## Introduction:

For more than 30 years, oxygenated compounds have been added to gasoline. The addition of these compounds provides two benefits: one, the reduction of pollution caused by car emissions as oxygenated gasoline burns more efficiently and two, the improvement of engine performance. However, there are also drawbacks to the use of oxygenated compounds. Due to the prolonged use of these compounds, there has been an increase in the contamination of ground water as underground storage tanks have been found to leak causing their contents to leach into the soil. Finally, due to the high solubility of these compounds, it is necessary to modify experimental conditions in order to receive optimum detection limits.

## Discussion:

This application note explores Purge and Trap experimental conditions in order to determine the most efficient and accurate technique to purge out these highly soluble compounds. The parameters examined were purge volume (5ml, 10ml and 25ml) and purge temperature (room temperature and 60°C). Experimental results were compared for calibration range, linearity, detection limits and compound response.

The Encon Evolution has a unique advantage in controlling the amount of moisture that can be introduced to the GC. Unlike other concentrators, the Evolution uses an 8 port valve. During the desorb process the analytes are transferred directly to the GC from the analytical trap through the transfer line, and the moisture reduction trap (MoRT) is excluded from the desorb pathway. This feature is especially advantageous when utilizing a heated purge as was done for this study. See Figures 1 and 2.
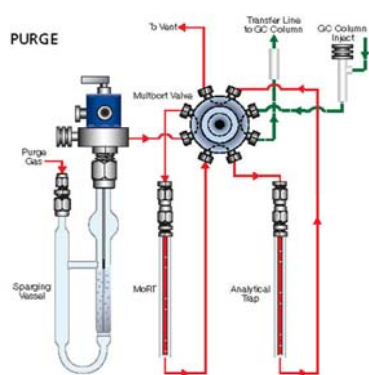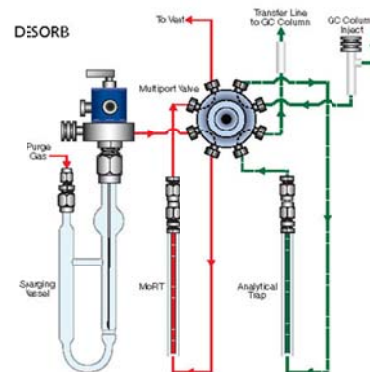


**Figure 1:  Purge Flow Path**



**Figure 2:  Desorb Flow Path**

**Experimental:**

The sampling system used for this study was the EST Analytical Centurion WS autosampler and Encon Evolution concentrator. The experiments were run in water mode and the method parameters are outlined in Table 1. The concentrator was configured to an Agilent 7890A GC and 5975 inert XL MS and the experimental conditions for the GC/MS are outlined in Table 2.

| Purge and Trap Concentrator | EST Encon Evolution |
|---|---|
| Trap Type | Vocarb 3000 |
| Valve Oven Temp. | 150ºC |
| Transfer Line Temp. | 150ºC |
| Trap Temp. | 35ºC |
| Moisture Reduction Trap (MoRT) Temp. | 39ºC |
| Purge Time | 11 min. |
| Purge Flow | 40mL/min |
| Purge Temp. (Room Temp. Purge) | Off |
| Purge Temp. (Heated Purge) | 60ºC |
| Dry Purge Temp. | ambient |
| Dry Purge Flow | 40mL/min |
| Dry Purge Time | 1.0 min. |
| Desorb Pressure Control | On |
| Desorb Pressure | 12psi |
| Desorb Time | 1.0 min. |
| Desorb Temp. | 250ºC |
| Moisture Reduction Trap (MoRT) Bake Temp. | 150ºC |
| Bake Temp | 265ºC |
| Sparge Vessel Bake Temp. | 130ºC |
| Bake Time | 8 |
| Bake Flow | 40mL/min |
| Purge and Trap Auto-Sampler | EST Centurion WS |
| Sample Size | 5mL, 10mL and 25mL |
| Internal Standard Volume | 5µL |

