

Fast Sub PPB GC/MS Analysis for Tert-Butanol in Gasoline Contaminated Well Water

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Key Words

- PolarisQ Ion Trap
- GC-MS/MS
- Environmental
- Water Quality

Introduction

Oxygenates have been added to gasoline since the mid 1980's as octane additives and to reduce atmospheric pollutants from incomplete combustion. The oxygenated additive compounds are alcohols and ethers that are very water soluble. They tend to migrate into drinking water aquifers much more rapidly than non-polar hydrocarbons, raising environmental concerns. Two of these compounds of interest are Methyl-tert-Butyl Ether (MTBE) and tertiary-Butanol (TBA). TBA was added to gasoline as a 50/50 blend with Methanol in the 1980's as leaded gasoline was being phased out. The mixture was typically blended at concentrations up to 10 % of the gasoline as a replacement octane additive.

Objective

The sample used for this evaluation was selected to represent typical contaminants found in shallow wells. The greatest contamination from gasoline spills comes from polar compounds in the gasoline, primarily aromatic and oxygenate compounds. To create the test mixture, the first 6 gases listed in EPA Method 524 and TBA were added to a Los Angeles County, CA Well Investigation Program standard containing 10 Aromatic hydrocarbons and MTBE. The chosen compounds are listed in Table 1. This sample was analyzed by Purge & Trap-GC/MS to determine the optimum parameters in drinking water. The gases were introduced to measure the effect of purged water on the resolution of these early eluting compounds. A calibration curve at low picogram levels was generated. Replicate injections were made to check the precision of the method.

Experimental Conditions

The Thermo Scientific PolarisQ GC-MS ion trap, (Figure 1), and Tekmar 3100 Concentrator were used for this study. As a part of this evaluation of purge & trap as a viable technique for the analysis of TBA, several method parameters were examined. Sample volumes of 5 mL and 25 mL were tested, since the purge & trap methods for drinking water analysis often recommend 25 mL samples as a way to increase sensitivity for volatile pollutants. Desorb times of 1, 2, and 4 minutes were evaluated to measure the effect of water on the resolution of the volatile gases.

Longer desorb times increase water loading on the trap, and this water can interfere with the chromatographic performance of the early eluting gases as it coelutes along with them. Two different capillary columns were evaluated to compare the performance of a fast, narrow bore column with the more traditional standard column. The standard column was a 60 meter x 0.32mm Rtx®-624 column from Restek. The fast column was a 20 meter x 0.18mm Rtx-VMS, also from Restek. Figure 2 shows that the VMS column took less than half the time to complete the analysis.

To configure a GC for sample introduction from a concentrator, carrier gas is diverted from the GC to a heated switching valve in the concentrator. This valve will divert the flow of the carrier gas across the trap to the inlet for sample introduction. For this evaluation the Purge and Trap Interface kit was installed into the Split/splitless inlet and the heated transfer line from the Tekmar 3100 connected to the top of the GC inlet just below the septum nut. The mass spectrometer was set up in the Segmented Scanning Mode for meeting the tuning criteria for BFB in EPA Method 524. A typical Tune report is shown in Figure 2. All compounds evaluated against the NIST library showed an excellent fit.

Dichlorodifluoromethane	<i>tert</i> -butanol	<i>m</i> + <i>p</i> -Xylene
Chloromethane	Dibromofluoromethane (surr)	<i>o</i> -Xylene
Vinyl chloride	Benzene	<i>p</i> -Bromofluorobenzene (surr)
Bromomethane	Toluene- <i>d</i> 8 (surr)	1,3-Dichlorobenzene
Chloroethane	Toluene	1,4-Dichlorobenzene
Trichlorofluoromethane	Chlorobenzene	1,2-Dichlorobenzene
MTBE	Ethylbenzene	Fluorobenzene (ISTD)

Table 1: Volatile Organics standard test mixture



Figure 1: PolarisQ external ionization ion trap

Instrument Parameters

TRACE GC Ultra

Column 1: Rtx 624 0.32 mm x 60 meter,

1.8 micron film thickness

Oven Ramp: 35 °C, 4.0 min.; 5 °C/min, 55 °C, 0.0 min.;

