Butadiene Selective Measurements Using NEO BENZ

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

* Methane or propane concentrations over 1% quench the 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.

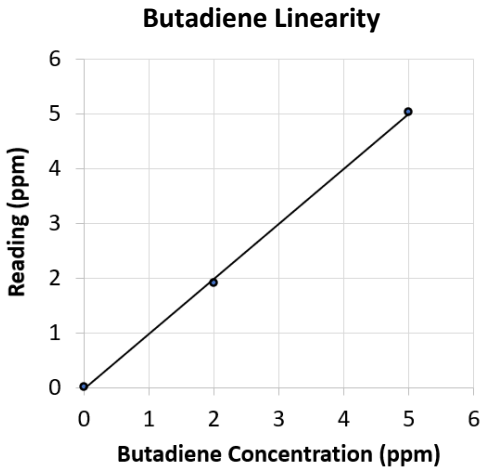
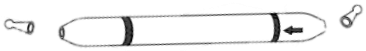


Fig. 1. Butadiene response as a pure vapor is linear to ≥5 ppm

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

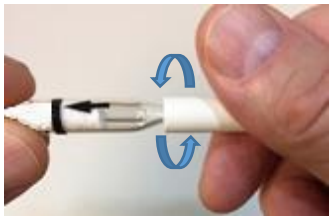
Zero and span calibration should be performed using a butadiene tube and near the temperature of the expected measurements, to compensate for the temperature effects of timing and magnitude of the response. If calibration is performed at room temperature a 20% error can be expected for measurements at 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.

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

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.