Technical White Paper

The Limit of Detection (LOD) Method: An FTIR Screening Tool for Evaluating Solvent Remaining after Extraction

Fundamental Properties of Asphalts and Modified Asphalts III Product: FP 03

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INTRODUCTION

At the Western Research Institute (WRI), asphalt mix and core extractions to recover the asphalt for additional laboratory testing are performed on a routine basis. The extraction procedure used at WRI is in general accordance with AASHTO T319, *Standard Method of Test for Quantitative Extraction and Recovery of Asphalt Binder from Asphalt Mixtures*. However, T319 is somewhat tedious, and equipment intensive. The method uses a complicated extraction vessel that was developed during the Strategic Highway Research Program (SHRP). The equivalent method in ASTM is D6847-02 and it was withdrawn in 2010 because there were too few labs performing it to establish required interlaboratory precision and bias. T319 is intended for use when the physical or chemical properties of the recovered asphalt binder are to be determined.

The current method used by WRI for extractions is a micro-extraction method that generates about 10 g of recovered binder. It is a straightforward, simple modification of AASHTO T 319. See Farrar et al. [2015] for details on the WRI method. The WRI method allows two solvents: (1) an 85:15 (v/v) mixture of toluene and 95 percent ethyl alcohol, and (2) trichloroethylene. Both solvents were considered in this study.

After the extraction process is completed, there are no AASHTO or ASTM methods to determine if the solvent has been removed to a "trace" level during the extraction process. Typically it is assumed that if the vacuum and temperature requirements for the rotary evaporator process are followed, then sufficient solvent has been removed. That is, enough solvent has been removed that any "trace" amount remaining will not have a significant influence on the chemical or rheological results of laboratory tests performed on the recovered asphalt.

To ensure the solvent has been removed to the "trace" level, AASHTO T319 requires a final rotary evaporator step of 25 min at 174°C (oil bath temperature) and vacuum of 700 mm of Hg below atmospheric pressure. ASTM D5404/D5404M – 12 *Standard Practice for Recovery of Asphalt from Solution Using the Rotary Evaporator* requires a final rotary evaporator step of 10 min at 155°C (oil bath temperature) and vacuum of 600 mm of Hg below atmospheric pressure.

The extraction method recently developed by WRI [Farrar et al. 2015] requires a final rotary evaporator step of 1 hour at 170°C (oil bath temperature) and vacuum of 600 mm of Hg below atmospheric pressure. These final steps discussed are in addition to initial rotary evaporator steps at lower temperature and pressure. The reason for the lower temperature and pressure in the beginning of the rotary evaporator process is to prevent "bumping" where the solvent/asphalt solution moves up into the condenser.

To ensure the level of solvent is below the threshold that could affect the asphalt's viscoelastic properties, the recovered asphalt is evaluated using Fourier transform infrared (FTIR or IR)

spectroscopy. If the solvent is above the detection threshold of the IR instrument, the final rotary evaporator step is repeated. IR spectroscopy is an ideal analytical tool for evaluating the presence of solvent in asphalt because of the simplicity of analysis coupled with the information-rich spectra that it provides.

To be clear, the IR analysis proposed here is a screening method and not intended to quantitate the concentration of solvent in the asphalt. The IR screening method is referred to as the limit of detection (LOD) method and is described in the next section of this report.

Our experience with the WRI extraction method is that the final rotary evaporator step removes the solvent to a "trace" level about 99 percent of the time. Occasionally recovered asphalt has to be sent back to the extraction lab because the asphalt was unusual in terms of polarity or its ability to retain the solvent. Often the exact reason why there is excessive solvent remaining in the sample is unknown. While the occurrence of excess solvent is rather uncommon, a procedure to detect excess solvent is crucial in order to have full confidence in the laboratory results of tests performed on the recovered asphalt.

The terminology "trace concentration level" of solvent is used here not in the analytical sense as an amount of a solvent in a unit amount of asphalt, instead trace concentration is defined here as the concentration level of solvent remaining in the asphalt that will not significantly affect the rheological test results performed on the recovered asphalt.

During the initial phase of this study, it was thought the main goal was to develop an analytical method using infrared spectroscopy to determine the concentration of solvent remaining in units such as part per million (ppm). Overall, it appeared that the detection threshold of toluene in asphalt using WRI's FTIR Instrument was roughly 500 to 1000 ppm.

Other more precise analytical methods such as gas chromatography/mass spectrometry GC/MS provide an order of magnitude better precision. The IR detection threshold is described as a very rough estimate because it is expected to vary drastically among labs with different types of IR equipment and accessories such as liquid cell or attenuated total reflectance (ATR). In addition, the detection threshold is affected by the selected IR test parameters such as resolution, number of co-added scans, apodization, path length, etc. So, even in the same lab, the LOD could vary significantly depending on how well the test parameters are optimized.

It became apparent during this phase of the study that simply developing an IR analytical method to determine the concentration of solvent remaining would not address the crucial question as to at what concentration does the solvent begin to have a significant effect on the chemical and rheological properties of the recovered binder. It is not uncommon in the literature to observe comments questioning the results of rheology on recovered asphalt which may have had a solvent level greater than the trace level. Of course, comments of this sort may or may not be telling, and it remains unresolved because of a lack of a standard method to assess the "trace" level of solvent. A method that simply reports the concentration level of the solvent remaining after extraction while useful, does not resolve the crucial "trace" issue.

If solvent is detected and is still present after extraction by an approximate method such as proposed in this study, the sample can simply be sent back to the extraction lab for further rotary evaporation and it is not necessary to quantitate the amount of solvent.

In routine testing of recovered asphalt to assess the level of solvent remaining, it would be impractical to determine the concentration of the solvent even using a relatively simple, straight forward technique such as IR. Recovered asphalt from a different source would involve preparing reference standards and development of calibration curves.

Developing calibration curves when using attenuated total reflectance, and other IR techniques such as photoacoustic spectroscopy, would be particularly difficult since a separate analytical method such as GC/MS would be required to determine the concentration of the toluene-spiked asphalts for the calibration curves. Also, very special precautions would be required to prevent or take into account differences in the duplicate spiked samples since the solvent even at low concentration levels evaporates from the asphalt at room temperature.

