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CENTER FOR TRANSPORTATION RESEARCH

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Use of X-Ray Fluorescence (XRF) to Determine Tire Rubber Content in Asphalt Binders

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16. Abstract

This work involved making a portable X-Ray Fluorescence Spectroscopy device available to district personnel and training them to use the device on a routine basis to analyze tire rubber-modified asphalt binder for tire rubber content. The Performing Agency worked with the Receiving Agency and producers from around the state to develop calibration standards that can be used to determine the tire rubber content using the portable XRF units and conducted a round-robin analysis of samples from across different laboratories. The Performing Agency also revised test procedure Tex 553-C, "Determination of Re-Refined Engine Oil Bottoms, Polyphosphoric Acid, and Tire Rubber Content in Asphalt using X-Ray Fluorescence Spectroscopy" to account for procedures to use in the field since the device is portable.

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CENTER FOR TRANSPORTATION RESEARCH

Use of X-Ray Fluorescence (XRF) to Determine Tire Rubber Content in Asphalt Binders

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ABSTRACT

This work involved making a portable X-Ray Fluorescence Spectroscopy device available to district personnel and training them to use the device on a routine basis to analyze tire rubber-modified asphalt binder for tire rubber content. The Performing Agency worked with the Receiving Agency and producers from around the state to develop calibration standards that can be used to determine the tire rubber content using the portable XRF units and conducted a round-robin analysis of samples from across different laboratories. The Performing Agency also revised test procedure Tex 553-C, "Determination of Re-Refined Engine Oil Bottoms, Polyphosphoric Acid, and Tire Rubber Content in Asphalt using X-Ray Fluorescence Spectroscopy" to account for procedures to use in the field since the device is portable.

EXECUTIVE SUMMARY

Tire rubber is required in certain TxDOT asphalt binders; e.g., AC-205TR, used for chip seal construction. These binders are specified and used in several districts across the state. Current Receiving Agency Standard Specification Item 300, Asphalts, Oils, and Emulsions, includes using test procedure Tex 553-C, "Determination of Re-Refined Engine Oil Bottoms, Polyphosphoric Acid, and Tire Rubber Content in Asphalt using X-Ray Fluorescence Spectroscopy."

This test procedure is currently only performed at the Receiving Agency Materials and Tests Division (MTD). This test can be implemented in the field with a portable XRF device and test procedure Tex-553-C can be used in conjunction with a calibration chart to evaluate and obtain a quantitative estimate of tire rubber at the district level.

This work involved making this device available to district personnel and training them to use the device on a routine basis to analyze tire rubber-modified asphalt binder for tire rubber content. The Performing Agency worked with the Receiving Agency and producers from around the state to develop calibration standards that can be used to determine the tire rubber content using the portable XRF units and conducted a round-robin analysis of samples from across different laboratories. The Performing Agency also revised test procedure Tex-553-C to account for procedures to use in the field.

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Chapter 1. XRF Purchase

On October 10, 2022, the University of Texas at Austin - Center for Transportation Research (CTR) received final approval for initiating this project. The first order of business was the purchasing of three XRF systems, as this was a key event that could be on the critical path for project execution. This purchase had several key elements described below.

- CTR had received a quote from Thermo Fisher Scientific for the XRF instruments, instrument cradles, and consumables.
- A proprietary purchase was selected to ensure a match of the purchased items to the existing TxDOT system at the Materials and Tests Division.
- On October 10, 2022, the Purchase Order for these systems (and consumables) was developed and entered the University of Texas Purchasing system.
- On November 11, the purchase order was issued to Thermo Fisher Scientific. The purchasing process involved some legal language differences and was finally signed on December 27, 2022.

Thermo Fisher Scientific initially indicated a lead time of 8-weeks for delivery. On December 28, this was revised to a shipment date of January 6, 2023, but this would be only the XRF instruments as the Field Mate Test Stands were back ordered and would take 4-months to receive.

CTR approved a partial shipment of the XRF instruments (guns) only, as the guns can be calibrated without cradles.

CTR received the XRF gun shipment on January 6, 2023. This did not include the Field Mate Test stands but did include a standard mobile test stand. Field Mate Test Stands were expected when available.

The next step was to assess the XRF guns and initiate a calibration process for each XRF gun before distributing to the Lufkin, Odessa, and Brownwood Districts.

Chapter 2. Review and Modify Existing Tex-553-C Test Procedure

This Chapter describes the work performed for Task 3, “Review and Modify Existing Tex-553-C Test Procedure”.

The project team acquired a MS Work version of the existing procedure from the Materials and Tests Division and reviewed the existing procedure for possible changes.

The review resulted in suggested changes in Tex-553-C relative to XRF detection of tire rubber, but also suggested more global revisions. These global revisions included combining developing calibration samples in one section instead of being repeated in each. There were also suggested changes to the concentrations for calibration standards.

The proposed version of Tex-553-C was submitted to TxDOT for review and comment.

The proposed version of Tex-553-C is shown in Appendix A. The proposed revisions resulted in shortening of the test procedure by approximately one page.

The existing version of Tex-553-C is shown in Appendix B.

TxDOT reviewed and edited the proposed version, making minor changes. The final version as edited and approved for publication by TxDOT is shown in Appendix C.

Chapter 3. Develop Training Protocol and Train Districts

This Chapter describes the work performed for Task 4, "Develop a training protocol and train three districts in the use of the portable XRF for determining tire rubber content in asphalt binder."

3.1. Calibration Standards

The calibration standards were acquired from multiple producers. These were specific blends of the base binder and tire rubber used by each producer. In most cases, these blends were provided by the producer to TxDOT.

The project team used the calibration standards to develop calibration curves for each of the XRF guns purchased for the three districts, and the existing XRF guns at MTD and CTR. These calibration curves were included in a consolidated spreadsheet. The consolidated spreadsheet, usable by all XRF guns, requires inputs of the specific XRF gun serial number, binder producer, and zinc content derived from the XRF analysis of that specific sample. The output is tire rubber content for that sample.

3.2. Training Video

Instead of a written layperson's procedure for the complete analysis, a video was developed for training. This video includes a demonstration of key steps:

- Heating and pouring binder into a sample cup.
- Applying a mylar film on the sample (after cooling).
- Placing the XRF gun in the test stand.
- Starting the XRF gun and the initiation sequence to prepare the gun for analysis.
- Placing the sample in the analysis zone of the test stand.
- Entering identifying information into the gun operational software.
- Initiating the analysis (depressing the trigger and analysis time).
- Reading the zinc content of the sample.

