

## METHOD 17

### STANDARDIZATION OF HYDROCARBON CALIBRATION GASES

#### 1. PRINCIPLE

- 1.1 Hydrocarbon gas standards used for calibrating source test instrumentation must be checked periodically for accuracy and quality assurance purposes. These standards usually consists of a single hydrocarbon compound such as; methane, propane, butane or hexane in parts per million (ppm) concentration.
- 1.2 The concentration of the hydrocarbon calibration gas is determined by comparing it with an EPA Protocol Gaseous Calibration Standard.
- 1.3 The analysis is performed using a gas chromatograph fitted with a flame ionization detector (FID) and a data station.
- 1.4 This method is also applicable to the speciation of hydrocarbon compounds in headspace samples with concentrations in the ppm range.
- 1.5 The detection limit of this method is 0.5 ppm for all hydrocarbon species in the samples.

#### 2. APPARATUS

- 2.1 Gas Chromatograph. This unit is equipped with a gas sampling valve, sample loop, a flame ionization detector, a temperature programmer and a compatible integrator or data station.
- 2.2 Analytical Columns. Any column capable of resolving the hydrocarbon of interest may be used. The recommended analytical columns for the determination of methane and other hydrocarbon compounds and the GC operating parameters are:

##### 2.2.1 For methane determination:

A 15' x 1/8" ID SS Column packed with Chromosorb 102, 100 to 120 mesh:

|                    |            |
|--------------------|------------|
| Initial Oven Temp. | 60° C      |
| Iso Time-1         | 3 min.     |
| Program Rate       | 15° C/min. |
| Final Oven Temp.   | 180° C     |
| Iso Time-2         | 10 min.    |
| Sample Loop Size   | 2.3 ml     |
| Carrier Gas        | He         |
| Carrier Gas Flow   | 20 ml/min. |

2.2.2 For propane, butane and hexane determination:

A 25 m x 0.53 mm I.D. Al<sub>2</sub>O<sub>3</sub>/KCl fused silica column:

|                    |            |
|--------------------|------------|
| Initial Oven Temp. | 35° C      |
| Iso Time-1         | 5 min.     |
| Oven Temp.-2       | 120° C     |
| Temp. Program Rate | 8° C/min.  |
| Iso Time-2         | 8 min.     |
| Final Oven Temp.   | 195° C     |
| Iso Time-3         | 22 min     |
| Sample Loop Size   | 0.5 ml     |
| Carrier Gas        | He         |
| Carrier Gas Flow   | 20 ml/min. |

2.3 Syringes. Use 5, 10 and 30 ml calibrated syringes.

2.4 Two stage regulator with a controlling valve.

### 3. REAGENTS

3.1 EPA Protocol Gaseous Calibration Standards. These standard mixtures are commercially available from any specialty gas and equipment company capable of preparing such gas standards.

3.2 Cylinder Nitrogen gas or air (< 1 ppm hydrocarbon)

### 4. STANDARDIZATION OF HYDROCARBON CYLINDER

4.1 Set up the gas chromatograph as described in (2.2.1) or (2.2.2)

4.2 Using a clean 20 ml syringe, inject the hydrocarbon standard into the gas chromatograph through the sampling valve. Record the retention time and the peak area of the hydrocarbon compound of interest. Retain the chromatogram.

4.3 Using a clean 20ml syringe, inject the sample into the gas chromatograph through the sampling valve. Record the retention time and the peak area of the hydrocarbon compounds of interest. Retain the chromatogram.

4.4 If the concentration of the hydrocarbon calibration gas in the cylinder is higher than 5,000 PPM, dilute the content of the cylinder in a six liter summa polished canister with either clean air or nitrogen to within ± 25% of the EPA Protocol Standard before analysis. Record the dilution factor, DF.

- 4.5. All sample injections must be done in duplicate and the area counts must not exceed (+/-) 2% of the average area count.

## 5. CALCULATION

- 5.1 Compare the chromatogram of (4.2) to (4.3) to confirm the identity of the compounds in the chromatogram. Quantitate the concentration of each compound and the % bias using the following equations:

$$5.1.1 \text{ ppm HC in the Cylinder} = \frac{PA_{(Sam)}}{PA_{(Std)}} \times \text{Conc.}_{(Std)} \times DF$$

Where:

$PA_{(Sam)}$  = Peak Area of the Sample

$PA_{(Std)}$  = Peak Area of the Standard

$\text{Conc.}_{(Std)}$  = Concentration of the hydrocarbon standard in ppm

DF = Dilution Factor. Where the sample was not diluted, DF = 1.0.

$$5.1.2 \text{ \% Bias} = \frac{\text{Assigned Conc. (ppm)} - \text{Analyzed Conc. (ppm)}}{\text{Assigned Conc. (ppm)}} \times 100$$

## 6. REFERENCE

- 6.1 Halzas, I. and Wegner, E.F., Gas Chromatographic Separation of Low Boiling Hydrocarbons. Nature, 57, 189, 1961.
- 6.2 EPA Method 18 – Measurement of Gaseous Organic Compound Emissions By Gas Chromatography, Environmental Protection Agency, CFR Part 60, Appendix A, Method 18.