This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.

Designation: D8554 – 24a

Standard Test Method for Determination of the Degree of Unsaturation of Butyl Rubber by FTIR and Multivariate Analysis[1]

This standard is issued under the fixed designation D8554; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the degree of unsaturation of butyl rubber as a molar percentage of the total sample. It is applicable to degrees of unsaturation from 1.00 to 2.40 mol% range.

1.2 The values stated in SI units of measurement are to be regarded as the standard. The values given in paratheses are for information only.

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

1.4 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D8321 Practice for Development and Validation of Multivariate Analyses for Use in Predicting Properties of Petroleum Products, Liquid Fuels, and Lubricants based on Spectroscopic Measurements

E168 Practices for General Techniques of Infrared Quantitative Analysis

E932 Practice for Describing and Measuring Performance of Dispersive Infrared Spectrometers

E1421 Practice for Describing and Measuring Performance of Fourier Transform Mid-Infrared (FT-MIR) Spectrometers: Level Zero and Level One Tests

E1655 Practices for Infrared Multivariate Quantitative Analysis

E2977 Practice for Measuring and Reporting Performance of Fourier-Transform Nuclear Magnetic Resonance (FT-NMR) Spectrometers for Liquid Samples

3. Terminology

3.1 *Definitions:*

3.1.1 *butyl rubber, n*—a synthetic rubber, a copolymer of isobutylene and isoprene.

3.1.2 *calibration transfer, n*—a method of applying a multivariate calibration developed on one analyzer to a different analyzer by mathematically modifying the calibration model or by instrument standardization.

3.1.3 *estimate, n*—the value for a component concentration or property obtained by applying the calibration model for the analysis of an absorption spectrum.

3.1.4 *multivariate calibration, n*—process of creating a model that relates component concentrations or properties to the absorbances of a set of known reference samples at more than one wavelength or frequency.

3.1.5 *reference material (RM), n*—a material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for use as the method calibration or validation samples. RMs are used to develop accurate methods of analysis, calibrate, and validate the method, institute quality control, determine performance characteristics, or measure a property at the state-of-the-art limit.

3.1.6 *reference method, n*—the analytical method that is used to estimate the reference component concentration or property value which is used in the calibration and validation procedures.

3.1.7 *reference values (RV), n*—the component concentrations or property values for the calibration or validation samples which are measured by the reference analytical method.

3.1.8 *standard error of validation (SEV), n*—a measure of the performance of a multivariate model obtained by analyzing

[1] This test method is under the jurisdiction of ASTM Committee D11 on Rubber and Rubber-like Materials and is the direct responsibility of Subcommittee D11.11 on Chemical Analysis.

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[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at www.astm.org/contact. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

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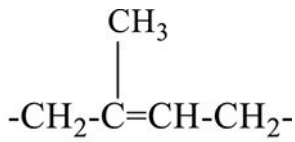
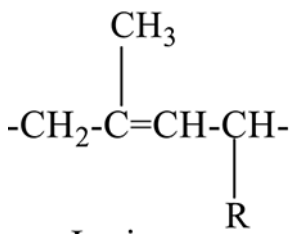
a set of model validation samples and comparing the specified values to predicted measured values.

3.1.9 *structure I (1, 4), mol%, n*—the molar percentage of 1, 4 isoprene units with double bond present in the butyl rubber.



I (1, 4)

3.1.10 *structure I (minor), mol%, n*—the molar percentage of 1, 4 isoprene units with a short side chain in the isoprene unit of the butyl rubber.



I minor

3.1.11 *total unsaturation, mol%, n*—the total molar percentage of isoprene units with double bond present in the butyl rubber.

3.1.12 *validation samples, n*—a set of samples used in validating the model. Validation samples are not part of the set of calibration samples. Reference component concentration or property values are known (measured by reference method) and are compared to those estimated using the model.