The video can be found at:

https://doi.org/10.18738/T8/GX7H0Y

The zinc content of the sample is used in the calibration spreadsheet (knowing the gun serial number and binder supplier) to calculate the tire rubber content.

Trips were organized to deliver the XRF guns to districts and conduct training using a district's delivered XRF gun.

3.3. Training Program

Each district training program involved delivering the XRF gun [with unique serial numbers (SN)] and other consumable materials (sample cups and mylar film) and watching the video. Then district personnel demonstrated pouring a sample in a sample cup (if the district had an oven and binder available) and applying the mylar film. CTR staff had several pre-made samples for testing (in the interest of time) and the district personnel demonstrated running XRF on these samples and putting the zinc content in the calibration spreadsheet to calculate tire rubber content.

On May 19, 2023, CTR staff traveled to the Brownwood District. They delivered an XRF gun, test stand, and testing consumables to district personnel and conducted training. Brownwood received XRF SN 133080

On June 1, 2023, CTR staff traveled to the Lufkin District. They delivered an XRF gun, test stand, and testing consumables to district personnel and conducted training. Lufkin received XRF SN 200125

On June 5, 2023, CTR staff traveled to the Odessa District. They delivered an XRF gun, test stand, and testing consumables to district personnel and conducted training. Odessa received XRF SN 200129.

CTR already had XRF SN 97393.

MTD already had XRF SN 100062

3.4. Correction and Update of Calibration Standards and Spreadsheet

Soon after distribution several districts reported what they believed to be significant errors in the TR content of some samples. Upon investigation, at least one supplier had made mistakes in mixing the calibration standards supplied to CTR. This necessitated having some new standards shipped to CTR. In addition, calibration samples were acquired for another supplier that had not submitted standards previously.

These new standards were shipped to the three districts and they and CTR retested them. A new calibration spreadsheet was developed with the new calibration standards and distributed to the districts.

Calibration data was plotted for all XRF SN – Binder Supplier combinations to determine the best line fit for the data, by XRF SN and Binder Supplier. An example is shown in Figure 1.

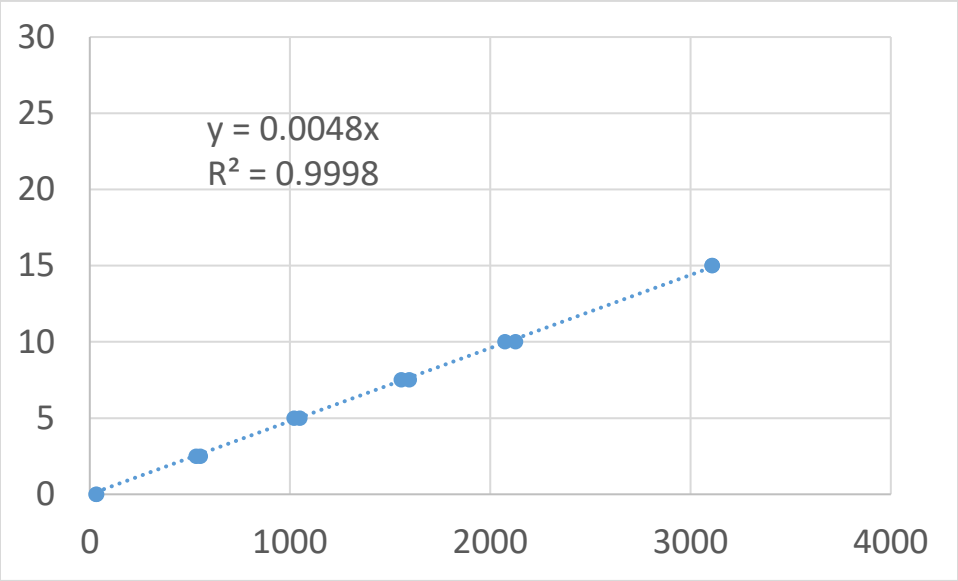

Figure 1. Calibration Plot for XRF SN = 97393 and Binder Supplier = Wright Asphalt

Table 1 shows the summary of calibration slopes determined for each XRF SN and Binder Supplier combination. The spreadsheet allows the selection of XRF Serial Number (each district has one), the binder supplier, and the zinc reading (ppm) from that XRF gun for a sample from the chosen supplier. The spreadsheet uses the zinc reading and multiplies it by the slope of the calibration curve for that XRF gun – Binder Supplier combination to calculate the TR percentage of that sample. Martin Batch 1 was replaced by Martin Batch 2

Table 1. Calibration Slope for XRF SN and Binder Supplier.

XRF SN	Wright	Polyco	Ergon	Jebro Waco	Martin	Valero Houston
200129	0.00488	0.00233	0.00434	0.00295	0.00271	0.0046
133080	0.00474	0.00239	0.00427	0.00295	0.00272	0.00446
200125	0.0049	0.0023	0.00432	0.00294	0.00273	0.00448
97393	0.0048	0.00273	0.00435	0.00292	0.0026	0.00445
100062	0.00500	0.00288	0.00454	0.00307	0.00279	0.00466

Chapter 4. Develop Round Robin

This Chapter describes the work performed for Task 5, "Develop Round Robin."

After Task 4 was completed and calibration standards were corrected for those suppliers that had made incorrect calibration samples, samples were analyzed for a round robin. Five blind samples at different TR concentrations were distributed to districts for analysis. These were from three different binder suppliers and were developed in the CTR lab. Samples were sent to all five labs and each sample was sample was evaluated twice. The round-robin data is shown in Table 2.

