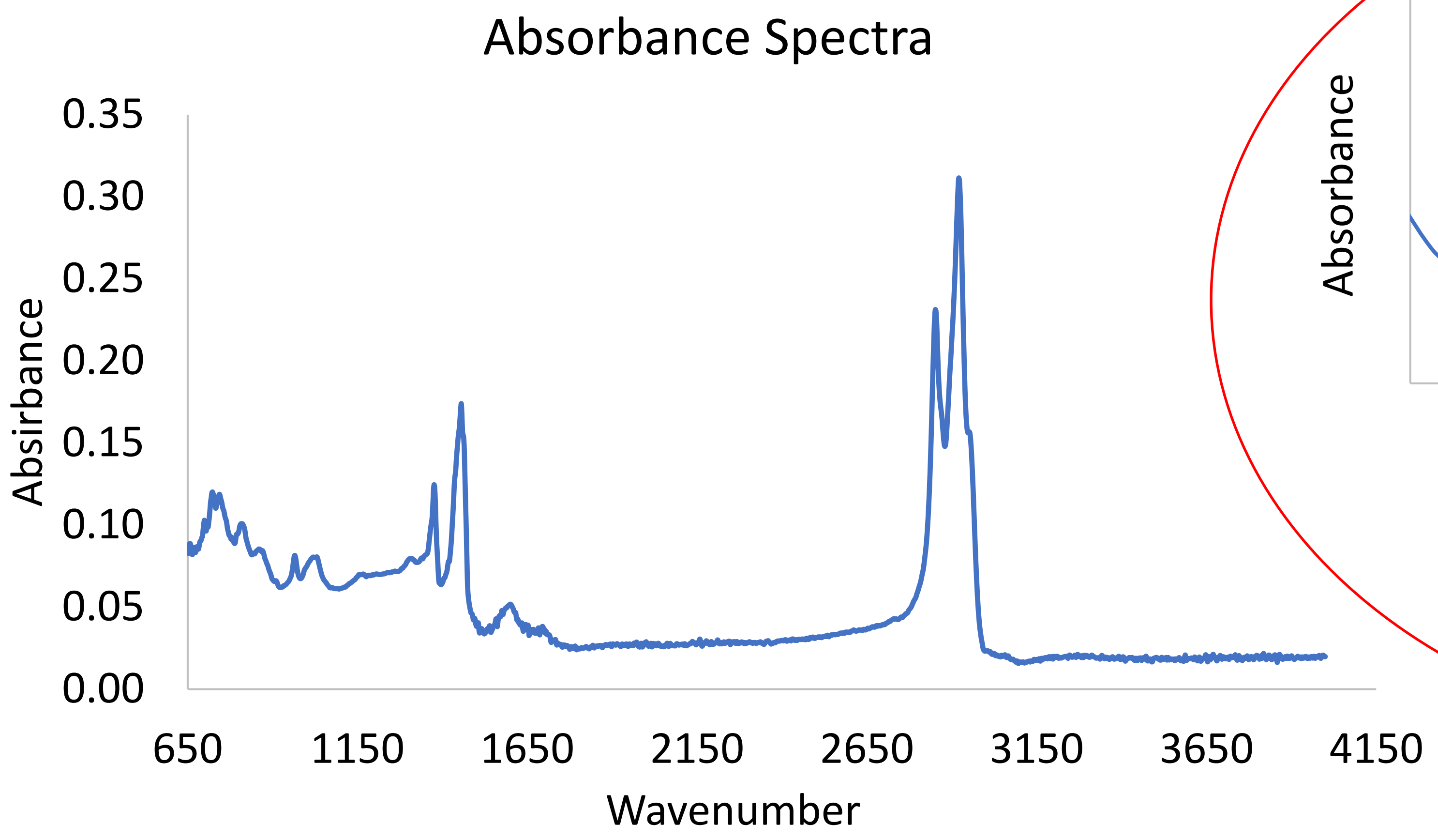
Longer Duration Aging

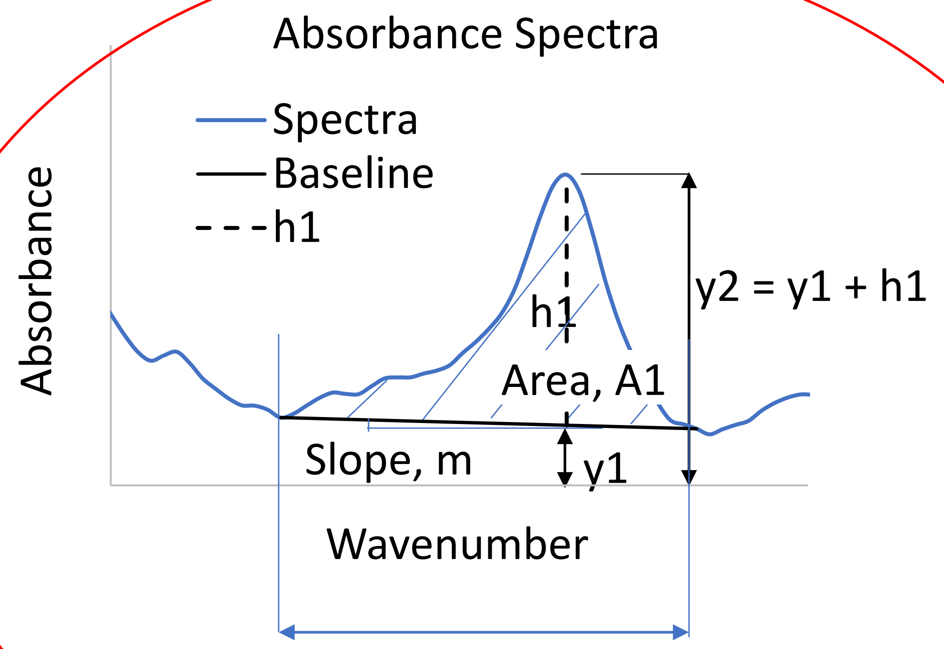
Temperature: 85 ^{o}C
Duration: 1, 3, 5 days

Aged mix required binder extraction to use in ATR-FTIR

Quantitative Analysis of FT-IR Spectra

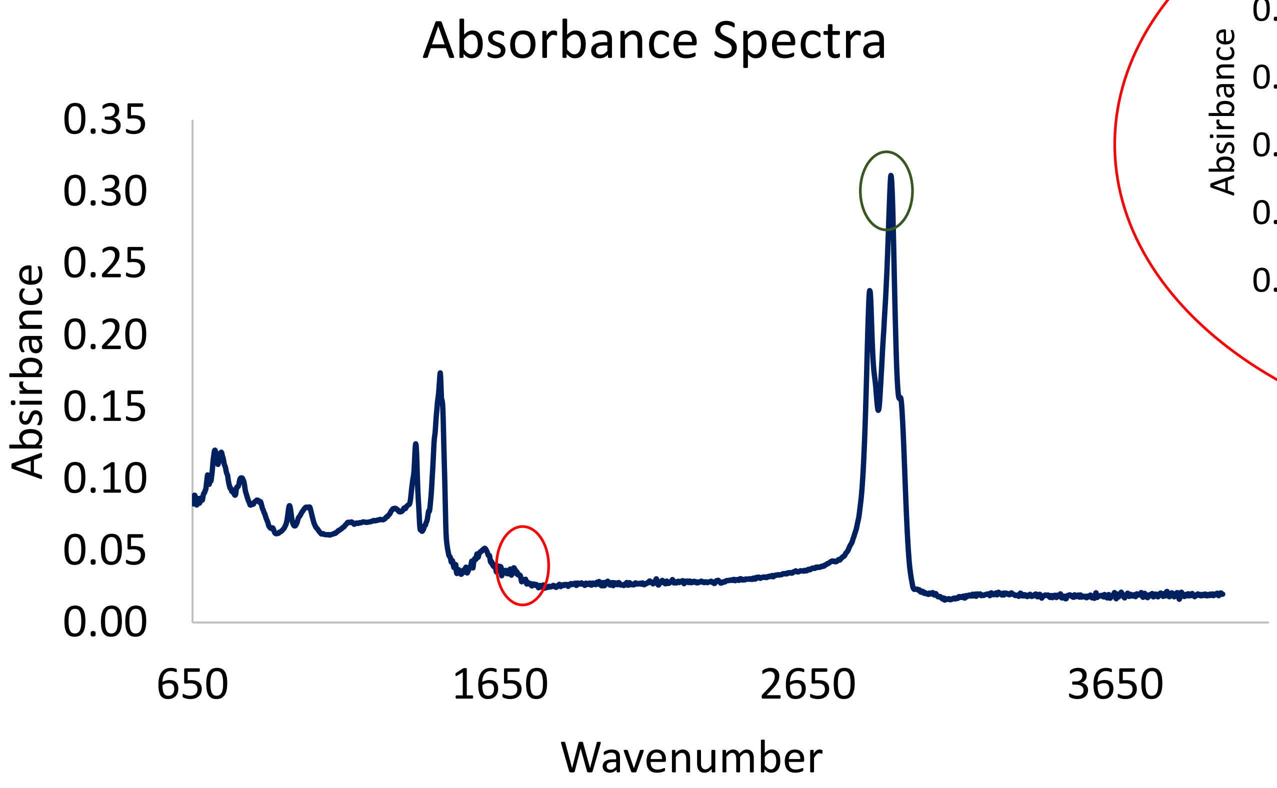
Spectra for the whole range of wavenumber

