# BENZENE-SPECIFIC MEASUREMENTS USING THE TIGER SELECT

Benzene selectivity, STEL accuracy, and TAC selectivity

### Introduction

The Ion Science Tiger Select PID together with the Draeger Benzene pre-filter tubes (p/n FD06-01-BENZTUBE) can be used to measure benzene specifically when present in a complex mixture of other hydrocarbons such as gasoline. As shown in Figure 1, the pre-filter tube oxidizes aromatics and olefins, and absorbs heavy components including alkanes. Lighter alkanes that pass through the tube do not respond on the 10.0 eV lamp. Only benzene passes through the tube unoxidized and unadsorbed, and is detected. This Technical Note describes the limiting conditions when interferences might occur.

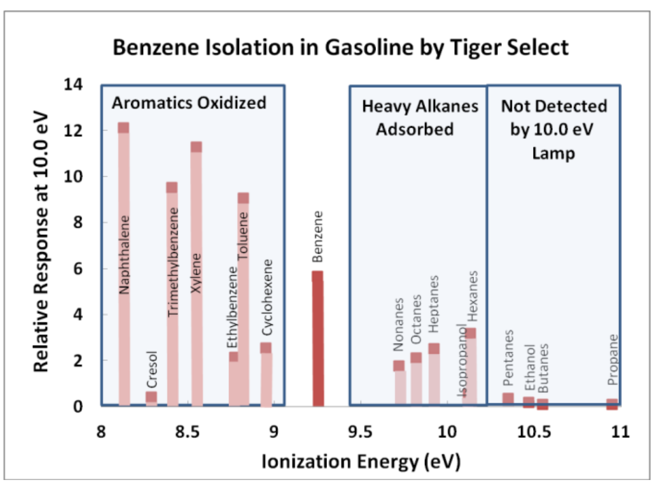


Figure 1. Benzene isolation in gasoline.

### Selectivity Quantification

The Tiger Select gives a spot concentration reading in about 2 minutes, but can also measure Short-Term Exposure Limit (STEL) readings after a 15-minute sampling period. Eventually the pre-filter tube will be used up, and components of a mixture will break through and be read as if they were benzene. The following tests were conducted to determine what concentrations of other potential components might interfere:

Table 1. Tiger Select Benzene Interference Tests†.

| Compound | Test Conc. (ppm) | 2-min Result | Max.Conc. 15-min |
|---|---|---|---|
| Toluene* | 400 | No effect | >25 |
| o-Xylene* | 200 | No effect | |
| n-Octane* | 300 | No effect | 100 |
| n-Heptane | 20 | No effect | >20 |
| n-Hexane | 20 | No effect | >20 |
| Pentanes | 24 | No effect | |
| Butanes | 47 | No effect | |
| Propane | 43 | No effect | |
| Cyclohexane* | 200 | Interferes | |
| Refined Fuels | 90 | No Effect | >90 |
| Acetone* | 100 | No effect | 100 |
| Ethanol* | 200 | No effect | 200 |
| Ethyl Acetate* | 400 | No effect | 400 |
| $H_2S$* | 25 | No effect | 25 |

† Measured effect on response using 0.4 to 5 ppm benzene

* Data estimated from Draeger tube specification sheet

### STEL Tests

Three samples were prepared at a major oil refinery in northern California. One sample was from a cooler where QA samples of refined fuels are stored. Another was prepared by injecting pure hexanes, heptane, toluene, and benzene liquids into a 20-liter Tedlar© gas bag filled with air. The third was diluted from a cylinder of calibration gas used in the laboratory to monitor light end streams. Table 2 shows the make-up of this calibration gas with estimated concentrations of each component based on the benzene measurement.

Each sample was analyzed 1) by granular activated carbon (GAC) using a Gillian sampling pump, with subsequent laboratory analysis, as a reference, 2) using the Tiger Select in standard benzene mode for 2 minutes, and 3) continuing the Tiger Select measurement in STEL mode for 15 minutes. The results are summarized in Table 3 and Figure 2.

Table 2. Calibration Gas Mixture

| Component | Vol% | ppm |
|---|---|---|
| Propane | 22.9 | 48.7 |
| n-Butane | 15.0 | 31.9 |
| Propylene | 14.7 | 31.2 |
| Isopentane | 11.9 | 25.3 |
| Isobutane | 10.1 | 21.5 |
| Isobutylene | 9.53 | 20.2 |
| 1-Butene | 4.99 | 10.6 |
| n-Heptane | 2.30 | 4.9 |
| Benzene | 2.26 | 4.8 |
| n-Hexane | 2.09 | 4.4 |
| cis-2-Butene | 1.04 | 2.2 |
| trans-2-Butene | 1.03 | 2.2 |
| n-Pentane | 1.01 | 2.1 |
| 1,3-Butadiene | 0.514 | 1.1 |
| Propadiene | 0.492 | 1.0 |
| 3-Methyl-1-butene | 0.0582 | 0.1 |
| Methylacetylene | 0.0342 | 0.1 |
| Total | | 212 |

Table 3. STEL Measurements on Refinery Samples

| Sample | TVOC† (ppm) | Benzene Response (ppm) by GAC | Benzene Response (ppm) by Tiger Select Initial* | Benzene Response (ppm) by Tiger Select STEL |
|---|---|---|---|---|
| **Cooler**: Refined fuel samples | 90 | 0.38 | 0.37 | 0.38 |
| **Standard Mix**: 20 ppm Hexane 19 ppm Heptane 26 ppm Toluene 0.3 ppm Benz.‡ | 65 | 0.45 | 0.44 | 0.44 |
| **Cal. Gas Mix** (see Table 2) | 212 | 4.8 | 4.2 | 4.4 |

