Benzene and Butadiene Selective Measurements using the NEO BENZ

Application Note 11

BENZENE SELECTIVE MEASUREMENTS

Introduction

Benzene is a highly toxic component of many fuels and chemical processes. It is classified as a known human carcinogen and has an ACGIH TWA of 0.5 ppm and a NIOSH REL of 0.1 ppm. Benzene is present at about 0.2 to 3% in automotive fuels, and when it is above about 1%, its concentration dominates the toxicity over all other components put together. If a conventional PID were used to measure the gasoline vapors, two different samples containing, say 1% and 2% Benzene would have the same PID reading, yet the second sample would be twice as toxic as the first. Therefore, it is important to measure the Benzene selectively in the mixture of some 300 or more components of typical fuels.

The NEO BENZ selectively measures Benzene (C_6H_6), in complex chemical mixtures, by two processes:

1) The 9.8 eV lamp removes response to nearly all compounds of 5 carbons or less

2)The Benzene Filter Tube removes nearly all compounds of 7 carbons or more by a combination of oxidation and adsorption

Of the remaining 6-Carbon compounds, most Hexanes do not respond on the 9.8 eV lamp, Cyclohexane gives a small interference, and Benzene alone passes through the filtering tube and is measured.

Table 1 shows that most compounds tested do not give any interference in Benzene measurements. All the components of gasoline, including the BTEX components Toluene, Ethylbenzene and Xylene, do not give any response until they are at very high concentrations of a few 100 ppm. The alkanes like Propane, Pentane, Hexane, Heptane and Isooctane also do not interfere. Only Cyclohexane, if present, can give a small response. Sulfur compounds, like Hydrogen Sulfide and Mercaptans, which are sometimes present in crude fuels, are completely absorbed by the tubes.

Table 1. Response of the NEO BENZ system to various possible interferences

Chemical	Concentration (ppm)	Response (ppm)
Toluene	200 300	0.0 ≤0.1
EthylBenzene	100	0.0
Xylenes	100	0.0
Methane*	100%	0.0
Ethylene	100	0.0
Propane*	10000 (1%)	0.0
Isobutylene	200	0.0
1,3-Butadiene	5	0.0
Pentane	1000	0.0
n-Hexane	100	0.0
Cyclohexane	10 50	0.1 0.5
Methyl Cyclohexane	100	0.0
n-Heptane	100	0.0
Iso-Octane	100	0.0
Decane	100	0.0
Hydrogen Sulfide	25	0.0
Methyl Mercaptan	20	0.0
Ethylene Oxide	10	0.0
Epichlorohydrin	50	0.0
Methanol	400	0.0
Ethanol	400	0.0
Acetone	100	0.0
Vinyl Chloride	100	0.4
Trichloroethylene	100	56
Perchloroethylene	100	90
Carbon Monoxide†	50	0.0

** Methane or propane concentrations over 1% quench the response of Benzene and other VOCs.*
† Benzene tubes can be used on a POLI to remove many VOCs that interfere in EC sensor CO measurements without affecting CO.

A few compounds such as Trichloroethylene and Perchloroethylene do pass through the tubes, at least partially. These Chlorinated compounds are not present in fuels, but in some cases are present together with Benzene at hazardous waste sites that are contaminated with complex solvent mixtures.

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Benzene Linearity as a Pure Vapor and in Gasoline

Figures 1a and 1b below show that Benzene response as a pure vapor is linear up to at least 5 ppm and has a detection limit of about 0.025 ppm.

