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METHOD 310B—DETERMINATION OF RESIDUAL HEXANE THROUGH GAS CHROMATOGRAPHY

1.0 Scope and Application

Analyte	CAS No.	Matrix	Method sensitivity (5.5g sample size)
Hexane	110-54-3	Rubber crumb	.01 wt%.
Applicable Termonomer		Rubber crumb	.001 wt%.

1.1 Data Quality Objectives:

In the production of ethylene-propylene terpolymer crumb rubber, the polymer is recovered from solution by flashing off the solvent with steam and hot water. The resulting water-crumb slurry is then pumped to the finishing units. Certain amounts of solvent (hexane being the most commonly used solvent) and diene monomer remain in the crumb. The analyst uses the following procedure to determine those amounts.

2.0 Summary of Method

2.1 The crumb rubber sample is dissolved in toluene to which heptane has been added as an internal standard. Acetone is then added to this solution to precipitate the crumb, and the supernatant is analyzed for hexane and diene by a gas chromatograph equipped with a flame ionization detector (FID).

3.0 Definitions

3.1 Included in text as needed.

4.0 Interferences

4.1 None known.

4.2 Benzene, introduced as a contaminant in the toluene solvent, elutes between methyl cyclopentane and cyclohexane. However, the benzene peak is completely resolved.

4.3 2,2-dimethyl pentane, a minor component of the hexane used in our process, elutes just prior to methyl cyclopentane. It is included as “hexane” in the analysis whether it is integrated separately or included in the methyl cyclopentane peak.

5.0 Safety

5.1 This procedure does not purport to address all of the safety concerns 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.

5.2 Chemicals used in this analysis are flammable and hazardous (see specific toxicity information below). Avoid contact with sources of ignition during sample prep. All handling should be done beneath a hood. Playtex or nitrile gloves recommended.

5.3 Hexane is toxic by ingestion and inhalation. Vapor inhalation causes irritation of nasal and respiratory passages, headache, dizziness, nausea, central nervous system depression. Chronic overexposure can cause severe nerve damage. May cause irritation on contact with skin or eyes. May cause damage to kidneys.

5.4 Termonomer may be harmful by inhalation, ingestion, or skin absorption. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Causes skin irritation.

5.5 Toluene is harmful or fatal if swallowed. Vapor harmful if inhaled. Symptoms: headache, dizziness, hallucinations, distorted perceptions, changes in motor activity, nausea, diarrhea, respiratory irritation, central nervous system depression, unconsciousness, liver, kidney and lung damage. Contact can cause severe eye irritation. May cause skin irritation. Causes irritation of eyes, nose, and throat.

5.6 Acetone, at high concentrations or prolonged overexposure, may cause headache, dizziness, irritation of eyes and respiratory tract, loss of strength, and narcosis. Eye contact causes severe irritation; skin contact may cause mild irritation. Concentrations of 20,000 ppm are immediately dangerous to life and health.

5.7 Heptane is harmful if inhaled or swallowed. May be harmful if absorbed through the skin. Vapor or mist is irritating to the eyes, mucous membranes, and upper respiratory tract. Prolonged or repeated exposure to skin causes defatting and dermatitis.

5.8 The steam oven used to dry the polymer in this procedure is set at 110 °C. Wear leather gloves when removing bottles from the oven.

6.0 *Equipment and Supplies*

6.1 4000-ml volumetric flask

6.2 100-ml volumetric pipette

6.3 1000-ml volumetric flask

6.4 8-oz. French Square sample bottles with plastic-lined caps

6.5 Top-loading balance

6.6 Laboratory shaker

6.7 Laboratory oven set at 110 °C (steam oven)

6.8 Gas chromatograph, Hewlett-Packard 5890A, or equivalent, interfaced with HP 7673A (or equivalent) autosampler (equipped with nanoliter adapter and robotic arm), and HP 3396 series II or 3392A (or equivalent) integrator/controller.