Table 2. Blind Round-Robin Samples

MATERIALS	Percentage of Tire Rubber [%]					Average	StDev
	CTR Lab 1	Brownwood Lab 2	Lufkin Lab 3	Odessa Lab 4	MTD Lab5		
Supplier 1 - Blind A - S1	15.2	15.3	14.9	15.3	15.2	15.17	0.18
Supplier 1 - Blind A - S2	15.2	15.4	15.2	14.8	15.2		
Supplier 1 - Blind B - S1	5.0	5.0	4.9	5.0	5.0	4.91	0.11
Supplier 1 - Blind B - S2	4.8	4.9	4.8	4.7	5.0		
Supplier 2 - Blind #1 - S1	4.8	4.9	n/a	4.9	4.9	4.86	0.05
Supplier 2 - Blind #1 - S2	4.8	4.9	n/a	4.8	4.9		
Supplier 3 - Blind #2 - S1	5.0	5.0	n/a	5.0	4.8	4.95	0.18
Supplier 3 - Blind #2 - S2	5.0	5.0	n/a	5.2	4.6		
Supplier 1 - Blind #3 - S1	5.6	5.5	n/a	5.5	5.6	5.55	0.05
Supplier 1 - Blind #3 - S2	5.6	5.5	n/a	5.5	5.6		

Since each asphalt sample was run twice, each measurement will be treated as a sample we have either 10 samples or 8 samples (Lufkin's XRF instrument failed, and they could not analyze the last three unknown samples). Using a two-tailed, 95% t-distribution:

For degrees of freedom (df) = number of observations (10) minus 1 = 9. From tabulated t-statistics, t = 2.262. Then the calculated 95% confidence intervals is:

$\overline{X} + \pm 2.262\ (\sigma/\sqrt{n})$, and

For degrees of freedom (df) = number of observations (8) minus 1 = 7. From tabulated t-statistics, t = 2.365. Then the calculated 95% confidence intervals is:

$\overline{X} + \pm 2.365\ (\sigma/\sqrt{n})$

Then applying these to the data, the variation can be estimated as:

Blind A = 15.17 +/- 0.13.

Blind B = 4.91 +/- 0.08

Blind #1 = 4.86 +/- 0.04

Blind #2 = 4.95 +/- 0.14

Blind #3 = 5.55 +/- 0.04

Some materials produce more repeatable results than others, and is likely dependent on the base asphalt and type of tire rubber used. Any changes would require developing a new calibration curve.

Chapter 5. Summary/Conclusions

This chapter provides a summary of the work performed and conclusions.

Work performed on this project included:

- CTR purchased three portable XRF analyzers and their operation was verified in the CTR lab.
- Calibration standards were acquired to develop a calibration spreadsheet for all instruments. Calibration is instrument specific.
- CTR revised test procedure Tex 553-C, "Determination of Re-Refined Engine Oil Bottoms, Polyphosphoric Acid, and Tire Rubber Content in Asphalt using X-Ray Fluorescence Spectroscopy" to improve the test method and allow for the use of portable XRF in the field.
- A training program (video) was developed for the operation of the XRF analyzer to determine TR content in asphalt according to Tex-553-C.
- Three TxDOT Districts were supplied with a portable XRF analyzer and trained in its operation.
- New calibration standards were acquired for some suppliers to modify the calibration spreadsheet, which was then supplied to the three districts to replace the original spreadsheet.
- A round robin on a blind sample from one producer showed that the accuracy of the output (with rounding up and only calculating to the nearest 0.1% TR) to be approximately +/- 0.1 % TR to +/- 0.2% TR. This equates to the multi-lab D2S that is published by AASHTO to indicate the repeatability between labs. Within lab accuracy is generally higher. Usually, thirty 30 data points or more are desired to get a better standard deviation.

Measurement of TR content can be accomplished with a portable XRF analyzer. One must use a calibration model unique for each instrument (XRF gun), using standards at various TR contents, that accounts for each base asphalt (producer) and TR combination that will be supplied. Any change in the source of the ingredients will necessitate developing a new calibration for that material.

Appendix A – Proposed Tex-553-C

Test Procedure for

DETERMINATION OF RE-REFINED ENGINE OIL BOTTOMS, POLYPHOSPHORIC ACID, TIRE RUBBER, AND TRICHLOROETHYLENE CONTENT IN ASPHALT BINDERS USING X-RAY FLUORESCENCE SPECTROSCOPY

TxDOT Designation: Tex-553-C

Effective Date: Draft

1. SCOPE

1.1 This test method covers the procedure for determining the Re-refined Engine Oil Bottoms (REOB), Polyphosphoric Acid (PPA), and Tire Rubber (TR) content in asphalt binder samples using X-Ray Fluorescence (XRF) Spectroscopy. In the case of obtaining asphalt binder sample from extraction process using Trichloroethylene (TCE), this test procedure can also be implemented to quantify the effect of TCE concentration in the asphalt binder residue on its mechanical properties such as stiffness and performance grade (PG).

1.2 Calibration curves are created for each additive using different asphalt binders and measuring the intensity of elements including calcium (Ca), zinc (Zn), molybdenum (Mo), phosphorous (P), silicon (Si), sulfur (S), vanadium (V), and chlorine (Cl) as the amount of additive added to the asphalt binders is varied.

1.3 In unknown samples, the concentration of all the elements necessary to estimate REOB, PPA, TR, and TCE content; can be measured in one analysis using XRF. However, each additive content to be estimated should have separate calibration curves as outlined in the method.

1.4 Using XRF Spectrometer to measure additive content in asphalt binders requires passing safety and technical training and following the test procedure provided in this document.

1.5 It is highly recommended to always wear a dosimetry finger ring on the hand that will be closest to the device, when using a handheld XRF, to quantify potential radiation exposure. Follow all radiation safety and safety precautions set out by the X-Ray instrument manufacturer and the testing facility.

1.6 The values given in parentheses (if provided) are not standard and may not be exact mathematical conversions. Use each system of units separately. Combining values from the two systems may result in nonconformance with the standard.

2. MATERIALS

2.1 Tapered Aluminum Briquetting Cup (Pellet Cups) with a minimum diameter of 25 mm and a minimum height of 8 mm for presenting samples to the XRF.

2.2 Oven capable of maintaining temperature at 160 ± 5 °C.

2.3 Mylar Thin-Films with 2.5 micrometer thickness and 6.35 cm diameter (precut circles).

2.4 XRF Analyzer; handheld, benchtop, or floor top.

Note 1 - If floor or benchtop XRF is used, the instrument will need to be able to operate in a helium atmosphere; otherwise, the sample may be pulled from the sample cup.

2.5 Class G2 Balance (according to Tex-901-K), with a capacity of 2,000 g.

2.6 Sample mixing can, 1-quart (1-liter).

2.7 Heating Mantle or Heating System, that can maintain the blending temperature of asphalt binder at 160 ± 5°C of a 1-quart (1-liter) sample mixing can.

