



Designation: D8154 – 17^{e1}

Standard Test Methods for ¹H-NMR Determination of Ketone-Ethylene-Ester and Polyvinyl Chloride Contents in KEE-PVC Roofing Fabrics¹

This standard is issued under the fixed designation D8154; 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.

^{e1} NOTE—Editorially added Research Report information in April 2019.

1. Scope

1.1 This test method pertains to the determination of the relative contents of Ketone-Ethylene-Ester (KEE) and Polyvinyl Chloride (PVC) after their extraction from reinforced roofing membranes, or fabrics. Based on Proton Nuclear Magnetic Resonance Spectroscopy (¹H-NMR), the method allows for the quantification of PVC with respect to an internal standard. The KEE content is then obtained by difference. The test method is not applicable to membranes or blends that contain high molecular weight polymers other than PVC and KEE.

1.2 *Units*—The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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

D1079 Terminology Relating to Roofing and Waterproofing
D6754/D6754M Specification for Ketone Ethylene Ester Based Sheet Roofing

¹ This test method is under the jurisdiction of ASTM Committee D08 on Roofing and Waterproofing and is the direct responsibility of Subcommittee D08.18 on Nonbituminous Organic Roof Coverings.

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

3. Terminology

3.1 *Definitions*—Terminology D1079 and Specification D6754/D6754M shall apply to this test method.

4. Summary of Test Method

4.1 *Test Methods*—There are two related test methods to quantify PVC and KEE in roofing fabrics. In both methods the polymer blend is extracted from the fabric and purified by a series of dissolution, centrifugation, and precipitation. After drying, the blend is dissolved in deuterated tetrahydrofuran along with a ¹H-NMR internal standard. In Method A, PVC content is quantified by comparing its ¹H-NMR signal with that of the internal standard, and KEE is obtained by difference. Method B adds to Method A a calibration curve the slope of which providing for a correction factor. This correction factor is applied to the polymer content obtained by Method A to provide for greater precision on the PVC and KEE contents.

5. Significance and Use

5.1 Determination of the percentage of KEE compound in sheet roofing is of concern to many specifiers and building owners. Method A, the faster method, is best used for quality control. Method B may apply better to research and development, or investigative work.

6. Interferences

6.1 The NMR analysis of the polymer blend extracted from the sheet roofing is sensitive to impurities, including plasticizer, filler, reinforcement, and trace solvent (other than the NMR solvent). The procedure here is meant to purify the blend for proper analysis.

7. Equipment and Apparatus

7.1 *Glassware*. Erlenmeyer flask and stopper, 125 mL. Weighing bottle, 25 mL.

7.2 *Porcelain ware*. Büchner funnel, 10 cm in diameter.

7.3 *Platform shaker*. Must accept 125 mL Erlenmeyer, and allow for swirling at 120 to 150 rpm.

7.4 *Metal spatula*. To stir the suspension during the precipitation step.

7.5 *Pasteur pipettes*. To transfer solubilized polymer and solvent from one flask to another.

7.6 *Centrifuge*. Capable of 10 000 RPM.

7.7 *Centrifuge tubes*. 50 mL. Must be resistant to THF, for example, Fluorinated Ethylene Propylene.

7.8 *Watch-glass*. To dry polymer in the oven.

7.9 *Vacuum Oven*. Adjustable to $65 \pm 2^\circ\text{C}$.

7.10 *Vacuum pump*. To provide for 100 kPa of vacuum in the oven.

7.11 *Balance*. Sensitive to 0.000001 g (1 microgram).

7.12 *NMR sample tubes*. 5 mm in diameter.

7.13 *NMR Fourier Transform Spectrometer*. Equipped with a proton probe. 400 MHz field strength or higher is recommended.

8. Reagents and Materials

8.1 *Water*. 500 mL, and crushed ice, 1 kg, for an ice bath.

8.2 *Whatman filter paper No. 2*. For the Büchner funnel.

8.3 *Lint-free paper towel*. To blot sample dry of solvent.

8.4 *Hexane*. Technical grade, 60 mL.

8.5 *Tetrahydrofuran (THF)*. Technical grade, 150 mL.

8.6 *Methanol*. Technical grade, 450 mL. Maintained near 5°C in an ice bath.

8.7 *Deuterated tetrahydrofuran (THF-d8)*. 99.5 % pure or better.

8.8 *1,2,4,5-Tetrachloro-3-nitro-benzene*. Certified reference material, TCNB, 99.7 % pure or better.

8.9 *Polyvinyl chloride (PVC) powder*. For calibration in Method B. It is ideally obtained from the membrane producer. If this fails, PVC could be obtained from a primary source, that is, a raw material producer, ascertaining that the product source and grade is the same as that used in actual sheet roofing production. PVC could be obtained for instance from OxyVinyls. For best precision in polymer quantification, the raw materials for calibration samples should be those used in the membrane fabrication.