3.2 *Abbreviations:*

3.2.1 *FTIR, n*—Fourier transform infrared

3.2.2 *NMR, n*—nuclear magnetic resonance

3.2.3 *PCR, n*—principal component regression

3.2.4 *PLS, n*—partial least square

4. Summary of Test Method

4.1 Multivariate mathematics is applied to correlate the spectra measured for a set of calibration samples to reference materials unsaturation concentrations values for the set of samples. The resultant multivariate calibration model is applied to the analysis of spectra of unknown samples to provide an estimate of the total unsaturation concentration value for the unknown sample. Multilinear regression (MLR), principal components regression (PCR), and partial least squares (PLS) multivariate mathematical techniques are commonly used for the development of the calibration model.

4.2 Validation of the calibration model is performed to analyze a set of validation samples and statistically comparing the estimates for the validation samples to reference values measured for these samples, to test for bias in the model and for agreement of the model with the reference method.

4.3 A test sample of butyl rubber film is prepared by pressing the sample in a FTIR card mold or a metal sample mold. The pressed sample is introduced to a standard FTIR transmission sample holder. A beam of infrared light is imaged through the sample onto a detector, and the detector response is recorded. The full or select regions of the spectrum is selected for the analysis and processed to remove areas of high absorbance. A multivariate mathematical analysis converts the detector response for the spectrum from an unknown sample to quantify molar percentage of the total unsaturation of the butyl rubber. The multivariate calibration model shall be developed using either a PCR or PLS algorithm. A calibration set using reference materials (RM) with known molar percentage for the total unsaturation of butyl rubber with reference values (RVs) should be used to generate the multivariate model. If such a calibration set with known values are unavailable, the user should develop a set of reference materials, should be analyzed using the ^{1}HNMR reference method (see Annex A2) to determine their molar percentage of total unsaturation to be used as RVs.

4.4 This test method uses a Fourier transform infrared spectrometer with a transmission sample holder. The absorption spectrum shall be used to calculate a multivariate calibration model, using partial least squares (PLS) or principal component regression (PCR) analyses. Chemical methods such as *(1)* ozone degradation, *(2)* radiochemical, *(3)* iodine index, etc., have been developed and have been used to determine the degree of unsaturation in butyl rubbers **(1-4)**.[3]

5. Significance and Use

5.1 This infrared absorbance method quantifies the total unsaturation structures in butyl rubber using the characteristic infrared absorbance regions and multivariate analysis. This method accounts for superimposing absorbances and is an extension of the typical method for infrared quantification, which correlates a single band absorbance height or area with concentration. This method measures the level of total unsat uration in butyl rubber by multivariate analysis Fourier Transform Infrared Spectroscopy. It is applicable for butyl rubber in the concentration range of 1.00 to 2.40 mol%. It can be expanded beyond these ranges with additional calibration RMs.

6. Interference

6.1 The composition of the rubber sample and additives present have a significant effect on the FTIR spectrum and therefore the calibration model. Thus, it is essential that butyl rubber in the unknown sample set is represented in the calibration model.

6.2 Proper choice of apparatus, use of appropriate calibration matrix and multivariate calibration models and evaluation routines as described in this standard, can minimize interferences.

6.3 *Water Vapor Interference*—As the entire spectral range may be used for the generation of the calibration model, the

[3] The boldface numbers in parentheses refer to a list of references at the end of this standard.

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bands associated atmospheric water vapor will be present. Thus, it is necessary to compensate for these by means of dry air and nitrogen purge. It is preferable to have the residual level of moisture in the rubber <0.4 wt.%.

6.4 *Rubber Additives Interference*—Certain additives such as antioxidant and anti-agglomeration agents may interfere with the unsaturated spectral regions. If any interference is present suitable correction factors in the calibration sets should be used.

6.5 *Carbon Dioxide Interference*—Similar to how atmospheric water vapor poses an interference, so does the ambient carbon dioxide. Compensation for this can also be achieved through dry air or nitrogen purge of the instrument.

NOTE 1—Ideally, the spectrometer should be purged with dry air or nitrogen to remove water vapor and carbon dioxide. The purge may be allowed to stabilize over several hours before analytical work is pursued, due to rapid changes in the air moisture and carbon dioxide content within the spectrometer during the early stages of the purge. In cases where water vapor and carbon dioxide prevention or elimination is not possible using a purge, the operator should measure a reference background spectrum for correction of the ratioed spectrum for each sample spectrum measured. This operation is generally automated in today's spectrometer systems and the operator should consult the manufacturer of the spectrometer for specific instructions for implementing automated background correction routines. The spectrometer should be sealed and desiccated to minimize the effect of water vapor variations and any accessory should be sealed to the spectrometer.