15C/min, 210 °C, 12 min

Carrier: 10 psi Helium, manual pressure control

Split Flow: 35 mL/min

MS Transfer line: 210 °C

Column 2: Rtx™ VMS 0.18 mm x 20 meter, 1.0 micron film thickness

Oven Ramp: 50 °C, 4.0 min.; 18 °C/min, 100 °C,

0.0 min.; 40 °C/min, 230 °C, 6 min

S/SL Inlet: 150 °C

Liner: Purge and Trap Interface

Carrier: 25 psi Helium, manual pressure control

Split Flow: 35 mL/min

MS Transfer line: 230 °C

Tekmar 3100 Concentrator

Trap: VOCARB 3000

Sample Volume: 5 and 25 mL

Purge Temperature: 30 °C

Purge: 40 mL/min; 11 min

Dry Purge Time: 2 min

Desorb: 245 °C preheat; 2 min. desorb

Bake: 260 °C; 6 min.

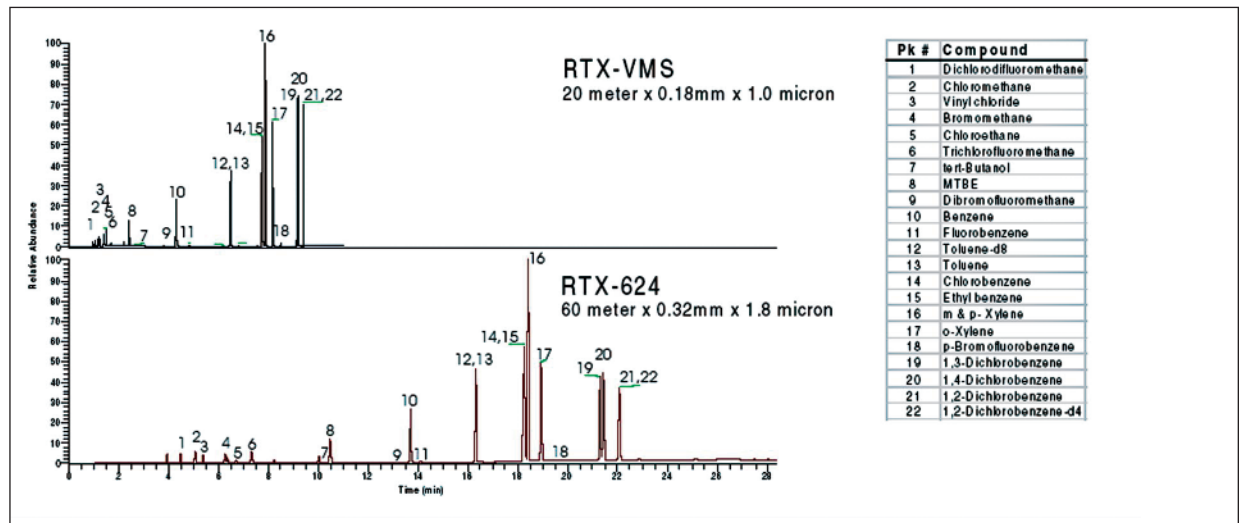


Figure 2: Comparison of 40 ppb Standard on Narrow bore Capillary vs Wide bore Column