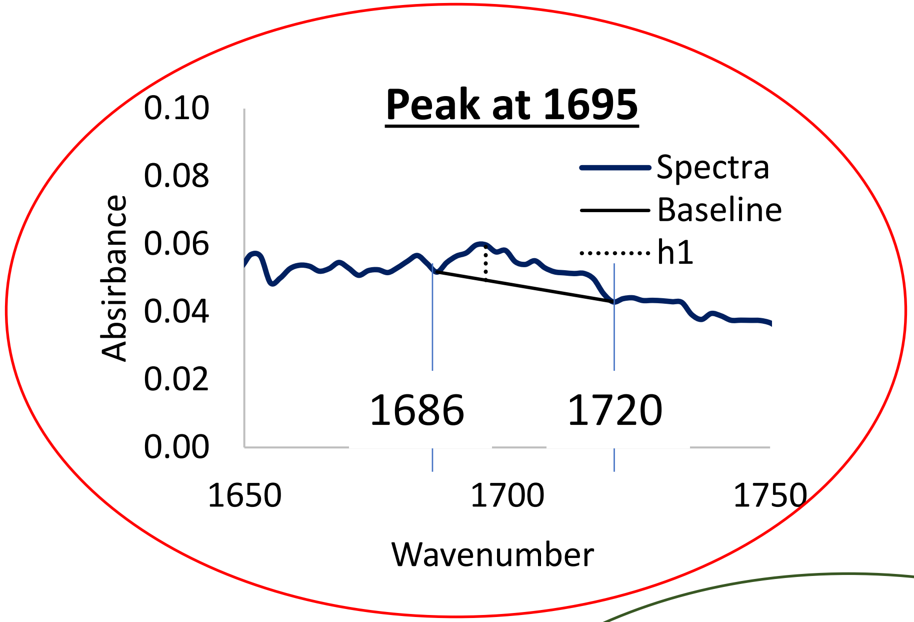


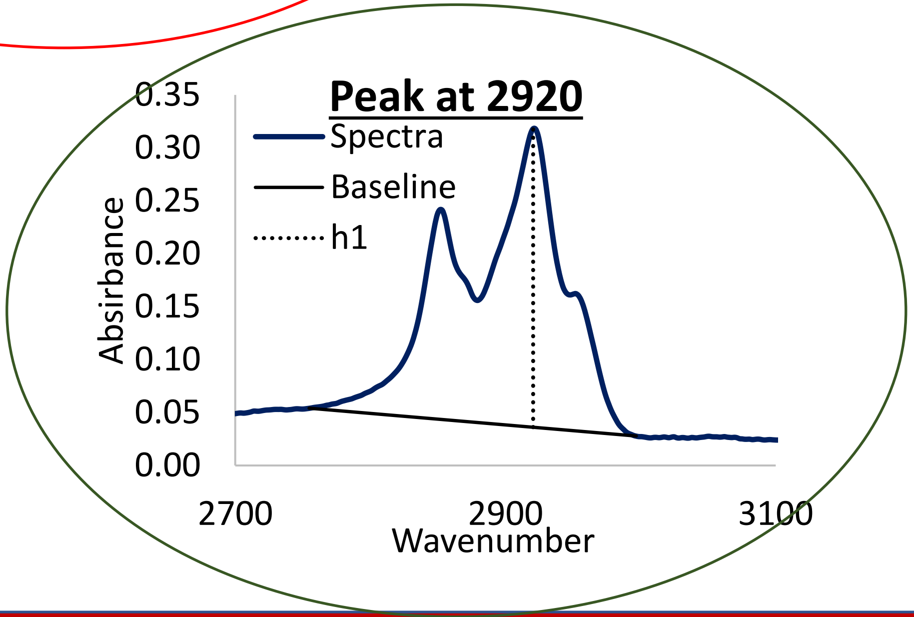


At certain wavenumber, location of Valley is unaffected by absorbance intensity

Data Analysis for Asphalt Aging







Indices Used to Quantify Aging

Vibration Type	Functional Group	Wavenumbers (cm^{-1})
Stretching	**S=O**	**1030**
Stretching	**C=O**	**1695**

Vibration Type	Functional Group	Wavenumbers (cm^{-1})
Bending vibration	**C=C**	**1600**
Asymmetric bending	**CH_2 and CH_3**	**1455**
Symmetric bending	**CH_3**	**1375**
asymmetric stretching	**CH_2**	**2920**

Based on Peak Height

$$Index = \frac{Peak\ Height_{at\ Wavenumber\ affected\ by\ Aging}}{Peak\ Height_{at\ Wavenumber\ unaffected\ by\ Aging}}$$

Based on Area Under Spectra

$$Index = \frac{Area_{under\ Wavenumber\ affected\ by\ Aging}}{Area_{under\ Wavenumber\ unaffected\ by\ Aging}}$$

Aging Indices Based on Peak Height

Based on Peak Height

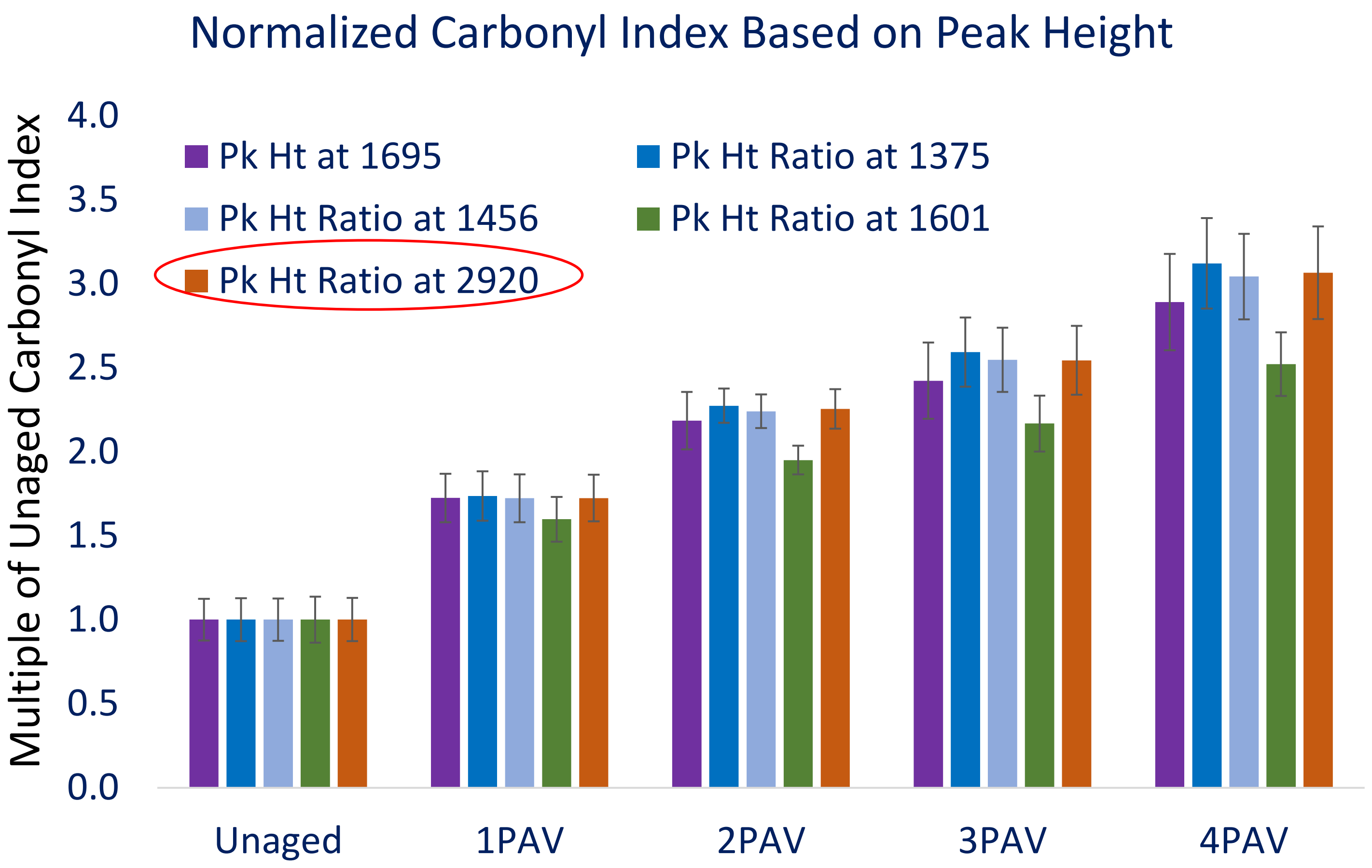
$$Carbonyl\ Index = Peak\ Height_{at\ 1695}$$

$$Carbonyl\ Index = \frac{Peak\ Height_{at\ 1695}}{Peak\ Height_{at\ 1375}}$$

$$Carbonyl\ Index = \frac{Peak\ Height_{at\ 1695}}{Peak\ Height_{at\ 1456}}$$

$$Carbonyl\ Index = \frac{Peak\ Height_{at\ 1695}}{Peak\ Height_{at\ 1601}}$$

$$\boldsymbol{Carbonyl\ Index = \frac{Peak\ Height_{at\ 1695}}{Peak\ Height_{at\ 2920}}}$$