6.9 GC column, capillary type, 50m × 0.53mm, methyl silicone, 5 micron film thickness, Quadrex, or equivalent.

6.10 Computerized data acquisition system, such as CIS/CALS

6.11 Crimp-top sample vials and HP p/n 5181-1211 crimp caps, or screw-top autosampler vials and screw tops.

6.12 Glass syringes, 5-ml, with “Luer-lock” fitting

6.13 Filters, PTFE, .45 µm pore size, Gelman Acrodisc or equivalent, to fit on Luer-lock syringes (in 6.12, above).

7.0 *Reagents and Standards*

7.1 Reagent toluene, EM Science Omnisolv (or equivalent)

Purity Check: Prior to using any bottle of reagent toluene, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and termonomer peak areas are less than 15 each (note that an area of 15 is equivalent to less than 0.01 wt% in a 10g sample).

7.2 Reagent acetone, EM Science Omnisolv HR-GC (or equivalent)

Purity Check: Prior to using any bottle of reagent acetone, analyze it according to section 11.2 of this method. Use the bottle only if hexane, heptane, and termonomer peak areas are less than 15 each.

7.3 Reagent heptane, Aldrich Chemical Gold Label, Cat #15,487-3 (or equivalent)

Purity Check: Prior to using any bottle of reagent heptane, analyze it according to section 11.2 of this method. Use the bottle only if hexane and termonomer peak areas are less than 5 each.

7.4 Internal standard solution—used as a concentrate for preparation of the more dilute Polymer Dissolving Solution. It contains 12.00g heptane/100ml of solution which is 120.0g per liter.

Preparation of internal standard solution (polymer dissolving stock solution):

Action	Notes
7.4.1 Tare a clean, dry 1-liter volumetric flask on the balance. Record the weight to three places	If the 1-liter volumetric flask is too tall to fit in the balance case, you can shield the flask from drafts by inverting a paint bucket with a hole cut in the bottom over the balance cover. Allow the neck of the flask to project through the hole in the bucket.
7.4.2 Weigh 120.00 g of n-heptane into the flask. Record the total weight of the flask and heptane as well as the weight of heptane added	Use 99 + % n-heptane from Aldrich or Janssen Chimica.
7.4.3 Fill the flask close to the mark with toluene, about 1 to 2" below the mark	Use EM Science Omnisolve toluene, Grade TX0737-1, or equivalent.
7.4.4 Shake the flask vigorously to mix the contents	Allow any bubbles to clear before proceeding to the next step.
7.4.5 Top off the flask to the mark with toluene. Shake vigorously, as in section 7.4.4 of this method, to mix well	
7.4.6 Weigh the flask containing the solution on the three place balance record the weight	
7.4.7 Transfer the contents of the flask to a 1 qt Boston round bottle	Discard any excess solution
7.4.8 Label the bottle with the identity of the contents, the weights of heptane and toluene used, the date of preparation and the preparer's name	Be sure to include the words " <i>Hexane in Crumb Polymer Dissolving Stock Solution</i> " on the label.
7.4.9 Refrigerate the completed blend for the use of the routine Technicians	

7.5 Polymer Dissolving Solution ("PDS")—Heptane (as internal standard) in toluene. This solution contains 0.3g of heptane internal standard per 100 ml of solution.

7.5.1 Preparation of Polymer Dissolving Solution. Fill a 4,000-ml volumetric flask about $\frac{3}{4}$ full with toluene.

7.5.2 Add 100 ml of the internal standard solution (section 7.4 of this method) to the flask using the 100ml pipette.

7.5.3 Fill the flask to the mark with toluene. Discard any excess.

7.5.4 Add a large magnetic stirring bar to the flask and mix by stirring.

7.5.5 Transfer the polymer solvent solution to the one-gallon labeled container with 50ml volumetric dispenser attached.

7.5.6 Purity Check: Analyze according to section 11.2. *NOTE:* You must “precipitate” the sample with an equal part of acetone (thus duplicating actual test conditions—see section 11.1 of this method, sample prep) before analyzing. Analyze the reagent 3 times to quantify the C₆ and termonomer interferences. Inspect the results to ensure good agreement among the three runs (within 10%).