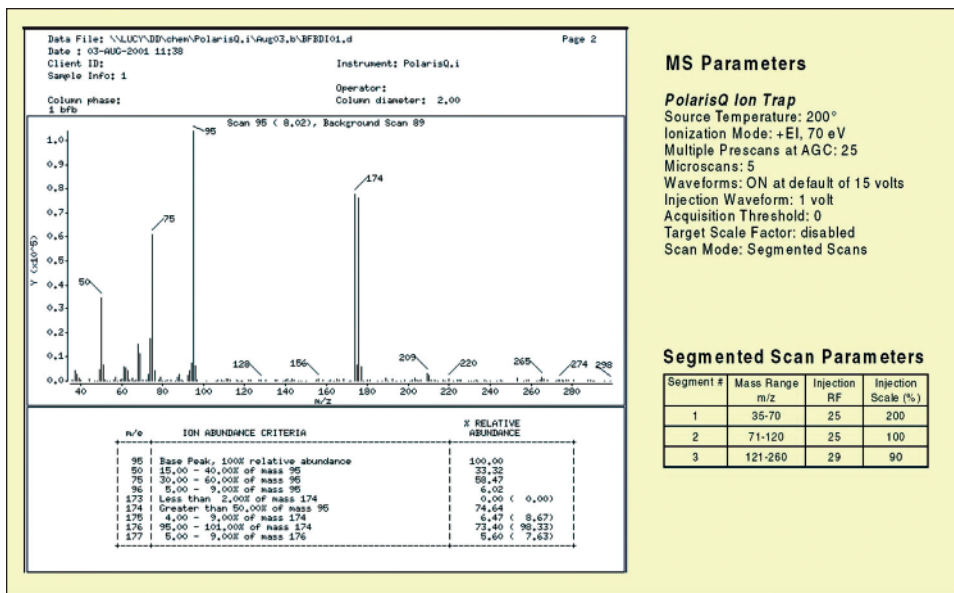


Figure 3: Mass Spectrometer tuning parameters for BFB

COMPOUNDS	CONCENTRATION							AVG CONC (ppb)	STD DEV	MDL (ppb)
Dichlorodifluoromethane	1.06	0.97	0.73	0.84	0.61	0.80	0.73	0.82	0.1500	0.4826
Chloromethane	0.65	1.21	1.03	1.15	0.93	1.05	1.12	1.02	0.1900	0.5924
Vinyl chloride	0.94	0.87	0.85	0.95	0.81	0.91	1.02	0.91	0.0700	0.2211
Bromomethane	2.65	1.61	2.42	1.87	2.94	1.62	2.03	2.16	0.5200	1.6226
Chloroethane	1.16	1.09	1.38	1.37	1.11	1.26	1.35	1.25	0.1300	0.4015
Trichlorofluoromethane	1.12	1.09	0.92	1.13	0.86	1.11	1.06	1.04	0.1100	0.3490
MTBE	1.01	0.92	0.94	0.98	0.99	1.05	1.05	0.99	0.0500	0.167
tert-butanol	0.96	0.89	1.06	1.12	1.11	0.99	0.90	1.00	0.0900	0.3019
Dibromofluoromethane	0.98	0.91	1.00	0.99	0.95	1.08	1.02	0.99	0.0500	0.175
Benzene	1.00	0.94	0.90	0.98	0.96	0.99	1.05	0.97	0.0500	0.145
Toluene - d8	0.99	0.97	0.92	0.94	0.97	1.03	1.06	0.98	0.0500	0.154
Toluene	1.06	1.00	0.96	1.07	1.02	1.13	1.14	1.05	0.0700	0.208
Chlorobenzene	1.05	0.98	0.95	1.01	0.96	1.02	1.01	1.00	0.0400	0.129
Ethylbenzene	1.00	0.95	0.91	0.92	0.89	1.03	1.00	0.96	0.0600	0.1811
m + p - xylene	2.03	2.12	1.81	1.88	1.91	1.95	1.92	1.95	0.1000	0.336
o - xylene	0.97	0.89	0.91	0.92	0.88	1.03	0.96	0.94	0.0500	0.1710
p-Bromofluorobenzene	0.97	0.89	0.92	0.90	0.099	0.85	0.89	0.91	0.0500	0.155
1,3 - Dichlorobenzene	1.00	1.05	0.93	0.98	1.00	1.06	1.02	1.01	0.0400	0.149
1,4 - Dichlorobenzene	1.07	1.03	0.87	0.97	0.92	1.06	1.07	1.00	0.0800	0.2512
1,2 - Dichlorobenzene	1.01	0.96	0.92	1.08	0.99	1.00	1.03	1.00	0.0500	0.1710