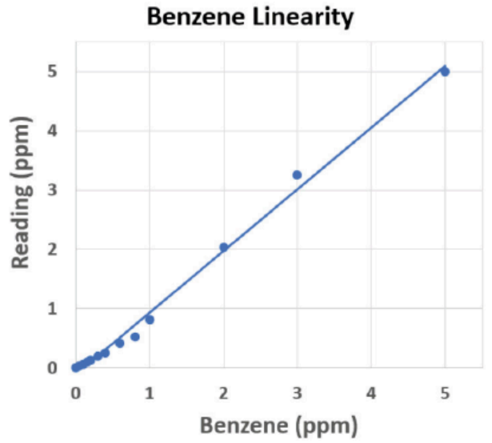


Fig. 1a. Benzene response as a pure vapor is linear to ≥5 ppm

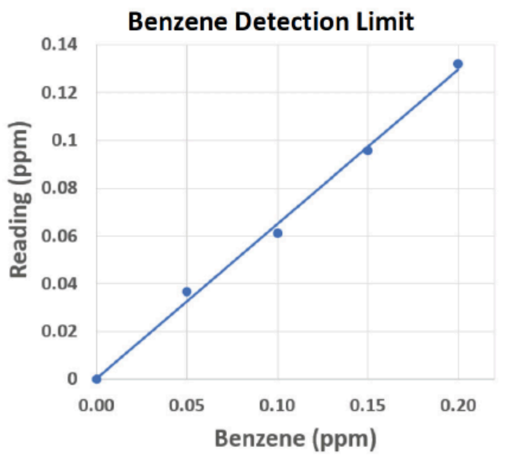
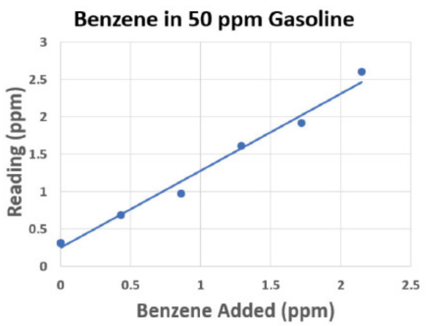


Fig. 1b. Benzene response as a pure vapor, showing detection limit of about 0.025 ppm

Figure 2 shows measurements of Benzene in samples of 50 ppm of gasoline vapors. The Gasoline itself contains about 0.3 ppm Benzene for the 50 ppm sample, or about 0.6%. Addition of pure Benzene to the sample shows a linear rise by the amounts added, with intercept of 0.3 ppm, showing that the hundreds of other components in the Gasoline do not interfere in the Benzene measurement.



Benzene Screening and Measurement

The NEO Benzene is first used for screening by making continuous VOC measurements without a filtering tube. If a reading of concern is encountered, a tube is broken open and inserted into the tube holder. The temperature is selected (see temp. effects below) and a reading initiated, which takes 45 seconds at room temperature. The single reading is displayed and the user can then select whether to continue to do a STEL measurement or to remove the tube and return to continuous Benzene screening.

STEL: Short-Term Exposure Limit

STEL is the average concentration over any 15-minute interval. After the initial 45-second reading, the user can continue sampling for a STEL measurement. To extend the working life of the tubes, the NEO runs at maximum flowrate during initial sampling and then changes to the lowest pump speed for the STEL reading. The figure on the right shows an example of a STEL measurement on a sample containing about 5 ppm Benzene. Table 2 below shows the maximum concentration of various chemicals that give less than 0.05 ppm interference in Benzene STEL measurements on the NEO.

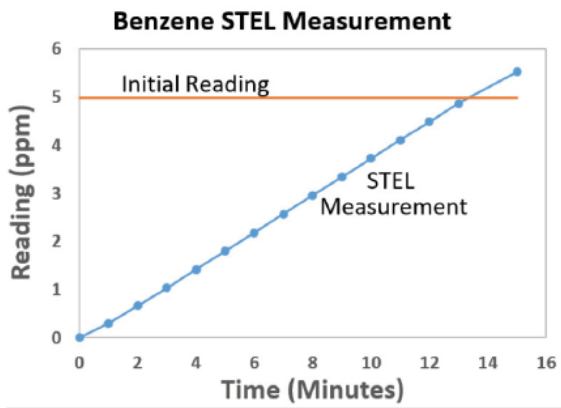


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Table 2. **Maximum concentration for <0.05 ppm interference in Benzene STEL measurements.**