† Total Volatile Organic Compounds

* Spot reading after the first two minutes of sampling

‡ Added benzene amount, plus unknown amounts present as a trace impurity in the other solvents

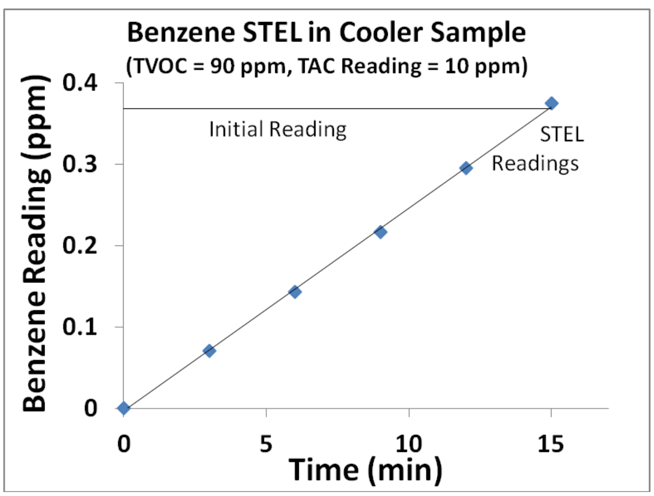


Figure 2. STEL value accumulation in Cooler sample.

Table 3 shows that benzene STEL can be accurately measured at sub-ppm levels in refinery mixtures containing 65 ppm hexane, heptane, & toluene, and in vapors from refined gasoline and diesel fuels up to at least 90 ppm. It can also be measured in over 200 ppm of mixed alkanes and olefins typical of light end streams in a refinery. Figure 2 shows the progression of STEL readings with time. If the sampling ends before the 15 minute period, the reading will be less than the average concentration by the fraction of the 15 minutes sampled.

**Pre-filter Tube Discoloration**

Figure 3 shows how the VOCs (volatile organic compounds) in the Cooler sample turn the tube to a greenish-brown color. In this sample, an accurate STEL reading was obtained even with the color beginning to change to the end of the tube. Nevertheless, it is generally recommended that the discoloration not be allowed to progress further than the ¾ mark indicated on the tube, as shown below.

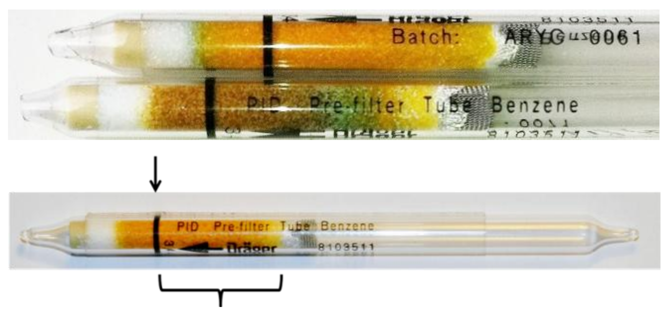


Figure 3. Tube discoloration with VOC exposure.

**How Well Does the TAC Reading Correlate to Actual Total Aromatic Hydrocarbons?**

The Tiger Select can be used in TAC mode to screen

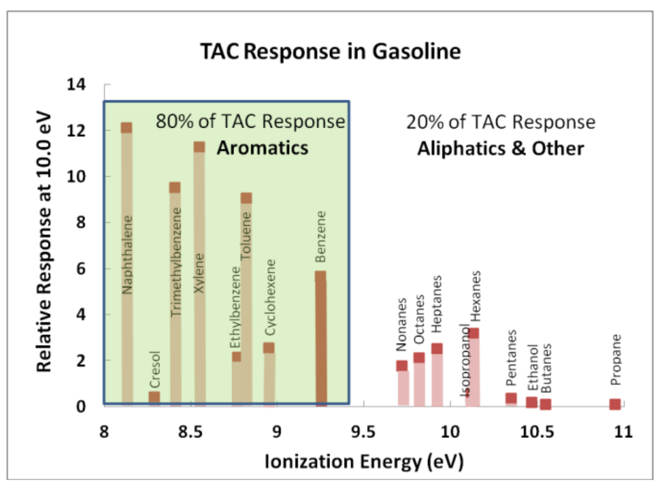


Figure 4. Calculated TAC response in gasoline.

for total aromatic hydrocarbons before applying a pre-filter tube to measure benzene selectively. Figure 4 shows the calculated TAC response on a 10.0 eV lamp for a typical gasoline mixture. About 80% of the response is due to aromatic compounds, while 20% is due to alkanes and other compounds. Thus, TAC gives a reasonable upper limit estimate of true total aromatic hydrocarbon concentrations when measuring gasoline-type samples. Table 4 shows a similar agreement for the Standard Mixture of hexane, heptane & toluene, which simulates gasoline. However, there was no agreement for the Calibration Gas Mixture, which contains more olefins than aromatics. These olefins, like propene and butadiene, respond on the 10.0 eV lamp when no pre-filter tube is present, and thus the so-called TAC reading is not representative of the aromatic concentration. Nevertheless, a high TAC reading is useful in that it provides an upper limit and thus a warning signal to insert a tube to measure benzene selectively.

Table 4. TAC Measurements on Refinery Samples

| Sample | TAC Calc. or Added | TAC Reading |
|---|---|---|
| **Cooler**: Refined fuel samples | --- | 10 |
| **Standard Mix**: 20 ppm Hexane 19 ppm Heptane 26 ppm Toluene | 26 | 19* |
| **Cal. Gas Mix** (see Table 2) | 4.8 | ~28 |

*This value was measured at high humidity and should be closer to 26 ppm after correction for humidity effects.

**Acknowledgments**

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