Test Procedure for

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

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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.