

BENZENE-SPECIFIC MEASUREMENTS IN PETROLEUM HYDROCARBONS USING THE RAE SYSTEMS ULTRARAE 3000

INTRODUCTION

Benzene is a known human carcinogen that is present in automotive gasoline and other fuels in concentrations typically 0.2 to 3%. Its regulated exposure limit is so low (proposed 8-hour day TWA of 0.5 ppm), that its concentration alone usually defines the toxicity of the fuel vapors as a whole. Thus, it is necessary to measure low concentrations of benzene (often ≤ 1 ppmv) in the presence of much higher concentrations (tens to hundreds of ppmv total) of the hundreds of aromatic and aliphatic compounds that make up gasoline.

SPECIFIC BENZENE MEASUREMENTS

RAE-Sep™ benzene tubes scrub nearly all components out of gasoline vapors except benzene. This is accomplished through a proprietary absorption medium in the tubes. Further selectivity is afforded by using a 9.8 eV lamp, which responds strongly to aromatics but weakly to many hydrocarbons. Table 1 shows the response of the combined system to various challenge gases.

Measurement Procedure

A separate tube is used for each measurement. The instrument is calibrated using a 5 ppm benzene standard with a RAE-Sep™ tube in place, following best practices. When ready to measure, a tube is opened, it is inserted into the UltraRAE 3000, and the start button is pushed. A pump draws in the air sample at about 330 cc/min. and the unit automatically fixes the display and logs the value after 30 to 280 seconds, depending on the temperature.

TUBE CAPACITY AND MATRIX EFFECTS

Benzene RAE-Sep™ tubes withstand 1000 ppm of toluene in dry air and 300 ppm at 50 to 80% RH (relative humidity). Tubes can be opened and left exposed to air for up to 1 hour without losing significant capacity.

Table 2 shows that humidity has no effect on the response to benzene. However, high humidity affects the capacity of the tube to remove interfering hydrocarbons.

Table 1. Response to potential benzene interferences.

| Compound | Concentration (ppmv) | Apparent Benzene Response |
|-------------------|----------------------|---------------------------|
| Toluene | 400 | 0.1 |
| p-Xylene | 200 | 0.0 |
| Ethylbenzene | 200 | 0.0 |
| Styrene | 100 | 0.0 |
| Nitrobenzene | 100 | 0.0 |
| Phenol | 100# | 0.0 |
| Chlorobenzene | 20 | 2.5 |
| Dichlorobenzene | 50 | 0.1 |
| Hydrogen Sulfide | 150 | 0.0 |
| Methane | 25,000** | 0.0 |
| Propane | 1,000 | 0.0 |
| Isobutane | 100 | 0.0 |
| Isobutylene | 500 | 0.0 |
| n-Pentane | 1,500 | 0.0 |
| 1,3-Butadiene | 300 | 0.0 |
| n-Hexane | 100# | 0.0 |
| Cyclohexane | 10 | 0.4 |
| n-Octane | 300 | 0.1 |
| β-Pinene | 50 | 0.0 |
| Ethanol | 50 | 0.0 |
| Isopropanol | 100 | 0.0 |
| Acetone | 100 | 0.0 |
| Cyclohexanone | 200 | 0.0 |
| Tetrahydrofuran | 100 | 0.0 |
| Ethyl acetate | 100 | 0.0 |
| Acrylonitrile | 100 | 0.0 |
| Epichlorohydrin | 100 | 0.0 |
| Trichloroethylene | 100 | 66 |
| Perchloroethylene | 50 | 38 |

* Not necessarily the maximum allowable concentration.

** No effect on tube capacity. Propane and higher hydrocarbons do affect capacity.

Higher concentrations may cause a reduced benzene response.

Methane has no effect on tube capacity, but it reduces the response of the PID to benzene, when the methane concentration is above about 1% by volume. Propane and higher hydrocarbons consume part of the capacity of the tubes even if they give no response.

Table 2. Humidity effect on 5 ppm benzene standards.

| Tube # | Relative Humidity | Reading (ppm) |
|--------|-------------------|---------------|
| 1 | Dry | 5.0 |
| 2 | Dry | 4.9 |
| 3 | 100% | 5.1 |
| 4 | 100% | 4.8 |

SAMPLE MEASUREMENTS

Figure 1 shows the linearity of the response when benzene is added to a sample of gasoline vapors. The correlation coefficient (r^2) for the line is 0.998. This excellent linearity allows the use of a fast and simple single-point calibration.

Benzene in 250 ppmv Gasoline

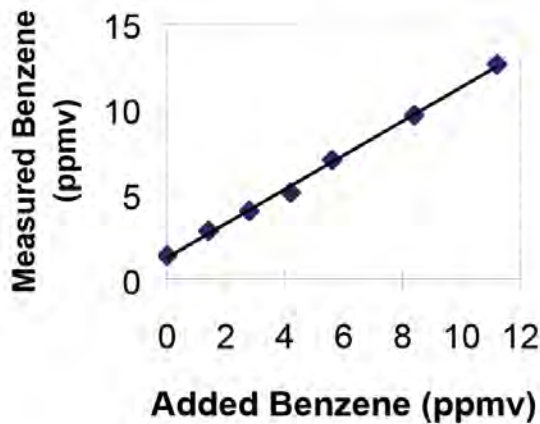


Figure 1. Linearity of benzene response added to 250 ppmv of 92 octane gasoline. The sample contains 1.4 ppmv of benzene from the gasoline itself.

Field Comparison

A study was conducted at four major oil refineries comparing the UltraRAE 3000 with three other benzene-specific portable measurement systems: the Photovac Snapshot handheld GC, the Dräger CMS, and laboratory GC. The results shown in Table 3 were obtained for the combined data from 18 different field samples and 24 standards, including BTEX mixtures:

Table 3. Field sample accuracies as percent of laboratory value ± standard deviation.

| Sample | UltraRAE | Snapshot | CMS |
|---------------|-----------|-----------|-----------|
| Standards | 101 ± 16% | 116 ± 23% | 120 ± 52% |
| Field Samples | 97 ± 29% | 84 ± 21% | 103 ± 92% |

The Snapshot and UltraRAE 3000 gave similar results while the CMS tended to have greater variability.