**Table 1: Purge and Trap Parameters**

| GC/MS | Agilent 7890A/5975 inert XL |
| --- | --- |
| Inlet | Split/Splitless |
| Inlet Temp. | 200ºC |
| Inlet Head Pressure | 17.311 psi |
| Mode | Split |
| Split Ratio | 40:1 |
| Column | Rtx-624 20m x 0.18mm I.D. 1µm film thickness |
| Oven Temp. Program | 45ºC hold for 1 min., ramp 18ºC/min to 220ºC, hold for 0.3 min. |
| Column Flow Rate | 0.8mL/min |
| Gas | Helium |
| Total Flow | 38.8mL/min |
| Source Temp. | 230ºC |
| Quad Temp. | 150ºC |
| MS Transfer Line Temp. | 180ºC |
| Scan Range | m/z 35-265 |
| Scans | 3.12 scans/sec |
| Solvent Delay | 0.7 min |

**Table 2:  GC/MS Parameters**

The Oxygenate standards were acquired from Restek.  The California Oxygenate mix contained diisopropyl ether (DIPE), ethyl-tert-butyl ether (ETBE), tert-amyl methyl ether (TAME), tert-butyl alcohol (TBA) and methyl tert-butyl ether (MTBE).  The ethers were at a concentration of 2000µg/ml, while the TBA was at a concentration of 10,000µg/ml.  The ethanol standard was also acquired from Restek at a concentration of 10,000µg/ml.

The linear range of each volume and temperature experiment was established by running a nine point calibration curve with a range of 0.5 to 200ppb for the ether compounds and 2.5 to 1000ppb for TBA and ethanol.  Method detection limits were also established for each compound by examining seven replicate standards of a low calibration point for every experiment.  Experimental results are summarized in Table 3 and Figures 3 and 4 display how volume and temperature affect the chromatographic results.

Upon analysis of the volume and temperature experimental results, it was determined that the larger the sample volume the better the compound response.  Also, the heated purge more than doubled the ethanol response.  However, the 10ml sample volume and 60°C purge temperature provided the optimum linear calibration range.  Thus, the 10ml sample volume and 60°C purge temperature was chosen for the full 8260 analysis.   An 8260 standard was then prepared.  Calibration, method detection limit and precision and accuracy studies were done on the full list of compounds, see Table 4 and Figures 5 and 6.

| Purge and Trap  Technique | Ave Curve %RSD | Ave Curve RF | Ave. Compound MDL | Ethanol Calibration Range (ppb) | Ether Calibration Range (ppb) | TBA Calibration Range (ppb) |
|---|---|---|---|---|---|---|
| 5ml Sample Vol., 25°C Purge Temp. | 6.20 | 1.96 | 1.74 | 25-1000 | 0.5-200 | 2.5-1000 |
| 5ml Sample Vol., 60°C Purge Temp. | 5.50 | 1.77 | 1.33 | 10-1000 | 0.5-200 | 2.5-1000 |
| 10ml Sample Vol., 25°C Purge Temp. | 6.18 | 2.26 | 1.64 | 25-1000 | 0.5-200 | 2.5-1000 |
| 10ml Sample Vol., 60°C Purge Temp. | 6.10 | 2.37 | 1.28 | 5-1000 | 0.5-200 | 2.5-1000 |
| 25ml Sample Vol., 25°C Purge Temp. | 6.54 | 3.67 | 3.11 | 50-1000 | 0.5-200 | 2.5-1000 |