Note 2 - For TR additive, the blending temperature may be increased up to 180°C.

2.8 Plastic squeeze bottle or syringe for adding liquid additives.

2.9 High Shear Mixer, capable of mixing 1-quart (1-liter) can of asphalt binder.

2.10 Various spatulas and sample holders for asphalt and additives

3. SAMPLE PREPARATION FOR XRF ANALYSIS

3.1 Prepare containers (pellet cups) to pour the samples:

- make sure they are new, dry, clean, and dust-free, and
- label outside wall and bottom of pellet cups.

3.2 Heat the asphalt binder in an oven set at 160 ± 5 °C until it becomes liquid enough to be easily poured.

3.3 After heating, stir the sample with a metal spatula to ensure the sample is homogenized.

3.4 Pour the sample into an aluminum pellet cup. Completely fill the cup without overflowing or having excess material on top of the container.

3.5 If needed, strike off the sample with a hot spatula to remove excess materials from the top and to ensure a flat surface for testing.

3.6 Allow the sample to cool to room temperature for 30 ± 5 min. To avoid contamination, cover the samples and prevent any contact with the surface of the sample.

3.7 Once the sample has cooled to room temperature, place a clean Mylar Thin-Film over the binder sample, avoiding air entrapment (bubble) and wrinkling of the film.

3.8 If necessary, stretch the film to remove any air bubble or wrinkle. If some air bubbles or wrinkles remain on the surface of the specimen, avoid these spots when conducting the test, as these could affect XRF readings.

4. DEVELOPING CALIBRATION CURVES

4.1 Use the XRF to develop individual calibration curves using blends of known concentration of Re-refined Engine Oil Bottoms (REOB), Polyphosphoric Acid (PPA), or Tire Rubber (TR). Use concentrations both above and below the limit of interest to allow for interpolation rather than extrapolation.

4.1.1 For REOB, analyze binder samples for calcium (Ca), zinc (Zn), molybdenum (Mo), sulfur (S), and vanadium (V). Since current specifications do not allow REOB, create standards for 0, 1, 2, 3, 5, and 10% REOB. Since binders and REOB may both contain S and V, use binders with varying S and V contents; such that multiple sets of binders can be used to generate calibration curves. For example, set 1 has a S and V content of xs and xv while set 2 has a S and V content of ys and yv.

4.1.2 For PPA, analyze binder samples for phosphorus (P). Since current specifications allow a maximum of 0.5% PPA, blend standards for 0, 0.1, 0.25, 0.5, 0.75, and 1.0% PPA.

4.1.3 For TR, analyze the binder sample for zinc (Zn) and molybdenum (Mo). Since current specifications require a minimum of 5% TR, create standards for 1, 3, 5, 8, and 10 % TR.

4.1.4 In order to quantify the effect of TCE on the PG grade of asphalt binders, see Section 6.

Note 3 - Calibration curves are asphalt binder source and XRF device dependent.

4.2 Blend a Calibration Standard.

4.2.1 Heat sufficient asphalt binder in a single can in an oven set at 160 ± 5°C for the minimum time necessary for it to be sufficiently fluid to pour. Avoiding overheating the material.

4.2.2 Thoroughly stir the asphalt binder with a clean metal spatula and pour xB grams of the heated binder (approximately of 400 g) into a 1-quart mixing can.

Note 4 – Approximately 400 g of asphalt is sufficient for REOB and TR, while approximately 700 g of asphalt is suggested for PPA because of the small amounts of PPA needed.

4.2.3 Immediately transfer the sample to the mixing assembly comprising a heating mantle and a high shear mixer and heat to a mixing temperature of 160 ± 5°C.

For TR additive, the mixing temperature may be increased up to 180°C.

4.2.4 Determine the amount of additive needed to blend the calibration concentration desired. (Additive concentration is based on the weight of the blend.)

Use the formula:

$xA = (AC \cdot xB) / (100 - AC)$

Where:

xA = weight of additive to be added for xB weight of binder

xB = weight of binder used

AC = percentage of additive to be used (i.e., 0.1, 1.0, 5.0, etc)

4.2.5 While maintaining the binder temperature at the mixing temperature, gradually add xA grams of the additive, such that the additive content of the mixture becomes the percent by total weight for the calibration standard, i.e., xB = 380 g binder and xA = 20 g for a 5% standard.

Note 5 –Add liquid additives by the drop from a squeeze bottle or syringe, and back weigh the bottle or syringe for the weight of additive used. For solid polymers, weigh the appropriate amount into a container and add about a third of the material at a time, allowing the additive to disperse for a few seconds between additions.

4.2.6 Blend the mixture with a high shear mixer for a minimum of 30 minutes. TR additive may require up to 2 hours of blending to ensure a smooth, uniform blend.

4.2.7 Repeat 4.2.1 through 4.2.6 to prepare all standard at the concentrations for the additive of interest.

4.3 Generate calibration curves.

4.3.1 Prepare XRF samples for analysis according to Section 3.

4.3.2 Use the XRF according to the manufacturer's instructions, analyze the standards for the elements of interest according to the additive of interest shown in Section 4.1.

4.3.3 Create a plot for each additive for the elements of interest using data from the appropriate series of standards. The XRF result should be on the y-axis and the percentage of additive in the standard on the x-axis.

4.3.4 Determine the equation of the best fit line for each element.

5. ESTIMATING ADDITIVE CONTENT OF AN UNKNOWN SAMPLE

5.1 Prepare a sample for presentation to the XRF according to Section 3.

5.2 Use the XRF to analyze the unknown sample for the additive of interest for the presence of the elements from Section 4.1.

5.3 Use the additive element calibration curve or best-fit equation to estimate the additive concentration of the unknown sample.

5.4 Report the estimated additive content of the unknown sample.

6. QUANTIFYING THE EFFECT OF TCE ON PG OF ASPHALT BINDERS

6.1 Use this test procedure to quantify the effect of Trichloroethylene (TCE) remaining in the asphalt binder residue from the extraction process on its mechanical properties; e.g., *stiffness* and continuous *high temperature performance grade* (High Temp. PG).

Note 6 - Samples are prepared by extracting asphalt binder as described in test procedure Tex-211-F, Abson process.