8.10 *Ketone ethylene ester (KEE) pellets*. For calibration in Method B. It is ideally obtained from the membrane producer. If this fails, KEE could be obtained from a primary source, that is, DuPontTM (Elvaloy[®] polymer), ascertaining that the product grade is that used in the sheet roofing fabrication.

9. Hazards

9.1 *Chemical Hazards*—Several solvents are used in this test method, including methanol, THF, hexane, along with TCNB. Check their material safety datasheet to identify specific hazards. Follow local regulations for proper disposal of spent chemicals.

9.2 *Centrifugation*—Centrifugation of dissolved sheet roofing involves high speeds and it must be balanced with counter weights for safe operation. Refer to the operator's manual for

details. Centrifugation flasks must be resistant to the fluid being used and must not swell.

9.3 *Magnetic Fields*—NMR spectroscopy involves strong magnetic fields. Analysis by NMR requires safety and equipment training. Follow local laboratory guidelines.

10. Sampling

10.1 Samples are obtained from sheet roofing, or from pre-production runs. Cut two pieces of 4 cm^2 taken 1 m apart along the length of the same roll. Each piece will be analyzed for polymer content to provide for duplicate analysis.

11. Sample Preparation

11.1 Polymer Extraction and Purification Procedure:

11.1.1 From each 4 cm^2 piece of sheet, cut about 0.5 g into small pieces, approximately $3 \text{ mm} \times 3 \text{ mm}$. Place cut pieces into a 125 mL Erlenmeyer flask and add 60 mL of hexane. Stopper the flask and place it on a platform shaker to swirl at 120 rpm for 24 hours.

NOTE 1—Hexane is used to clean the sheet and extract low molecular weight plasticizer that would affect the PVC and KEE contents measured by NMR.

11.1.2 Filter off the hexane into a Büchner funnel with cellulose Whatman filter paper No-2. Place the pieces of sample onto a lint free paper towel and blot them dry.

11.1.3 Place sample pieces into a 125 mL Erlenmeyer flask, add 45 mL of tetrahydrofuran (THF) and close the flask with its stopper. Place the flask on a platform shaker and stir its content at 150 rpm until sample polymer has completely dissolved and there is no evidence of gel.

NOTE 2—Dissolution time depends on composition. It may take up to 5 hours for the sample to dissolve.

11.1.4 Transfer dissolved sample to a 50 mL centrifugation tube. Rinse the Erlenmeyer flask with 5 mL of THF and use this rinse solvent to completely fill the centrifugation tube. Cap the tube and centrifuge its content for 30 minutes at 10 000 rpm. After centrifugation, carefully transfer the supernatant liquid with a Pasteur pipette to a 125 mL Erlenmeyer flask (for transport and storage, if necessary), leaving the precipitated solid at the bottom of the centrifugation tube.

11.1.5 Precipitate the dissolved polymer by pouring the supernatant THF into 150 mL of cold methanol (5°C) in a 400 mL beaker and stir with a metal spatula for 5 minutes. Allow the mixture to stand for another 5 min at 5°C (for example, in an ice bath) to allow for the polymer to precipitate out of solution.

11.1.6 Filter the polymer precipitate through a vacuum funnel over No. 2 Whatman filter paper. Remove the polymer from the filter paper while it is still damp, and place the polymer onto a watch-glass to dry the excess of THF in an oven at 65°C for 15 minutes.

11.1.7 Repeat 11.1.3 – 11.1.6 twice for a total of three iterations to retain a polymer sample free of interference as defined in Section 6.

11.1.8 After three iterations as per 11.1.7, place the extracted and purified polymer sample into a 20 mL sample vial and dry it free of THF by heating it to 60°C for 8 hours under vacuum.

NOTE 3—Thorough drying is required to remove traces of THF, which will interfere with the calculated PVC-KEE content NMR analysis. THF will be readily visible in the ^1H -NMR spectrum. Before dissolution of the sample in deuterated-THF as per 11.2.1, the absence of protonated-THF may be verified by means of Fourier-transform infrared spectroscopy, or thermo-gravimetric analysis.

11.1.9 Reserve the polymer dried as per 11.1.8 in a flask to protect it from contaminant until it is used to prepare the NMR sample.

11.2 Preparation of NMR Sample:

11.2.1 *Polymer Sample*—Weigh in a small weighing pan and with a precision of 0.001 mg about 20 mg of TCNB and about 30 mg of polymer dried as per 11.1.8. Transfer these solids to a 5 mL weighting glass bottle. Use about 1 mL of THF-d₈ to wash residual solid in the weighing pan and pipet it out to the glass bottle. Close the weighing glass bottle with its lid, and leave the polymer-TCNB solid mixture to dissolve overnight. With a pipette, transfer the solution into a 5 mm NMR tube.

NOTE 4—Keep aside the weights of TCNB and the dried polymer for use in the calculation of PVC and KEE content in Section 13.