**Table 3:  Sample Volume and Temperature Experimental Results Summary**
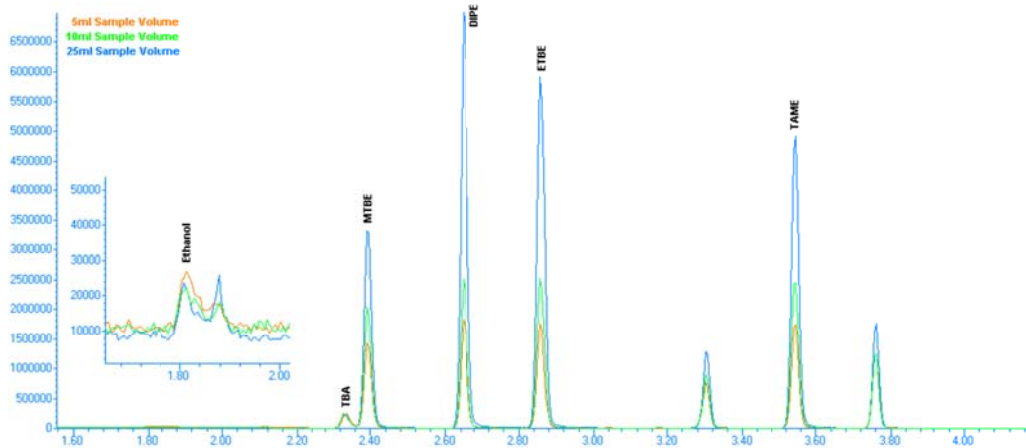


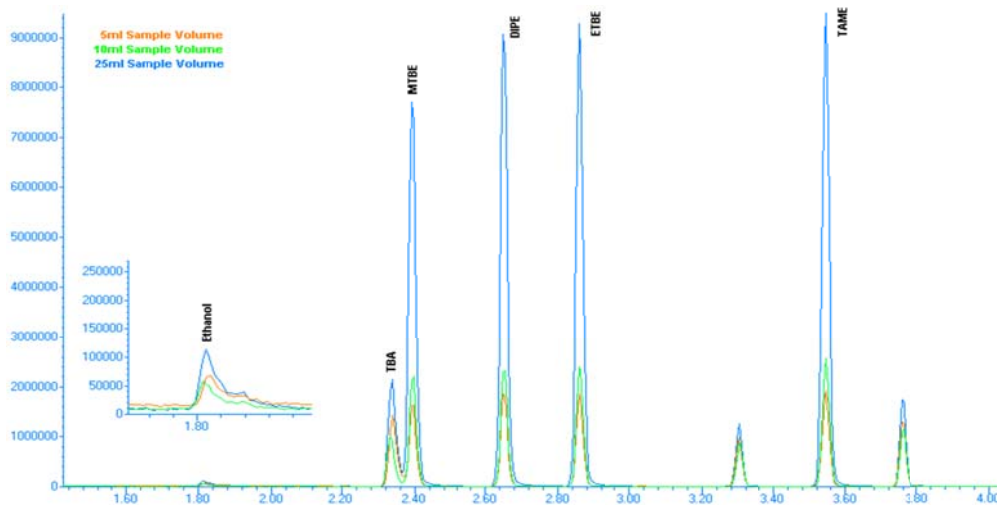**Figure 3:  50ppb Chromatogram with Room Temperature Purge**