It should be mentioned in this discussion that if a common calibration curve could be used for all asphalt/toluene mixtures, it might be possible to rapidly quantitate the toluene concentration with IR. The first phase of this study suggested that Beer's molar absorption coefficient (absorbance divided by the absorption path length and concentration) for toluene in unmodified asphalt at 694 cm^{-1} is relatively constant. However, that hasn't been fully established nor has the error involved in assuming an average molar absorption coefficient for toluene or trichloroethylene in asphalt. And again, simply determining the concentration of solvent does not answer the larger, more important question about the concentration level where the chemical or rheological properties may be significantly affected during testing, i.e., the "trace" amount.

The above discussion has led to a proposed method which is a screening tool to evaluate if the remaining solvent is above or below the "trace" amount. It is referred to here as the limit of detection (LOD) method.

Another approach considered to detect the presence of solvent remaining after extraction was spectral subtraction. Spectral subtraction is a technique where the absorbances of a reference spectrum are subtracted from the absorbance of a sample. The idea is to remove the bands due to the reference materials from the sample [Smith 2011].

Spectral subtraction, while useful, has several limitations and was not applied in this study because: (1) spectral effects can lead to distortions in the subtraction result, (2) the variability in the subtraction process from user to user can lead to uncertainty, and (3) the subtraction process requires a pure spectrum of, e.g., the spectrum of the asphalt without toluene … something not typically available when performing routine extractions.

The above discussion has led to development of the LOD method which does not attempt to quantify the amount of solvent remaining after extraction. It simply requires that the solvent remaining after extraction be close to the limit of detection of the instrument, and that through a set of experiments the LOD be near the trace amount. If the amount of solvent is detected above the LOD then it is returned to the extraction lab for further processing.

EXPERIMENTAL

Infrared

Liquid cell IR analysis was performed on a PerkinElmer Spectrum One IR Spectrometer in the transmission mode with a 1.0 mm solution cell with 50 mg asphalt per 1 mL carbon disulfide. Thirty-two scans were co-added, at a resolution of 4 cm^{-1}. Note the 4 cm^{-1} resolution was varied to evaluate the effect on signal-to-noise ratio (SNR). A background single beam spectrum was obtained for every sample single beam spectrum. The reported sample absorbance spectra were obtained by ratioing the single beam background and sample spectrums.

Dynamic Shear Rheometry

Dynamic shear tests were performed with a Malvern Kinexus controlled stress dynamic shear rheometer (DSR). Four mm diameter plate geometry was used because it only takes approximately 25 mg asphalt between the parallel plates. This greatly facilitated preparation of test samples. A single oscillatory shear frequency sweep from 0.1 to 50 rad/s was performed at 30°C.

Reagents

Toluene (Pharmco-Aaper, ACS, 99.97 percent); trichloroethylene (Fisher, ACS, 99.5 percent min.); carbon disulfide (Fisher, Spectranalyzed®, ACS, 99.9 percent), Ethanol (95%)

Solvents

Two extraction solvents were used: an 85:15 (v/v) mixture of toluene and ethanol (95%); and trichloroethylene.

Materials

Table 1 describes the three asphalt binders used in this study. They were tank asphalts collected during construction and then RTFO and PAV aged. The YNP asphalt binder was modified at the refinery with a low percent of styrene butadiene styrene (SBS) copolymer.

Table 1. Asphalt binders used in this study.

Project Location	Date Constructed	Asphalt Binder Label	PG	Extent of Oxidative Aging	Description
Yellowstone National Park	2007	YNP	58 - 34	RTFO/PAV (20 hr, 300 psi, 100°C)	SBS modified binder
Olmsted County, MN, CR 113	2006	MN1-3	58 - 28	RTFO/PAV (48 hr, 300 psi, 100°C)	Unmodified binder.
Olmsted County, MN, CR 113	2006	MN1-4	58 - 28	RTFO/PAV (48 hr, 300 psi, 100°C)	Unmodified binder.

Preparation of Spiked Samples for the LOD Method

Three grams of the aged asphalt binders were dissolved completely in 3 mL of toluene/ethanol trichloroethylene in small Erlenmeyer flasks. These were then poured into pre-cleaned 57 mm disposable aluminum tins and allowed to evaporate overnight in the hood. They were then placed in a vacuum oven at 90°C at moderate vacuum (~15 inches mercury). The temperature was increased as necessary and IR samples collected periodically to evaluate the toluene or trichloroethylene concentration in terms of a relative amount. Note: toluene forms an azeotrope with ethanol and water so it was assumed that as the toluene was removed, so too were the ethanol and water. After the desired concentration of solvent was achieved, the samples were tested in the DSR. The desired concentration in terms of the relative amount of toluene, for example, remaining after this process is > 80% but < 120%.

THE LOD METHOD

The LOD method does not attempt to quantify the amount of solvent remaining after extraction. It simply requires that the solvent remaining after extraction be close to the limit of detection of the instrument, and that, through a set of experiments, the LOD be near the trace amount. If the amount of solvent is detected above the LOD, then it is returned to the extraction lab for further processing.

It is useful at this point to (1) define the LOD as commonly used in analytical chemistry, (2) define how the term is used here and (3) discuss several of the factors or instrument parameters in terms of infrared spectroscopy that can affect the LOD. The LOD is the point or concentration where it becomes difficult to distinguish a substance from the absence of that substance. In this case, the substance is the solvent, and the signal in the absence of the solvent is the asphalt spectrum. This is a somewhat nuanced definition, as generally the absence of the solvent is the blank or background. In this case the solvent is part of a matrix consisting of asphalt moieties that have strong absorbance in a number of regions in the mid-infrared spectrum, and there is considerable potential for interference with the solvent signal.

In analytical chemistry there are a number of detection limits common in use beyond LOD such as the instrument detection limit (IDL), the method detection limit (MDL), the limit of quantification (LOQ), etc. The definition of these "limits" varies in the literature. The intent here is to use the LOD to evaluate, thru a set of experiments, if the LOD is near the trace amount of solvent.

The proposed LOD method consists of preparing an asphalt sample with solvent spiked at a concentration well above the instrument's LOD. Then DSR frequency sweeps at 30°C are performed with the control asphalt (no solvent) and the spiked sample. The two frequency sweeps of the asphalt samples are used to establish the relationship between the LOD and the trace amount. The trace amount is defined as a maximum reduction (softening) of the complex shear modulus, G*(10 rad/s) by 10 percent. Typically, 5% variation in G* in a series of replicates is considered acceptable, so the trace amount was set at 10% to be above the test precision limits.

