Technical/Application Article 11

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Benzene-Specific Measurements Using the Tiger Select

Introduction

The Ion Science Tiger Select PID together with the benzene pre-filter tubes, part no. 861614 (formerly 5/FD-01), 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 adsorbs 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 unabsorbed, and is detected. This article describes the limiting conditions when interferences might occur.

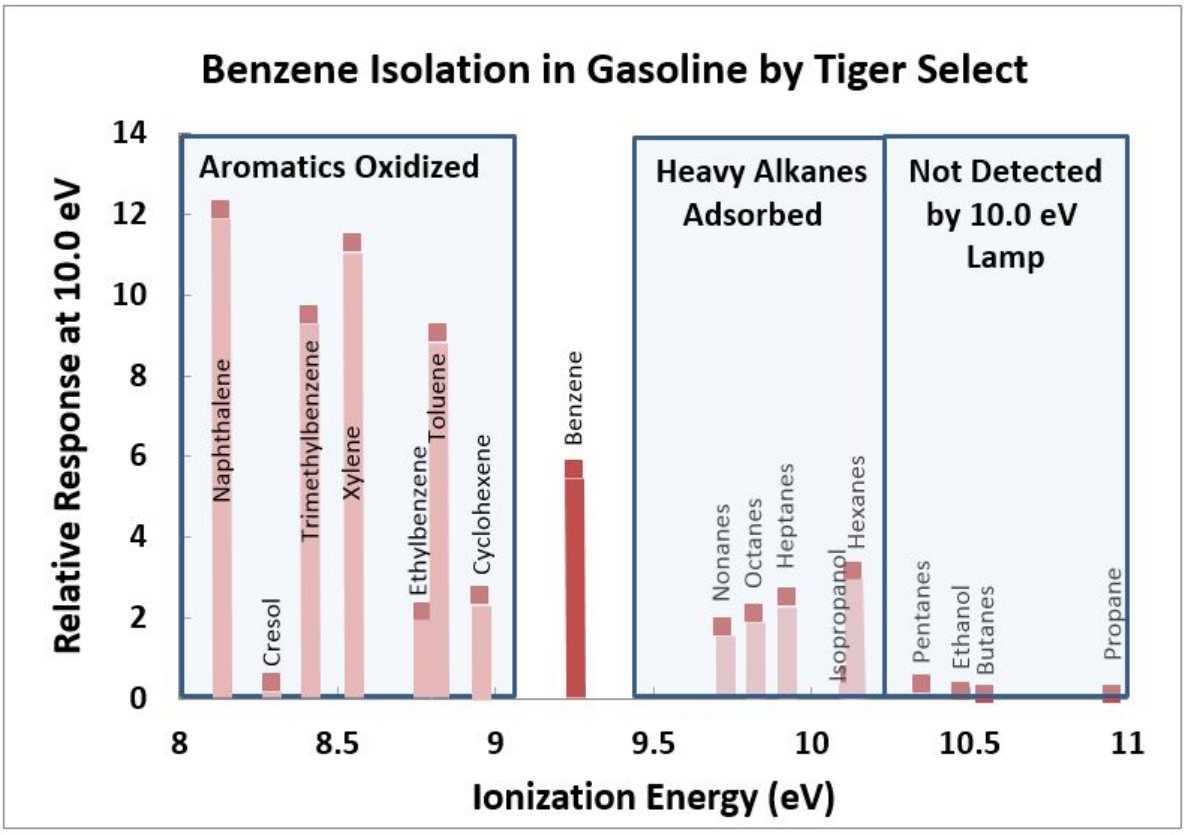

Figure 1. Benzene isolation from gasoline.

Selectivity Quantification

The Tiger Select gives a spot concentration reading in about two minutes (times vary depending on temperature), 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 then 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	0	100
Xylene	200	0	100
Ethylbenzene	200	0	100
n-Octane	300	0	200
n-Heptane	20	0	>20
n-Hexane	100*	0	20
Pentane	1500	0	
Butane	100	0	
Propane	1000	0	
Methane	25000	0	10000**
Cyclohexane	50*	0	
Isobutylene	100	0	
Refined Fuels	50	No effect†	50
Acetone	400	0	200
Ethanol	450	0	>400
Isopropanol	400	0	>400
Ethyl Acetate	400	0	400
H_2S	25	0	>25
CO	100	0	>100
Chlorobenzene	20	2.9	
Trichloroethylene	100	1.8	
Perchloroethylene	50	>11	

† Benzene is present in refined fuels and thus gives a response.