6.2 Developing Calibration or Correction Curves.

6.2.1 Virgin binder should be extracted, and the extraction process stopped at various times to measure:

- the continuous high temperature PG of the extracted binder using a DSR, and
- the amount of Cl in the sample using XRF using samples prepared according to Section 3.

6.2.2 From testing according to Sections 3 and 4, plot the continuous high temperature PG of the samples on the *x*-axis and the corresponding Cl content or intensity measurements on the *y*-axis.

6.2.3 Determine the equation of the best fit line for the data.

6.3 Testing an Unknown sample.

6.3.1 Determine the Cl content in the sample using XRF according to the manufacturer's instructions.

6.3.2 Measure the continuous high temperature PG of the extracted binder using a Dynamic Shear Rheometer (DSR).

6.3.3 Use the calibration curve or best fit equation to estimate the adjusted continuous high temperature PG of the sample for the binder with no TCE.

Note 7 - For accuracy, the above procedure should be used to generate separate plots for asphalt binders with different performance grades.

Appendix B – Existing Tex-553-C

Test Procedure for

DETERMINATION OF RE-REFINED ENGINE OIL BOTTOMS, POLYPHOSPHORIC ACID, AND TIRE RUBBER CONTENT IN ASPHALT BINDERS USING X-RAY FLUORESCENCE SPECTROSCOPY

TxDOT Designation: Tex-553-C

Effective Date: February 2022

1. SCOPE

This test method covers the procedure for determining the re-refined engine oil bottoms (REOB), Polyphosphoric Acid (PPA), and Tire Rubber (TR) content in asphalt binder samples using X-Ray Fluorescence (XRF) Spectroscopy. In the case of obtaining asphalt binder sample from extraction process using Trichloroethylene (TCE), this test procedure can also be implemented to quantify the effect of TCE concentration in the asphalt binder residue on its mechanical properties such as stiffness and performance grade (PG).

1.1 Calibration curves are created for each additive using different asphalt binders and measuring the intensity of elements including calcium (Ca), zinc (Zn), molybdenum (Mo), phosphorous (P), silicon (Si), sulfur (S), vanadium (V), and chlorine (Cl) as the amount of additive added to the asphalt binders is varied.

1.2 In unknown samples, the concertation of all the elements necessary to estimate REOB, PPA, TR, and TCE content; can be measured in one analysis using XRF. However, each additive content to be estimated should have separate calibration curves as outlined in the method.

1.3 Using XRF Spectrometer to measure additive content in asphalt binders requires passing safety and technical trainings and follow the test procedure provided in this document.

1.4 It is highly recommended to always wear a dosimetry finger ring on the hand that will be closest to the device, when using a handheld XRF, to quantify potential radiation exposure. Follow all radiation safety and safety precautions set out by the X-Ray instrument manufacturer and the testing facility.

1.5 The values given in parentheses (if provided) are not standard and may not be exact mathematical conversions. Use each system of units separately. Combining values from the two systems may result in nonconformance with the standard.

2. MATERIALS

2.1 Tapered Aluminum Briquetting Cup (Pellet Cups) with a minimum diameter of 25 mm and a minimum height of 8 mm.

2.2 Spatula with approx. 15.2 -20.3 cm blade and wooden or PVC handle

2.3 Oven capable of maintaining temperature at 135 ± 5 °C for 3 hr.

2.4 Mylar Thin-Films with 2.5 micrometer thickness and 6.35 cm diameter (precut circles).

2.5 XRF Analyzer; handheld, benchtop, or floor top.

Note 1 - If floor or benchtop XRF is used, the instrument will need to be able to operate in a helium atmosphere; otherwise, the sample may be pulled from the sample cup.

2.6 Balance, with a capacity of 2,000 g readable to 0.1g.

2.7 Heating Mantle, that can maintain the blending temperature of asphalt binder at 135 ± 5°C.

2.8 High Shear Mixer, capable of mixing 1 pt. to 1 gal. can of asphalt binder.

3. SAMPLE PREPARATION

3.1 Prepare containers (pellet cups) to pour the samples:

- make sure they are new dry, clean, and dust-free, and
- label outside wall and bottom of pellet cups.

3.2 The asphalt binder should be heated in an oven set at a temperature lower than 140°C until it becomes liquid enough to be easily poured.

3.3 After heating, slowly stir the sample with a clean and dry wooden tongue depressor or a metal trimmer and make sure that the sample is well homogenized.

3.4 Pour the sample into an aluminum pellet cup; completely fill the cup without overflowing or having excess material on top of the container.

3.5 If needed, the sample is then struck off with a hot spatula to remove excess materials from the top and to ensure a flat surface for testing.

3.6 Allow the sample to cool to room temperature for almost 30 ± 5 min. To avoid contamination, cover the samples and prevent any contact with the surface of the sample.

3.7 Once the sample has cooled to room temperature and right before testing, place a clean Mylar thin-film over the binder sample, avoiding air entrapment (bubble) and wrinkle of the film.

3.8 If necessary, stretch the film to remove any air bubble or wrinkle. If some air bubbles or wrinkles remain on the surface of the specimen, avoid these spots when conducting the test; as these could affect XRF readings.

4. ESTIMATING REOB CONTENT

To estimate the REOB content of an unknown sample, first calibration curves should be developed based on the instructions in Section 4.4 Then following the instructions in Sections 4.1 through 4.3, REOB content can be estimated.

Note 2 - Calibration curves are asphalt binder source and XRF device dependent.

4.1 Use the XRF to analyze the binder sample for calcium (Ca), zinc (Zn), molybdenum (Mo), sulfur (S), and Vanadium (V) according to the manufacturer's instructions.

Note 3 - The test results are not valid if the spot chosen on the surface of the sample for evaluation is too close to the edge of the container. Make every effort to run the test at the central portion of the sample. This applies to samples tested for REOB, PPA, TR and TCE.

4.2 Based on the analysis of the unknown sample, determine which calibration set is closest in S and V content using a plot of the standards with the S result on the y-axis and the V result on the x-axis.

4.3 Use the calibration curve for the closest matching set determined from 4.2 to estimate the % REOB present in the unknown sample.

4.3.1 Compare the calculated REOB content based on each element and verify that there is some agreement between Ca, Zn, and Mo. Use the Student t test, as outlined in 7.1.1 through 7.1.3 of ASTM E 178, to determine if any results are outliers.