The concentration of solvent that causes a 10 percent reduction in G*(10 rad/s) must be greater than the concentration at the LOD. G*(10 rad/s) is determined from the frequency sweep data at the 30°C. Relative amounts of solvent are determined in absorption units since Beer's molar absorption coefficient is not determined.

An initial attempt was made to determine the LOD from the signal-to-noise ratio (SNR) of the analyte (the solvent) measured in the matrix (the asphalt). The absorbance spectrum of toluene is shown in figure 1. There are two pronounced peaks at approximately 730 cm^{-1} and 694 cm^{-1} in the toluene spectrum. The peak at 694 cm^{-1} is due to ring bending and the peak at 730 cm^{-1} is due to aromatic C-H out-of-plane bending [Smith 1999]. These peaks were selected to evaluate the presence of toluene in asphalt. The toluene peak wave numbers vary slightly when comparing spectra of for example toluene alone, or toluene in asphalt or toluene in SBS modified asphalt because of factors such as hydrogen bonding, π-π stacking, etc.
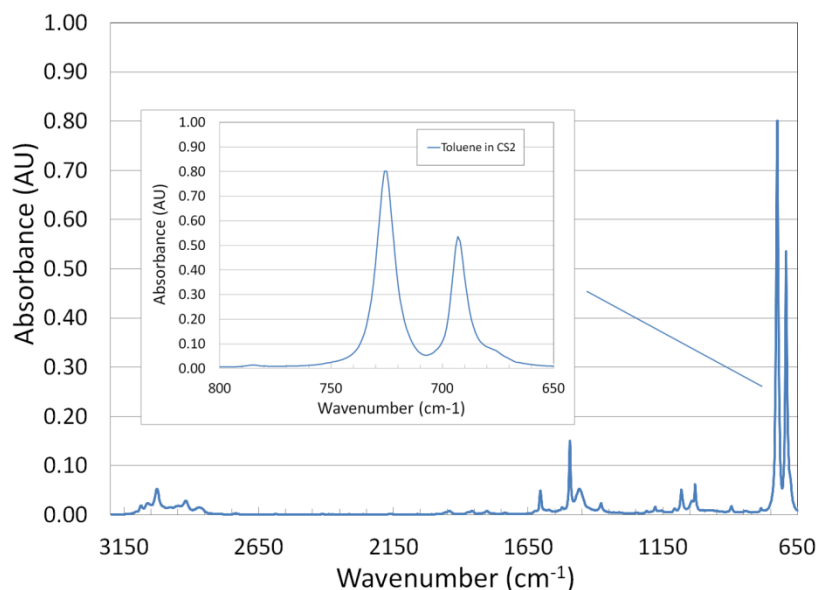

Figure 1. Graph. Infrared absorbance spectrum of toluene. Note: during the rotary evaporator process the toluene azeotropes with any water present in the original extraction solvent or asphaltic material, and since the water concentration is much lower than the solvent concentration, the water is typically removed during the rotary evaporation process.

The LOD is affected when the asphalt or additive(s) in the asphalt significantly absorb in the same regions as the solvent. At low concentration of toluene in asphalt, the infrared signal due to the solvent at 694 cm^{-1} and 730 cm^{-1} are difficult to distinguish from the asphalt/additive infrared signal, and this defines the LOD. Figure 2 compares the infrared absorbance spectra of toluene, SBS, unmodified asphalt, and SBS modified asphalt. Unmodified asphalt does not strongly absorb in the 694 cm^{-1} region so the 694 cm^{-1} peak is a good peak to use to evaluate the presence of toluene in unmodified asphalt. However, in the region of the toluene peak at 730 cm^{-1}, there is an asphalt peak at about 722 cm^{-1}, and the two absorbance bands are sufficiently broad that they

overlap one another. The peak at 722 cm^{-1} is associated with asphalt straight chain methylene (CH$_2$) groups at least four units long [Musser and Kilpatrick 1998]. The peak is attributed to the presence of waxes in the asphalt and will be referred to here as the asphalt "wax" peak.

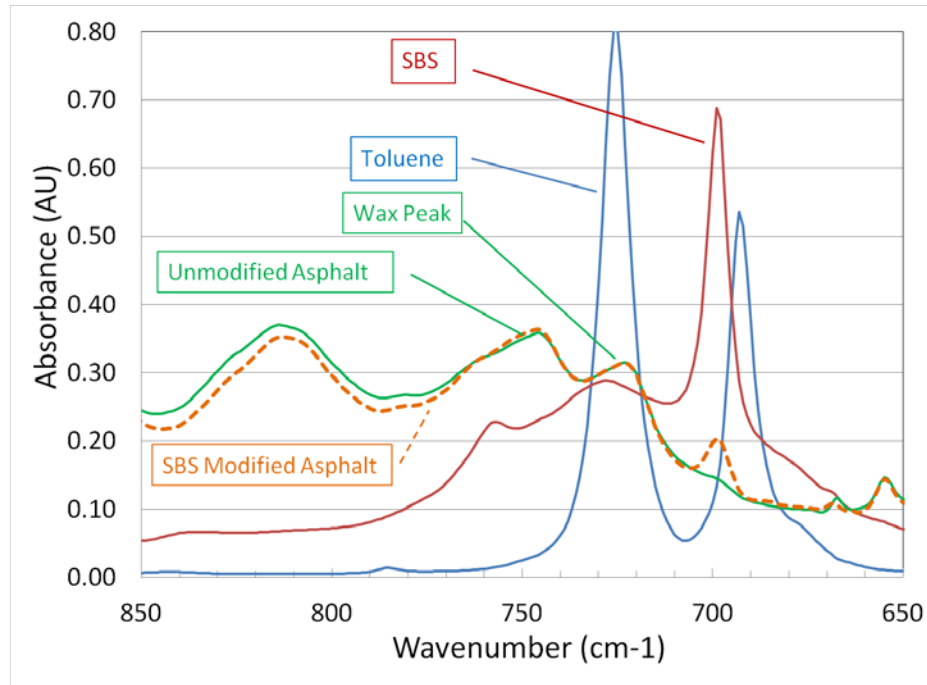
Figure 2. Graph. Infrared absorbance spectrum of toluene, SBS, unmodified and SBS modified asphalt binder.