* Higher concentrations may decrease benzene response.

** Methane does not decrease tube capacity or give a response, but above 10,000 ppm it will decrease benzene readings.

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 a) by granular activated carbon (GAC) using a Gillian sampling pump, with subsequent laboratory analysis, as a reference, b) using the Tiger Select in standard benzene mode for two minutes, and c) 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

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 some refined gasoline and diesel fuels up to 90 ppm. It can also be measured in over 200 ppm of mixed alkanes and alkenes typical of light end streams in a refinery (cal. gas mix). Figure 2 shows the progression of STEL readings with time. If the sampling ends before the 15 minute period, the reading equals the average concentration times the fraction of the 15 minutes sampled, as expected.

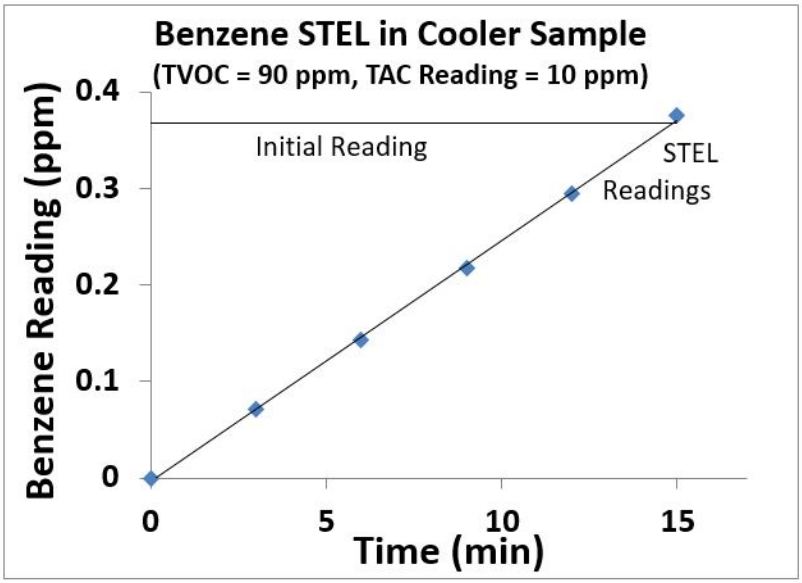

Figure 2. STEL value accumulation in Cooler sample.

Pre-filter Tube Discoloration and Re-Use of Tubes

Figure 3 shows how VOCs (volatile organic compounds) turn the tube to a greenish-brown color as the reagent is consumed. Ion Science recommends that a new tube be used with each tube measurement for best accuracy and performance. Tubes can be re-used for more than one short-term (~2 min.) measurement provided that the tube has not been exposed to high humidity, and tube discoloration has not exceeded the ¾ mark indicated on the tube, as below, to prevent interference in the benzene reading. Please note, however, that the re-use of tubes is done so at the user's own risk. If tubes are re-used it is important that they are purged in clean air for two minutes, to remove any benzene from the tube before starting another benzene measurement. Never use a tube for more than one 15-minute STEL even if there is no discoloration of the tube or the displayed reading is zero. The Tiger Select should not be stored with tubes connected.

Figure 3. Tube discoloration with VOC exposure.

Humidity Considerations

Variations in humidity do not affect the benzene readings because the tube absorbs moisture from the air. However, tubes that have been open to the ambient air for more than an hour or have been used for multiple air samples will turn a dull orange color and have reduced capacity for removing organic interferences. **CAUTION: Do not use tubes that have excessive moisture absorbed onto them, as liquid acids may be drawn into the instrument, causing corrosion and severe damage to the PID.** Again, it is always safest to use a new tube for each measurement, and never use a tube for more than one 15-minute STEL to avoid liquid acid formation.

