# METHOD 312C - DETERMINATION OF RESIDUAL STYRENE IN SBR LATEX PRODUCED BY EMULSION POLYMERIZATION

## 1.0 SCOPE

1.1  This method is applicable for determining the amount of residual styrene in SBR  latex as produced in the emulsion polymerization process.

## 2.0 PRINCIPLE OF METHOD

2.1  A weighed sample of latex is coagulated in 2-propanol which contains alpha-methyl styrene as an Internal Standard. The extract from the coagulation will contain the alpha-methyl styrene as the Internal Standard and the residual styrene from the latex.  The extract is analyzed by a Gas Chromatograph.  Percent styrene is calculated by relating the area of the styrene peak to the area of the Internal Standard peak of known concentration.

## 3.0 DEFINITIONS

**3.1**  The definitions are included in the text as needed.

## 4.0 INTERFERENCES

(Reserved)

## 5.0 SAFETY

**5.1**    When using solvents, avoid contact with skin and eyes. Wear hand and eye protection.  Wash thoroughly after use.

**5.2**    Avoid overexposure to solvent vapors.  Handle only in well ventilated areas.

## 6.0 EQUIPMENT AND SUPPLIES

**6.1**    <u>Gas Chromatograph</u> - Hewlett Packard 5890, Series II with flame ionization detector, or equivalent.

<u>Column</u> - HP 19095F-123, 30m x 0.53mm, or equivalent. Substrate HP FFAP (cross-linked) film thickness 1 micrometer.  Glass injector port liners with silanized glass wool plug.

<u>Integrator</u> - HP 3396, Series II, or equivalent.

**6.2**   Wrist action shaker

**6.3**   Automatic dispenser

**6.4**   Automatic pipet, calibrated to deliver 5.0 $\pm$0.01 grams of latex

**6.5**   Four-ounce wide-mouth bottles with foil lined lids

**6.6**   Crimp cap vials, 2ml, teflon lined septa

**6.7**   Disposable pipets

**6.8**   Qualitative filter paper

**6.9**   Cap crimper

**6.10**  Analytical balance

**6.11**  10ml pipette

**6.12**  Two-inch funnel

**7.0   REAGENTS AND STANDARDS**

**7.1**   2-Propanol (HP2C grade)

**7.2**   Alpha methyl styrene (99+% purity)

**7.3**   Styrene (99+% purity)

**7.4**   Zero air

**7.5**   Hydrogen (chromatographic grade)

**7.6**   Helium

**7.7**   Internal Standard preparation

**7.7.1** Weigh 5.000-5.005 grams of alpha-methyl styrene into a 100ml volumetric flask and bring to mark with 2-propanol to make Stock "A" Solution.

          Note:  Shelf life - 6 months

**7.7.2** Pipette 10ml of Stock "A" Solution into a 100ml volumetric flask and bring to mark with 2-propanol to

2

prepare Stock "B" Solution.

**7.7.3** Pipette 10ml of the Stock "B" solution to a 1000ml volumetric flask and bring to the mark with 2-propanol.  This will be the Internal Standard Solution (0.00005 grams/ml).

**7.8**  Certification of Internal Standard - Each batch of Stock "B" Solution will be certified to confirm concentration.

**7.8.1** Prepare a Standard Styrene Control Solution in 2-propanol by the following method:

**7.8.1.1**  Weigh 5.000 $\pm$.005g of styrene to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock "A" Solution.

**7.8.1.2**  Pipette 10ml of Styrene Stock "A" Solution to a 100ml volumetric flask and fill to mark with 2-propanol to make Styrene Stock "B" Solution.

**7.8.1.3**  Pipette 10ml of Styrene Stock "B" soluion to a 250ml volumtric flask and fill to mark wtih 2-propanol to make the Certification Solution.

**7.8.2** Certify Alpha-Methyl Styrene Stock "B" Solution.

**7.8.2.1**  Pipette 5ml of the Certification Solution and 25ml of the Alpha Methyl Styrene Internal Standard Solution to a 4-oz. bottle, cap and shake well.

**7.8.2.2**  Analyze the resulting mixture by GC using the residual styrene method. (11.4-11.6 of this method)

**7.8.2.3**  Calculate the weight of alpha methyl styrene present in the 25ml aliquat of the new Alpha Methyl Styrene Standard by the following equation:

$$W_x = F_x x W_{is}(A_x/A_{is})$$

where    $A_x$  = Peak area of alpha methyl styrene

3

$$A_{is} = \text{Peak area of styrene}$$
$$W_x = \text{Weight of alpha methyl styrene}$$
$$W_{is} = \text{Weight of styrene (.00100)}$$
$$F_x = \text{Analyzed response factor} = 1$$

The Alpha Methyl Styrene Stock Solution used to prepare the Internal Standard Solution may be considered certified if the weight of alpha methyl styrene analyzed by this method is within the range of .00121g to .00129g.