6.6 *^{1}HNMR Interference*—Residual polymerization solvents, certain additives such as antioxidant, anti-agglomeration agents, and other processing aids can interfere with the unsaturated spectral regions. The ^{1}H NMR analyst should cross check these additives and impurities and make appropriate corrections needed.

6.7 *Sample Thickness*—Samples need to be analyzed on the FTIR immediately after preparation to avoid sample swelling, change in thickness. Sample thickness can become inconsistent because of rubber relaxation. Inconsistent sample thickness can have a significant effect on the consistency of results.

7. Apparatus

7.1 *Press*—Carver-type, capable of pressing films at 80°C and 10 MPa or higher.

7.1.1 *Sample Card Mold*—A cardboard mold with a rectangular specimen slot, typically a photograph backing cardboard sheet mold, with a slot 7.5 cm × 5 cm × 0.060 sized for pressing the butyl rubber specimen, described in 6.1. The cardboard mold should have approximately the same dimensions as the FTIR instrument sample holder. A sample card mold is shown in Fig. 1.

7.1.2 *Alternate Mold*—Alternatively, a metal sample mold with the above dimensions may be used.

7.1.3 *Sheets for Molding*—Sheets for molding, either PTFE-coated aluminum sheets or polyester film, or aluminum film may be used.

7.2 *Specimen Film Holder*—The film molded using cardboard mold or the metal mold, described in 7.1.1 and 7.1.2 may be directly used, that fit in the spectrometer specimen compartment, with the film without removal after pressing.

7.3 *Infrared Fourier Transform Spectrophotometer*—An instrument capable of measuring absorbances in the range 400 to 6000 cm^{-1} with a transmittance specification (accuracy) of ± 1 % T or better. The instrument should be capable of spectral resolution of minimum 2 cm^{-1} (see "Specification for Evaluation of Research Quality Analysis of Infrared Spectra"). A

