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Application Note

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Analysis of BTEX-MTBE by Purge and Trap (P&T) Concentration and Determination by GC/PID

PETROCHEMICAL SERIES

Introduction

The analysis of Benzene, Toluene, Ethylbenzene, Xylenes, and Methyl-tert-butyl ether is a common analysis performed in many laboratories. BTEX compounds are naturally occurring constituents in crude oil and are created and used during the processing of refined petroleum products and during the production of chemical intermediates for many consumer products.[1] BTEX compounds represent some of the most hazardous components in gasoline and are considered toxins of concern in fuels. These compounds, as well as MTBE a fuel oxygenate, are very mobile in soil and groundwater and are used as indicator compounds in various monitoring and clean-up programs such as the Underground Storage Tank (UST) Program.[2]

There are technology improvements available for analysis using the BTEX-MTBE method.

Figure 1. OI Analytical Eclipse 4760 Purge and Trap and the 4551A Autosampler and LV20 Detector

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Instrumentation

Purge and trap concentration was performed with an OI Analytical 4760 purge and trap with a 4551A autosampler. The LV-20 Standard Additions Module was used to inject 5 µl of internal standard and surrogate standard to each sample. The LV-20 employs high-speed valves that inject a programmed volume of standard with no excess or waste. GC separation and detection utilized an Agilent 7890A GC and OI Analytical 4450 tandem photoionization/flame ionization detector (PID/FID). The column used was a Restek Rxi-624Sil MS which can be programmed up to 320 ˚C if samples with very heavy compounds are being analyzed. Please see Table 1 for instrument parameters.

Experimental

A seven-point calibration of 0.5-200 ppb was analyzed. MTBE and m, p-Xylenes were run at 1-400 ppb. Each analytical sample was spiked with 30 ppb α,α,α-Trifluorotoluene internal standard and 30 ppb 1, 4-Difluorobenzene and Bromofluorobenzene surrogate standards. A Method Detection Limit (MDL) study was performed at 0.25 (0.5) ppb. An Initial Demonstration of Proficiency (IDP) was performed at 50 (100) ppb. A Lower Limit of Quantitation (LLOQ) verification was run at 0.5 (1) ppb.

Results

Data was processed with Agilent OpenLab software. The %RSD and correlation co-efficient were calculated for each analyte and all Method 8021B/ 8000D criteria of ≤ 20% RSD for average response and correlation coefficient of ≥ to 0.99 were met for the calibration. The MDL's met 40CFR criteria and IDP and LLOQ met Method 8021B/8000D criteria of 70-130% for the IDP and +/-20% for the LLOQ.