The height of the wax peak at 722 cm^{-1} varies considerably among asphalts and can be used to estimate the wax content. Figure 3 compares the SHRP core asphalts AAM-1 and AAK-1. AAM-1 is known to contain considerable wax and AAK-1 only a slight to moderate amount [Pauli et al. 2012].
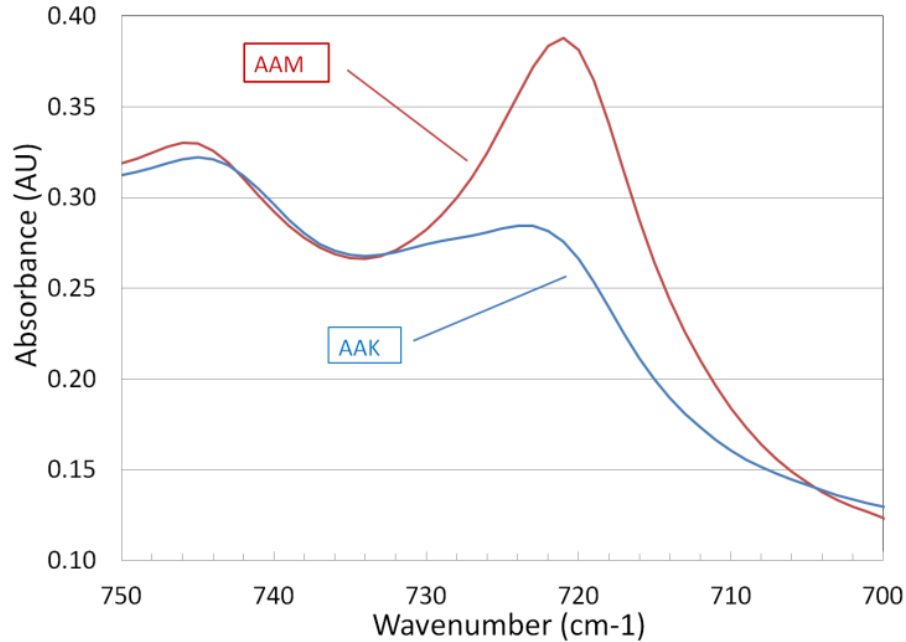
Figure 3. Graph. Infrared absorbance spectra comparing AAK-1 and AAM-1 wax content.

SBS modified asphalt has a strong absorbance peak at 699 cm^{-1}, which is relatively close to the toluene peak at 694 cm^{-1}, and the two absorbance bands are sufficiently broad that they tend to overlap one another. The absorption band at 699 cm^{-1} is attributed to the C-H out of plane bending in the polystyrene [Masson et al. 2001].

The spectral resolution is an important measurement parameter when considering two peaks that are fairly broad and sufficiently close that they tend to overlap. Of course, ideally, if the toluene molecule had a major absorbance band that did not overlap SBS absorbance bands or asphalt absorbance bands, then the issue would be moot, but unfortunately that is not the case.

Resolution in the context of IR analysis is defined as a measure of how well an infrared spectrometer can distinguish spectral features that are close together; that is, the minimum peak interval that can be distinguished [Smith 2011]. The resolution test parameter determines the number of data points in the spectrum and is the inverse of the optical path difference (OPD). The resolution can typically be set to values ranging from 0.5 to 16 cm^{-1} depending on the instrument. Increased resolution means a better ability to distinguish absorbance peaks that are close together, but there is a trade-off since increasing the resolution tends to increase the noise and therefore reduce the SNR. Various criteria have been applied in quantifying the SNR limit, but the generally accepted rule is that the signal must be at least three times greater than the background noise.

When performing infrared analysis on asphalt it is not always desirable to increase the resolution beyond a certain point because it can result in lower SNR and not necessarily improve the ability to distinguish between two close peaks. Figure 4 illustrates the increase in resolution from 4 to 0.5 cm^{-1} and the increase in noise due to increased resolution. Of course the noise could be

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reduced somewhat by increasing the number of co-added scans, but there is a trade-off in terms of the time to perform the test. Increased resolution did not appear to improve the ability to detect the two bands present: the toluene band at about 730 cm^{-1} and the asphalt wax band at 722 cm^{-1}.
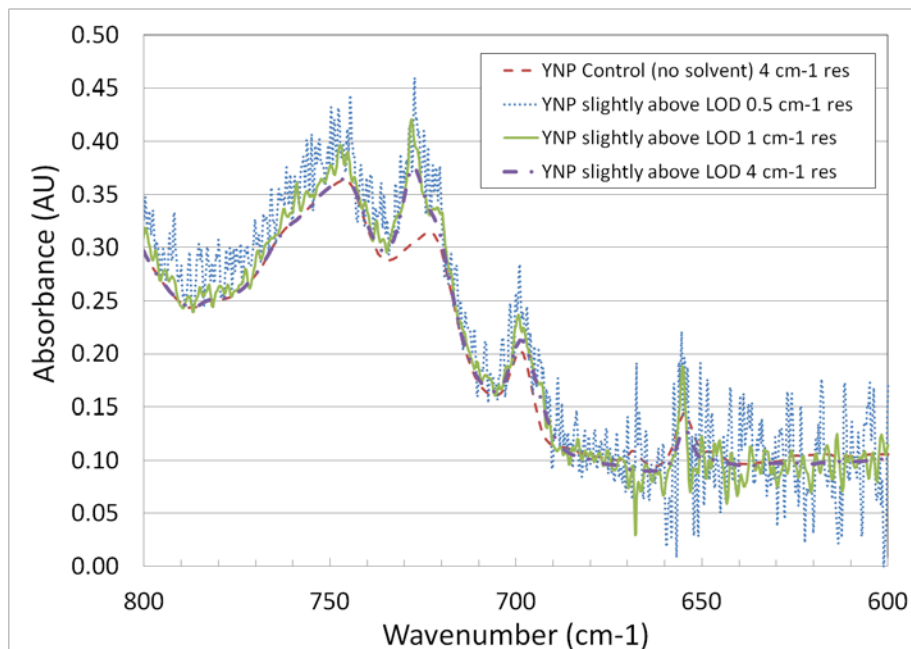

Figure 4. Graph. Infrared absorbance spectra of YNP asphalt at various resolutions.