Aging Indices Based on Area Under the Spectra

Based on Peak Area

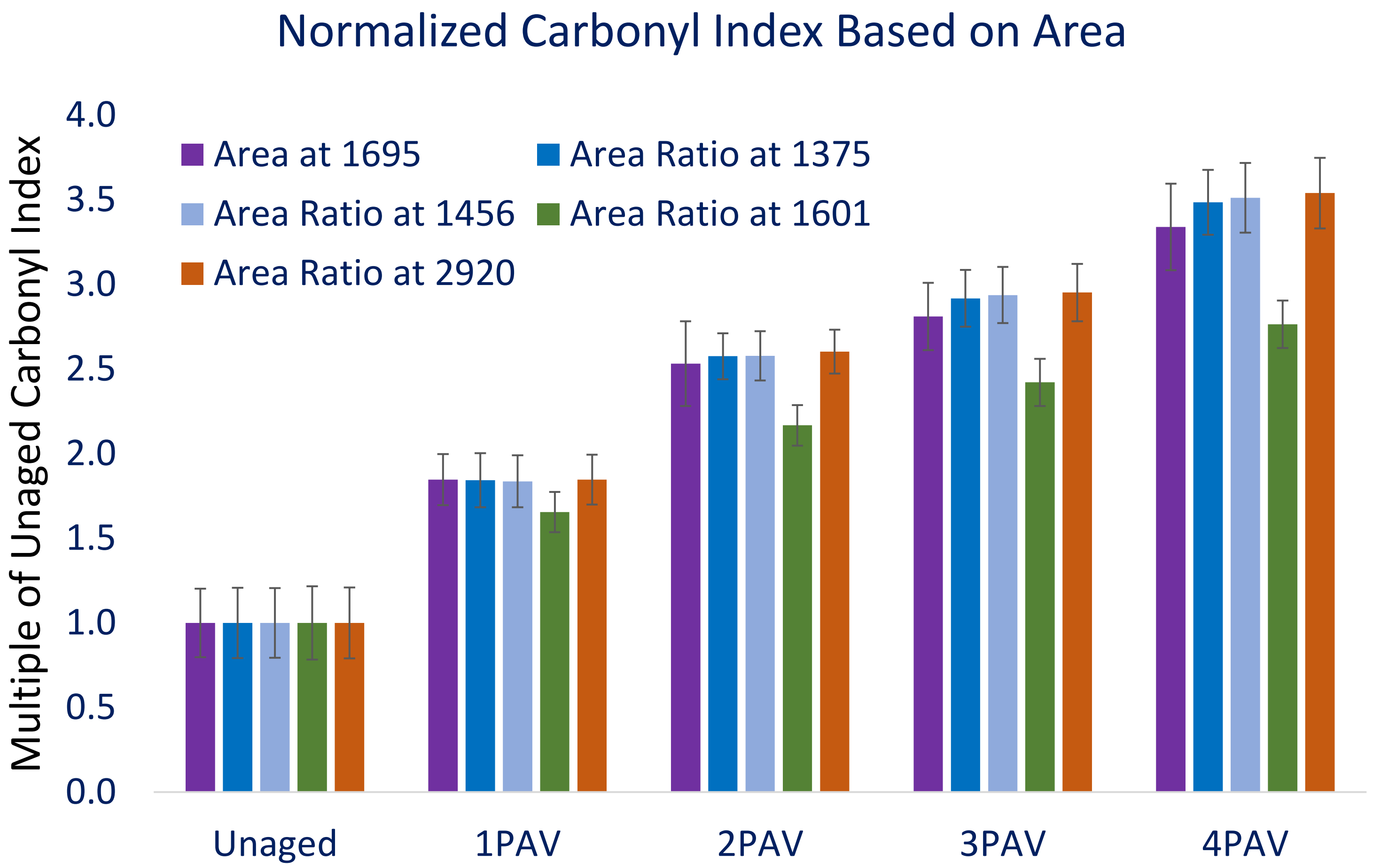
$$Carbonyl\ Index = Area_{at\ 1695}$$

$$Carbonyl\ Index = \frac{Area_{at\ 1695}}{Area_{at\ 1375}}$$

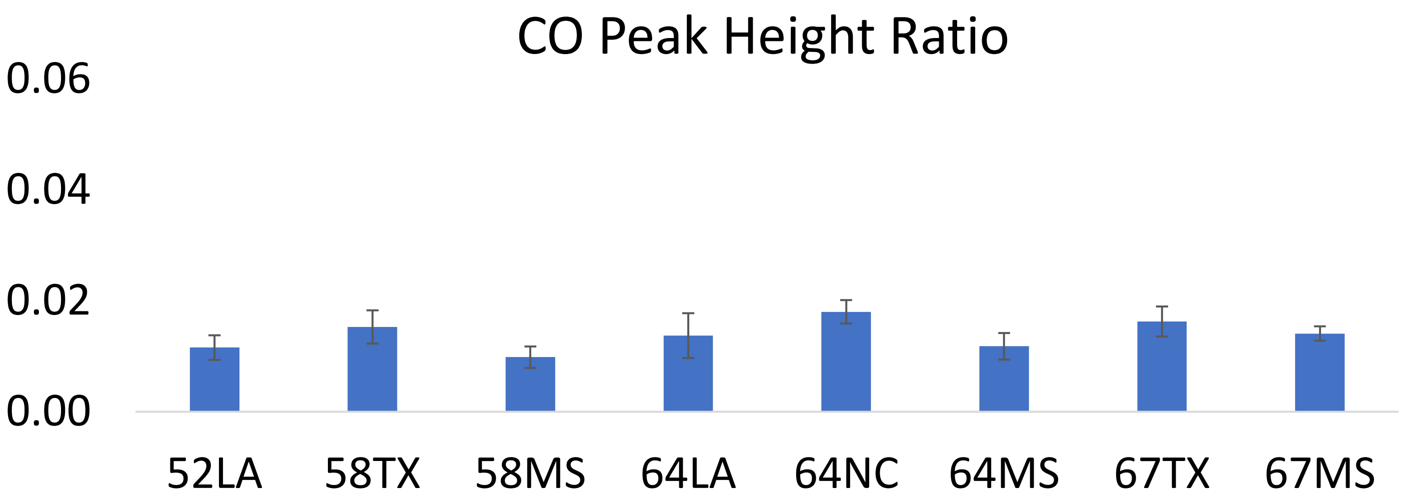
$$Carbonyl\ Index = \frac{Area_{at\ 1695}}{Area_{at\ 1456}}$$

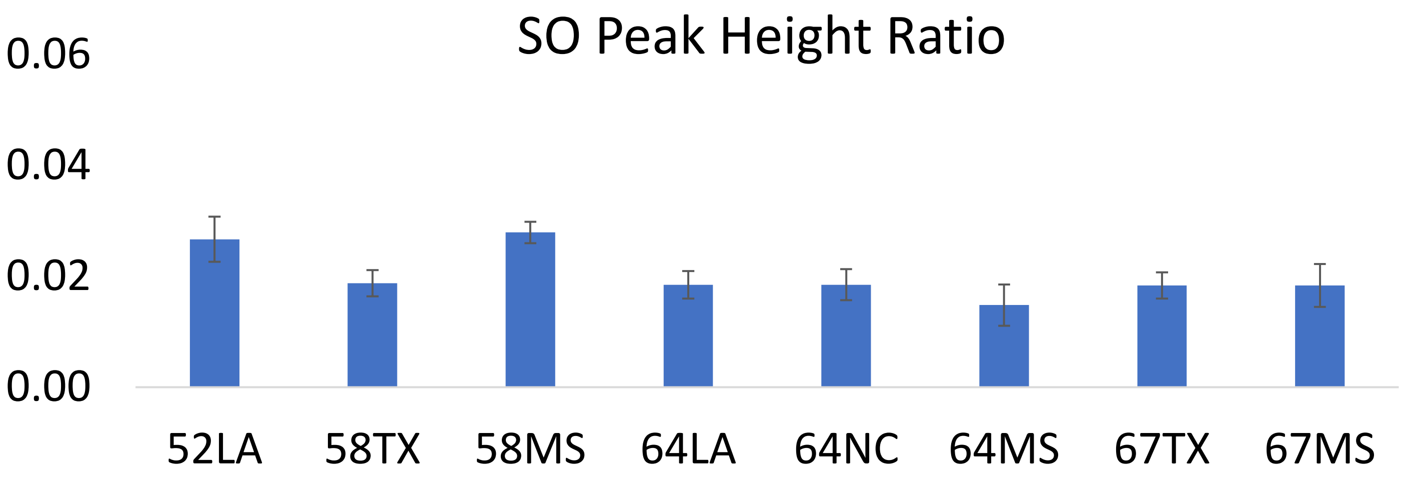
$$Carbonyl\ Index = \frac{Area_{at\ 1695}}{Area_{at\ 1600}}$$

$$Carbonyl\ Index = \frac{Area_{at\ 1695}}{Area_{at\ 2920}}$$



Indices are not Dependent on Binder Grade

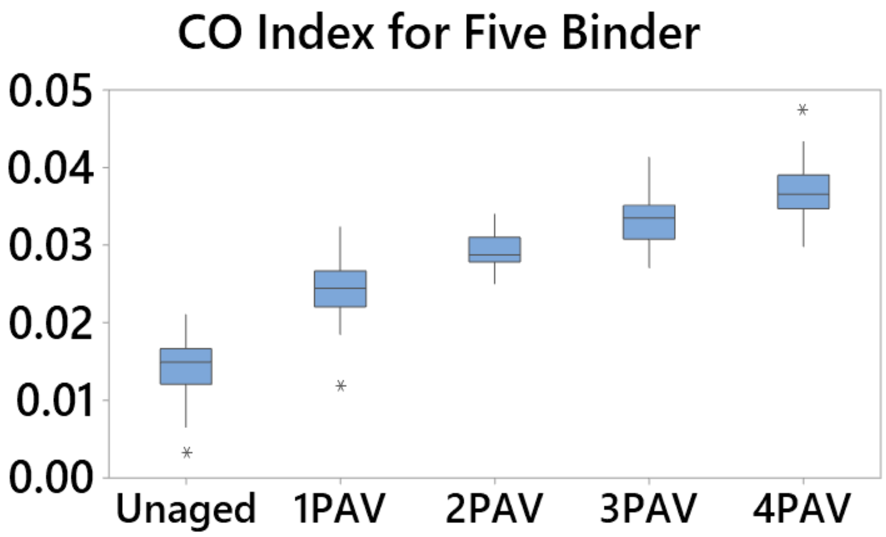




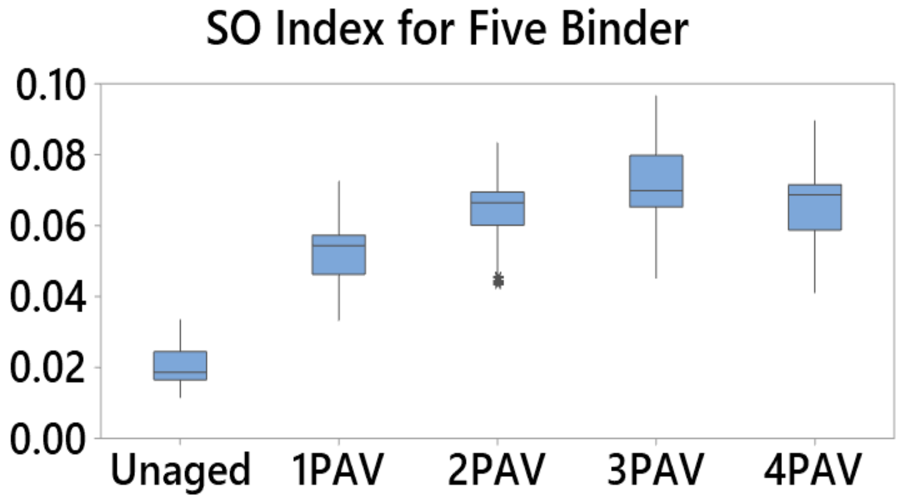
- Four different binder grade, Three sources and Ten sample of each binder are tested
- No visible trend is observed between binder grade and the Carbonyl as well as Sulfoxide Index
- **Carbonyl Index of unaged binders are Not Statistically different**

Carbonyl and Sulfoxide Index

- **Indices are calculated based on Peak Height Ratio at wavenumber 2920 cm^{-1}**
- Both the indices are changing because of aging

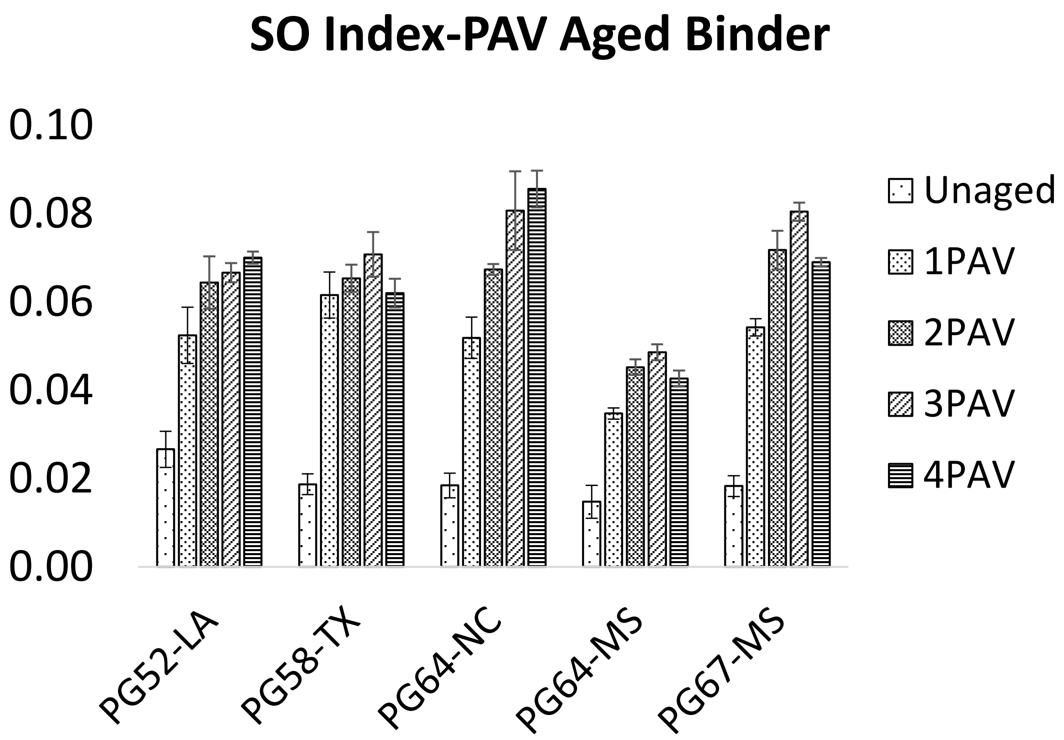


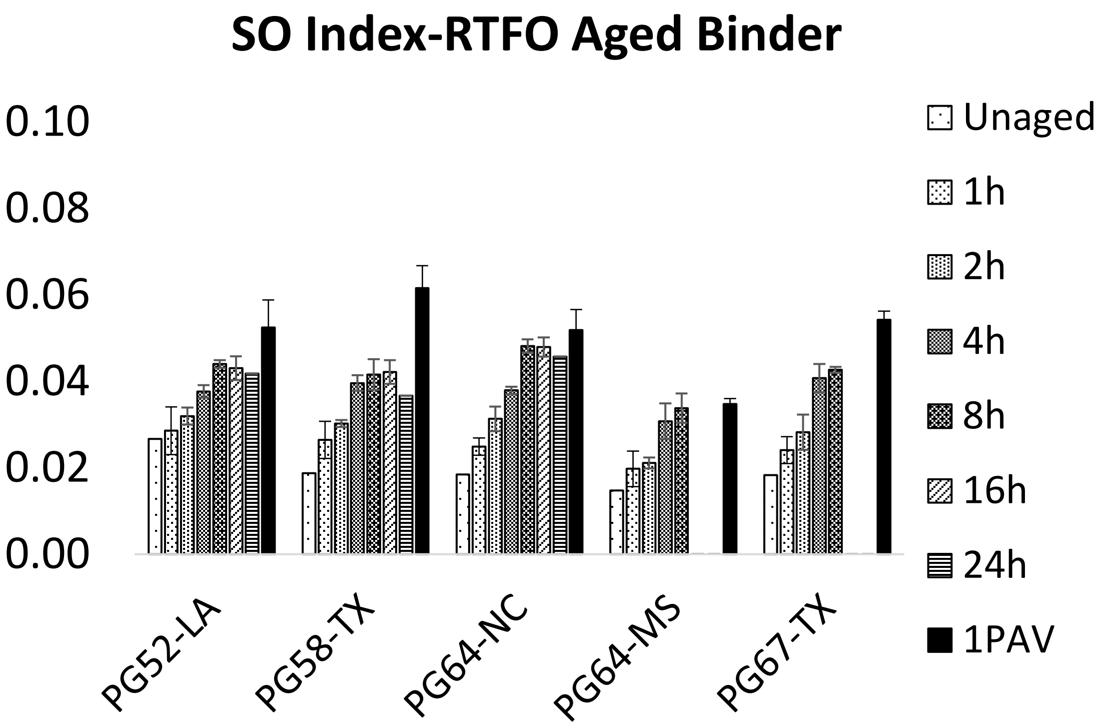
Carbonyl Index Changes consistently with aging duration



