ILLINOIS TEST PROCEDURE 601

ATR-FTIR Spectroscopy and Comparison Method

Effective Date: September 1, 2021

1.0 SCOPE

This test procedure covers the collection of infrared spectra using Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) including the parameters that shall be used to collect the spectra. The test procedure also covers the methodology to compare the IR spectra of two different samples. The degree of similarity between sample spectra can be measured by the correlation value which can be used for Quality Assurance by determining changes in the material composition.

1.1 The values stated in SI units are to be regarded as the standard.

1.2 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this procedure to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2.0 METHOD FOR COLLECTING ATR-FTIR SPECTRA

This procedure outlines a general method for obtaining the characteristic infrared spectrum of a material. A sample can be analyzed as-is (as received) or as prepared below. The universal Smart iTR accessory is an attenuated total reflectance (ATR) accessory which has a diamond crystal upon which the sample is deposited. The infrared spectrum is a result of the absorption of infrared light by molecules in the sample. The absorption is specific to the chemical bonds or functional groups that are present in the molecular structure.

2.1 Refer to the FTIR instrument manual for appropriate settings for maximum performance, and proper use.

2.2 For each material a minimum of 16 scans should be conducted to acquire the IR spectrum.

2.3 Sample Preparation/Analysis

2.3.1 For liquid samples, place enough sample to completely cover the diamond crystal of the ATR accessory.

2.3.2 For paste samples, use a spatula to cover the diamond crystal with enough sample to cover the crystal. Tap lightly on the deposited sample to ensure complete contact between the sample and the crystal.

2.3.3 For powder samples, finely grind the powder using a mortar and pestle or grinder. Attach a concave tip by screwing it to the pressure rod of the ATR apparatus. Use a spatula to put a small mound of the powder on top of the diamond crystal. Use the concave pressure tip to ensure complete contact between the powder and the crystal.

2.3.4 For films, place enough film to cover the diamond crystal. Attach a flat tip by screwing it to the pressure rod of the ATR apparatus. Use the flat pressure tip to complete the contact between the film and the crystal.

2.3.5 For asphalt, heat sample in a 135°C oven for approximately 30 minutes or until the sample is fluid enough to pour. Use a spatula to transfer enough sample to completely

cover the diamond crystal. While acquiring the spectrum, use a spatula to apply gentle pressure to the asphalt sample to ensure optimum contact with the diamond crystal. Apply pressure throughout the collection of the IR spectrum. Enough pressure should be applied to acquire the transmittance or absorbance spectrum in accordance with Section 3.1.

2.4 Instrumentation and Materials

2.4.1 Nicolet FTIR spectrometer Model 6700 or any similar instrument capable of obtaining spectrum in the mid-IR region of 600-4000 cm^{-1} range.

2.4.2 OMNIC Software or any compatible software that allows full operation of the FTIR spectrometer.

2.4.3 Instrument software shall either have a performance verification feature to demonstrate reliability and suitability or have a Spectrometer Performance Verification (SPV) tool.

2.4.4 Smart iTR or equivalent ATR accessory with diamond crystal

2.4.5 Miscellaneous Laboratory Accessories: Spatula, mortar and pestle, mixer/mill for grinding samples to fine particle size, disposable plastic transfer pipets, isopropyl alcohol, mineral spirits, oven and Kim wipes.

3.0 SUMMARY OF SPECTRAL COMPARISON PROCEDURE

This procedure outlines a rapid and accurate quality verification of highway materials by comparing their ATR-FTIR spectra. The verification is accomplished by comparison of the IR spectra of a verification sample against that of a reference material or previously approved sample. This comparison method uses a basic algorithm to calculate a correlation value based on the IR peak positions and peak intensities of the spectra. This correlation value is a measure of the degree of similarity between two spectra. This procedure can identify samples, detect any formulation changes, and detect the presence of any contamination.

3.1 Obtain the IR spectrum of the verification or field sample. A satisfactory IR spectrum should have the major peaks at a transmittance between 5 – 35% or absorbance units between 0.5 – 1.0.

3.2 In the same collection window, retrieve and open the stored IR spectrum of the reference sample.

3.3 Both the field sample and the reference sample spectra should be obtained using the same IR analysis conditions.

3.4 Highlight both spectra and under the Analyze Menu of the OMNIC software, click on QCheck.

3.5 Record the correlation value between the two spectra. Compare the correlation value to the allowed minimum correlation value to determine the PASS/FAIL status. Software can

also be used to automatically report as PASS/FAIL if the specification or threshold is included in the analysis set up.

3.6 For aqueous solutions, the IR spectrum of water shall be subtracted using the OMNIC Subtraction Processing Feature.

3.6.1 Highlight both the sample and water spectra and under the Process Menu, click on Subtract. (Check for the proper setting. The order of subtraction should be sample spectrum minus water spectrum). The OMNIC software will automatically determine the subtraction factor to best eliminate water peaks from the sample spectrum.

3.6.2 The two main water peaks are at wavelengths 3300 cm-1 and 1640 cm-1.

3.6.3 Manual adjustments can be made to the subtraction factor to eliminate as much of the water peaks as possible without subtracting important components from the sample spectrum.

3.6.4 Repeat steps 3.4 and 3.5 to obtain the correlation value between the subtracted spectrum of the sample and the reference sample spectrum.

4.0 PERFORMING A VERIFICATION CHECK ON FIELD SAMPLES

For the analysis of most materials, a correlation value ≥ 0.85 is acceptable. There are many variables that can affect this value though. For example, the signal strength of the sample's spectrum is very important. Very dilute samples will have a very weak signal, and this will greatly affect the correlation value.

5.0 SYSTEM PERFORMANCE VERIFICATION

Confirmation of the instrument performance for reliability and suitability of the analysis. Perform regular internal verification of the instrument.

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