MEASURING THE RELATIVE AMOUNT OF TOLUENE PRESENT AFTER EXTRACTION, COMPARING THE RELATIVE AMOUNT TO THE LOD AND CONFIRMING THE LOD IS BELOW THE TRACE AMOUNT

Definitions

Toluene: Limit of Detection (LOD) – The general definition of LOD with respect to solvent in asphalt is the point or concentration where it becomes difficult to distinguish the presence of solvent from the absence of solvent. Specifically, for toluene the relative amount of toluene where it becomes difficult to determine if toluene is present has been assigned a value of 50 percent. The 50 % value is based on our experience with reviewing numerous IR spectra for solvent contamination and the potential for false positives due to absorbance by compounds other than toluene in the same region. The relative amount of toluene is defined as the ratio (in percent) of the absorbance at 730 cm^{-1} divided by the absorbance at 747 cm^{-1}. The absorbance at 730 cm^{-1} and 747 cm^{-1} are measured from a baseline established at the trough between the bands at about 735 cm^{-1}. The functional groups associated with these peaks and an example of how to determine the relative amount of toluene is provided in the discussion below.

Trace amount – The trace amount is defined as the amount of solvent present in the asphalt after extraction that would cause a reduction or softening of the of the complex shear modulus by 10 percent.

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Measuring the Relative Amount of Toluene Present

Figure 5A demonstrates the calculation of the relative amount of toluene for the MN1-4 control asphalt (no solvent). As shown in figure 5A and table 2, the relative amount of toluene is 31.3 percent, and since this amount is less than 50 percent the sample is deemed to be below the LOD. The reason the relative amount of toluene is not zero percent is due to interference from the asphalt's "wax" absorbance band at 722 cm^{-1}. This interference will occasionally lead to false-positives. Also, as apparent in figure 2, SBS has a relatively minor absorbance peak at 728 cm^{-1} which could contribute to the absorbance measure at 730 cm^{-1}. The peak at 728 cm-1 is attributed to bending vibrations (wagging) of the CH groups in the SBS polybutadiene [Munteanu and Vasile 2005] and could contribute to false-positives albeit to a much less degree than asphalt wax absorbance. Overall, based on testing on a wide range of asphalts over the last several years, false positives occur rather infrequently.

Further, the MN1-4 asphalt has considerable wax, which is apparent by the significant peak in the figure 5A control spectrum at 722 cm^{-1}. Even with the significant amount of wax present the relative amount of solvent present was well below the LOD. The relative amount of toluene present in the MN1-4 sample is tabulated in table 2, as well as the other two asphalts studies (MN1-3 and YNP).

Figure 5B is the MN1-4 asphalt spectrum where the asphalt has been spiked with toluene. The relative amount of toluene is 72.7 percent, and since this amount is greater than 50 percent, the sample is deemed to be above the LOD. When the relative amount of toluene present is above the LOD the sample is simply sent back to the extraction lab for additional rotary evaporation.

If the asphalt is unmodified and the relative amount of toluene is greater than the LOD, before returning the asphalt for further extraction, evaluate the spectrum in the 694 cm^{-1} region. As mentioned previously, there are two pronounced peaks at approximately 730 cm^{-1} and 694 cm^{-1} in the toluene spectrum. The peak at 694 cm^{-1} is due to ring bending and the peak at 730 cm^{-1} is due to aromatic C-H out-of-plane bending [Smith 1999]. If there isn't an absorbance band detectable at about 694 cm^{-1}, then additional rotary evaporation is unnecessary. The presence of SBS polymer can be assessed by checking for the butadiene characteristic absorbance band at 966 cm^{-1} [Mouillet et al. 2000].

When using the WRI extraction method [Farrar et al. 2015], the asphalt is recovered in the final rotary evaporator step in a wide-mouth bottle, not a large round-bottom flask. It is a simple operation to reattach the bottle to the rotary evaporator and continue the evaporation at high temperature and vacuum. The solvent level is too small to cause "bumping", and the bottle can be lowered rapidly into the rotary evaporator hot oil bath.

After the additional rotary evaporation, a new infrared spectrum is obtained. This repeat spectrum and the first spectrum are compared, and if there is slight to no change, then it is concluded that it was a false positive and the sample is deemed to be at the trace level.
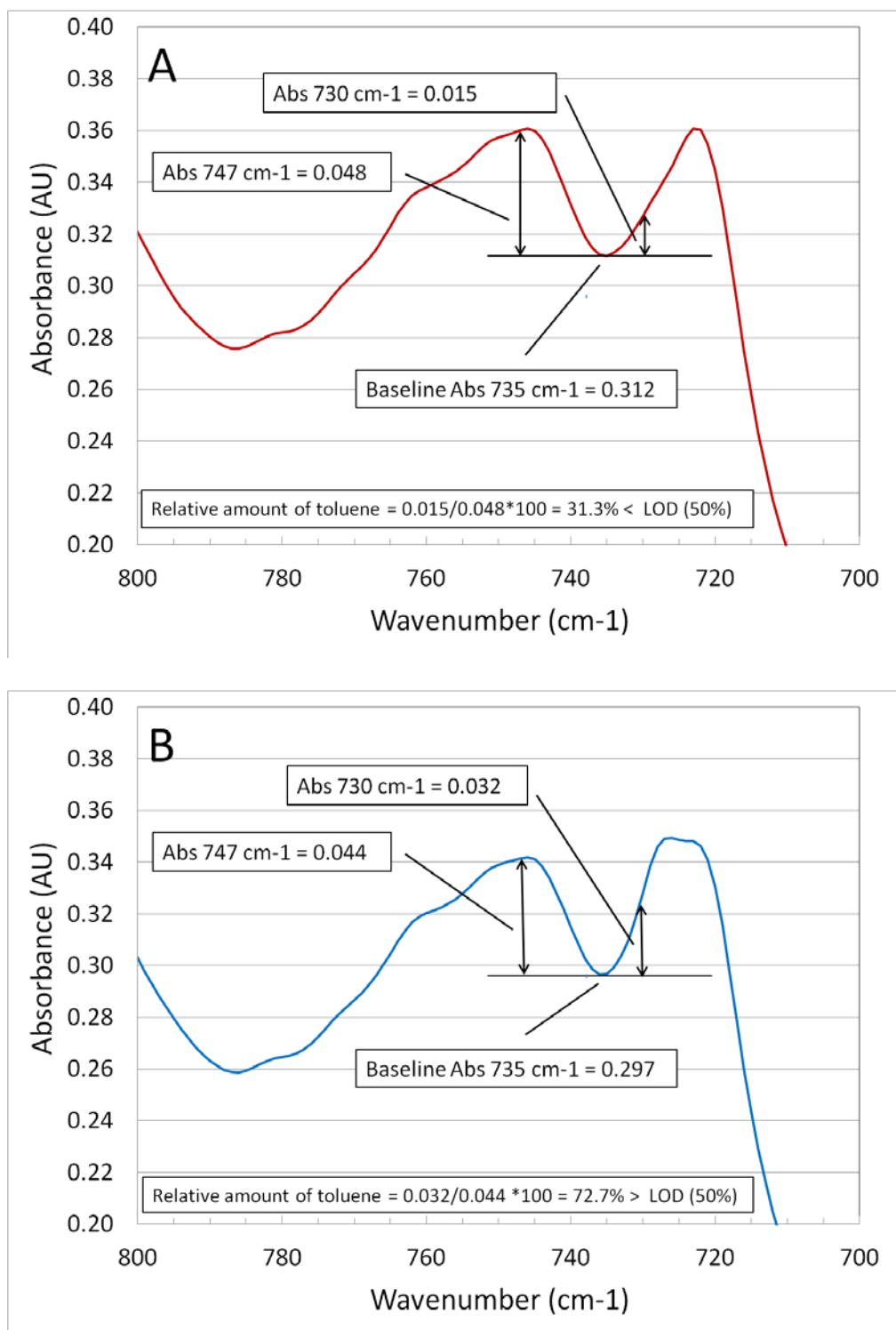
Figure 5. Graph. Infrared absorbance spectra MN1-4: (A) control (no toluene), and (B) spiked with toluene. The spiked sample should have a relative amount of toluene between 80 and 120%.