Inconsistent change in Sulfoxide Index

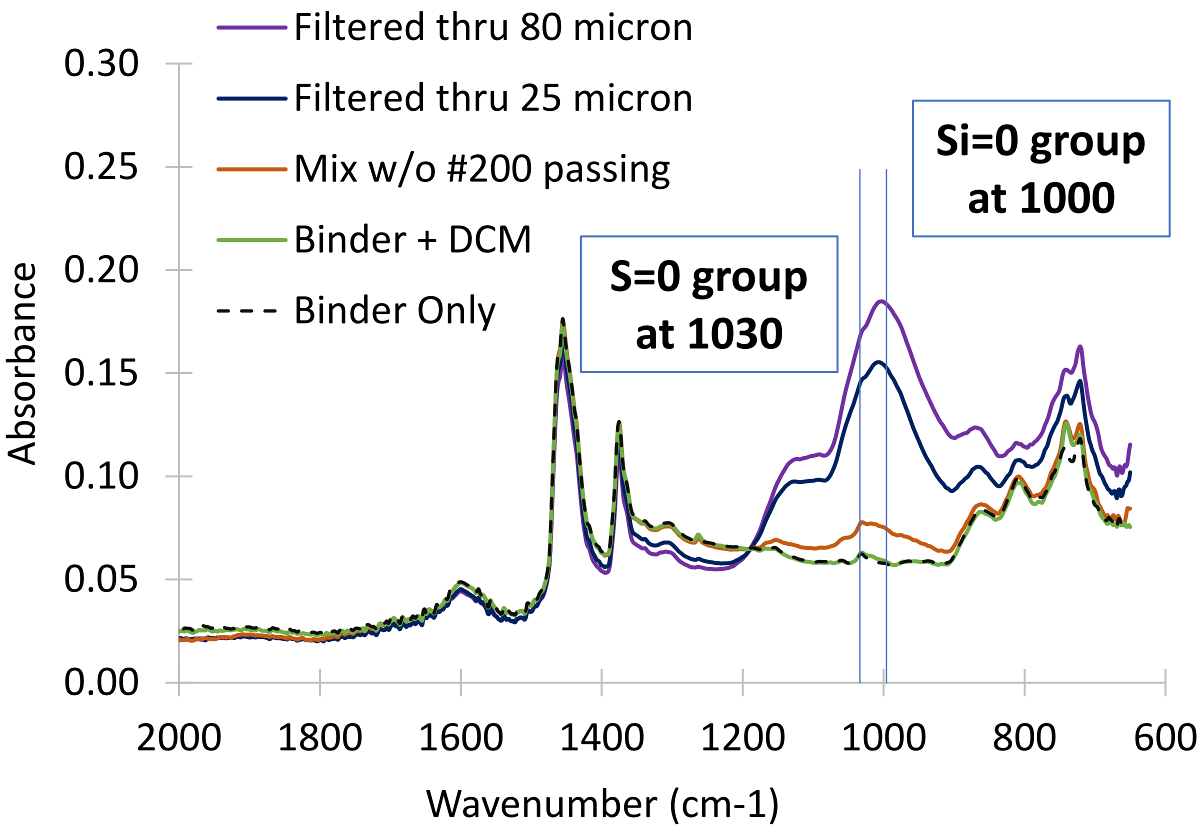
Inconsistent Change in Sulfoxide Index

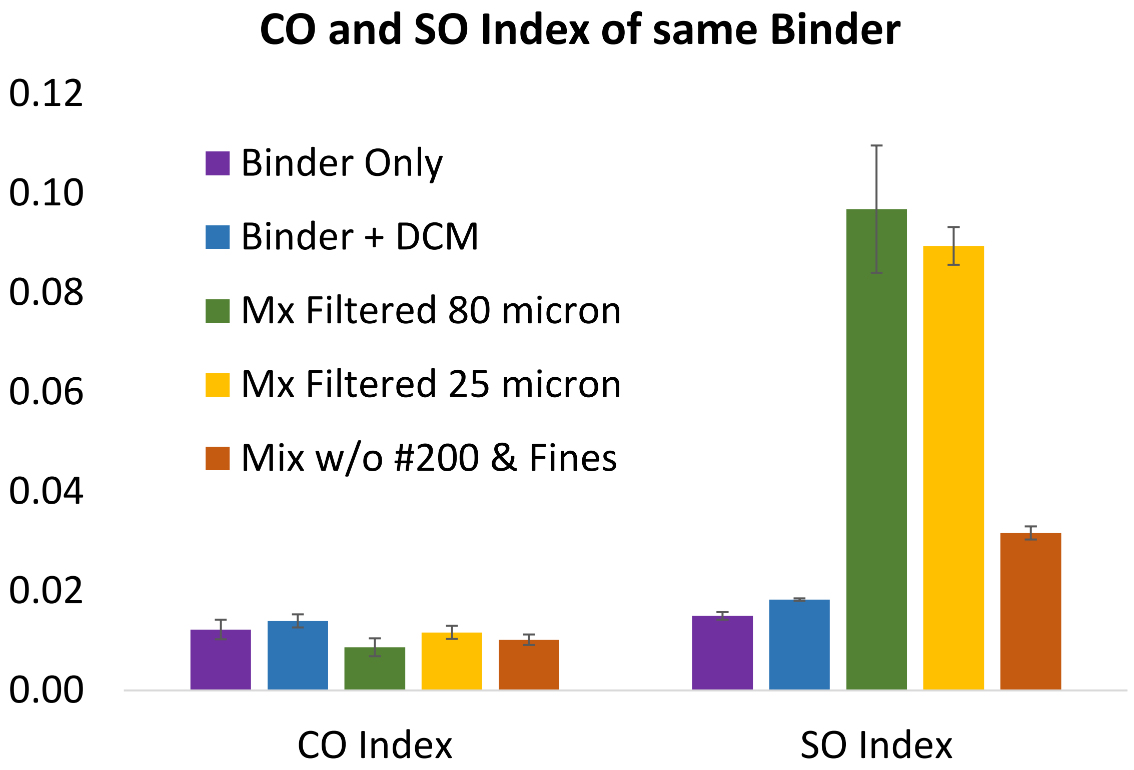




- Sulfoxide index starts to decrease after certain duration of aging
- Sulfoxide can be decomposed to Sulfones resulting to reduced Sulfoxide Index
- Sulfoxide Index for RTFO aged binder NEVER equals the Index of PAV aged binder

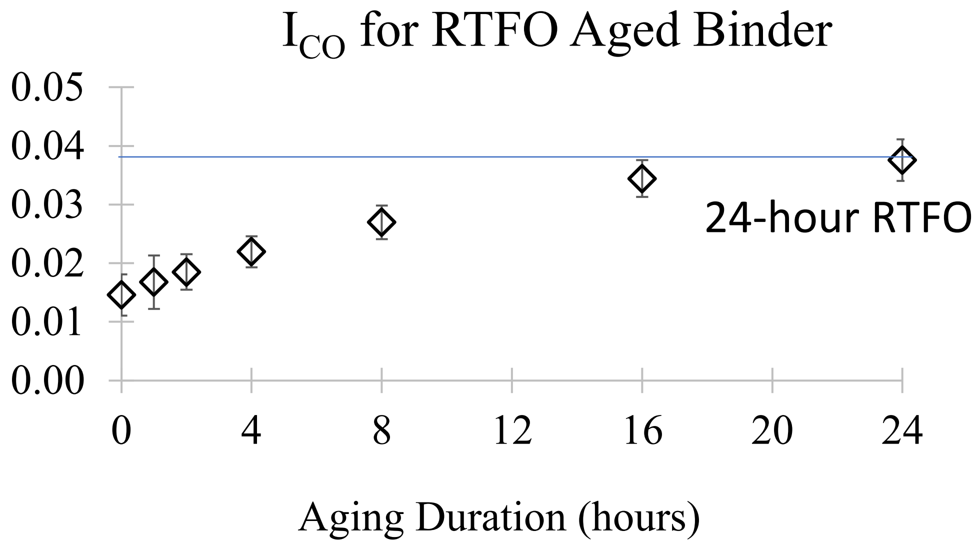
Effects of Fine in Extracted Binder

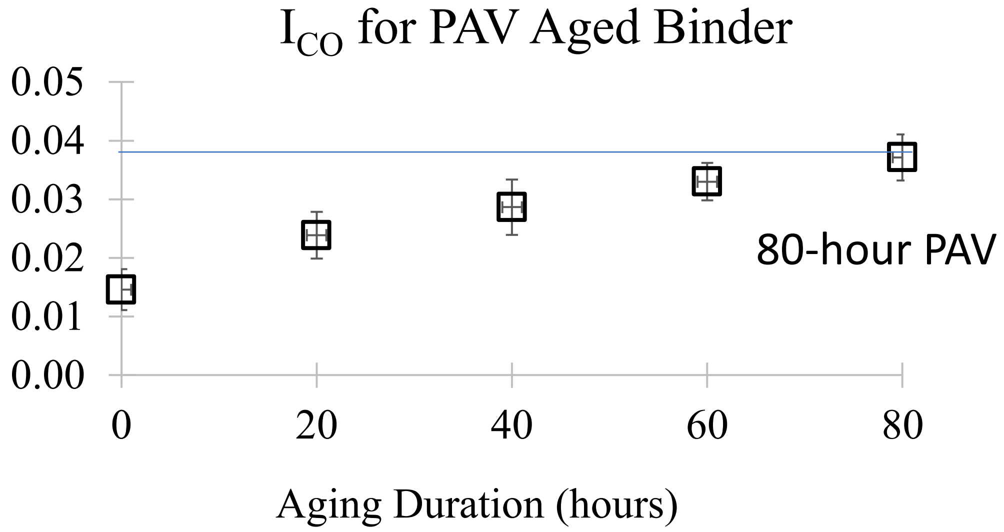




- Fine particle from mix contain Si=O which interferes with S=O
- **Carbonyl Index** is not affected by the fines : **Suitable** for quantifying Mix Aging
- **Sulfoxide Index** is influenced by the fines: **Not suitable** for quantifying Mix