## 8.0 SAMPLING

**8.1** Collect a latex sample in a capped container. Cap the bottle and identify the sample as to location and time.

**8.2** Deliver sample to Laboratory for testing within one hour.

**8.3** Laboratory will test within two hours.

**8.4** No special storage conditions are required.

## 9.0 QUALITY CONTROL

**9.1** The laboratory is required to operate a formal quality control program. This consists of an initial demonstration of the capability of the method as well as ongoing analysis of standards, blanks, and spiked samples to demonstrate continued performance.

**9.1.1** When the method is first set up, a calibration is run and the recovery efficiency for each type of sample must be determined.

**9.1.2** If new types of samples are being analyzed, then recovery efficiency for each new type of sample must be determined. New type includes any change, such as polymer type, physical form or a significant change in the composition of the matrix.

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

**9.2.1** In determining the recovery efficiency, the quadruplet sampling system shall be used. Six sets of samples (for a total of 24) shall be taken. In each

4

quadruplet set, half of the samples (two out of the four) shall be spiked with styrene.

**9.2.2** Prepare the samples as described in section 8 of this method.  To the vials labeled "spiked", add a known amount of styrene that is expected to be present in the latex.

**9.2.3** Run the spiked and unspiked samples in the normal manner.  Record the concentrations of styrene reported for each pair of spiked and unspiked samples with the same vial number.

**9.2.4** For each hydrocarbon, calculate the average recovery efficiency (R) using the following equation:

$$R = \mathbf{E}(R_n)/12$$

$$R_n = (M_s - M_u)/S$$

where: n = sample number
$M_s$ = total mass of compound (styrene) measured in spiked sample (µg)
$M_u$ = total mass of compound (styrene) measured in unspiked sample (µg)
S = theoretical mass of compound (styrene) spiked into sample (µg)
R = fraction of spiked compound (styrene) recovered

**9.2.5** A different R value should be obtained for each sample type.  A value of R between 0.70 and 1.30 is acceptable.

**9.2.6** 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** - A styrene control sample will be tested weekly to confirm the FID response and calibration.

**10.1**  Using the Styrene Certification Solution prepared in 7.8.1, perform test analysis as described in 7.8.2

using the equation in 7.8.2.3 to calculate results.

**10.2**   Calculate the weight of styrene in the styrene control sample using the following equation:

$$W_{sty} = (F_x \, x \, A_{sty} \, x \, W_{is}) / A_{is}$$

The instrument can be considered calibrated if the weight of the styrene analyzed is within range of 0.00097 – 0.00103gms.

## 11.0  PROCEDURE

**11.1**   Using an auto pipet, add 25ml of Internal Standard Solution to a 4 oz. wide-mouth bottle.

**11.2**   Using a calibrated auto pipet, add 5.0 ±0.01g latex to the bottle containing the 25ml of Internal Standard Solution.

**11.3**   Cap the bottle and place on the wrist action shaker. Shake the sample for a minimum of five minutes using the timer on the shaker.  Remove from shaker.

**11.4**   Using a disposable pipet, fill the 2ml sample vial with the clear alcohol extract.  (If the extract is not clear, it should be filtered using a funnel and filter paper.)  Cap and seal the vial.

**11.5**   Place the sample in the autosampler tray and start the GC and Integrator.  The sample will be injected into the GC by the auto-injector, and the Integrator will print the results.

**11.6**   <u>Gas Chromatograph Conditions</u>

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Oven Temp                   70°C
Injector Temp               225°C
Detector Temp               275°C
Helium Pressure             500 KPA
Column Head Pressure        70 KPA
Makeup Gas                  30 ml/min.
Column - HP 19095F - 123, 30m x 0.53mm
     Substrate: HP - FFAP (cross-linked)
     1 micrometer film thickness
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## 12.0 CALCULATIONS

**12.1** The integrator is programmed to do the following calculation at the end of the analysis:

$$\%ResidualStyrene = (A_x x W_{is})/(A_{is} x W_x) x F_x x 100$$

Where: $A_x$ = Peak area of styrene
$A_{is}$ = Peak area of internal standard
$W_x$ = Weight of sample = 5g
$W_{is}$ = Weight of internal std. = 0.00125g
$F_x$ = Analyzed response factor = 1.0

**12.2** The response factor is determined by analyzing a solution of 0.02g of styrene and 0.02g of alpha methyl styrene in 100ml of 2-propanol. Calculate the factor by the following equation:

$$F_x = (W_x x A_{is})/(W_{is} x A_x)$$

where: $W_x$ = Weight of styrene
$A_x$ = Peak area of styrene
$W_{is}$ = Weight of alpha methyl styrene
$A_{is}$ = Peak area of alpha methyl styrene

## 13.0 METHOD PERFORMANCE

**13.1** Performance must be determined for each sample type by following the procedures in section 9 of this method.

## 14.0 WASTE GENERATION

**14.1** Waste generation should be minimized where possible.

## 15.0 WASTE MANAGEMENT

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

## 16.0 REFERENCES

(Reserved)