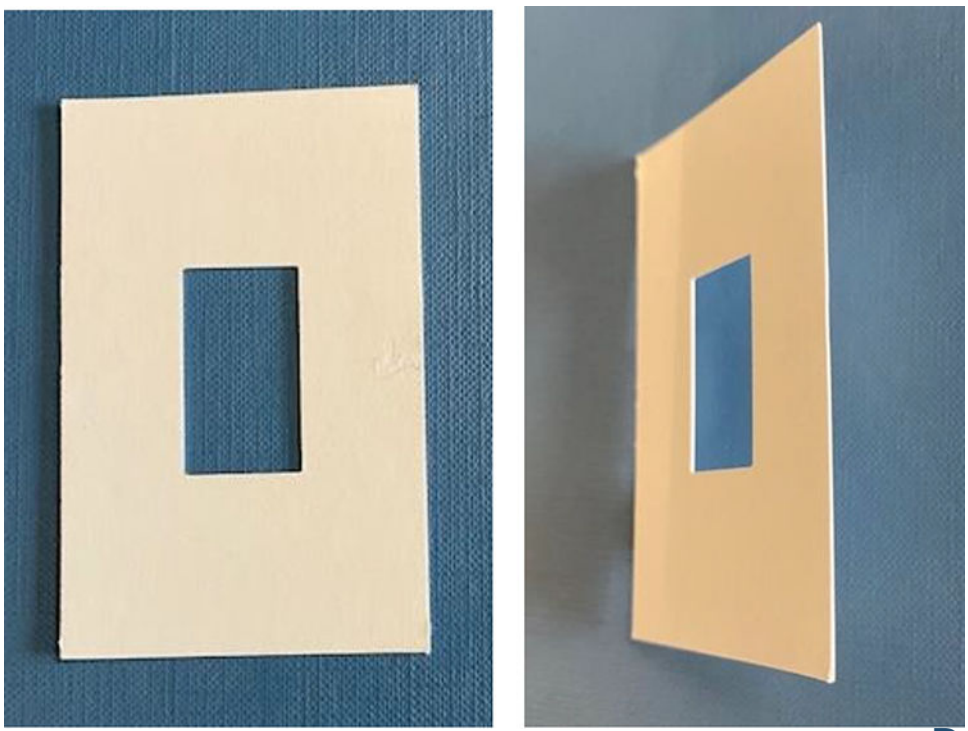

FIG. 1 Photograph of a Cardboard Mold with a Rectangular Specimen Slot

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deuterated triglycine sulfate (DTGS) detector is preferred. The instrument must operate in accordance with Practices E168, E932 and E1421. The type of apparatus suitable for use in this test method employs an IR source, a transmission sample holder, a scanning interferometer, a detector, an A-D converter, a microprocessor, and a method to introduce the sample. The following performance specification shall be met:

Scan Range: 6000 cm^{-1} to 400 cm^{-1}

Resolution: minimum 2 cm^{-1}

Scan count: minimum 16

7.3.1 The noise level shall be established by acquiring a single beam spectrum using air or nitrogen. The single beam spectrum obtained must be the average of 16 FTIR scans to match the sample analysis procedure. If interference from water vapor or carbon dioxides is a problem, the instrument shall be purged with dry air or nitrogen. The use of an atmospheric compensation algorithm to compensate for interference from moisture and carbon dioxide is advisable.

7.3.2 The instrument should be capable of spectral accumulation, averaging, and subtraction. Water is the primary source of interference in this method. Methods, physical and electronic, that minimize moisture level and variation are required to obtain the highest precision. The preferred method is use of an instrument equipped with a dry gas purge and a specimen shuttle, which permits alternating and repetitive collection of single beam specimen and background spectra. Alternatively, should a specimen shuttle be unavailable, careful purging of the sample compartment with dry nitrogen can yield satisfactory results. High precision of calibration RMs data is indicative of adequate purging. When moisture interference is not removed by purging, spectral subtraction of water vapor may be used. To obtain improved instrument measurement consistency which in turn leads to more robust and dependable analytical results, an instrument with an Absolute Virtual Instrument (AVI) capable of line shape and wavenumber calibration is recommended. The AVI is intended to allow users to effectively lock the instrument back into calibration after any inadvertent user actions that affects the performance for the instrument.

8. Test Specimen Preparation

8.1 *Primary Method*—Place the sample mold in between two sheets of aluminum foil or nylon or polytetrafluoroethylene coated sheets or polyester film, or a suitable equivalent film. Place approximately 0.24 ± 0.03 g of sample in the center of the slot (7.5 cm × 5 cm × 0.060 cm) and press the sample positioned in the center of a sample card or sample mold using carver-type press using pressing conditions ~25 MPa (3500 psi or 5 tons) and no hotter than 90°C ± 10 for 10 to 60 s. If metal mold used, a sample of 1 ± 0.01 g of sample at ~50 MPa (7000 psi or 10 tons) and no hotter than 90°C ± 10 for 60 s, may be used. If press conditions exceed 90°C or 60 s, ensure that structural changes in unsaturation types do not occur by checking the unsaturation level using NMR. Release the pressure, remove from the press, cool, and carefully remove the film or foil from the molded sample. Acetone may be used as a release agent from the polyester film for especially sticky or weak films. Ensure that the molded film sample inside slot has a smooth surface, uniform thickness and no cracks or holes in the testing area. Samples with too much moisture or other additive may look cloudy, in such cases the sample need to be dried before test specimen preparation. Hold the assembly up to the light and inspect for bubbles or voids, or both. Should there be imperfections, repeat the sample preparation with a larger amount of sample. Mount the molded specimen in the sample holder of the spectrophotometer.

