METHOD 45

DETERMINATION OF BUTANES AND PENTANES IN POLYMERIC MATERIALS

REF: Reg. 8-52

1. PRINCIPLE

1.1 The butanes and pentanes are solubilized in toluene or any appropriate solvent, and the mixture is injected into a gas chromatograph equipped with a liquid injection port, a flame ionization detector (GC-FID) and a compatible integrator or a data station.

1.2 The concentrations of the organic compounds are calculated based on a standard made in the laboratory using the same matrix.

1.3 The limit of detection of this method is 0.05% (w/w).

2. APPARATUS

2.1 Gas Chromatograph. This unit is fitted with a liquid injection port, a flame ionization detector, a temperature programmer and a compatible integrator or data station. The recommended GC operating parameters are:

Initial Oven Temperature (^{o}C)	40
Initial Hold Time (min)	8
Temperature Program Rate (^{o}C/min)	5
Final Temperature (^{o}C)	200
Final Hold Time (min)	5
Injector Temperature	250
Detector Temperature (^{o}C)	250
Carrier Gas	He
Carrier Gas Flow Rate (ml/min)	3
Injection Sample Size (μl)	1

2.2 Analytical Column: Any analytical column capable of resolving the compounds of interest is acceptable. The recommended analytical columns for this method are:

2.2.1 Primary Column: 60 m x 0.32 mm DB-1 Column, 5.0 μm film thickness (J & W Scientific).

2.2.2 Alternate Column: 12' x 1/8" O.D. SS Column packed with 20% SP 2100/0.1% Carbowax 1500 on 100/120 mesh Supelcoport. **(**Note 1**)**

Note 1: It is necessary to modify the suggested gas chromatographic parameters if the alternate column is used.

2.3 Analytical balance, capable of weighing to ±0.0001 g.

2.4 Syringes, various sizes as needed.

2.5 Micro syringe, 10 µl capacity.

2.6 Vials, crimp top, clear glass, 30 ml and 120 ml capacity.

2.7 Seals, tear–away, to fit vials.

2.8 Septa-jars, I-Chem, short wide mouth jars, with caps/septa (Teflon/silicone septa are bonded into the open top caps), 125 ml capacity.

2.9 Plastic bags with seals.

2.10 Refrigerator.

2.11 Rubber gloves.

3. REAGENT

3.1 n-Butane, 99+% Purity.

3.2 Isobutane, 99+% Purity.

3.3 n-Pentane, Reagent Grade, 99+% Purity.

3.4 Isopentane, Reagent Grade, 99+% Purity.

3.5 Cyclopentane, Reagent Grade, 99+% Purity.

3.6 n-Hexane, Reagent Grade, 99+ % Purity.

3.7 Toluene, Reagent Grade, 99+% Purity.

3.8 Toluene/n-Hexane Solution. To 1000 ml of toluene, add 2 ml n-hexane. N-hexane is the internal standard used in this method.

Note 2: Before preparing this solution, follow the screening procedure in Note (6). If n-hexane or a co-eluting compound is present in the screening sample, use a different internal standard such as n-heptane.

3.9 Acetone, pentane/hexane free.

3.10 Compressed Air. (Note 3)

3.11 Carrier Gas, helium or nitrogen, 99.99% or higher purity. (Note 3)

3.12 Fuel Gas, hydrogen, 99.9% or higher purity. (Note 3)

Note 3: The carrier and fuel gases are compressed under high pressure. Hydrogen is an extremely flammable gas. Compressed air supports combustion. Read the precautionary labels before handling these materials.

4. SAMPLING PROCEDURE

4.1 Preparation of Vial Sets **(2.6 and 2.7)**

4.1.1 Use dry, clean gloves to handle the vials and samples in order to minimize contamination.

4.1.2 Rinse the vials, septa and seals at least three times with pentane-free acetone. Air dry for about two hours under a clean hood.

4.1.3 Place the septa in a desiccator.

4.1.4 Dry the vials and seals in an oven at 105^0C for one hour.

4.1.5 After the oven drying, keep the vials and seals in the desiccator until ready for use.

4.1.6 When ready to use, take one vial set (one vial, one septum and one seal) from the desiccator and weigh them. Record the weight.

4.1.7 Immediately place the tarred vial set in a plastic bag. Seal the bag and give it to the person who will obtain the expandable polystyrene sample.

4.2 Preparation of Septa-jar sets **(2.8)**

4.2.1 Use dry clean gloves to handle the jars and samples in order to minimize contamination.

4.2.2 Rinse the jars and caps/septa at least three times with pentane-free acetone. Air dry for about two hours under a clean hood.

4.2.3 Place the caps/septa in a desiccator.

4.2.4 Dry the jars in an oven at 105^0C for one hour.

4.2.5 After the oven drying, keep the jars in the desiccator until ready for use.

4.2.6 When ready to use, take Septa-jar set (one jar, one cap/septum from the desiccator, and weigh them. Record the weight.

4.2.7 Immediately place the tarred Septa-jar sets in a plastic bag. Seal the bag and give it to the person who will obtain the expandable polystyrene sample.

4.3 Sample Collection

4.3.1 Remove the vial sets **(4.1)** or Septa-jar sets **(4.2)** from the plastic bag and collect the samples as follows: **(Note 4)**

Note 4: When sampling, use dry, clean gloves or scoops to avoid contamination. Take an additional sample for preliminary screening to check for peaks that co-elute with the internal standard (n-hexane).

4.3.1.1 For unexpanded, prepuff and molded part samples, fill the vial to the top with samples. Use the Septa-jar if the sample size is too large to fit in the mouth of the vial.