4.3.2 Once any outliers have been removed, average the remaining results to estimate REOB content of the sample.

4.4 Developing Calibration Curves

Binders with varying S and V contents should be used along with commonly used REOB additions; such that multiple sets of binders can be used to generate calibration curves. For example, set 1 has a S and V content of x_S and x_V while set 2 has a S and V content of y_S and y_V.

4.4.1 Heat 1500 ± 100 g of asphalt binder in a single can at a temperature of 135 ± 5°C in an oven until it becomes fully liquid while avoiding overheating the material.

4.4.2 After thoroughly stirring the asphalt binder with a clean and dry wooden tongue depressor or a metal trimmer, pour x_B grams of the heated binder (a minimum of 700 g) into a mixing container.

4.4.3 Immediately transfer the sample to the mixing assembly comprising a heating mantle and a high shear mixer.

4.4.4 While maintaining the binder temperature at 135 ± 5°C, gradually add x_R grams of the REOB, such that the REOB content of the mixture becomes 5% by total weight, i.e., x_B = 760 g binder and x_R = 40 g REOB.

4.4.5 Blend the mixture with a high shear mixer for 30 min.

4.4.6 Repeat 4.4.1 through 4.4.5 to prepare standards that contain 10%, 20%, and 25% REOB.

4.4.7 Analyze the standards for calcium (Ca), zinc (Zn), molybdenum (Mo), sulfur (S), and vanadium (V) using XRF according to the manufacturer's instructions.

4.4.8 Create a plot for each element (Ca, Zn, Mo) analyzed by XRF. The XRF result should be on the y-axis and the % REOB in the standard on the x-axis.

4.4.9 Determine the equation of the best fit line for each element.

5. ESTIMATING PPA CONTENT

To estimate the PPA content of an unknown sample, first calibration curves should be developed following the instructions in Section 5.3. Then following the instructions in Sections 5.1 – 5.2, PPA content can be estimated.

Note 4 - Calibration curves are asphalt binder source and XRF device dependent.

5.1 Use the XRF to analyze the binder sample for phosphorus (P) according to the manufacturer's instructions.

5.2 Use the calibration curve generated in 5.3 to estimate the PPA content of an unknown sample.

5.3 Developing Calibration Curves

5.3.1 Heat 1500 ± 100 g of asphalt binder in a single can at a temperature of 135 ± 5°C in an oven until it becomes fully liquid while avoiding overheating the material.

5.3.2 After thoroughly stirring the asphalt binder with a clean and dry wooden tongue depressor or a metal trimmer, pour x_B g of the heated binder (a minimum of 700 g) into a mixing container.

5.3.3 Immediately transfer the sample to the mixing assembly comprising a heating mantle and a high shear mixer.

5.3.4 While maintaining the binder temperature at 135 ± 5°C, gradually add x_P g of the PPA, such that the PPA content of the mixture becomes 0.25% by total weight, i.e., x_B = 798 g binder and x_P = 2 g PPA.

5.3.5 Blend the mixture with the high shear mixer for 30 min.

5.3.6 Repeat 5.3.1 through 5.3.5 to prepare standards that contain 0.5%, 0.75%, 1%, 1.25%, 1.5%, and 1.75% PPA.

5.3.7 Use the XRF to analyze the standards for phosphorus (P) according to the manufacturer's instructions.

5.3.8 Create a plot for P analyzed by XRF. The XRF result should be on the y-axis and the % PPA in the standard on the x-axis.

5.3.9 Determine the equation of the best fit line.

6. ESTIMATING TR CONTENT

To estimate the TR content of an unknown sample, first calibration curves should be developed following the instructions in Section 6.3. Then following the instructions in Sections 6.1 through 6.2, TR content can be estimated.

Note 5 - Calibration curves are asphalt binder source and XRF device dependent.

6.1 Use the XRF to analyze the binder sample for zinc (Zn) and molybdenum (Mo) according to the manufacturer's instructions.

6.2 Use the calibration curve generated, following Section 6.3, to estimate the TR content of an unknown sample.

Note 6 - If no molybdenum (Mo) is found in the sample, then the measured zinc (Zn) concentration is solely from the addition of tire rubber.

6.3 Developing Calibration Curves

6.3.1 Heat 1500 ± 100 g of asphalt binder in a single can at a temperature of 135 ± 5°C in an oven until it becomes fully liquid while avoiding overheating the material.

6.3.2 After thoroughly stirring the asphalt binder with a clean and dry wooden tongue depressor or a metal trimmer, pour x_B g of the heated binder (a minimum of 700 g) into a mixing container.

6.3.3 Immediately transfer the sample to the mixing assembly comprising a heating mantle and a high shear mixer.

6.3.4 While maintaining the binder temperature at 135 ± 5°C, gradually add x_T g of the TR such that the TR content of the mixture becomes 5% by total weight, i.e., x_B = 760 g binder and x_T = 40 g TR.

6.3.5 Blend the mixture with the high shear mixer for 60 min. while the sample sits on a hot plate.

6.3.6 Repeat 6.3.1 through 6.3.5 to prepare standards that contain 10%, 15%, and 20% TR.

6.3.7 Use the XRF to analyze the standards for zinc (Zn) and molybdenum (Mo) according to the manufacturer's instructions.

6.3.8 Create a plot for each element analyzed by XRF. The XRF result should be on the y-axis and the % TR in the standard on the x-axis.

6.3.9 Determine the equation of the best fit line for each element.

7. QUANTIFYING THE EFFECT OF TCE ON PG OF ASPHALT BINDERS

In case of obtaining asphalt binder sample from extraction process using Trichloroethylene (TCE), this test procedure can be implemented to quantify the effect of TCE remaining in the asphalt binder residue on its mechanical properties; e.g., *stiffness* and *high temperature of performance grade* (High Temp. PG). This would be helpful in accounting for softening effect of TCE remaining in the extracted asphalt binder residues, leading to a correct or adjusted estimation of asphalt binders High Temp. PG. To this end, first calibration or correction curves should be developed following the instructions in Section 7.4. Then following the instructions in Sections 7.1 through 7.3, adjusted High Temp. PG of the asphalt binder, with no TCE, can be estimated.

Note 7 - Samples are prepared by extracting asphalt binder as described in test procedure Tex-211-F, Abson process.