Table 2: Replicate response and calculated MDLs

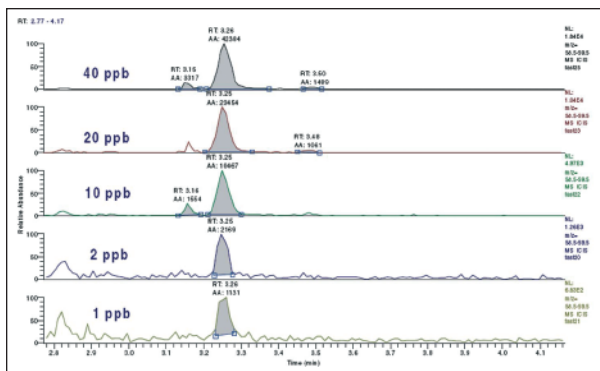


Figure 4a: Extracted Ion Profiles for t-Butanol (59 m/z)

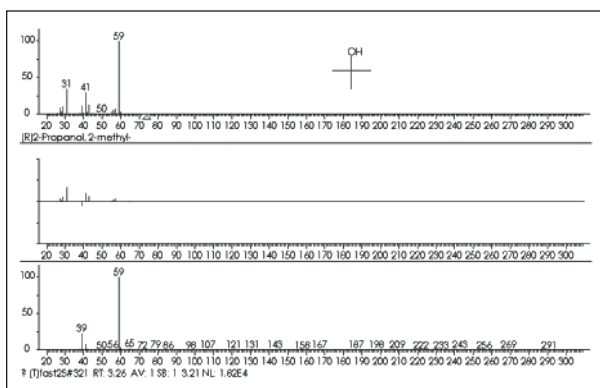


Figure 4b: NIST Library match for t-Butanol

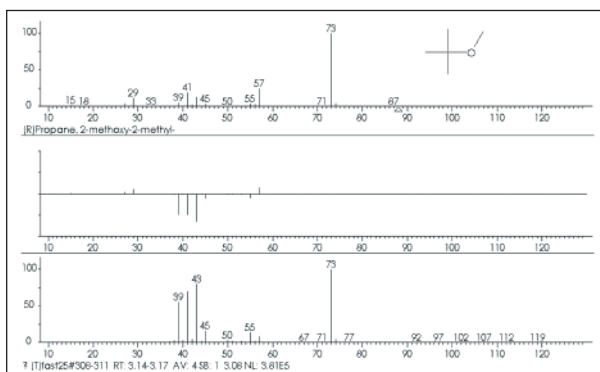


Figure 4c: NIST Library match for MTBE

The linearity of the method was evaluated by running a 5-point curve (1, 2, 10, 20, 40 µg/L) and determining the relative percent standard deviation (%RSD) across the points. The %RSD for all analytes was calculated. Table 2 shows the results of the linearity study on Column #2. The extracted ion profile for TBA at each level of the curve on Column #2 is shown in Figure 4a. The NIST Library spectra for TBA and MTBE are shown in Figures 4b and 4c.

Results

Surprisingly, the lowest MDL for TBA was achieved with a 5 mL water sample. This may be due to a greater purge gas to sample ratio for this highly water-soluble compound. The less soluble gases and aromatics gave lower MDL values for the 25 mL sample, as expected from the greater sample volume extracted. The recovery of TBA was not affected by varying desorb times, and less water interference of the gases was present with the shorter times. A two-minute desorb was chosen as the optimum time for this analysis.

Conclusion

The PolarisQ proved to be an excellent mass spectrometer for the analysis of TBA in the low ppb range. The tuning criteria for BFB were easily met by using segmented scans. The pre-column split injection minimized the adverse effects of water and methanol. MDLs of less than 0.5 µg/L were easily achieved for TBA and MTBE. The linearity was very good, and the tune and response were stable over the test period of three weeks. In order to facilitate the start up of this environmental application, a detailed user's guide with copies of the instrument method, tune file, and calibration curve data are included with the Xcalibur™ software, which arrives with each PolarisQ.

Acknowledgement

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