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

The Tiger Select can be used in TAC mode to screen 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.

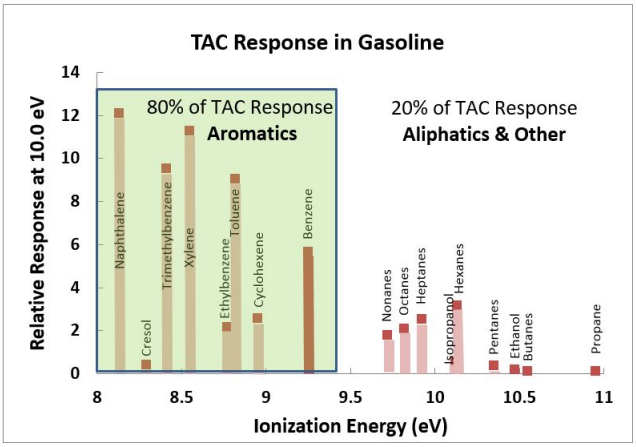

Figure 4. Calculated TAC response in gasoline.

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 may be closer to 26 ppm after correction for humidity effects.

Environmental Compliance Measurements

Although the Tiger Select is designed to measure benzene at the low ppm range near TWA levels, for environmental compliance concentrations of 200 ppm or more may need to be measured. Figure 5 shows that 200 ppm benzene comes to a stable reading within 90 seconds, which is a normal response time for the Tiger Select. Figure 6 demonstrates that readings are linear up to at least 300 ppm benzene. However, that at such high benzene levels, the concentration of other hydrocarbons may also be high, and the capacity of the pre-filter tubes should be considered. If the tubes are discolored past the ¾ mark (see Figure 3), the benzene readings may be high, but as long as the response is below the test limit (e.g., 200 ppm) the result still within environmental compliance and the work activity can continue.

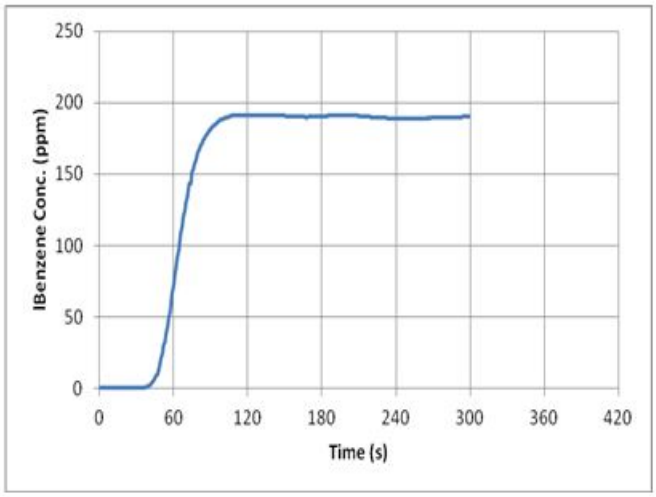

Figure 5. Benzene response time at 200 ppm.

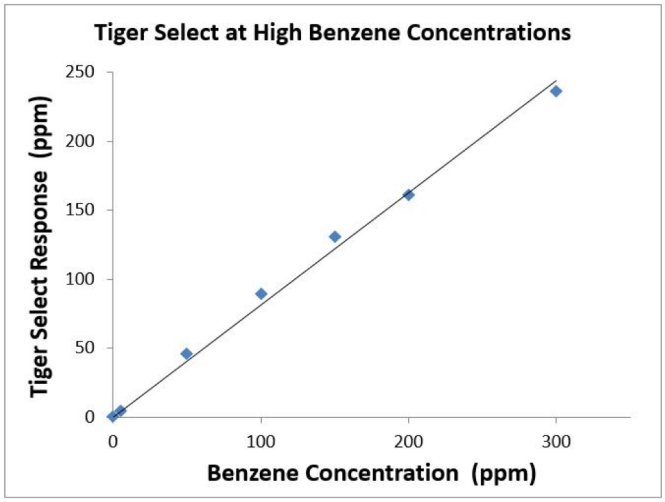

Figure 6. Linear response at high benzene levels.

Acknowledgments

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