Table 2. Relative amounts of toluene present in the control and spiked samples.

| Sample | Trough 735 cm^{-1}, Abs | Asphalt 747 cm^{-1}, Abs | Wax + Toluene 730 cm^{-1}, Abs | Using Absorbance at 735 cm^{-1} as the baseline | | Relative Amount A730/A747, % |
				Asphalt 747 cm^{-1}, Abs	Wax + Toluene 730 cm^{-1}, Abs	
MN1-4 Control	0.312	0.360	0.327	0.048	0.015	31.3
MN1-4 Spiked	0.297	0.341	0.329	0.044	0.032	72.7
MN1-3 Control	0.289	0.357	0.296	0.068	0.007	10.3
MN1-3 Spiked	0.303	0.363	0.372	0.060	0.069	115.0
YNP Control	0.289	0.361	0.297	0.072	0.008	11.1
YNP Spiked	0.316	0.361	0.671	0.045	0.355	788.9

Determine the Trace Amount of Toluene

Figure 6 illustrates the relationship between G*(10 rad/s) and the relative amount of toluene based on the control and spiked binders. By interpolating the linear fit, G*(10 rad/s) at the LOD and the relative amount of toluene at the trace level can be determined. Both interpolated values are listed in table 3.
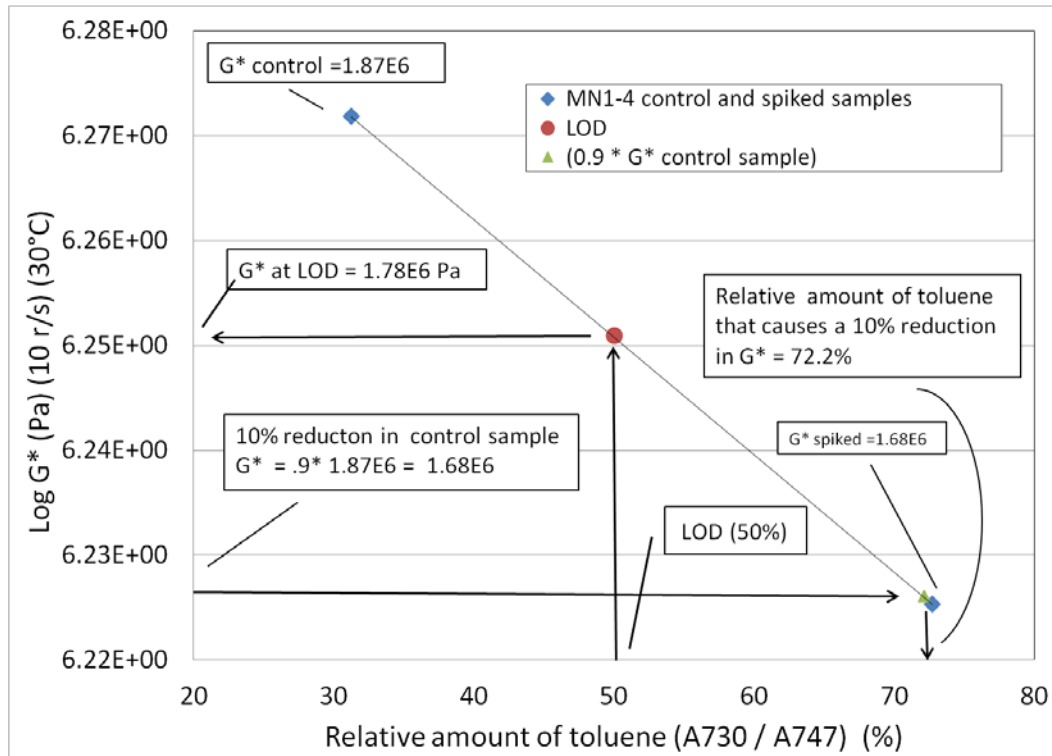

Figure 6. Graph. MN1-4: Interpolation to determine G*(10 rad/s) at the LOD, and the relative trace amount of Toluene where G*(10 rad/s) = 0.9 *(G*(10 rad/s) control sample).

Table 3. Relative amounts of toluene in the control and spiked samples, at the LOD, and at the trace level [G*(10 rad/s) = 0.9 * (G*(10rad/s) control sample)] and the corresponding G*(10 rad/s).

