

# Determination of Anthraquinone in Crude Tall Oil by Gas Chromatography

## 1. Scope

- 1.1 The purpose of this method is to determine the amount of anthraquinone(AQ) in crude tall oil. It has been demonstrated at levels of approximately 100-2000 ppm AQ.

## 2. Applicable Documents

- 2.1 ASTM Standards

D804 standard definition of terms relating to naval stores and related products  
D5974, Gas chromatography of fatty and rosin acids

## 3. Summary of Methods

- 3.1 The gas chromatographic method is based on internal standard quantitation utilizing a flame ionization detector and capillary column. Eicosane(C20) is used as the internal standard, with 9-anthracenecarboxylic acid as an alternate.

## 4. Purity of Reagents

- 4.1 Chloroform or tetrahydrofurane ACS grades
- 4.2 Tetramethylammonium hydroxide, or diazomethane reagents (See D5974-96)
- 4.3 Eicosane (C20), 99+% or 9-anthracenecarboxylic acid (internal standard) 4.4 Anthraquinone (AQ), 99+%

## 5. Apparatus

- 5.1 Suitable GC equipped with an FID split or splitless flow injector and integration capabilities
- 5.2 Column: 30 meter Restek 2330, 0.25 mm I.D., 0.2  $\mu$  film, or functional equivalent
- 5.3 Analytical balance capable of measuring to  $\pm 0.0001$  g.
- 5.4 Derivatization equipment for GC analysis of fatty and rosin acids (D5974-96)
- 5.5 20 mL scintillation vial or equivalent
- 5.6 Syringe compatible with injector and capable of accurately delivering 1  $\mu$ l.
- 5.7 100 mL volumetric flasks
- 5.8 Pipette capable of accurately delivering 1 mL.

## 6. Chromatographic Conditions

- 6.1 He carrier gas, 10 psi head pressure
- 6.2 Split flow 25 mL/min.
- 6.3 Injector and Detector Temp. 275°C
- 6.4 Initial Column Temp. 150°C (5 min hold)
- 6.5 Rate 15°C/min
- 6.6 Final Column Temp. 250°C (30 min hold)

## Procedure

### **I. Preparation of Calibration Standards and Determination of Response Factor**

- 6.7 Accurately weigh out approximately equal amounts of internal standard and anthraquinone (typically between 35 and 50mg each) into a 20 mL scintillation vial and record the weight of each to the nearest 0.0001 g.
- 6.8 Dissolve the mixture in approximately 10 mL of chloroform (mild heat may be used if necessary)
- 6.9 Determine the % of eicosane (C20) and anthraquinone (AQ) using equations I and 2 respectively.
- 6.10 Inject 1.0  $\mu$ l of this solution into the GC using the conditions described above and determine the retention time of AQ and C20. Repeat as needed.
- 6.11 Determine the response factor from equation 3 and enter this value as the RF in the integration data file if needed.

### **II. Preparation of Internal Standard Stock and Samples**

- 6.12 Prepare a C20 internal standard stock solution by weighing out approximately 0.1g (record exact weight to the nearest 0.0001g) into a 100 mL volumetric flask and dilute to volume with chloroform. Shake well until complete dissolution is achieved.
- 6.13 Weigh out approximately 1.0g of CTO (record exact weight to the nearest 0.0001 g) into a 20mL scintillation vial. Accurately pipette 1.0 mL of the C20 internal stock solution into the vial. Determine the amount of C20 internal standard using equation 4.
- 6.14 Derivatize the sample using one of the techniques for conversion to methyl esters, as in D5974.
- 6.15 Dilute the sample to approximately 10mL with chloroform and mix well until the entire sample is dissolved. Mild heat (i.e. steam bath) may be used if necessary to completely dissolve the sample.
- 6.16 Inject 1  $\mu$ l of the sample and determine the amount of AQ by internal standard quantitation using equation 5. This calculation (Eq 5) may be performed manually, or in the integration software.

## Calculations

### **Equation 1: % C20 in Standard**

$$\% \text{ C20} = \frac{(\text{Wt.C20}) \times 100}{(\text{Wt.C20} + \text{Wt.Aq})}$$

### **Equation 2: %AQ in Standard**

$$\% \text{ AQ} = 100\% - \% \text{ C20}$$

### Equation 3: Response factor for AQ

$$Rf (AQ) = \frac{\%AQ \text{ weighed in (eq. 2)}}{\%AQ(GC)}$$

$$\text{where \%AQ(GC)} = \frac{(\text{area AQ}) * 100}{(\text{area AQ} + \text{area C20})}$$

### Equation 4: Determination of IS amount in sample

(This calculation is based on adding exactly 1.0 mL of the C20 Internal Standard Stock Solution to the sample)

$$\mu\text{g C20/ g CTO} = \frac{\text{Wt.C20is} \times 10,000}{\text{Wt.CTO}}$$

### Equation 5: Concentration of AQ in CTO Samples

$$\mu\text{g AQ/g CTO} = \frac{(\mu\text{g C20/ g CTO}) \times (\text{Area Count AQ}) \times Rf (AQ)}{\text{Area count C20}}$$

## 7. Report

- 7.1 Report the anthraquinone content as  $\mu\text{g AQ/g CTO}$  ( parts per million, ppm) for each sample.

## 8. Precision and Bias

- 8.1 During a preliminary interlaboratory study a single sample of CTO was analyzed 5 times with an average of 755.8 ppm AQ and a standard deviation of 18.5 ppm. The same sample was spiked with 300 ppm of AQ and analyzed 5 times with an average value of 1035.8 with a standard deviation of 31.2 ppm.