9. Spectral Acquisition

9.1 Place the sample in the sample beam of the spectrophotometer with air in the reference beam and acquire the absorption spectrum from 6525–400 cm^{-1} with a minimum 16 scans; this number of scans determined by the manufacturer for optimal quantitative analysis. The optimal conditions for the method are defined as giving the lowest sigma for a quality control butyl rubber sample and the best agreement of FTIR test result with ^{1}H NMR result for total unsaturation. Follow the instrument manufacturer's recommendations for quantitative infrared spectroscopy and use the control settings as advised. Particularly, control the scan speed, the gain, and the slit width according to the recommendations to give consistent results. Recommended settings include resolution (2 or 4 cm^{-1}), 16 scans, TGS detector, and boxcar or strong apodization, but these typical FTIR parameters, descriptions could be different with different vendors.

9.2 Spectral regions characteristic of unsaturation types (1700–1600 cm^{-1} C=C stretching, 900–600 cm^{-1} vinylic H deformations, and 2200–1800 cm^{-1} overtone regions), of most interest, should have absorbances less than 1.5A and preferably between 0.5 and 1.2 A. Although for MVA analysis, this requirement may not be necessary, saturated areas of interest are to be avoided. They should be verified during re-processing of the spectra (Reference – Handbook of Instrumental Techniques for Analytical Chemistry by Frank Settle; Chapter 14; p. 271). It may be necessary to decrease the thickness of the specimen by decreasing the thickness of the mold to satisfy this condition. See Fig. 2 for a typical FTIR spectrum of butyl rubber.

10. Reference Method: ^{1}H NMR Spectrometry

10.1 Primary RMs shall be established via use of ^{1}H Nuclear Magnetic Resonance (^{1}HNMR). The unsaturation mol% of the calibration RMs employed in the development of this method were determined by a ^{1}HNMR, utilizing samples dissolved in deuterated chloroform at 25°C.

10.2 ^{1}H NMR spectra may be obtained on a high field spectrometer at 25°C. Suggested parameters are a tip angle of 30°, with a 5-s delay, and 128 transients. It is recommended to follow Practice E2977 procedures for measuring and reporting the performance of Fourier-transform nuclear magnetic resonance spectrometers (FT-NMRs).

10.3 A typical procedure for the collection of a quantitative ^{1}H NMR spectrum of butyl rubber is given in Annex A1.

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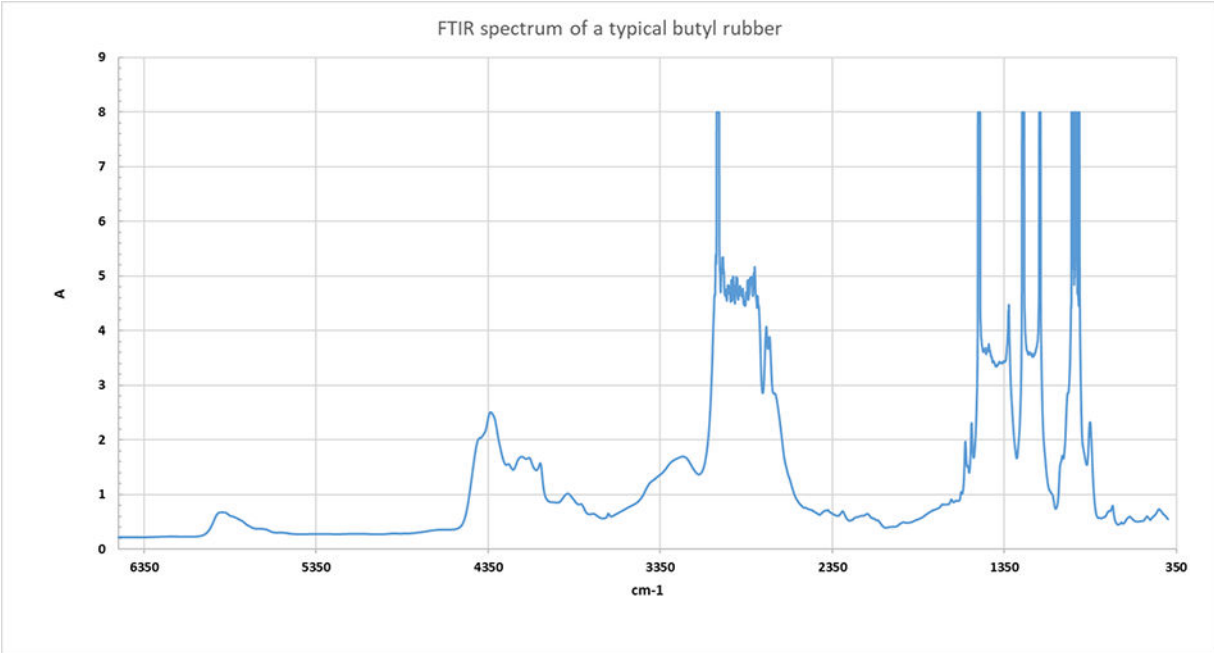