4.3.1.2 Take bead samples within 5 minutes after opening a carton and from at least 6 inches beneath the surface of the beads. **(Note 5)**

Note 5: Follow manufacturer's directions if, due to safety reasons, the manufacturer recommends a different sampling time after opening a carton.

4.3.1.3 Select representative sections of the molded part for the sample. Avoid edges and sections of poor fusion.

4.3.1.4 Do not take samples from edges that have been hot wire cut.

4.3.1.5 Immediately set a septum over the top of the vial with the Teflon side toward the sample, place a seal over it and crimp tightly. If using Septa-jars, immediately cap the jars tightly.

4.3.1.6 Keep the samples in a container at about 4^0C, if possible, or under ice and transport to the laboratory as soon as possible.

5. PREPARATION OF SAMPLES

5.1 Set up the gas chromatograph as described in **(2.1) and (2.2).**

5.2 Using a 10 μl syringe, inject 1 μl of the solvent into the gas chromatograph to check for contamination. If the solvent is contaminated, discard it and open a fresh bottle of solvent. The solvent for the preparation of samples and standards must be free of contamination.

5.3 Take the samples out of the refrigerated container. Wipe the outside surfaces of the vial dry and allow to equilibrate in a desiccator for at least one hour.

5.4 For unexpanded beads, weigh 1 to 1.5 grams (to ±0.0001 gram) aliquot of the sample from **(5.3)** (Ws), into a clean 30 ml vial with crimp top Teflon septum, cap and seal.

5.5 Immediately add 25 ml of toluene/n-hexane solution (3.8) through the septum using a syringe. Mix to dissolve the sample **(Notes 6 and 7).**

Note 6: Mixtures containing butanes must be kept in a refrigerator.

Note 7: Add 25 ml of toluene (without the internal standard to the screening sample. Follow step (7.1). If n- hexane is present in the sample, use a different internal standard such as n-heptane).

5.6 For pre-puff and molded part samples:

5.6.1 Weigh out sample from **(5.3).**

5.6.2 Subtract the tare weight obtained in **(4.1.6)** or **(4.2.6)** from that obtained in **(5.6.1).** The resulting value is the sample weight (Ws).

5.6.3 Follow **(5.5).**

6. STANDARD PREPARATION

6.1 Using a 5 ml syringe, inject 1ml each of iso-pentane, n-pentane cyclopentane and n-hexane (internal standard) into a tarred 5 ml vial with a septum. Determine and record the weight of each compound after it was added into the vial. **(Note 8)**

Note 8: If n-hexane, neohexane or other hydrocarbons are present in the sample, add the appropriate amount of the standard in the standard mixture. Use a compound that is not present in the sample as internal standard.

6.2 Using a calibrated syringe, add exactly 50 ml of toluene through the septum of an empty, capped 120 ml vial. Place in a refrigerator (4 ^{o}C) for at least one hour to cool. **(Note 9)**

Note 9: If butanes are not present in the sample, it is not necessary to add them to the calibration standard and the solvent does not have to be cooled.

6.3 To the vial prepared in **(6.2)**, add the following compounds:

6.3.1 Inject exactly 25 ml of isobutane directly into the toluene solvent. Determine and record the weight of the compound added to the vial.

6.3.2 Inject exactly 25 ml of n-butane directly into the toluene solvent. Determine and record the weight of the compound added to the vial.

6.3.3 Add 400 μl of the hydrocarbon mixture **(6.1).**

6.3.4 The calibration standard contains approximately:
59 mg isobutane, 59 mg n-butane, 62 mg iso-pentane,
63 mg n-pentane, 75 mg cyclopentane and 66 mg n-hexane
(internal standard). **(Note 8)**

6.4 The calibration standard **(6.3)** should be kept in a refrigerator and is stable for three days. If the sample does not contain isobutane or n-butane, they do not have to be added to the standard. This extends the stability of the standard to seven days.

7. ANALYTICAL PROCEDURE.

7.1 Using a 10 μl syringe, inject 1 μl of the standard (**6.3)** into the gas chromatograph. Integrate and record the retention times and peak areas of the hydrocarbon compounds in the standard. Retain the chromatogram. The order of elution is isobutane, n-butane, isopentane, n-pentane, cyclopentane and n-hexane. **(See Figure 1)**

7.2 Inject, separately, 1 μl of each of the samples from **(5.5 and 5.6)** into the gas chromatograph and record the retention times and peak areas of the hydrocarbons found. Retain the chromatograms.

7.3 Run the analysis in duplicate. Reanalyze the sample if the results on the butanes vary by more than 12% relative and/or the pentanes by more than 10% relative.

8. CALCULATION FOR COMPLIANCE

8.1 Compare the chromatograms obtained in **(7.1)** and **(7.2)** to confirm the identity of the compounds in the sample. Quantitate the concentration of the compounds using the following equations:

8.1.1 Calculate the response factors for each component using the following formula:

$$RF = \frac{Wi \times Ast}{Wst \times Ai}$$

Where:
Wi = weight of the internal standard in grams.
Wst = weight of the standard in grams.
Ai = ~~weight~~ area of the internal standard.
Ast = area of the standard.

8.1.2 Calculate the concentration of each component present in the sample by the following:

$$\text{Concentration (\%w/w)} = \frac{As \times Wis \times 100}{Ais \times Ws \times RF}$$

Where:

Wis = weight of the internal standard in the sample in grams.

Ws = weight of the sample in grams.

Ais = area of the internal standard in the sample.

As = area of the component in the sample.

8.1.3 Calculate the Total VOC of the sample by the following:

Total %VOC (w/w) = Sum of the concentration (% w/w) of each component in the sample

9. REFERENCE

9.1 "SCAQMD Laboratory Methods of Methods Analysis for Enforcement Samples," SCAQMD 306.