**Figure 4:  50ppb Chromatogram with 60°C Purge**

| Compound | Curve %RSD | MDL | 50ppb %Recovery | 50ppb %RSD | Compound | Curve %RSD | MDL | 50ppb %Recovery | 50ppb %RSD |
|---|---|---|---|---|---|---|---|---|---|
| Dichlorodifluoromethane | 11.38 | 0.25 | 82.93 | 4.47 | trans-1,3-Dichloropropene | 3.48 | 0.09 | 103.71 | 2.80 |
| Chloromethane | 9.90 | 0.20 | 84.26 | 1.93 | 1,1,2-Trichloroethane | 3.06 | 0.13 | 101.07 | 2.39 |
| Vinyl Chloride | 5.29 | 0.30 | 94.85 | 5.18 | Tetrachloroethene | 2.08 | 0.19 | 100.53 | 3.26 |
| Bromomethane | 11.89 | 0.30 | 87.88 | 3.39 | 1,3-Dichloropropane | 2.25 | 0.08 | 102.23 | 2.00 |
| Chloroethane | 6.56 | 0.28 | 91.56 | 4.20 | Dibromochloromethane | 9.86 | 0.09 | 106.96 | 2.19 |
| Trichlorofluoromethane | 5.14 | 0.18 | 92.67 | 4.39 | 2-Hexanone | 8.31 | 0.14 | 100.22 | 3.59 |
| ethanol*** | 11.00 | 8.96 | 99.65 | 9.23 | 1,2-Dibromoethane | 4.73 | 0.13 | 100.11 | 2.47 |
| 1,1-Dichloroethene | 7.38 | 0.16 | 95.45 | 4.21 | Chlorobenzene | 3.48 | 0.19 | 98.92 | 2.54 |
| Acetone | 9.41 | 0.48 | 89.12 | 6.01 | 1,1,1,2-Tetrachloroethane | 3.82 | 0.21 | 102.14 | 2.58 |
| Carbon Disulfide | 11.23 | 0.20 | 95.01 | 3.73 | Ethylbenzene | 2.29 | 0.19 | 101.20 | 3.43 |
| Methylene Chloride | 5.88 | 0.21 | 96.28 | 2.88 | Xylene (m+p)** | 9.37 | 0.33 | 211.30 | 2.12 |
| tert butyl alcohol | 6.65 | 1.22 | 96.05 | 5.21 | Styrene | 4.64 | 0.11 | 103.96 | 1.43 |
| MTBE** | 3.71 | 0.21 | 101.60 | 1.87 | Xylene (o) | 3.45 | 0.15 | 100.89 | 2.95 |
| trans-1,2-Dichloroethene | 4.22 | 0.20 | 102.67 | 3.71 | Bromoform | 12.41 | 0.07 | 107.22 | 2.28 |
| isopropyl ether | 2.57 | 0.11 | 104.70 | 2.82 | Isopropylbenzene | 3.55 | 0.17 | 103.28 | 2.29 |
| 1,1-Dichloroethane | 2.87 | 0.18 | 102.71 | 3.86 | Bromobenzene | 3.83 | 0.06 | 96.81 | 2.40 |
| ethyl tert butyl ether | 2.99 | 0.11 | 103.81 | 2.21 | 1,2,3-Trichloropropane | 3.70 | 0.18 | 99.45 | 2.43 |
| 1,4-Dioxane*** | 12.34 | 6.01 | 114.74 | 14.30 | 1,1,2,2-Tetrachloroethane | 9.93 | 0.19 | 98.36 | 3.94 |
| cis-1,2-Dichloroethene | 3.31 | 0.20 | 99.26 | 3.89 | n-Propylbenzene | 4.39 | 0.17 | 101.32 | 2.30 |
| 2-Butanone | 2.79 | 0.27 | 100.33 | 4.43 | 2-Chlorotoluene | 3.65 | 0.15 | 98.37 | 2.32 |
| 2,2-Dichloropropane* | 0.997 | 0.35 | 114.32 | 9.62 | 4-Chlorotoluene | 3.74 | 0.17 | 99.04 | 2.20 |
| Bromochloromethane | 4.85 | 0.18 | 104.31 | 1.88 | 1,3,5-Trimethylbenzene | 2.64 | 0.18 | 99.24 | 2.62 |
| Chloroform | 4.12 | 0.17 | 104.63 | 2.26 | tert-Butylbenzene | 3.80 | 0.20 | 98.31 | 2.20 |
| 1,1,1-Trichloroethane | 2.75 | 0.13 | 102.01 | 2.37 | sec-Butylbenzene | 2.53 | 0.21 | 98.61 | 2.74 |
| 2-Chloroethylvinylether | 3.41 | 0.18 | 96.85 | 2.55 | 1,2,4-Trimethylbenzene | 1.88 | 0.09 | 100.51 | 2.18 |
| Carbon Tetrachloride | 4.41 | 0.18 | 102.23 | 4.12 | 1,3-Dichlorobenzene | 3.56 | 0.16 | 98.43 | 1.95 |
| tert amyl methyl ether | 3.88 | 0.08 | 104.17 | 2.36 | 1,4-Dichlorobenzene | 5.18 | 0.11 | 96.21 | 2.88 |
| 1,1-Dichloropropene | 3.79 | 0.18 | 104.29 | 2.93 | Isopropyltoluene | 2.11 | 0.22 | 100.98 | 2.26 |
| Benzene | 2.18 | 0.15 | 102.27 | 3.58 | 1,2,-Dichlorobenzene | 3.18 | 0.10 | 97.58 | 2.40 |
| 1,2-Dichloroethane | 3.42 | 0.12 | 100.61 | 1.62 | n-Butylbenzene | 2.31 | 0.19 | 100.16 | 3.06 |
| Trichloroethene | 5.93 | 0.12 | 95.64 | 3.91 | 1,2-Dibromo-3-chloropropane | 7.50 | 0.28 | 97.22 | 4.00 |
| 1,2-Dichloropropane | 4.91 | 0.05 | 101.68 | 2.75 | 1,2,4-Trichlorobenzene | 2.88 | 0.12 | 96.30 | 2.16 |
| Dibromomethane | 3.31 | 0.13 | 100.76 | 2.35 | Naphthalene | 4.03 | 0.08 | 98.77 | 2.87 |
| Bromodichloromethane | 4.55 | 0.14 | 102.30 | 2.66 | Hexachlorobutadiene | 3.12 | 0.15 | 95.37 | 3.75 |
| cis-1,3-Dichloropropene | 3.77 | 0.15 | 102.52 | 2.98 | 1,2,3-Trichlorobenzene | 5.25 | 0.12 | 96.02 | 2.22 |
| Toluene | 3.66 | 0.15 | 100.48 | 2.39 | | | | | |