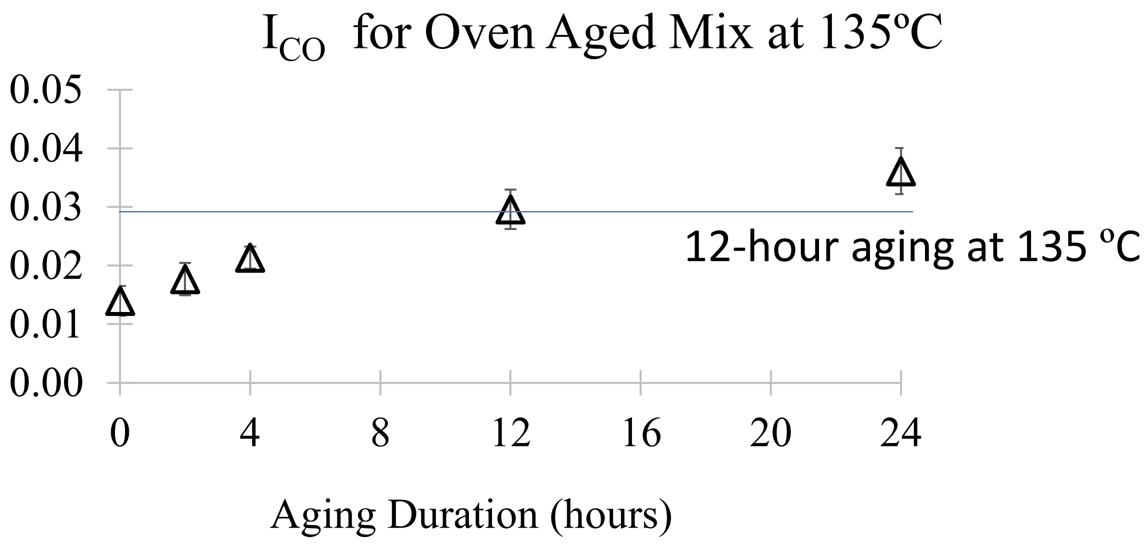
Carbonyl Index of Aged Binder and Mix

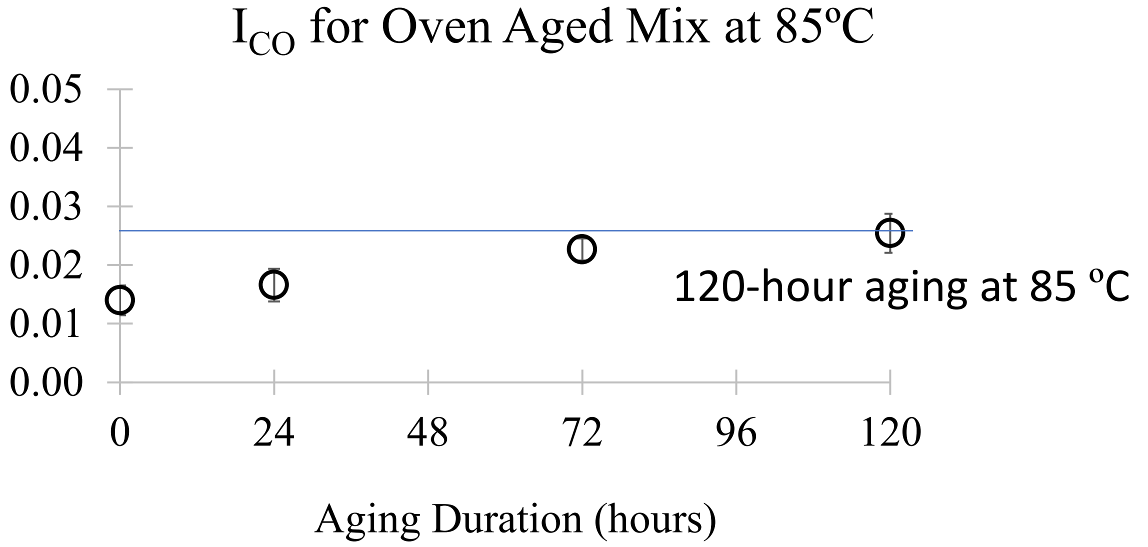




- 24-hour RTFO: $I_{CO} = 0.0376$
- 80-hour PAV: $I_{CO} = 0.0372$
- RTFO aging: higher initial rate of aging
- Change in I_{CO} *is NOT Linear*

Carbonyl Index of Aged Binder and Mix

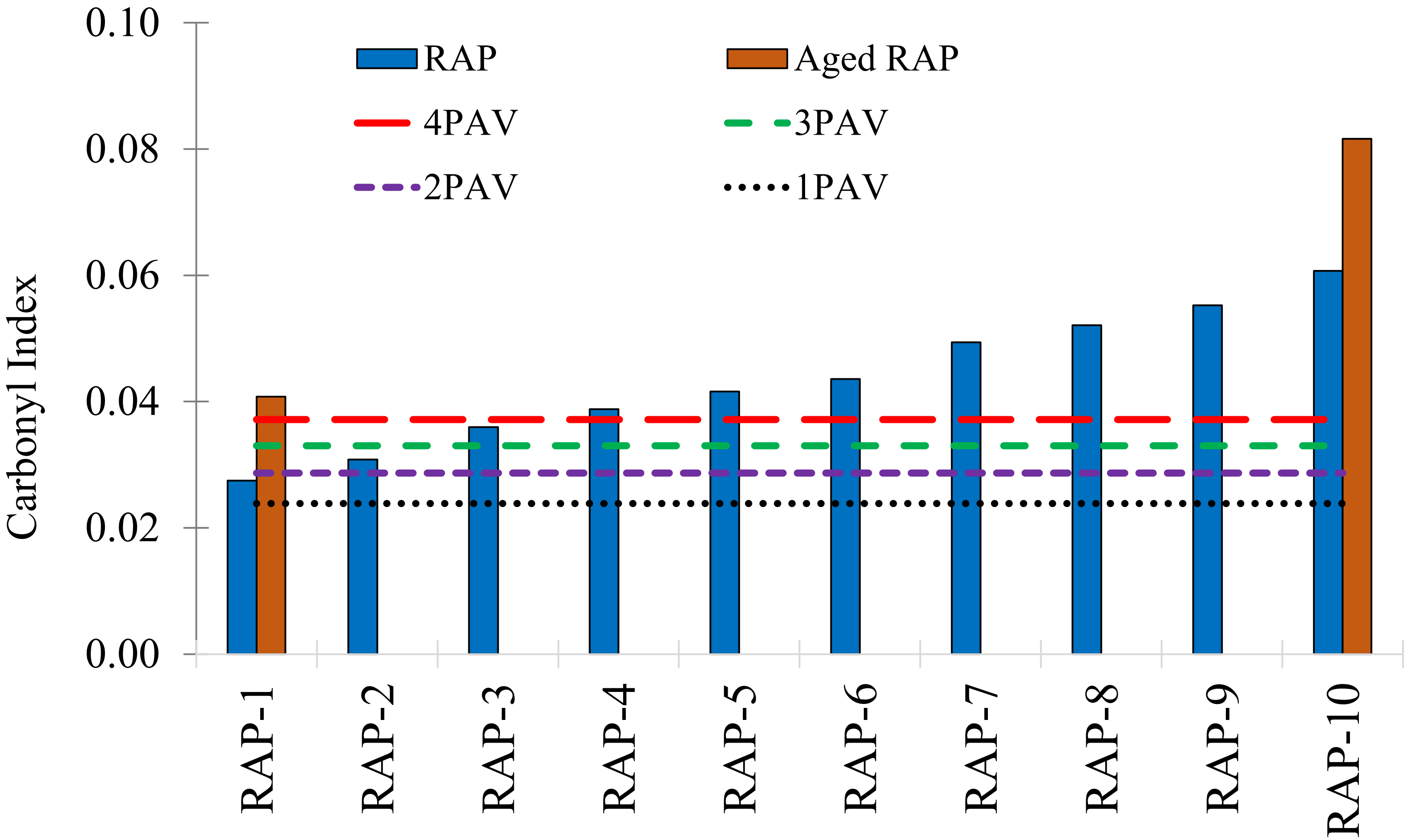




- 12-hour aging at 135 ºC: $I_{CO} = 0.0296$
- 120-hour aging at 85 ºC: $I_{CO} = 0.0254$
- Aging at higher temperature creates higher rate
- Change in I_{CO} *is NOT Linear*

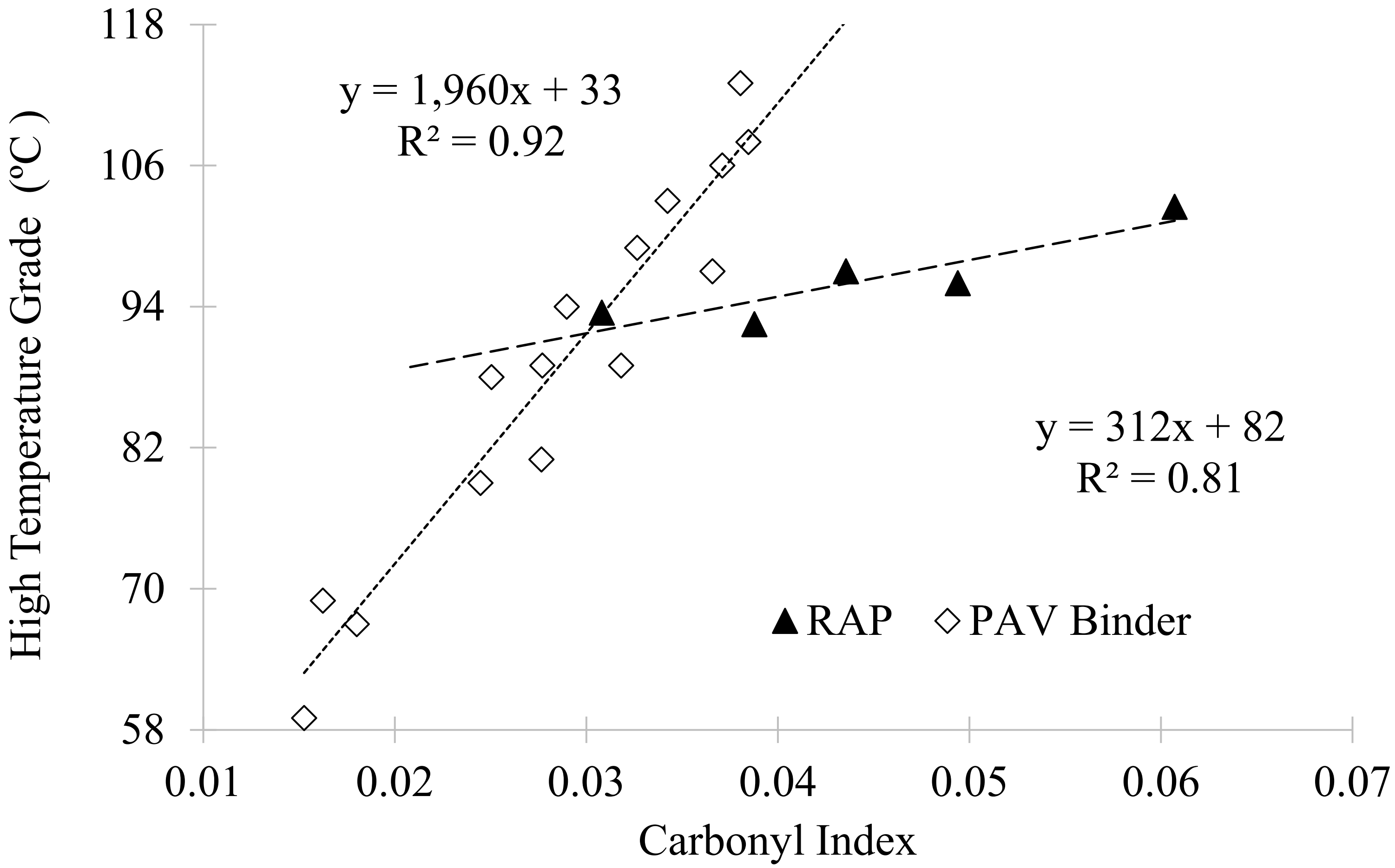
Aging Extent of RAP

- 10 different RAPs from different locations
- Carbonyl index of RAP is much higher than that of even 4-PAV aged binder
- Further aging of RAP increases the Carbonyl Index; In this plot RAP is aged at 135 ºC for 12 hours