Note 8 - Calibration curves are asphalt binder source and XRF device dependent.

7.1 Determine the Cl content in the sample using XRF according to the manufacturer's instructions.

7.2 Measure the continuous high temperature PG of the extracted binder using a Dynamic Shear Rheometer (DSR).

7.3 Estimate the adjusted continuous high temperature PG of the sample using the equation obtained in 7.4.3 and considering the binder with no TCE.

7.4 Developing Calibration or Correction Curves

7.4.1 Virgin binder should be extracted, and the extraction process stopped at various times to measure:

- the continuous high temperature PG of the extracted binder using a DSR, and
- the amount of Cl in the sample using XRF according to the manufacturer's instructions.

7.4.2 Plot the continuous high temperature PG of the samples from 7.4.1 on the *x*-axis and the corresponding Cl content or intensity measurements on the *y*-axis.

7.4.3 Determine the equation of the best fit line for the data.

Note 9 - For accuracy, the above procedure should be used to generate separate plots for asphalt binders with different performance grades.

Appendix C – Tex-553-C Approved for Posting

Test Procedure for

DETERMINATION OF RE-REFINED ENGINE OIL BOTTOMS, POLYPHOSPHORIC ACID, TIRE RUBBER CONTENT, AND TRICHLOROETHYLENE IN ASPHALT BINDERS USING X-RAY FLUORESCENCE SPECTROSCOPY

TxDOT Designation: Tex-553-C

Effective Date: September 2023

1. SCOPE

1.1 This test method covers the procedure for determining the re-refined engine oil bottoms (REOB), Polyphosphoric Acid (PPA), and Tire Rubber (TR) content in asphalt binder samples using X-Ray Fluorescence (XRF) Spectroscopy. In the case of obtaining asphalt binder sample from extraction process using Trichlorcethylene (TCE), this test procedure can also be implemented to quantify the effect of TCE concentration in the asphalt binder residue on its mechanical properties such as performance grade (PG).

1.2 Calibration curves are created for each additive using different asphalt binders and measuring the intensity of elements including calcium (Ca), zinc (Zn), molybdenum (Mo), phosphorous (P), sulfur (S), vanadium (V), and chlorine (Cl) as the amount of additive added to the asphalt binders is varied.

1.3 In unknown samples, the concertation of all the elements necessary to estimate REOB, PPA, TR, and TCE content; can be measured in one analysis using XRF. However, each additive content to be estimated should have separate calibration curves as outlined in the method.

1.4 Using XRF Spectrometer to measure additive content in asphalt binders requires passing safety and technical trainings and follow the test procedure provided in this document.

1.5 It is highly recommended to always wear a dosimetry finger ring on the hand that will be closest to the instrument, when using a handheld XRF, to quantify potential radiation exposure. Follow all radiation safety and safety precautions set out by the X-Ray instrument manufacturer and the testing facility.

1.6 The values given in parentheses (if provided) are not standard and may not be exact mathematical conversions. Use each system of units separately. Combining values from the two systems may result in nonconformance with the standard.

2. MATERIALS

2.1 XRF Analyzer; handheld, benchtop, or floor top.

Note 1 - If floor or benchtop XRF is used, the instrument will need to be able to operate in a Helium atmosphere; otherwise, the sample may be pulled from the sample cup.

2.2 Tapered Aluminum briquetting cup (Pellet Cups) with an approx. diameter of 25 mm and height of 8 mm.

2.3 XRF manufacturer-recommended precut thin polymer films such as the Mylar films with 2.5 micrometer thickness and 6.35 cm diameter (precut circles).

2.4 Various wooden or metal spatulas and sample holders for asphalt binder and additives.

2.5 Plastic squeeze bottle or syringe for adding liquid additives.

2.6 Oven capable of maintaining temperature at least up to 175°C.

2.7 Class G2 Balance (according to Tex-901-K), with a capacity of 2,000 g.

2.8 Metal cans, 1-quart. to 1-gal.

2.9 Heating Mantles, that can maintain the blending temperature at ± 5°C of the target value.

2.10 High Shear Mixer, capable of blending 1-quart. to 1-gal. can of asphalt binder.

3. SAMPLE PREPARATION FOR ESTIMATING REOB, PPA AND TR CONTENTS

3.1 Prepare containers (pellet cups) to pour the samples:

- make sure they are new dry, clean, and dust-free, and
- label outside wall and bottom of pelle: cups.

3.2 Heat the asphalt binder in an oven at 163 ± 5 °C until it becomes liquid enough to be easily poured.

Note 2 – For high TR content, the blending temperature may be increased up to 175°C.

3.3 Stir the sample with a clean and dry spatula and make sure that the sample is well homogenized.

3.4 Pour the sample into an aluminum pellet cup; completely fill the cup without overflowing or having excess material on top of the container.

3.5 If needed, strike off the sample with a hot spatula to remove excess materials from the top and to ensure a flat surface for testing.

3.6 Allow the sample to cool to room temperature for almost 30 ± 5 min. To avoid contamination, cover the samples and prevent any contact with the surface of the sample

3.7 Once the sample has cooled to room temperature and before testing, place a clean XRF manufacturer-recommended film (such as Mylar thin film) over the asphalt binder sample, avoiding air entrapment (bubble) and wrinkle of the film.

3.8 If necessary, stretch the film to remove any air bubble or wrinkle. If some air bubbles or wrinkles remain on the surface of the specimen, avoid these spots when conducting the test as these could affect XRF readings.

4. ESTIMATING REOB, PPA OR TR CONTENT

4.1 Use the XRF to develop individual calibration curves using blends of known concentration of REOB, PPA, or TR. Use concentrations both above and below the limit of interest to allow for interpolation rather than extrapolation.

4.1.1 For REOB, prepare calibration standards with at the minimum 0.0, 5.0, 15.0 and 25.0% REOB and analyze Ca, Mo, Zn, S, and V contents. Since asphalt binders and REOB may both contain S and V, use asphalt binders with varying S and V contents; such that multiple sets of asphalt binders can be used to generate calibration curves. For example, set 1 has a S and V content of x_A and x_V while set 2 has a S and V content of y_A and y_V.

4.1.2 For PPA, prepare calibration standards with a the minimum 0.00, 0.25, 0.50, 0.75, and 1.00% PPA and analyze S, V and P content.