FIG. 2 Typical FTIR Spectrum of Butyl Rubber Sample

11. Hazards

11.1 This procedure uses a heated hydraulic press. Be careful of hot surfaces and keep hands and clothing free of the pinch points.

11.2 The FTIR instrument has a helium-neon laser. Do not look directly into the laser because doing so may cause eye damage.

11.3 *Caution*—Chloroform-d Acute Dermal and Inhalation Toxicity; corrosive, and possibly carcinogenic. Refer to the SDS and PHS of $CDCl_3$ for chemical hazards.

12. Sampling and Sample Handling

12.1 Samples for testing should be free of external contaminants such as oils, grease, other rubber contaminates, etc. The sample can be from a pre-pressed bale or crumbs. If the sample is too porous, a pre-pressing on a heated carver-type press, preferably less than 90°C may help to obtain a bubble free sample for molding the test specimen. It is recommended that the moisture content in the sample be less than 0.4 weight percent.

13. Calibration and Standardization

13.1 Obtain a set of butyl rubber RMs[4,5] covering the range of unsaturation values of interest, e.g., 1.00–2.40 mol% range. Such a set may be called as a training set or spectral library set. This set is to represent all the chemical and physical variation normally encountered for routine analysis of the butyl rubber. Selection of the calibration set is discussed in Annex A1.

13.2 Calibration RMs whose unsaturation content is known should be established using an absolute analytical technique, such as NMR, for determining percent unsaturation in polymers. The primary RMs for this method shall be established via use of ^{1}H Nuclear Magnetic Resonance (^{1}HNMR). See Annex A2 for the procedure. The unsaturation assignment should be exclusively based on the olefinic protons of isoprene (1,4) and isoprene (minor) units. Although 1, 2 and 3, 4 type isoprene insertions are possible, in a typical butyl rubber the concentrations of them are negligible, thus not considered in this method.

13.3 For the preparation and qualification of butyl rubber as RMs, the same butyl rubber specimen used for FTIR scan should be used for ^{1}HNMR test, to determine the absorbance spectrum and molar percent of unsaturation, respectively. The ^{1}HNMR data used in the model must be correlated to the respective the FTIR sample spectrum while preparing the calibration curve and model.

13.4 The user must develop a set of primary RMs of butyl rubber with the necessary percentage unsaturation range via the use of ^{1}H Nuclear Magnetic Resonance (^{1}HNMR), if RMs with known ^{1}HNMR results are not available. Secondary RMs may be qualified using this method for using as quality control materials.

13.5 Before testing samples, calibration models need to be created for the instrument according to the procedure described in Annex A1. If for whatever reason (such as instrument maintenance) the calibration needs to be repeated, the qualification procedure will also need to be repeated.

13.6 If a set of RMs without reference values is used to generate the multivariate calibration model, the same set of

[4] Limited supply of the butyl rubber standards is currently available, the source known to the committee at this time is ExxonMobil Chemical Polymer Laboratories, P.O. Box 5200, Baytown, TX 77520. Contact Sunny Jacob, sunny.jacob@exxonmobil.com for standards with known HNMR values.

[5] Spectra of the RM and validation samples is currently available, for calibration transfer describe in the method, the source known to the committee at this time is ExxonMobil Chemical Polymer Laboratories, P.O. Box 5200, Baytown, TX 77520. Contact Sunny Jacob, sunny.jacob@exxonmobil.com for electronic copies of the spectra.

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