Chemical	Max Concentration for 15-min. STEL
Toluene	100 ppm
EthylBenzene	150 ppm
Xylenes	150 ppm
Methane*	100%
Ethylene	>100 ppm
Propane*	10000 (1%)
Isobutylene	250 ppm
Methanol	400 ppm
Ethanol	320 ppm
Pentane	500 ppm
Cyclohexane	5 ppm
n-Hexane	50 ppm
n-Heptane	50 ppm
Methyl Cyclohexane	50 ppm
Iso-octane	50 ppm
Decane	100 ppm

Tube Discoloration and Re-Use

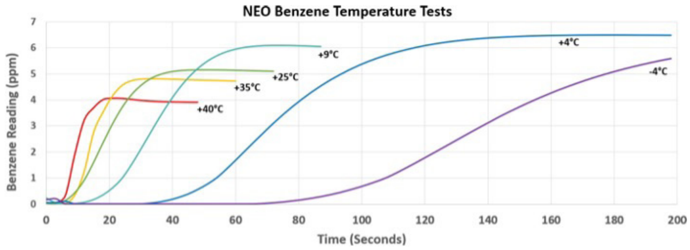
Benzene filtering tubes are designed to be used for only a single measurement. The figures below show that tube color changes can be quite variable depending on the sample gas humidity and type and concentration of VOCs. Therefore it is often difficult to tell from the color change if the tube capacity has been used up or not. Generally, if the color change extends beyond about ¾ of the reagent length, it is likely that VOCs will break through and begin interfering in the Benzene measurements. A tube can be re-used for a second, and possibly third, measurement as long as the earlier readings were close to zero. But as soon as a re-used tube shows a significant response, the results are suspect and the measurement should be repeated using a new tube. The same tube can be used for the initial zero and span calibration because the zero gas should contain no VOCs; however, the tube should not be left in the holder with the pump on for more than a few minutes between zero and span operations, to avoid humidity absorption. Tubes that are broken open but not inserted into an instrument can usually hold capacity for a few hours before the need to be used or discarded.

New tube
Humidity exposed
VOC exposed
VOC exposed

New tube
Humidity exposed
VOC exposed
VOC exposed

Temperature Effects

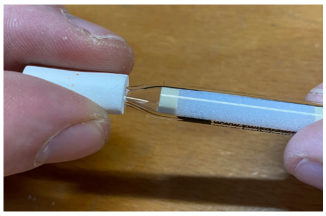
It takes a bit of time for the Benzene to saturate the tube, and therefore the response is not instantaneous. The required sampling time depends on the temperature of the ambient air sampled and the tubes, as indicated in the figure and table below. Most measurements are made in the 20-30°C range, where a sampling time of only 45 seconds is needed.



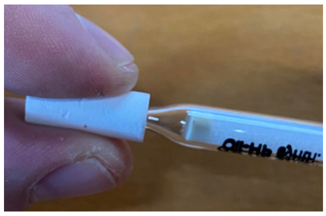
Temp. °C	+31 to +50°C	+20 to +30°C	+10 to +19°C	+5 to +9°C	0 to +4°C	-5 to -1°C	-10 to -6°C
Temp. °F	88 to 122°F	68 to 86°F	50 to 66°F	41 to 48°F	32 to 39°F	+23 to 30°F	+14 to 21°F
Run Time	30 s	45 s	60 s	110 s	170 s	240 s	360 s

Zero and span calibration should be performed using a Benzene tube and near the temperature of the expected measurements, to compensate for the temperature effects of timing and magnitude of the response. As shown if the figure above, 5 ppm Benzene calibrated at 25°C would give a response of only 4 ppm at 40°C and over 6 ppm when below 5°C if the unit weren't calibrated at the measurement temperature. If calibration is performed at room temperature a 20% error can be expected for measurements at the extremes of the temperature range.

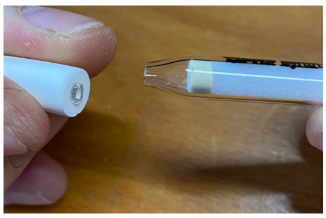
Tips on Opening Tubes



Insert tube fully into ceramic tip breaker and rotate to etch glass



Pull breaker away slightly from etch mark



Grip tube close to end and snap off tip

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Benzene filtering tubes contain compounds that can form corrosive chromic acid on reaction with moisture in the air. Tubes should be removed immediately after a 15-minute STEL measurement; if left in the tube holder for extended periods with the pump on, liquid acids can be drawn into the instrument causing significant damage.