7.5.7 Tag the bottle with the following information:

POLYMER DISSOLVING SOLUTION FOR C₆ IN CRUMB ANALYSIS

PREPARER'S NAME

DATE

CALS FILE ID'S OF THE THREE ANALYSES FOR PURITY (from section 7.5.6 of this method)

7.6 Quality Control Solution: the quality control solution is prepared by adding specific amounts of mixed hexanes (barga hexane), n-nonane and termonomer to some polymer dissolving solution. Nonane elutes in the same approximate time region as termonomer and is used to quantify in that region because it has a longer shelf life. Termonomer, having a high tendency to polymerize, is used in the QC solution only to ensure that both termonomer isomers elute at the proper time.

First, a concentrated stock solution is prepared; the final QC solution can then be prepared by diluting the stock solution.

7.6.1 In preparation of stock solution, fill a 1-liter volumetric flask partially with polymer dissolving solution (PDS)—see section 7.5 of this method. Add 20.0 ml barga hexane, 5.0 ml n-nonane, and 3 ml termonomer. Finish filling the volumetric to the mark with PDS.

7.6.2 In preparation of quality control solution, dilute the quality control stock solution (above) precisely 1:10 with PDS, i.e. 10 ml of stock solution made up to 100 ml (volumetric flask) with PDS. Pour the solution into a 4 oz. Boston round bottle and store in the refrigerator.

8.0 *Sample Collection, Preservation and Storage*

8.1 Line up facility to catch crumb samples. The facility is a special facility where the sample is drawn.

- 8.1.1 Ensure that the cock valve beneath facility is closed.
- 8.1.2 Line up the system from the slurry line cock valve to the cock valve at the nozzle on the stripper.
- 8.1.3 Allow the system to flush through facility for a period of 30 seconds.
- 8.2 Catch a slurry crumb sample.
 - 8.2.1 Simultaneously close the cock valves upstream and downstream of facility.
 - 8.2.2 Close the cock valve beneath the slurry line in service.
 - 8.2.3 Line up the cooling tower water through the sample bomb water jacket to the sewer for a minimum of 30 minutes.
 - 8.2.4 Place the sample catching basket beneath facility and open the cock valve underneath the bomb to retrieve the rubber crumb.
 - 8.2.5 If no rubber falls by gravity into the basket, line up nitrogen to the bleeder upstream of the sample bomb and force the rubber into the basket.
 - 8.2.6 Close the cock valve underneath the sample bomb.
- 8.3 Fill a plastic "Whirl-pak" sample bag with slurry crumb and send it to the lab immediately.
- 8.4 Once the sample reaches the lab, it should be prepped as soon as possible to avoid hexane loss through evaporation. Samples which have lain untouched for more than 30 minutes should be discarded.

9.0 *Quality Control*

Quality control is monitored via a computer program that tracks analyses of a prepared QC sample (from section 7.6.2 of this method). The QC sample result is entered daily into the program, which plots the result as a data point on a statistical chart. If the data point does not satisfy the "in-control" criteria (as defined by the lab quality facilitator), an "out-of-control" flag appears, mandating corrective action.

In addition, the area of the n-heptane peak is monitored so that any errors in making up the polymer dissolving solution will be caught and corrected. Refer to section 12.4 of this method.

- 9.1 Fill an autosampler vial with the quality control solution (from section 7.6.2 of this method) and analyze on the GC as normal (per section 11 of this method).
- 9.2 Add the concentrations of the 5 hexane isomers as they appear on the CALS printout. Also include the 2,2-dimethyl-pentane peak just ahead of the methyl cyclopentane (the fourth major

isomer) peak in the event that the peak integration split this peak out. Do not include the benzene peak in the sum. Note the nonane concentration. Record both results (total hexane and nonane) in the QC computer program. If out of control, and GC appears to be functioning within normal parameters, reanalyze a fresh control sample. If the fresh QC is not in control, check stock solution for contaminants or make up a new QC sample with the toluene currently in use. If instrument remains out-of-control, more thorough GC troubleshooting may be needed.