Sample	Relative Amount A730/A747 *100, %	G*(10 rad/s), Pa	Log G*, Pa
MN1-4 Control	31.3	1.87E+06	6.2718
MN1-4 Spiked	72.7	1.68E+06	6.2253
MN1-4 LOD	50.0	1.78E+06	6.2509
MN1-4 0.90 * (Control G*)	72.2	1.68E+06	6.2261
MN1-3 Control	10.3	3.04E+06	6.4829
MN1-3 well Spiked	115.0	2.87E+06	6.4579
MN1-3 LOD	50.0	2.99E+06	6.4753
MN1-3 0.90 * (Control G*)	240.9	2.74E+06	6.4371
YNP Control	11	2.92E+06	6.4654
YNP Spiked	789	1.24E+06	6.0934
YNP LOD	50.0	2.79E+06	6.4454
YNP 0.90 * (Control G*)	101.5	2.63E+06	6.4196

Definitions

Trichloroethylene: Limit of Detection (LOD) – The relative amount of trichloroethylene where it becomes difficult to determine if trichloroethylene is present has been assigned a value of 15 percent. The 15 % value is based on our experience with reviewing numerous IR spectra for solvent contamination and the potential for false positives due to absorbance by compounds other than trichloroethylene in the same region. The relative amount of trichloroethylene is defined as the ratio (in percent) of the absorbance at 930 cm^{-1} divided by the absorbance at 870 cm^{-1}. The absorbance 930 cm^{-1} and 870 cm^{-1} are measured from a baseline established at the trough between the bands at about 920 cm^{-1}. These absorbance bands are defined below.

Trace amount – The trace amount is defined as the amount of solvent present in the asphalt after extraction that would cause a reduction or softening of the of the complex shear modulus by 10 percent.

Measuring the Relative Amount of Trichloroethylene Present

Figure 7A for the control and figure 7B for the spiked sample illustrate the procedure. Draw a baseline parallel to the x-axis at the trough which occurs typically at about 920 cm^{-1} between the absorbance band at 870 cm^{-1} and the trichloroethylene band at about 930 cm^{-1}. The band at 930 cm^{-1} is mainly due to CCl$_3$ deformation vibrations and C-Cl stretching [Colthup et al. 1964]. The band at 870 cm^{-1} is due to rocking in the C-H moiety in asphalt. Measure the height of the absorbance peak 870 cm^{-1} and the height of the absorbance at 930 cm^{-1} from the baseline.
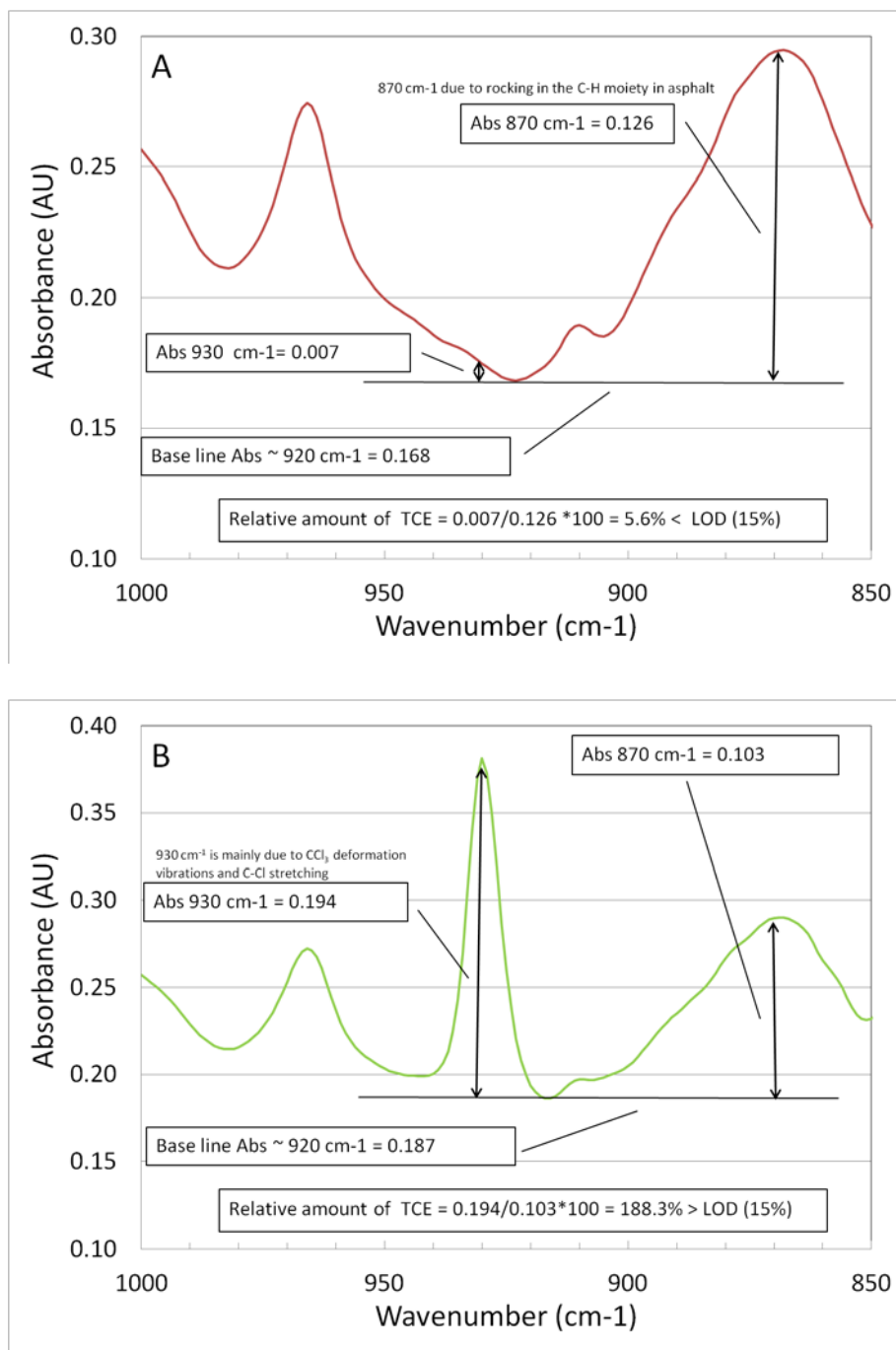
Figure 7. Graph. Infrared absorbance spectra: (A) YNP Control (no trichloroethylene) and (B) trichloroethylene spiked sample.

As shown in figure 7A and reported in table 4, the relative amount of trichloroethylene for the control samples 5.6 percent, and since this amount is less than the 15 percent, the sample is deemed to be below the LOD. The reason the relative amount of trichloroethylene is not zero percent is due to interference from the asphalt spectrum in this area. This interference could occasionally lead to false-positives, however the interference is relatively minor and false-positives should be rare.

