BENZENE-SPECIFIC MEASUREMENTS IN PETROLEUM HYDROCARBONS USING THE ULTRARAE

Introduction

Benzene is a known human carcinogen that is present in automotive gasoline and other fuels in concentrations typically 0.2 - 3%. Its regulated exposure limit is so low (proposed 8-h 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 (10s to 100s of ppmv total) of the hundreds of aromatic and aliphatic compounds that comprise 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 the use of 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. When ready to measure, a tube is opened, inserted into the UltraRAE and the start button 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 75 seconds. The final value is an average of the concentration over the 75-second sampling period in the 400-cc sample.

Table 1. Response to potential benzene interferences.

Compound	Concentration (ppmv)	Apparent Benzene Response
Toluene	500	0.0
o-Xylene	200	0.0
Ethylbenzene	500	0.0
Styrene	100	0.0
Nitrobenzene	100	0.0
Chlorobenzene	100	0.0
Dichlorobenzene	50	1.0
Methane	25000*	0.0
Propane	1000	0.0
Isobutane	100	0.0
Isobutylene	500	0.1
n-Hexane	300	0.0
Cyclohexane	50	0.2
n-Octane	500	0.0
β-Pinene	50	0.0
Ethanol	50	0.0
Isopropanol	100	0.0
Acetone	100	0.0
Cyclohexanone	300	0.0
Tetrahydrofuran	300	0.0
Ethyl acetate	25	0.0
Acrylonitrile	100	0.0
Epichlorohydrin	100	0.0
Perchloroethylene	100	27

* Methane has no effect on tube capacity. Propane and higher hydrocarbons do affect capacity.

Tube Capacity and Matrix Effects

Benzene RAE-SEP™ tubes withstand 1000 ppm of toluene in dry air and 300 ppm at 50-80% RH. Tubes can be opened and left exposed to air for up to 8 hours 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.

Methane has no effect on tube capacity, but will reduce 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.

	Relative	Reading

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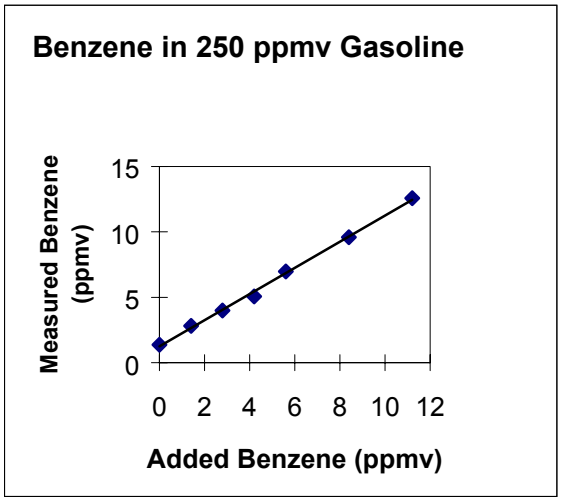
www.raesystems.com | rev.1.6-97

Tube #	Humidity	(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.

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.



Refinery Samples

Petroleum refineries have a variety of process streams that contain a broad range of benzene concentrations. Table 3 compares the results of the benzene-specific UltraRAE, obtained in one minute, with those of 2-hour gas chromatography (GC) runs in the laboratory. The good correlation between the two measurement systems shows the benefit of the time savings afforded by the UltraRAE.

Table 3. Benzene in refinery samples.

Sample	Benzene by GC/FID (mole %)	Benzene by UltraRAE (mole %)
87 Octane Gasoline	0.86	0.63
Reformer Feed	1.2	1.0
Reformer Product	6.3	7.2
Benzene Light Ends	22	24

Field Comparison

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

Table 4. 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 gave similar results while the CMS tended to have greater variability. Complete results of the study are available on request.