Stiffness of RAP and PAV Aged Binder

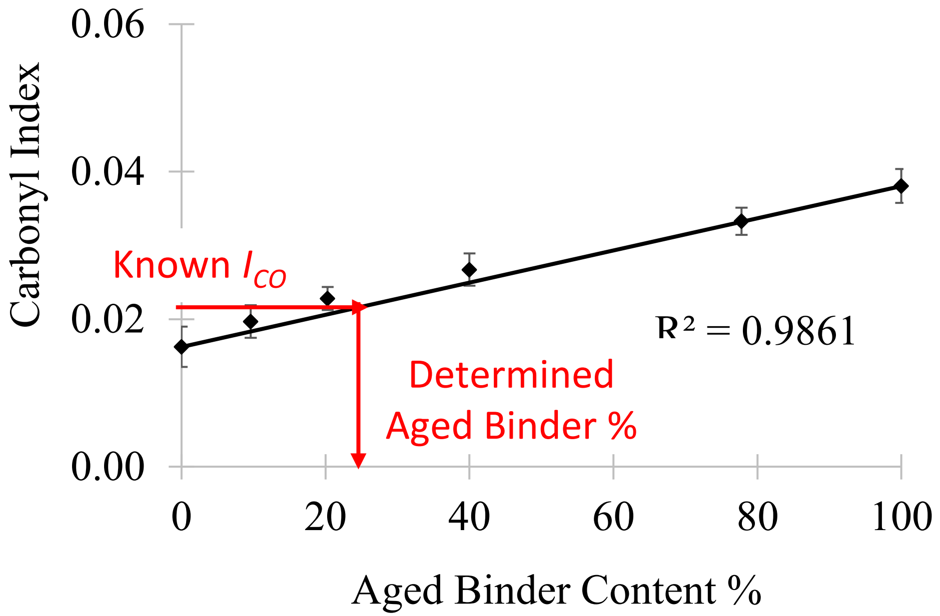
- Laboratory aging: Stiffness increases at faster rate with compared to Carbonyl Index
- Real Aging: Stiffness increases at slower rate with compared to Carbonyl Index
- Measuring Stiffness Only cannot determine the aging extent of the RAP



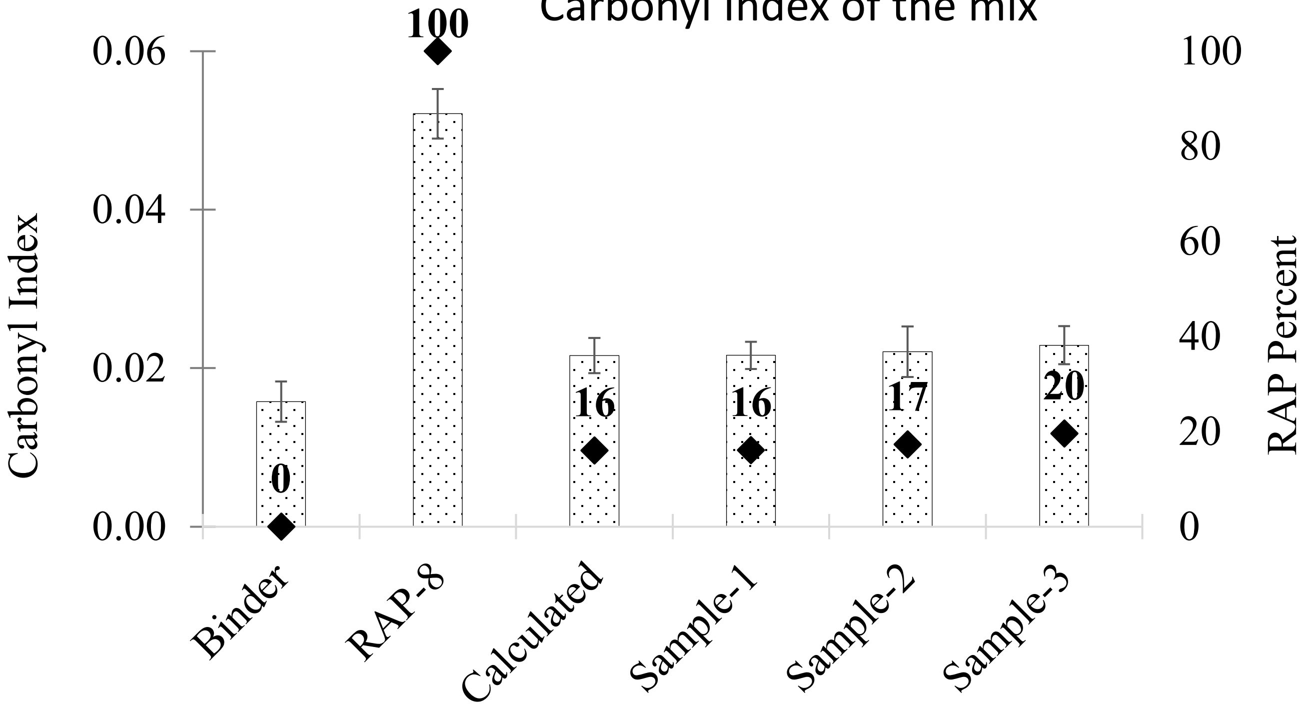
Carbonyl Index and RAP Content

- 4-PAV Aged binder was mixed with unaged binder at different ratio
- Change in Carbonyl Index of the binder blend is linear with the concentration of aged binder
- Using this plot, Aged binder content can be determined from known Carbonyl Index:

$$RAP\% = \frac{I_{CO\ (Mix)} - I_{CO\ (Unaged\ bInder)}}{I_{CO\ (RAP)} - I_{CO\ (Unaged\ bInder)}} * 100$$



Example of Determination of RAP content from Carbonyl Index of the mix



Suitable Index for Mix

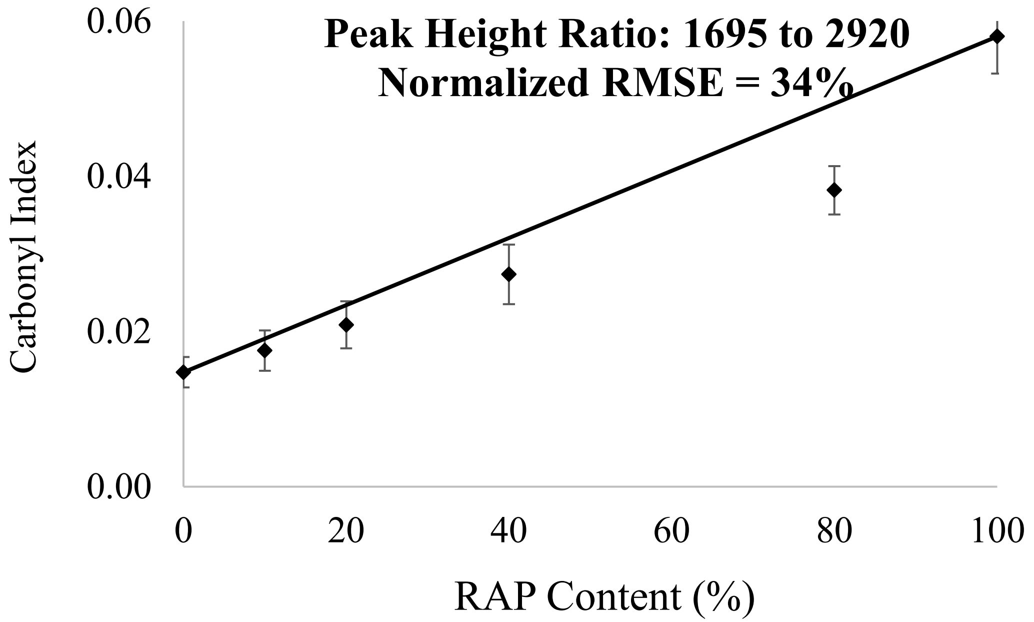
- RAP is added to the mix at different ratio
- Carbonyl Index is calculated using different methods
- Change in I_{CO} *should be linear*
- Root Mean Square Error is calculated:

$$RMSE = \sqrt{\frac{\sum[(Predicted - Measured)^2]}{Number\ of\ data\ points}}$$

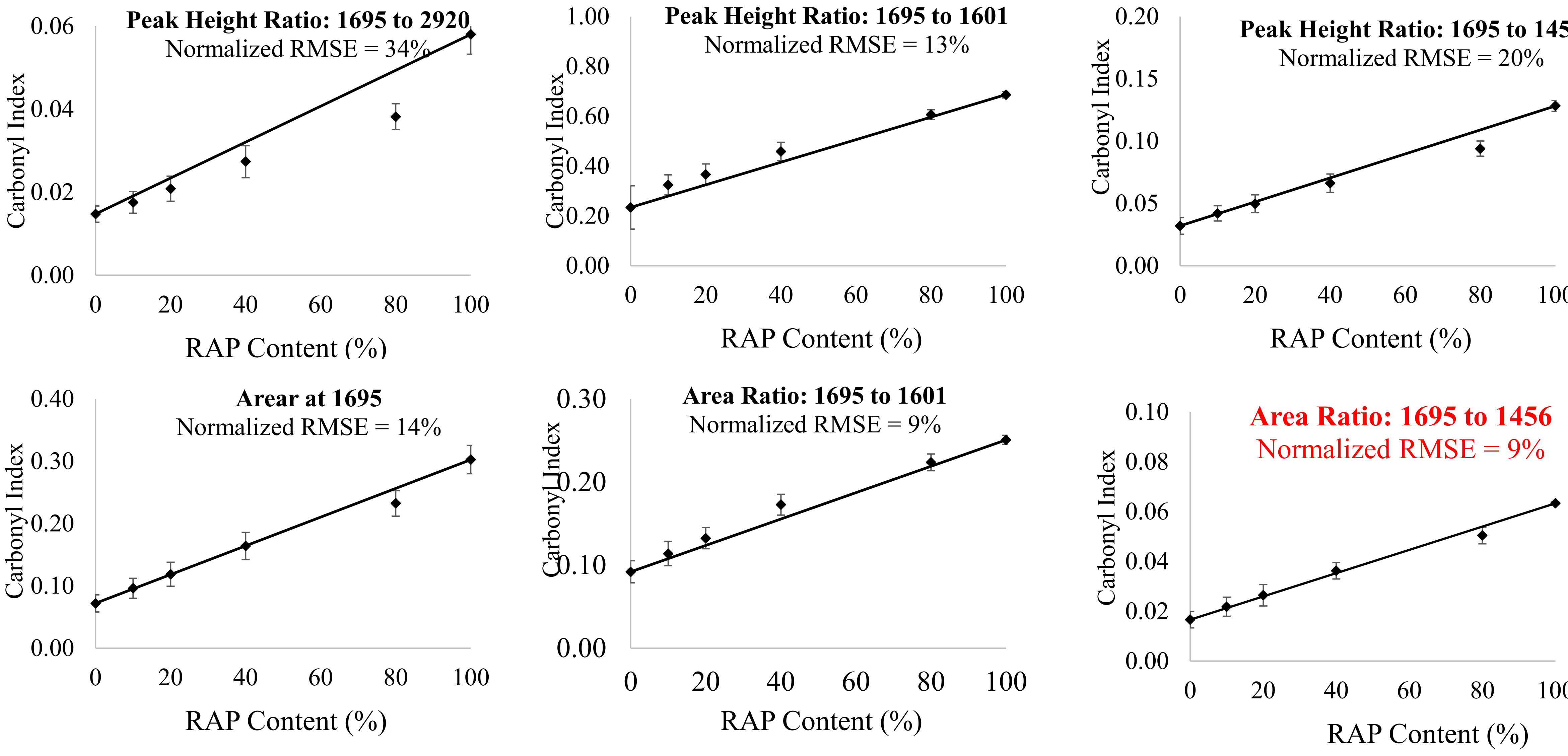
- Normalize the RMSE by Carbonyl Index of Unaged Mix