Figure 7B is the YNP asphalt spectrum after spiking with trichloroethylene. The relative amount of toluene is 188.3 percent, and since this amount is greater than 15 percent the sample is deemed to be above the LOD. When the relative amount of toluene present is above the LOD the sample is simply sent back to the extraction lab for additional rotary evaporation.

After the additional rotary evaporation, a new infrared spectrum is obtained. This repeat spectrum and the first spectrum are compared and if there is slight to no change, then it is concluded that it was a false positive and the sample is deemed to be at the trace level.

Table 4. Relative amounts of trichloroethylene present in the control and spiked samples.

| Sample | Trough 920 cm^{-1}, Abs | Asphalt 870 cm^{-1}, Abs | Trichloroethylene 930 cm^{-1}, Abs | Using Absorbance at 920 cm^{-1} as the baseline | | Relative Amount A930/A870, % |
				Asphalt 870 cm^{-1}, Abs	Trichloroethylene 930 cm^{-1}, Abs	
MN1-4 Control	0.206	0.313	0.211	0.107	0.005	4.7
NN1-4 Spiked	0.191	0.345	0.348	0.154	0.157	101.9
MN1-3 Control	0.183	0.308	0.193	0.125	0.010	8.0
MN1-3 Spiked	0.183	0.330	0.481	0.147	0.298	202.7
YNP Control	0.168	0.294	0.175	0.126	0.007	5.6
YNP Spiked	0.187	0.290	0.381	0.103	0.194	188.3

Determine the Trace Amount of Trichloroethylene

Figure 8 shows the relationship between G*(10 rad/s) and the relative amount of trichloroethylene based on the control and spiked binders. By interpolating the linear fit, G*(10 rad/s) at the LOD and the relative amount of trichloroethylene at the trace level can be determined. Both interpolated values are listed in table 5.
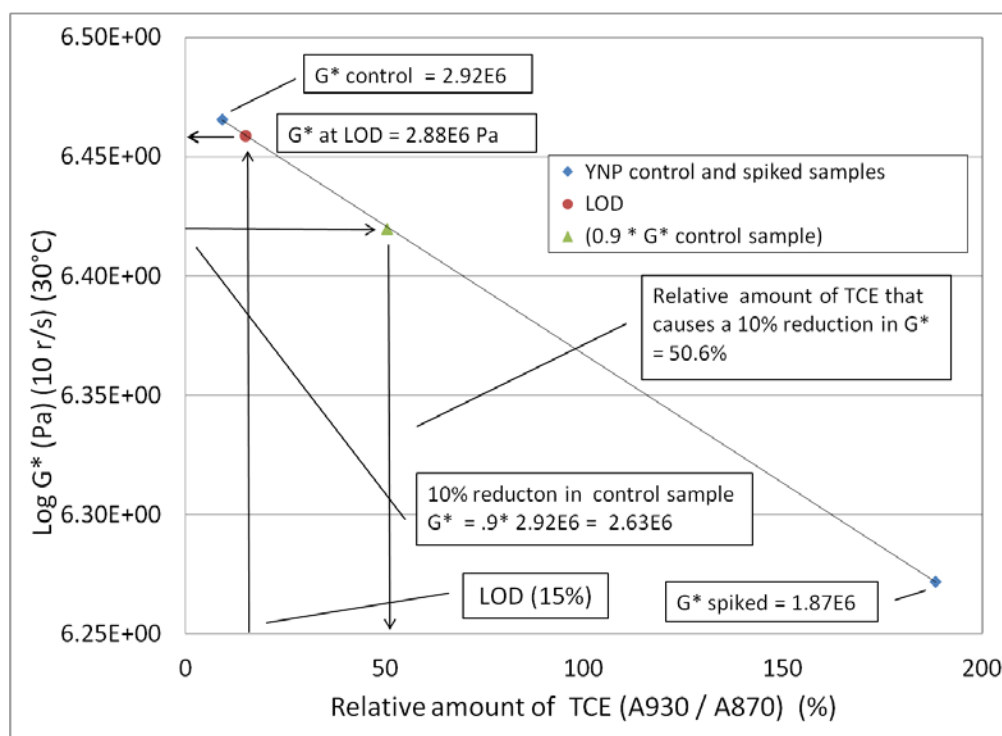
Figure 8. Graph. YNP: Interpolation to determine G*(10 rad/s) at the LOD, and the relative trace amount of trichloroethylene where G*(10 rad/s) = 0.9 * [G*(10 rad/s) control sample].

Table 5. Relative amounts of trichloroethylene in the control, spiked samples, at the LOD, and at the trace level [G*(10 rad/s) = 0.9 * (G*(10 rad/s) control sample)] and the corresponding G*(10 rad/s).

Sample	Relative Amount A730/A747 *100, %	G*(10 rad/s), Pa	Log G*, Pa
MN1-4 Control	4.7	1.87E+06	6.2718
MN1-4 Spiked	101.9	1.49E+06	6.1732
MN1-4 LOD	15.0	1.83E+06	6.2616
MN1-4 0.90 * (Control G*)	50.5	1.68E+06	6.2261
MN1-3 Control	8.0	3.04E+06	6.4829
MN1-3 well Spiked	202.7	1.72E+06	6.2355
MN1-3 LOD	15.0	2.98E+06	6.4735
MN1-3 0.90 * (Control G*)	43.0	2.74E+06	6.4371
YNP Control	9.2	2.92E+06	6.4654
YNP Spiked	188.3	1.87E+06	6.2718
YNP LOD	15.0	2.88E+06	6.4588
YNP 0.90 * (Control G*)	50.6	2.63E+06	6.4196

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CONCLUSIONS

This study demonstrates an infrared spectrometer screening tool to assess the level of solvent remaining in the recovered asphalt in terms of whether or not it will have a significant effect on the recovered asphalt's rheological properties.

The screening tool is referred to as the Limit of Detection (LOD) method. The test matrix to develop and evaluate the LOD method included two common solvents used to perform asphalt extractions (an 85:15 (v/v) mixture of toluene and 95 percent ethyl alcohol; and trichloroethylene), and two types of asphalt (unmodified and SBS modified).

This method is approximate since the "trace" concentration level may not completely consistent from one rheological test to another, and, even in performing dynamic shear oscillatory frequency sweeps in the linear viscoelastic range, the "trace" amount at -30°C may not be same as at 60°C. Further work is necessary to sort out the variation in the "trace" concentration among asphalts and the time dependency.

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DISCLAIMER

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