Also, verify that the instrument has detected both isomers of termonomer (quantification not necessary—see section 7.0 of this method).

9.3 Recovery efficiency must be determined for high ethylene concentration, low ethylene concentration, E-P terpolymer, or oil extended samples and whenever modifications are made to the method. Recovery shall be between 70 and 130 percent. All test results must be corrected by the recovery efficiency value (R).

9.3.1 Approximately 10 grams of wet EPDM crumb (equivalent to about 5 grams of dry rubber) shall be added to six sample bottles containing 100 ml of hexane in crumb polymer dissolving solution (toluene containing 0.3 gram n-heptane/100 ml solution). The polymer shall be dissolved by agitating the bottles on a shaker for 4 hours. The polymer shall be precipitated using 100 ml acetone.

9.3.2 The supernatant liquid shall be decanted from the polymer. Care shall be taken to remove as much of the liquid phase from the sample as possible to minimize the effect of retained liquid phase upon the next cycle of the analysis. The supernatant liquid shall be analyzed by gas chromatography using an internal standard quantitation method with heptane as the internal standard.

9.3.3 The precipitated polymer from the steps described above shall be redissolved using toluene as the solvent. No heptane shall be added to the sample in the second dissolving step. The toluene solvent and acetone precipitant shall be determined to be free of interfering compounds.

9.3.4 The rubber which was dissolved in the toluene shall be precipitated with acetone as before, and the supernatant liquid decanted from the precipitated polymer. The liquid shall be analyzed by gas chromatography and the rubber phase dried in a steam-oven to determine the final polymer weight.

9.3.5 The ratios of the areas of the hexane peaks and of the heptane internal standard peak shall be calculated for each of the six samples in the two analysis cycles outlined above. The area ratios of the total hexane to heptane (R1) shall be determined for the two analysis cycles of the sample set. The ratio of the values of R1 from the second analysis cycle to the first cycle shall be determined to give a second ratio (R2).

10.0 Calibration and Standardization

The procedure for preparing a Quality Control sample with the internal standard in it is outlined in section 7.6 of this method.

10.1 The relative FID response factors for n-heptane, the internal standard, versus the various hexane isomers and termonomer are relatively constant and should seldom need to be altered. However Baseline construction is a most critical factor in the production of good data. For this reason, close attention should be paid to peak integration. Procedures for handling peak integration will depend upon the data system used.

10.2 If recalibration of the analysis is needed, make up a calibration blend of the internal standard and the analytes as detailed below and analyze it using the analytical method used for the samples.

10.2.1 Weigh 5 g heptane into a tared scintillation vial to five places.

10.2.2 Add 0.2 ml termonomer to the vial and reweigh.

10.2.3 Add 0.5 ml hexane to the vial and reweigh.

10.2.4 Cap, and shake vigorously to mix.

10.2.5 Calculate the weights of termonomer and of hexane added and divide their weights by the weight of the n-heptane added. The result is the known of given value for the calibration.

10.2.6 Add 0.4 ml of this mixture to a mixture of 100 ml toluene and 100 ml of acetone. Cap and shake vigorously to mix.

10.2.7 Analyze the sample.

10.2.8 Divide the termonomer area and the total areas of the hexane peaks by the n-heptane area. This result is the “found” value for the calibration.

10.2.9 Divide the appropriate “known” value from 10.2.5 by the found value from 10.2.8. The result is the response factor for the analyte in question. Previous work has shown that the standard deviation of the calibration method is about 1% relative.