*Compound was linear regressed

**MDL at 2ppb and 100ppb for %Recovery and %RSD

***MDL at 10ppb and 250ppb for %Recovery and %RSD
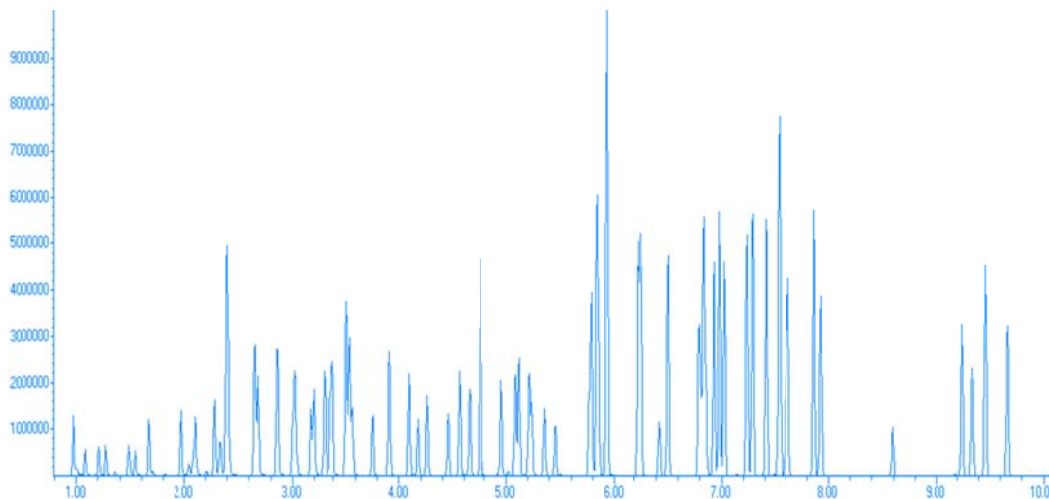
**Table 4:  Summary of 8260 and California Oxygenate Data**

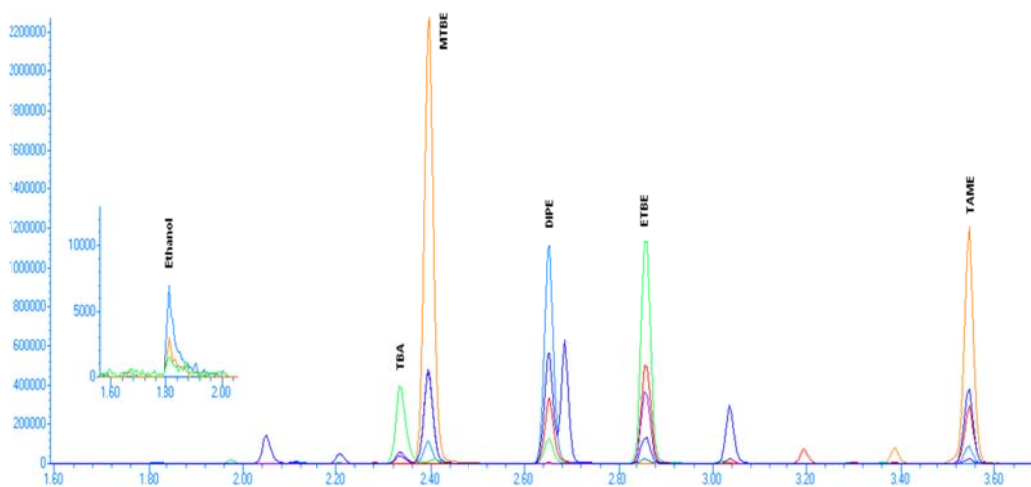**Figure 5:  50ppb Standard of 8260 and Fuel Oxygenates**



**Figure 6:  Extracted Ion Chromatogram of the 50ppb Standard of the Fuel Oxygenate Compounds in the 8260 Mix**

**Conclusions:**

Overall, the fuel oxygenate compounds had higher responses when the sample volume was increased.  Sample purge temperature had the greatest effect on the polar compounds, TBA and the ethanol.  The linear calibration range proved to be consistent between all of the compounds with the exception of Ethanol.  Optimum linear calibration for the ethanol was accomplished when using the 10ml volume and 60°C heat.  The Encon Evolution, with its Moisture Reduction Trap (MoRT), proved to be an excellent system for the determination of the Fuel Oxygenate compounds. Furthermore, as seen with the 8260 results, the system met or exceeded all of the method criteria.