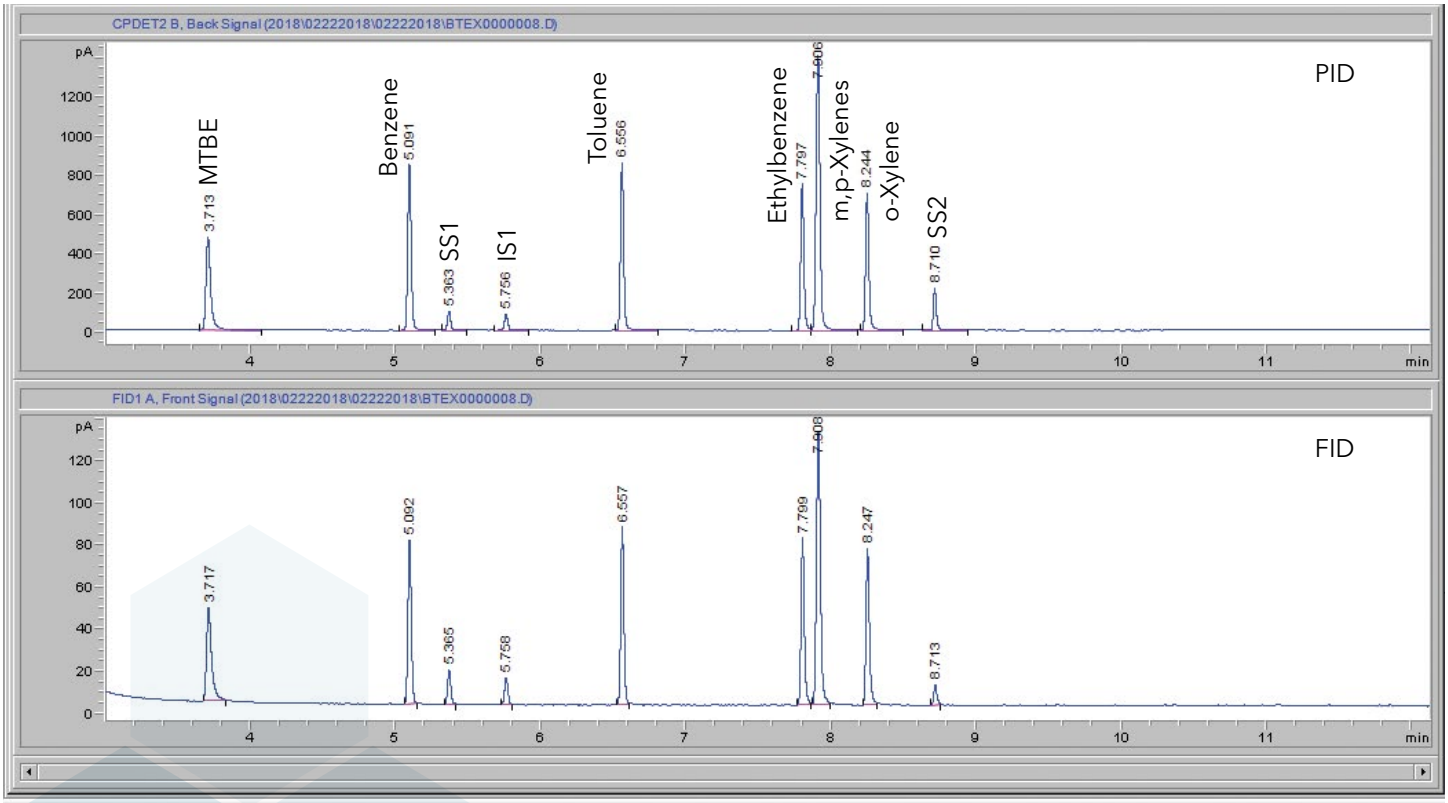
Table 1. Instrument Parameters

Purge-and-Trap	**Eclipse 4760 P&T Sample Concentrator**
Trap	#7 trap; Tenax
Purge Gas	Zero grade Helium at 40 mL/min
Purge Time	8 min
Purge Temperature	45 ˚C
Sparge Mount Temperature	45 ˚C
Desorb Time	0.5 min
Bake Time	3 min
OI #10 Trap Temperature	20 ˚C during purge 170 ˚C during desorb pre-heat 180 ˚C during desorb 200 ˚C during bake
Water Management	120 ˚C during purge Ambient during desorb 240 ˚C during bake
Transfer Line Temperature	140 ˚C
Six-port Valve Technique	140 ˚C
Gas Chromatograph	**Agilent 7890A**
Column	Resktek Rxi-624Sil MS 30 meters, 0.25 mm ID, 1.4 µm film
Carrier Gas	Zero grade helium
Inlet Temperature	240 ˚C
Inlet Liner	1 mm straight
Column Flow rate	0.8 mL/min
Split Ratio	50:1
Oven Program	50 ˚C for 1.5 min 16 ˚/min to 160 ˚C 40˚ /min to 230 ˚C Hold 2.0 minutes Total GC run time is 12.125 minutes
Detector	**4450 PID/FID**
Base Temperature	220 ˚C
Sweep Flow (H2)	35 mL/min
Air flow	170 mL/min
Make up flow (Helium)	25 mL/min
Lamp	5

Table 2. Calibration Data

Compound	RL (ppb)	Avg RF	% RSD	Coeff. of Det (R^2)	MDL (ppb)	IDP Precision (% RSD)	IDP Accuracy (% Rec)	LLOQ (% Rec)
α,α,α-Trifluorotoluene	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
MTBE	1.0	1.257	4.75	0.9992	0.486	2.70	108	104
Benzene	0.5	3.389	4.22	0.9992	0.034	0.89	95.4	92.0
1,4-Difluorobenzene (SS)	N/A	1.172	0.52	0.9999	N/A	0.45	97.5	N/A
Toluene	0.5	3.124	4.37	0.9992	0.052	1.22	93.6	86.6
Ethylbenzene	0.5	2.632	5.89	0.9993	0.016	0.91	98.0	92.2
m,p-Xylenes	1.0	3.033	5.47	0.9992	0.072	1.03	97.7	89.4
o-Xylene	0.5	2.561	4.93	0.9994	0.050	0.79	99.5	90.0
Bromofluorobenzene (SS)	N/A	2.474	1.93	0.9999	N/A	1.57	99.6	N/A

Figure 2. BTEX-MTBE 100 (200) ppb Standard



Conclusions

The 4760/4551A purge and trap system coupled with the 4450 PID/FID gave excellent results using a very simple and rugged methodology. The total GC cycle time from injection to injection totaled 15 minutes, making this a fast method as well.

References

1. Leusch, F. and Barktow, M. 2010. A Short Primer on Benzene, toluene, Ethylbenzene, and Xylenes (BTEX) in the Environment and in Hydraulic Fracturing Fluids. Griffith University.

2. Irwin, R. 1997. Environmental Contaminants Encyclopedia. National Park Service

3. USEPA Method 8021B. 2014 Aromatic and Halogenated Volatiles by Gas Chromatography Using Photoionization and/or Electrolytic Conductivity Detectors. Revision 3.

4. USEPA Method 8000D. 2014. Determinative Chromatographic Separation. Revision 4.

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