11.0 Procedure

11.1 Sample Preparation

11.1.1 Tare an 8oz sample bottle—Tag attached, cap off; record weight and sample ID on tag in pencil.

11.1.2 Place crumb sample in bottle: RLA-3: 10 g (gives a dry wt. of ~5.5 g).

11.1.3 Dispense 100ml of PDS into each bottle. Sample should be placed into solution asap to avoid hexane loss—Using “Dispensette” pipettor. *Before dispensing, “purge” the dispensette (25% of its volume) into a waste bottle to eliminate any voids.*

11.1.4 Tightly cap bottles and load samples into shaker.

11.1.5 Insure that “ON-OFF” switch on the shaker itself is “ON.”

11.1.6 Locate shaker timer. Insure that toggle switch atop timer control box is in the middle (“off”) position. If display reads “04:00” (4 hours), move toggle switch to the left position. Shaker should begin operating.

11.1.7 After shaker stops, add 100 ml acetone to each sample to precipitate polymer. Shake minimum of 5 minutes on shaker—Vistalon sample may not have fully dissolved; nevertheless, for purposes of consistency, 4 hours is the agreed-upon dissolving time.

11.1.8 Using a 5-ml glass Luer-lock syringe and Acrodisc filter, filter some of the supernatant liquid into an autosampler vial; crimp the vial and load it into the GC autosampler for analysis (section 11.2 of this method)—The samples are filtered to prevent polymer buildup in the GC. Clean the syringes in toluene.

11.1.9 Decant remaining supernatant into a hydrocarbon waste sink, being careful not to discard any of the polymer. Place bottle of precipitate into the steam oven and dry for six hours—Some grades of Vistalon produce very small particles in the precipitate, thus making complete decanting impossible without discarding some polymer. In this case, decant as much as possible and put into the oven as is, allowing the oven to drive off remaining supernatant (this practice is avoided for environmental reasons). WARNING: OVEN IS HOT—110 °C (230 °F).

11.1.10 Cool, weigh and record final weight of bottle.

11.2 GC Analysis

11.2.1 Initiate the CALS computer channel.

11.2.2 Enter the correct instrument method into the GC's integrator.

11.2.3 Load sample vial(s) into autosampler.

11.2.4 Start the integrator.

11.2.5 When analysis is complete, plot CALS run to check baseline skim.

12.0 Data Analysis and Calculations

12.1 Add the concentrations of the hexane peaks as they appear on the CALS printout. Do not include the benzene peak in the sum.

12.2 Subtract any hexane interferences found in the PDS (see section 7.5.6 of this method); record the result.

12.3 Note the termonomer concentration on the CALS printout. Subtract any termonomer interference found in the PDS and record this result in a “% termonomer by GC” column in a logbook.

12.4 Record the area (from CALS printout) of the heptane internal standard peak in a “C7 area” column in the logbook. This helps track instrument performance over the long term.

12.5 After obtaining the final dry weight of polymer used (Section 11.1.10 of this method), record that result in a “dry wt.” column of the logbook (for oil extended polymer, the amount of oil extracted is added to the dry rubber weight).

12.6 Divide the %C6 by the dry weight to obtain the total PHR hexane in crumb. Similarly, divide the % termonomer by the dry weight to obtain the total PHR termonomer in crumb. Note that PHR is an abbreviation for “parts per hundred”. Record both the hexane and termonomer results in the logbook.

12.7 Correct all results by the recovery efficiency value (R).

13.0 Method Performance

13.1 The method has been shown to provide 100% recovery of the hexane analyte. The method was found to give a 6% relative standard deviation when the same six portions of the same sample were carried through the procedure. Note: These values are examples; each sample type, as specified in Section 9.3, must be tested for sample recovery.

14.0 Pollution Prevention

14.1 Dispose of all hydrocarbon liquids in the appropriate disposal sink system; never pour hydrocarbons down a water sink.

14.2 As discussed in section 11.1.9 of this method, the analyst can minimize venting hydrocarbon vapor to the atmosphere by decanting as much hydrocarbon liquid as possible before oven drying.

15.0 Waste Management

15.1 The Technician conducting the analysis should follow the proper waste management practices for their laboratory location.

16.0 References

16.1 Baton Rouge Chemical Plant Analytical Procedure no. BRCP 1302

16.2 Material Safety Data Sheets (from chemical vendors) for hexane, ENB, toluene, acetone, and heptane