$$Normalized\ RMSE = \frac{RMSE}{I_{CO\ for\ 0\%\ RAP}}$$

- Lower the Normalized RMSE is Better the Correlation



Selection of Suitable Index for RAP Content Determination



Sample Collection from Plants

RAP Collection from Pile

Mix Collection from Truck

Details Information of the Plant Mix

NMS (inch)	**0.5**
RAP %	15.0
Design Asphalt %	4.8
Binder from RAP %	0.8
RAP to Binder Ratio	0.167
Binder PG	67-22
Virgin Binder I_{CO}	0.0219
RAP Binder I_{CO}	0.0758
Mix Collected From	Drum

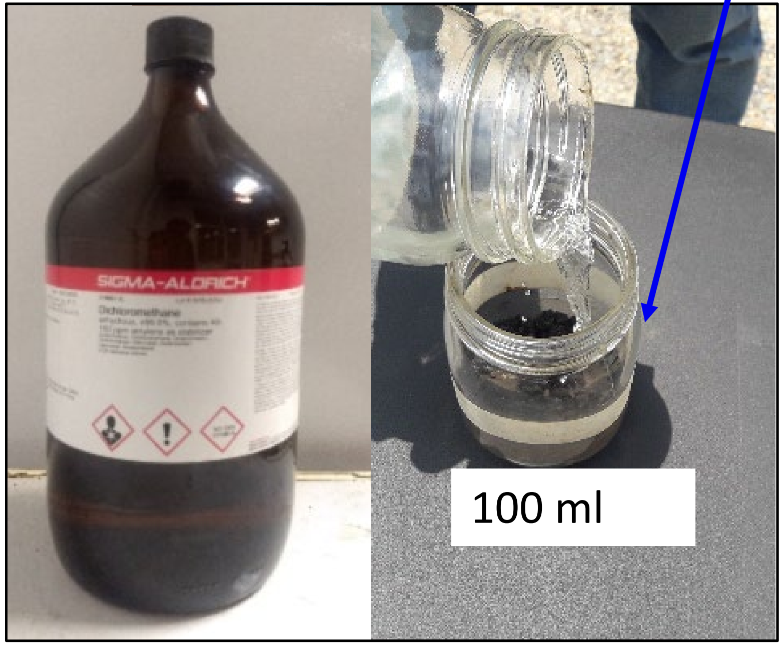
- Total Mix: 12 different mix
- Mixing Plants: 5 different plants in North Louisiana
- RAP content: 15% to 24%
- NMS: 0.50 to 1.0 inch
- Sampling Location: Outlet of Mixing Drum and Truck
- Binder Grade: PG 64-22, PG 67-22, PG 70-22, PG 76-22

Field/ Quick Extraction Process

HMA Collection in the Plant

Shake gently and wait for 5 minutes

Adding DCM in the Loose Mix



Field/ Quick Extraction Process

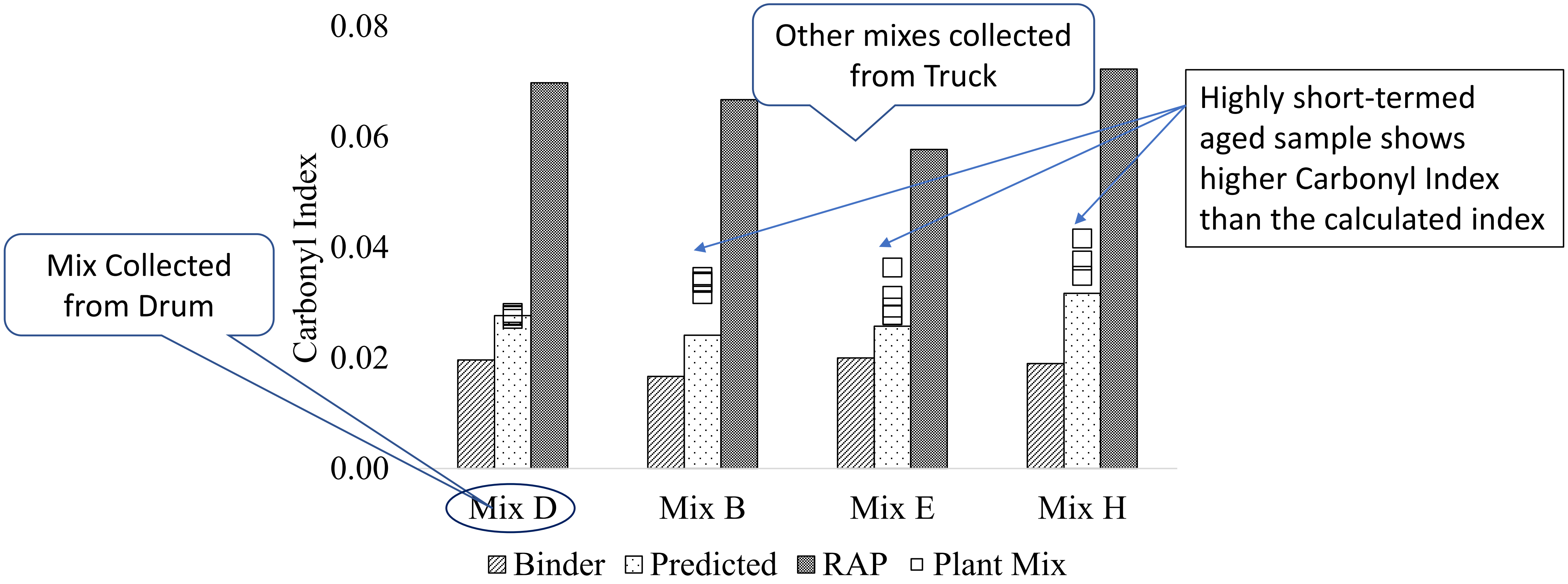
Extracted Mix

Filtration through 80-micron Nylon filter

5 min

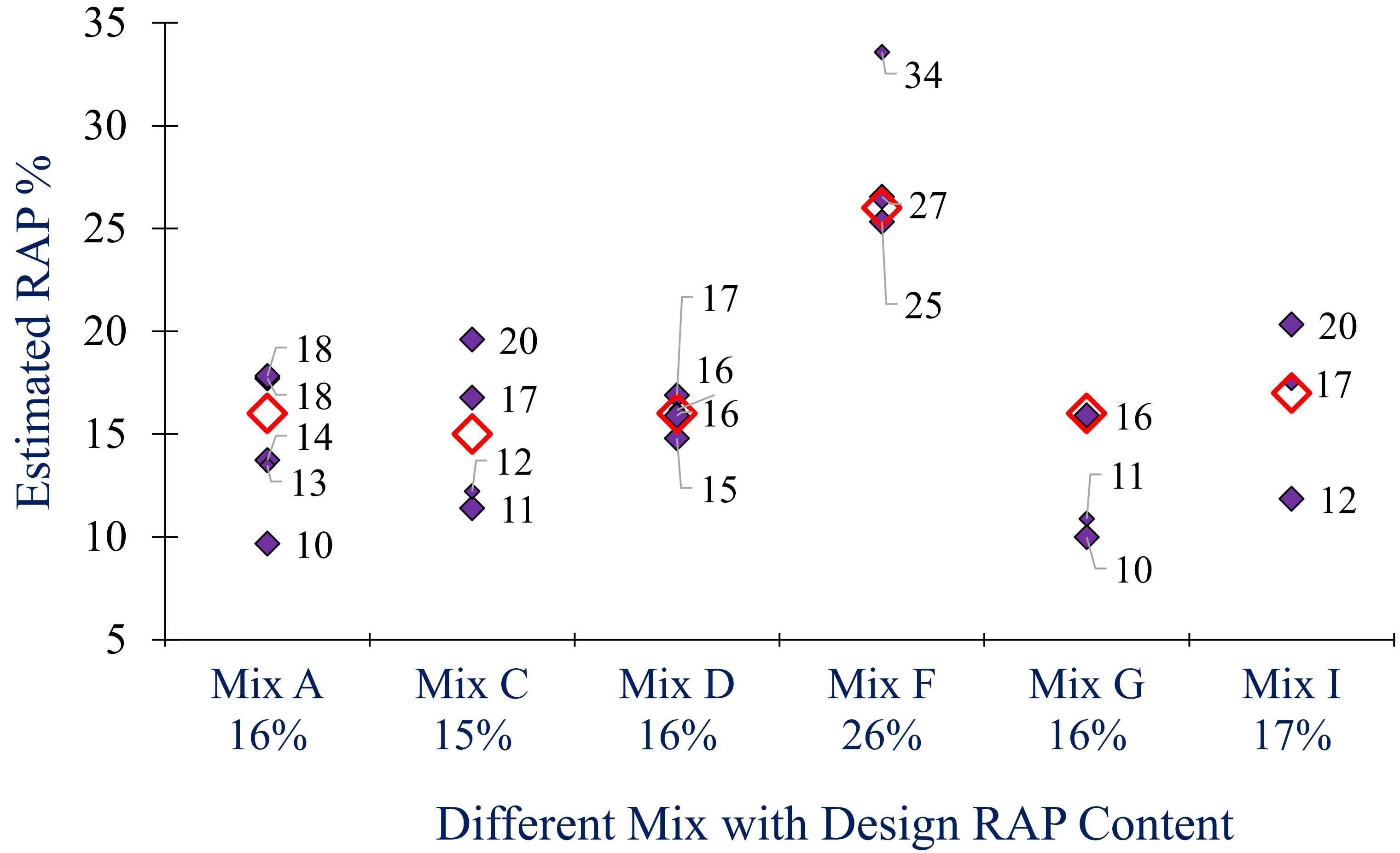
5 min

Effect of Short-term Aging in the Plant



- **Carbonyl Index is significantly affected by the Short-Term aging of the mix during production and storage**

Validation of RAP Content Determination in the Plant



Determined RAP content varies within maximum 8% of the designed RAP

Time Required

30 minutes is enough to determine the RAP percentage in the field

Work Step	Required Time					
	5 min	5 min	5 min	5 min	5 min	5 min
RAP Extraction						
Mix Extraction						
FT-IRS of 3 Replicates (1 Binder)						
FT-IRS of 3 Replicates (1 Extracted RAP)						
FT-IRS of 3 Replicates (1 Extracted HMA w/ RAP)						
Data Transfer and Analysis						