4.1.3 For TR, prepare calibration standards with at the minimum 0.0, 1.0, 2.5, 5.0, 7.5, 10.0, 15.0 and 25.0% TR and analyze S, V and Zn content.

Note 3 - Calibration curves are asphalt binder source, additive source, and XRF instrument dependent. It is highly recommended to prepare calibration standards using multiple asphalt binder and additive sources. When there is a change in XRF instrument, the same calibration standards can be used to create calibration curves for that instrument.

4.2 **Prepare a Calibration Standard.**

4.2.1 Heat 1500 ± 100 g of asphalt binder in a single can at a temperature of 163 ± 5°C in an oven until it becomes fully liquid while avoiding overheating the material.

4.2.2 Thoroughly stir the asphalt binder with a clean and dry spatula and pour x_B grams of the heated asphalt binder (a minimum of 400 g) into a blending can.

Note 4 – Approximately 400 g of asphalt binder is sufficient for REOB, while higher than 400 g of asphalt binders might be added for PPA and TR to allow better blending.

4.2.3 Immediately transfer the sample to the blending assembly comprising a heating mantle and a high shear mixer and maintain a blending temperature of 163 ± 5°C for REOB and PPA blends. For TR additive, the blending temperature may be increased up to 175°C.

4.2.4 Determine the amount of additive needed to prepare calibration standard at desired concentration. (Additive concentration is based on the weight of the blend.)

Use the formula:

$$x_A = x_B \cdot p_A / (100 - p_A)$$

Where:

x_A = weight of additive to be added,

x_B = weight of asphalt binder, and

p_A = desired percentage of additive (such as 0.0, 5.0, 15.0, and 25.0% REOB).

4.2.5 While maintaining the blending temperature, gradually add x_A grams of the additive of interest, such that the additive content of the mixture meets the target percent by total weight, i.e., x_B = 760 g of asphalt binder and x_A = 760 x 5 / 95 = 40 g of additive for a 5.0% calibration standard.

Note 5 –For liquid additives, add them by the drop from a squeeze bottle or syringe, and back weigh the bottle or syringe for the weight of additive used. For solid polymers, weigh their appropriate amount into a container and add about a third of the material at a time, allowing the additive to disperse for a few seconds between additions.

4.2.6 Blend the mixture with a high shear mixer for a minimum of 30 minutes and the sample is smooth and homogeneous. TR may require up to 2 hours of blending to ensure a smooth, uniform blend.A

4.2.7 Repeat 4.2.1 through 4.2.6 to prepare standards at the concentrations of interest (such as 0.0, 5.0, 15.0, and 25.0% REOB).

4.3 **Generate calibration curves.**

4.3.1 Prepare XRF samples for analysis according to Section 3.

4.3.2 Analyze the standards for the elements of interest using XRF according to the manufacturer's instructions.

4.3.3 Create a plot for each element of interest (such as Ca, Zn, Mo in the case of REOB) using data from the appropriate series of standards analyzed by XRF. The XRF result should be on the y-axis and the percentage of additive in the standard on the x-axis.

4.3.4 Determine the equation of the best fit line for each element.

5. ESTIMATING REOB, PPA OR TR CONTENT

5.1 Prepare a sample with unknown percentage of additive according to Section 3.

5.2 Use the XRF to analyze the asphalt binder sample for all elements of interest (S, V, Mo, Ca, Zn, P).

Note 6 - The test results are not valid if the spot chosen on the surface of the sample for evaluation is too close to the edge of the container. Make every effort to run the test at the central portion of the sample. This applies to samples tested for REOB, PPA, and TR.

5.3 Use the calibration set for the closest matching set determined from 4.1 to estimate the percent of additive of interest in the unknown sample.

5.3.1 If the source of asphalt binder is known, use the calibration set corresponding to that source.

5.3.2 If the source of asphalt binder is unknown and calibration sets with multiple sources of asphalt binders and additives are available, determine which calibration set is closest in S and V contents using a plot of the standards with the S result on the y-axis and the V result on the x-axis.

5.4 Compare the percentages of additives in the unknown sample calculated based on calibration curve of each element of interest and verify that there is some agreement between each other if there are more than one element of interest (such as Ca, Mo, Zn for REOB). Use a valid statistical analysis such as the student t-test as outlined in ASTM E 178 to determine if any results are outliers.

5.5 Once any outliers have been removed, use the average of the remaining results to estimate the percentage of additive of interest in the sample. Apply if any correction factors are applicable.

5.6 Report the estimated additive content of the unknown sample to 1 decimal place.

6. QUANTIFYING THE EFFECT OF TCE ON PG OF ASPHALT BINDERS

6.1 In case of obtaining asphalt binder sample from extraction process using TCE, this test procedure can be implemented to quantify the effect of TCE remaining in the asphalt binder residue on its mechanical properties, e.g., *high temperature of performance grade* (High Temp. PG). This would be helpful in accounting for softening effect of TCE remaining in the extracted asphalt binder residues, leading to a correct or adjusted estimation of asphalt binders High Temp. PG.

Note 7 - Samples are prepared by extracting asphalt binder as described in test procedure Tex-211-F, Abson process.

6.2 **Developing Calibration or Correction Curves**

6.2.1 Extract the virgin asphalt binder, and stop the extraction process at various times to measure:

- the continuous High Temp. PG of the extracted asphalt binder using a Dynamic Shear Rheometer (DSR), and
- the Cl content in the sample using XRF according to the manufacturer's instructions.

6.2.2 Plot the continuous high temperature PG of the samples on the *x*-axis and the corresponding Cl content or intensity measurements on the *y*-axis.

6.2.3 Determine the equation of the best fit line for the data.

Note 8 - Calibration curves are asphalt binder source, additive source, and XRF instrument dependent.

6.3 **Testing an Unknown asphalt binder sample.**

6.3.1 Measure the continuous High Temp. PG of the extracted asphalt binder using a DSR.

6.3.2 Determine the Cl content in the sample using XRF according to the manufacturer's instructions.

6.3.3 Estimate and report the adjusted continuous high temperature PG of the sample (in 1 decimal place) using the equation obtained in 6.2.3 and considering the asphalt binder with no TCE.

Note 9 - For accuracy, the above procedure should be used to generate separate plots for asphalt binders with different performance grades.