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METHOD 312A—DETERMINATION OF STYRENE IN LATEX STYRENE-BUTADIENE RUBBER, THROUGH GAS CHROMATOGRAPHY

1. Scope and Application

1.1 This method describes a procedure for determining parts per million (ppm) styrene monomer (CAS No. 100-42-5) in aqueous samples, including latex samples and styrene stripper water.

1.2 The sample is separated in a gas chromatograph equipped with a packed column and a flame ionization detector.

2.0 Summary of Method

2.1 This method utilizes a packed column gas chromatograph with a flame ionization detector to determine the concentration of residual styrene in styrene butadiene rubber (SBR) latex samples.

3.0 Definitions

3.1 The definitions are included in the text as needed.

4.0 Interferences

4.1 In order to reduce matrix effects and emulsify the styrene, similar styrene free latex is added to the internal standard. There are no known interferences.

4.2 The operating parameters are selected to obtain resolution necessary to determine styrene monomer concentrations in latex.

5.0 Safety

5.1 It is the responsibility of the user of this procedure to establish appropriate safety and health practices.

6.0 Equipment and Supplies

6.1 Adjustable bottle-top dispenser, set to deliver 3 ml. (for internal standard), Brinkmann Dispensette, or equivalent.

6.2 Pipettor, set to 10 ml., Oxford Macro-set, or equivalent.

6.3 Volumetric flask, 100-ml, with stopper.

6.4 Hewlett Packard Model 5710A dual channel gas chromatograph equipped with flame ionization detector.

6.4.1 11 ft. \times $\frac{1}{8}$ in. stainless steel column packed with 10% TCEP on 100/120 mesh Chromosorb P, or equivalent.

6.4.2 Perkin Elmer Model 023 strip chart recorder, or equivalent.

6.5 Helium carrier gas, zero grade.

6.6 Liquid syringe, 25- μ l.

6.7 Digital MicroVAX 3100 computer with VG Multichrom software, or equivalent data handling system.

6.6 Wire Screens, circular, 70-mm, 80-mesh diamond weave.

6.7 DEHA—(N,N-Diethyl hydroxylamine), 97 + % purity, CAS No. 3710-84-7

6.8 p-Dioxane, CAS No. 123-91-1

7.0 Reagents and Standards

7.1 Internal standard preparation.

7.1.1 Pipette 5 ml p-dioxane into a 1000-ml volumetric flask and fill to the mark with distilled water and mix thoroughly.

7.2 Calibration solution preparation.

7.2.1 Pipette 10 ml styrene-free latex (eg: NBR latex) into a 100-ml volumetric flask.

7.2.2 Add 3 ml internal standard (section 7.1.1 of this method).

7.2.3 Weigh exactly 10 μ l fresh styrene and record the weight.

7.2.4 Inject the styrene into the flask and mix well.

7.2.5 Add 2 drops of DEHA, fill to the mark with water and mix well again.

7.2.6 Calculate concentration of the calibration solution as follows:

$$\text{mg/l styrene} = (\text{mg styrene added})/0.1 \text{ L}$$

8.0 Sample Collection, Preservation, and Storage

8.1 A representative SBR emulsion sample should be caught in a clean, dry 6-oz. teflon lined glass container. Close it properly to assure no sample leakage.

8.2 The container should be labeled with sample identification, date and time.

9.0 Quality Control

9.1 The instrument is calibrated by injecting calibration solution (Section 7.2 of this method) five times.

9.2 The retention time for components of interest and relative response of monomer to the internal standard is determined.

9.3 Recovery efficiency must be determined once for each sample type and whenever modifications are made to the method.

9.3.1 A set of six latex samples shall be collected. Two samples shall be prepared for analysis from each sample. Each sample shall be analyzed in duplicate.

9.3.2 The second set of six latex samples shall be analyzed in duplicate before spiking each sample with approximately 1000 ppm styrene. The spiked samples shall be analyzed in duplicate.

9.3.3 For each hydrocarbon, calculate the average recovery efficiency (R) using the following equations:

where:

$$R = \Sigma(R_n) / 6$$

where:

$$R_n = (c_{ns} - c_v) / S_n$$

n = sample number

c_{ns} = concentration of compound measured in spiked sample number n.

c_{nu} = concentration of compound measured in unspiked sample number n.

S_n = theoretical concentration of compound spiked into sample n.

9.3.4 A value of R between 0.70 and 1.30 is acceptable.

9.3.5 R is used to correct all reported results for each compound by dividing the measured results of each compound by the R for that compound for the same sample type.

10.0 Calibration and Instrument Settings

10.1 Injection port temperature, 250 °C.

10.2 Oven temperature, 110 °C, isothermal.

10.3 Carrier gas flow, 25 cc/min.

10.4 Detector temperature, 250 °C.

10.5 Range, 1X.

11.0 Procedure

11.1 Turn on recorder and adjust baseline to zero.

11.2 Prepare sample.

11.2.1 For latex samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask. Pipet 10 ml sample into the flask using the Oxford pipettor, dilute to the 100-ml mark with water, and shake well.

11.2.2 For water samples, add 3 ml Internal Standard (section 7.1 of this method) to a 100-ml volumetric flask and fill to the mark with sample. Shake well.

11.3 Flush syringe with sample.

11.4 Carefully inject 2 µl of sample into the gas chromatograph column injection port and press the start button.

11.5 When the run is complete the computer will print a report of the analysis.

12.0 Data Analysis and Calculation

12.1 For samples that are prepared as in section 11.2.1 of this method:

$$\text{ppm styrene} = A \times D$$

Where:

A = "ppm" readout from computer

D = dilution factor (10 for latex samples)

12.2 For samples that are prepared as in section 11.2.2 of this method, ppm styrene is read directly from the computer.

13.0 Method Performance

13.1 This test has a standard deviation (1) of 3.3 ppm at 100 ppm styrene. The average Spike Recovery from six samples at 1000 ppm Styrene was 96.7 percent. The test method was validated using 926 ppm styrene standard. Six analysis of the same standard provided average 97.7 percent recovery. Note: These are example recoveries and do not replace quality assurance procedures in this method.

14.0 Pollution Prevention

14.1 Waste generation should be minimized where possible. Sample size should be an amount necessary to adequately run the analysis.

15.0 Waste Management

15.1 All waste shall be handled in accordance with Federal and State environmental regulations.

16.0 References and Publications

16.1 40 CFR 63 Appendix A—Method 301 Test Methods Field Validation of Pollutant Measurement

16.2 DSM Copolymer Test Method T-3060, dated October 19, 1995, entitled: *Determination of Residual Styrene in Latex*, Leonard, C.D., Vora, N.M.*et al*