Used tubes should be disposed of according to local environmental regulations. Single tubes contain de minimus quantities of hazardous chemicals and small numbers of tubes can usually be placed in the regular trash, but quantities greater than a several boxes may need to be treated as hazardous waste.

BUTADIENE SELECTIVE MEASUREMENTS

Introduction

1,3-Butadiene is a toxic gas that is used to manufacture polymers such as rubber and acrylonitrile-Butadiene-styrene (ABS) plastics. It is also a component of many fuels and oil refinery processes. It is classified by IARC as a known human carcinogen, and has a low OSHA PEL of 1 ppm and an ACGIH TWA of 2 ppm. 1,3-Butadiene is recognized as a Highly Reactive Volatile Organic Compound (HRVOC) for its potential to readily form ozone, and as such, emissions of the chemical are highly regulated by TCEQ in parts of the Houston-Brazoria-Galveston Ozone Non-Attainment Area. Therefore, it is important to measure the Butadiene for a variety of reasons and to do so selectively as it is often present together with other, less toxic compounds.

Achieving Butadiene-Specificity

The NEO BENZ selectively measures 1,3-Butadiene (C_4H_6), in chemical mixtures, by two processes:

1) The 9.8 eV lamp removes response to aliphatic compounds of 5 carbons or less.

2) The Butadiene Filter Tube adsorbs nearly all compounds of 6 carbons or more.

Low-molecular weight olefins like Ethylene, Propylene, Butenes, Vinyl Chloride and Butadiene pass through the filtering tube and are measured.

Table 1 shows that most compounds tested do not give any interference in Butadiene measurements. Acrylonitrile and styrene do not respond, nor do hydrocarbons like hexane, propane or methane. Of the BTEX components of gasoline, only Benzene gives a slight response. Vinyl chloride passes through the tube, while trichloroethylene does not interfere significantly.

Table 1. Response of the NEO Butadiene system to various possible interferences

Chemical	Concentration	Response
Acrylonitrile	100 ppm	0.0 ppm
Styrene	100 ppm	0.0 ppm
EthylBenzene	100 ppm	0.0 ppm
Toluene	100 ppm	0.3 ppm
Benzene	5 ppm	0.2 ppm
Methanol	300 ppm	0.0 ppm
Carbon Monoxide	50 ppm	0.0 ppm
Ethylene Oxide	10 ppm	0.4 ppm
Methane*	2.5%	0.0 ppm
Propane*	10000 ppm (1%)	0.0 ppm
n-Hexane	100 ppm	0.0 ppm
Ethylene	100 ppm	13.2 ppm
Isobutylene	10 ppm	7.4 ppm
Vinyl Chloride	32 ppm	7.4 ppm
Trichloroethylene	40 ppm	0.2 ppm
Hydrogen Sulfide	25 ppm	0.0 ppm
Methyl Mercaptan	20 ppm	12 ppm

**Methane or propane concentrations over 1% quenchthe response of Butadiene and other VOCs.*

A few compounds such as trichloroethylene and perchloroethylene do pass through the tubes, at least partially. These chlorinated compounds are not present in fuels, but in some cases are present together with Benzene at hazardous waste sites that are contaminated with complex solvent mixtures.

Butadiene Linearity

Figure 1 below shows that Butadiene response as a pure vapor is linear up to at least 5 ppm. The detection limit is about 0.05 ppm.