11.2.2 *Calibration Samples*—Calibration samples have PVC/KEE weight ratios close to 20/80, 30/70, 40/60, 50/50, and 60/40. Samples are prepared by individually weighting between about 5 mg to 25 mg of PVC and KEE for a total polymer content near 30 mg. Weigh in a small weighing pan and with a precision of 0.001 mg about 20 mg of TCNB and about 30 mg of the PVC/KEE mixture with a set ratio. Transfer these solids to a 5 mL weighting glass bottle. Use about 1 mL of THF-d₈ to wash residual solid in the weighing pan and pipet it out to the weighing bottle. Close the weighing bottle with its lid, and leave the polymer-TCNB solid mixture to dissolve overnight. With a pipette, transfer the solution into a 5 mm NMR tube. Table X1.1 in Appendix X1 provides an example of calibration sample compositions.

NOTE 5—Keep aside the weights of TCNB, PVC, and KEE for use in the calibration curve and calculation of PVC and KEE as per 13.1.2.

12. NMR Analysis

12.1 *Acquisition Parameters*—The proton-NMR probe temperature is to be set to 30°C and sample is to be left to stabilize for 20 minutes in the probe prior to testing. Measure spin-lattice relaxation, T_1 , by inversion recovery. Set the relaxation delay to about six times the value of T_1 to ascertain that full relaxation is achieved in the quantitative experiment. For instance, a 60 s relaxation delay is used for a T_1 of 9.9 s.

NOTE 6—Probe tuning and 90 degree pulse width determination must be done for every sample prior to acquisition, for example 9.3 μs at 53 dB.

12.1.1 Collect the quantitative ^1H -NMR spectrum at a spectral width of 8.0 kHz, acquisition time of 3.75 s, and co-add 32 scans (transients).

12.2 *Spectrum Analysis*—Reference the spectrum at 3.570 ppm with respect to the proton trace in THF-d₈. Upon spectrum processing as per 12.3, set to 100 the integral regions from 7.80 to 8.40 ppm for TCNB, and obtain the integration from 4.12 to 4.75 ppm for PVC. Fig. X1.1 in Appendix X1 provides an example of a spectrum with integration.

12.3 *Spectrum Processing*—For quantitative NMR, the peaks must be as narrow and symmetric as possible and the integral line must reflect the surface area of spectral lines as well as the absence of spectral lines (flat baseline). Note, for instance, the flat baseline on the TCNB integration in Fig. X1.1.

12.3.1 *Phasing*—It is first necessary to greatly expand the vertical scale of the spectrum to see the base of the peaks and make them as symmetric as possible by adjusting the phase so that the tails on each side of the peaks are as short and symmetric as possible. Phasing is done by adjusting two parameters: the zero order and the first order phase and the process vary depending on the NMR software.

12.3.2 *Integration*—Once properly phased, the spectrum must be processed for baseline correction for the integral line to reflect the baseline; the integral line should increase when a peak is present and should be flat in the absence of peaks. Once again, the process is different depending on the software used for data processing, but it is similar to phasing in the sense that a zero and first order parameter must be adjusted.

13. KEE Calculations

13.1 Two methods may be used to quantify the ratio of KEE and PVC in the extracted polymer blend. Both methods are based on the NMR integration values of peaks from the internal standard TCNB and PVC. In Method A, the polymer ratio is obtained from the analysis of a single sample. In Method B, the polymer ratio is obtained after the development of a calibration curve.

NOTE 7—The TCNB signal between 7.80 to 8.40 ppm arises from a single proton, and it is assumed that the PVC signal between 4.12 to 4.75 ppm also arises from a single proton, from $\text{CH}_2\text{-CHCl}$.

13.1.1 Method A

13.1.1.1 *Calculation of PVC Content*—In this method, the polymer and TCNB weights from 11.2.1, and the NMR integration values from TCNB and PVC in 12.2 are used to calculate the PVC weight content as per Eq 1, where MW is the molecular weight. The MW of TCNB is 260.89 g/mol, whereas that of PVC is 62.50 g/mol.

$$\text{PVC content \%} = 100 * \frac{\text{PVC mass}}{\text{sample mass}} \quad (1)$$

$$= 100 * \frac{\text{molar quantity PVC} * \text{MW of PVC}}{\text{sample mass}}$$

$$= 100 * \frac{\text{molar quantity TCNB} * \left(\frac{\text{integration PVC}}{\text{integration TCNB}} \right) * \text{MW of PVC}}{\text{sample mass}}$$

$$= 100 * \frac{\left(\frac{\text{mass TCNB}}{\text{MW of TCNB}} \right) * \left(\frac{\text{integration PVC}}{\text{integration TCNB}} \right) * \text{MW of PVC}}{\text{sample mass}}$$

Taking for instance a TCNB mass of 0.019938 g, a polymer mass of 0.029673 g, and a PVC integration of 242.61, and a TCNB integration of 100 leads to a percent PVC content of 39.0 %.

$$\begin{aligned} \text{PVC content \%} &= 100 * \\ &= 100 * \frac{0.011588 \text{ g}}{0.029673 \text{ g}} = 39.0 \end{aligned}$$