Conclusions: Quality Control of RAP Mixture

- Carbonyl index can successfully quantify binder and mix aging
- Sulfoxide index is not adequate to conclusively determine the aging of asphalt
- RAPs possess much higher carbonyl index than that of the laboratory aged binder or mix
- A quick extraction process can produce enough binder from the mix for testing in FT-IR.
- The amount of RAP can be determined by spectral analysis of fresh mix

Overall Layout of the Presentation

- ❑ Part I : Polymer Content Determination in Binder
- ❑ Part II : Quality Control of RAP Mixture
- ❑ **Part III : Rejuvenator Identification and Quantification**

Use of Rejuvenator

- Application of Rejuvenator in aged binder can improve the binder performance
- Aromatic Oil and Bio Oils are two widely used rejuvenator

Objective

- To quantify the amount of rejuvenator present in asphalt binder by analyzing absorbance spectra

Materials

- Binder: PG 58-28
- Rejuvenator:
  - Plant-based bio oil (0%, 5%, 15% of total binder)
  - Petroleum-based aromatic oil (0%, 15, 35% of total binder)
- Polymer: SBS
- RAP: Hight Temperature Grade 98 (20% RAP binder added to base binder)

Analysis Method

- Peak Height
- Area Under the Spectra

Absorption Spectra of Rejuvenator and Binder

Bio Rejuvenator

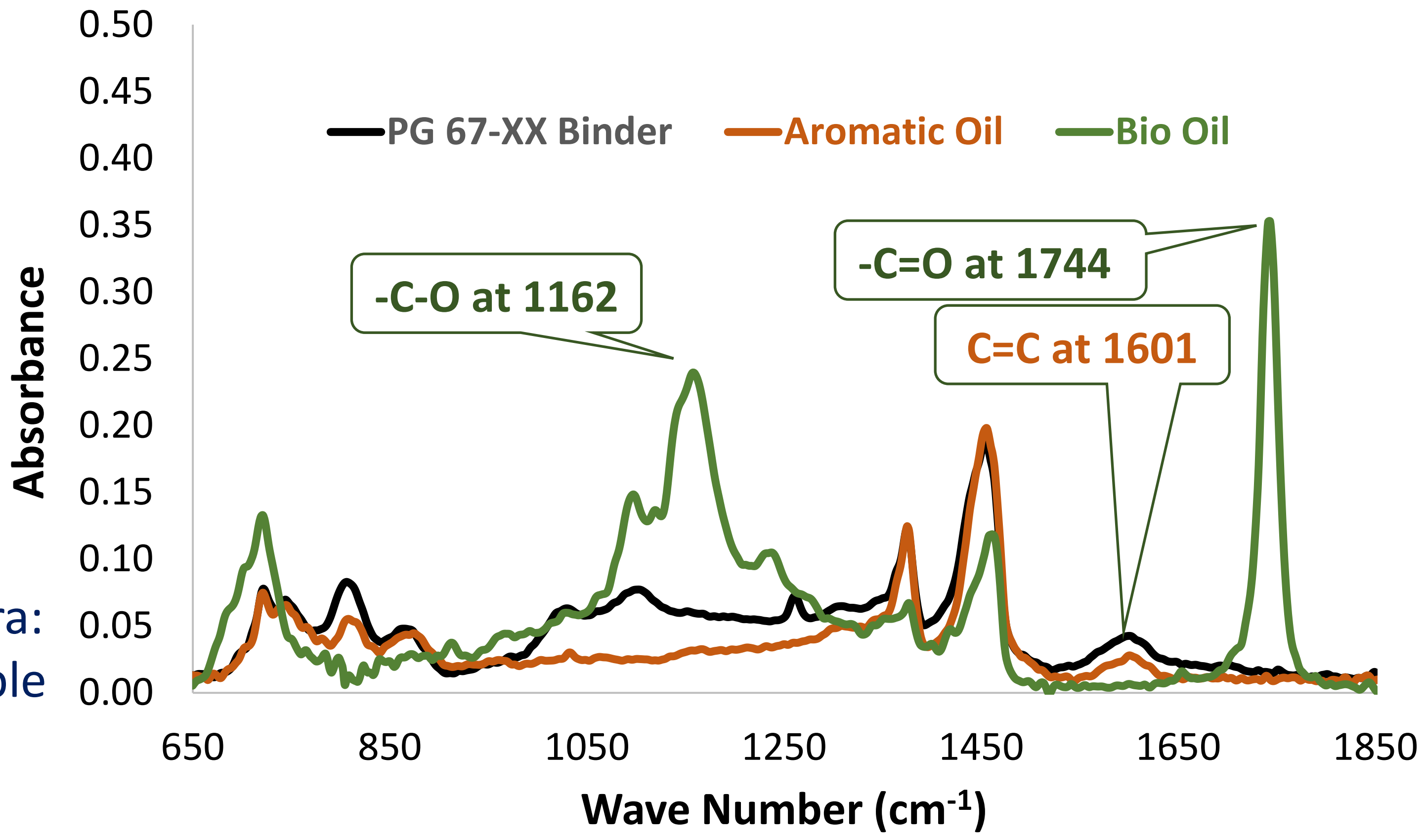
1162 : -C-O Stretching

1744 : -C=O Stretching

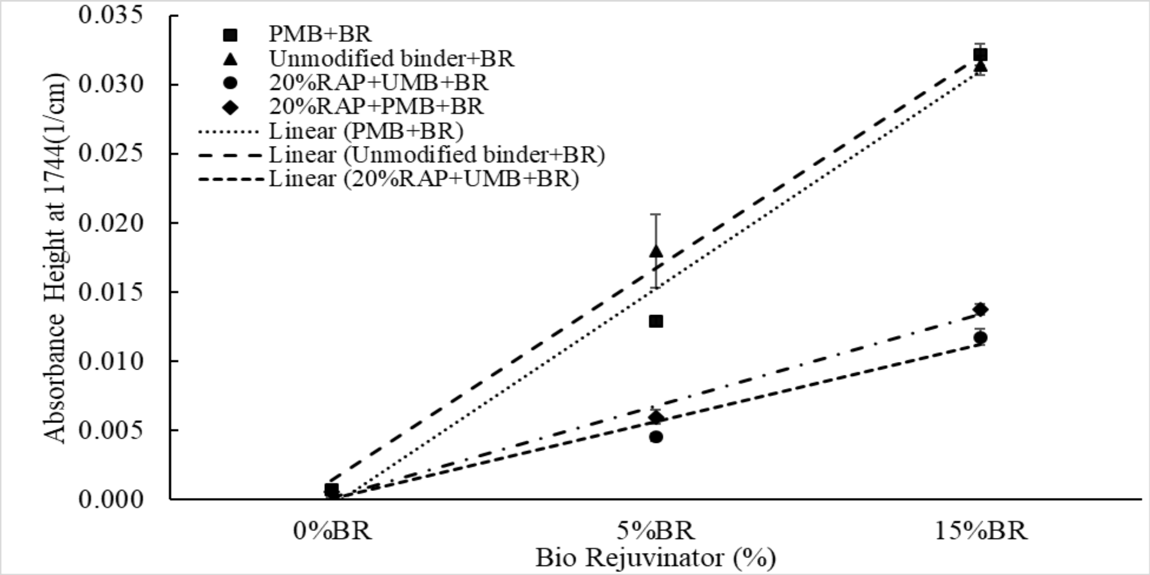
Aromatic Oil

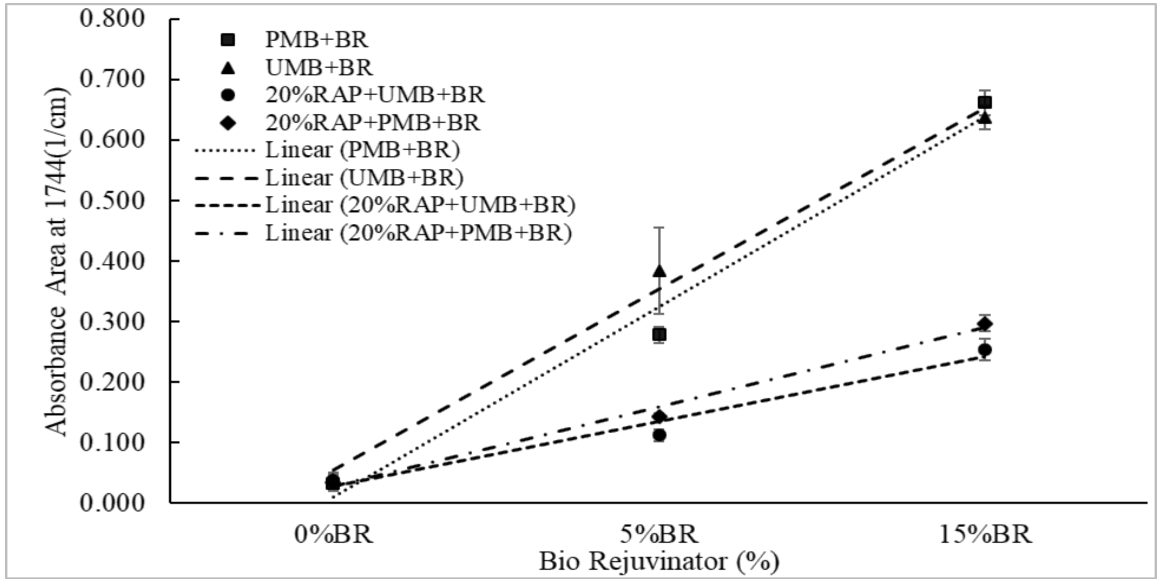
1601 : C=C Aromatic

Bio Rejuvenator add **new peaks** in spectra: Identification and Quantification is Possible



Quantitative Analysis of Rejuvenated binder





Absorbance Height at 1744 (1/cm) with Bio Rejuvenator %

Absorbance Area at 1744 (1/cm) with Bio Rejuvenator %

- Absorbance Area provides better linear relationship (R^2 = 0.96)
- Presence of polymer does nor affect the quantification process
- Presence of RAP reduce the absorbance value but does not affect the quantification process

Conclusion: Rejuvenator Identification

- **Bio Rejuvenator** add a **new peak** in the absorbance spectra, but Aromatic Rejuvenator does not
- FT-IRS can identify Bio Rejuvenator
- **Area method** provides better correlation to quantify the rejuvenator content
- **Quantification** of rejuvenator is unaffected by added **polymer or RAP binder**

Overall Recommendations

- In future, study should be performed on **DR-FT-IR (diffuse reflectance)** method
- FT-IR method has the potential to be used for **pavement maintenance** purposes
- Potential use of FT-IRS for identifying cracking susceptible **extremely aged surface**
- **Forensic analyses** can be performed to find the possible causes of premature failure
    - Detect segregation of polymer
    - Degradation of polymer
    - Excessive usage of RAP, & extremely oxidized RAP usage
    - Presence of rejuvenators
- Immediate **implementation** of FT-IR spectrometer is recommended
    - Polymer content determination
    - Quality control of RAP mixture
    - Identifying bio rejuvenators
- **Viability of extensive usage** of handheld FT-IR spectrometer in various applications should be studied

Acknowledgement

Louisiana Transportation Research Center

Field Implementation of Handheld FTIR Spectrometer for Polymer Content Determination and for Quality Control of RAP Mixtures