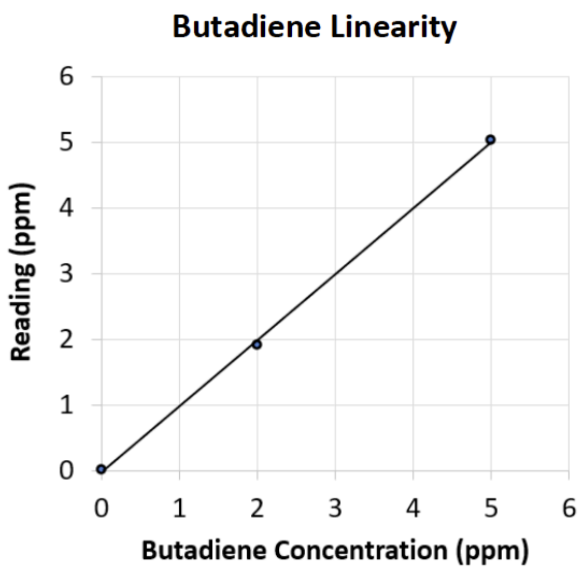

Fig. 1. Butadiene response as a pure vapor is linear to ≥5 ppm

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Butadiene Screening and Measurement

The NEO Butadiene is first used for screening by making continuous VOC measurements without a filtering tube. If a reading of concern is encountered, a tube is broken open and inserted into the tube holder. The temperature is selected (see temperature effects below) and a reading initiated, which takes 3 minutes at room temperature. The single reading is displayed and the user can then select whether to continue to do a STEL measurement or to remove the tube and return to continuous Butadiene screening.

STEL: Short-Term Exposure Limit

STEL is the average concentration over any 15-minute interval. After the initial 3-minute reading, the user can continue sampling for STEL by measuring for an additional 12 minutes . To extend the working life of the tubes, the NEO runs at maximum flowrate during initial sampling and then changes to the lowest pump speed for the STEL reading.

Tube Discoloration, Humidity Effects and Re-Use

Butadiene filtering tubes are designed to be used for only a single measurement. The tubes do not change color when adsorbing VOCs and thus there is no visual indication if the tube capacity has been used up or not. A tube can be re-used for a second, and possibly third, measurement as long as the earlier readings were close to zero. But as soon as a re-used tube shows a significant response, the results are suspect and the measurement should be repeated using a new tube. The same tube can be used for the initial zero and span calibration because the zero gas should contain no VOCs. Tubes do not absorb water vapor significantly but do exhibit moderate losses of capacity in high-humidity environments. Therefore tubes can be broken open up to a few hours before use, but we recommend discarding them if left open for more than one day.

Temperature Effects

Readings are not instantaneous because it takes a few minutes for Butadiene to saturate the tube and stabilize. The required sampling time depends on the temperature of the ambient air sampled and the tubes, as indicated in the table below. Most measurements are made in the 20-30°C range, where a sampling time of 3 minutes is needed. Lower temperatures give higher final response while higher temperatures give lower final response.

Butadiene Tube Measurement Time vs Temperature

Temp. °C	0 to +4	+5 to +9	+10 to +19	+20 to +34	+35 to +50
Temp. °F	32 to 39	41 to 48	50 to 66	68 to 93	95 to 122
Run Time	360 s	300 s	240 s	180 s	120 s

Calibration

Zero and span calibration should be performed using a Butadiene tube and near the temperature of the expected measurements, to compensate for the temperature effects of timing and magnitude of the response. If calibration is performed at room temperature a 20% error can be expected for measurements at the extremes of the temperature range. For typical conditions, we recommend using 5 ppm Butadiene gas for calibration. For highly accurate work at concentrations below 2 ppm, we recommend using a 2 ppm Butadiene standard gas, which is available from various calibration gas suppliers.

Isobutylene Calibration

If Butadiene is not available, isobutylene may be used. For 10 ppm isobutylene set the span value to 7.4 ppm or for 5 ppm isobutylene set the span value to 3.7 ppm (this compensates for the difference in response between isobutylene and 1,3-Butadiene. Again, the calibration should be performed using a Butadiene tube for zero and span, and as close as practical to the expected measurement temperature.

Tube Hazards and Disposal

Butadiene filtering tubes contain no toxic or corrosive chemicals and can be disposed of in the regular trash after taking precautions for sharp glass edges. Unlike Benzene tubes, Butadiene tubes may be left in the tube holder for extended periods with the pump on without threat of damage to the instrument, and will only need replacement when their capacity for VOCs is used up.

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