Analysis of Low Concentration Oxygenates in Environmental Water Samples Using Purge and Trap Concentration and Gas Chromatography/Mass Spectrometry

Environmental

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Abstract

The frequent use of oxygenate additives in gasoline to produce clean burning fuels has led to widespread and well documented contamination of ground water and drinking water supplies. The phasing out of methyl tert-butyl ether (MTBE) as the oxygenate of choice has led to an increased interest in testing for other common additives. These other additives may be ethers, other than MTBE, but also methanol or ethanol may be considered. Traditional techniques used for the analysis of volatile organic compounds in drinking and ground waters frequently employ the use of a purge and trap concentrator interfaced with a gas chromatograph. Detectors being used range from photoionization detectors (PID) and electrolytic conductivity detectors (ELCD) to mass selective detectors (MSD). Mass spectrometry is becoming the detection mode of choice for these additives, as it provides an additional level of confirmatory confidence in the presence of many potential matrix interferences. However, the challenge of extracting extremely polar analytes from an aqueous matrix requires modification and optimization of the purge and trap concentrator from its typical settings. As laboratories are seeking to determine these polar additives in the low part-per-billion (ppb) range, it is important that all aspects of the system be optimized. This application note will discuss system settings necessary for achieving low level quantitation of additives such as methanol and ethanol.

Experimental

This work was performed using a 6890 Plus gas chromatograph equipped with a 5973 mass spectrometer (Agilent Technologies, Inc. Wilmington DE). The purge and trap (P&T) used in the study was a model 3100 obtained from Tekmar/Dohrman (Cincinnati, OH). The J&W Scientific brand capillary column used, DB-VRX, was obtained from Agilent Technologies Inc. (Folsom, CA).

All standards used were prepared in-house from neat materials. Standard solutions were prepared in purified water.

Discussion

More and more frequently environmental laboratories are being asked to analyze for oxygenated analytes in drinking, ground and wastewater samples using pre-existing P&T GC/MS technology. Analytes such as acetone, ethyl ether, methyl-*tert*-butyl ether (MTBE), *tert*-butanol (TBA) and 2-butanone (MEK) are common, but now labs are beginning to receive an increasing number of requests for methanol and ethanol. As some laboratories are reporting very low method detection limits for these polar analytes, it is becoming apparent to others that not matching these low levels may eventually result in a loss of business. This work was performed for two primary reasons:

- To optimize P&T system conditions in order to achieve the best sensitivity possible for oxygenates in water
- To ascertain whether or not the low detection levels being reported by laboratories are realistic and achievable

The basic study design was as follows: Multiple replicates of an oxygenate standard (Table 1) were run using typical P&T conditions to establish a base response and to assure that reproducible results were being obtained. The %RSD for the multiple runs averaged 0.6%–0.8%. Once the base response was established analysts made modifications to the method parameters and charted any response changes for the same standard solution. Once the most significant modifications were defined they were combined to provide the best possible response enhancement. At this point a calibration curve was performed to establish that this technique was truly valid for quantitative work spanning a wide range of concentrations.

The oxygenate standard shown in Table 1 was prepared from neat materials in purified water and was used for all of the response enhancement work. Analytes are in solution at concentrations ranging from 5 to 500 µg/L. These concentrations were derived through experimentation using typical labratory P&T condtions so that all of the peaks of interest were on the same scale at the beginning of the study.

Table 1. Maximizing Oxygenate Response Analyte Concentrations in Purged Standard

Compound	Concentration (µg/L)
Methanol	500
Ethanol	500
Acetone	50
Ethyl ether	5
tert-Butanol (TBA)	50
Methyl-*tert*-butyl ether (MTBE)	5
Methyl ethyl ketone (MEK)	50

All stock solution prepared in purified water

Figure 1 shows the chromatogram obtained for the oxygenates standard using typical P&T concentrator conditions. Note that the abundance counts on the Y axis range up to approximately 35,000. This is an extracted ion chromatogram for *m/z* values of 31, 43, 73, and 59.

The primary variables considered in this work were:

- Purge gas flow
- Sample volume
- Sample temperature
- Matrix modification

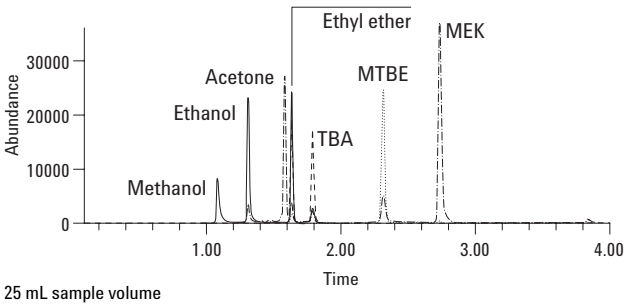


Figure 1. Oxygenates standard run using typical P&T conditions and DB-VRX capillary column.

Purge Gas Flow

The purge-gas flow was not adjusted or modified from typical settings as in most cases the laboratory will use the same P&T/GC/MS system for this analysis as well as for their standard 8260B and 524.2 work. Purge flow in most, if not all, P&T systems is a manual adjustment. Purge flow has a definite impact upon analyte recovery and if it is not kept constant calibration curves may become invalid and need to be rerun. If purge flow were manually increased for the oxygenate work and manually adjusted back down to return to 8260B or 524.2 work, it may jeopardize the current calibration curve. In addition, excessive purge flow can lead to trap breakthrough for some of the more volatile analytes contained in such methods. It was deemed more important that laboratories be able to easily adopt the changes suggested here without causing any loss in productivity for other methods of interest. As such, a purge flow of 40 mL/min for 11 minutes was maintained.

Sample Volume

It was shown in O.I. Analytical application note number 13271198 that utilization of a 25 mL sample volume vs. the typical 5 mL results in better sensitivity and improved calibration reproducibility. In its simplest form, five times the sample means five times the nanogram amount in solution. This does not mean five times the response will be achieved for all analytes, but for most a significant increase in response will be noted. All subsequent work was performed using a 25 mL sample size.

Sample Temperature

Multiple runs were performed with the sample temperature at ambient, 45 °C, 55 °C, 65 °C, 75 °C and 85 °C. Figure 2 shows the response enhancement with temperature increase for each analyte in the oxygenate standard. The responses graphed are all relative to the sample purged at ambient temperature, which is considered 100% recovery. There is a consistent response increase with temperature up to 75 °C but at 85 °C a dramatic increase is noted. As the response increase was so significant at 85 °C, this temperature was considered optimum. The sample preheat (heating prior to purge) was set for 1 minute for all temperatures. In reality, after 1 minute the purge temperature had only reached approximately 55 °C. After 2 minutes the temperature was around 65 °C, 3 minutes was 75 °C and not until the 4-minute mark did the vessel actually reach 85 °C. While the temperature was not at the set-point when purging began, it was deemed as acceptable as the heating rate of the sample was very consistent and even in the worst case, with an 85 °C set-point, the sample was purged for 8 minutes at full temperature. Increasing the preheat time to 3 and 4 minutes did not result in any significant response improvement, but definitely increased the overall purge and trap cycle time, thus reducing sample throughput. One minute of preheat gave excellent response with a minimal cycle time.

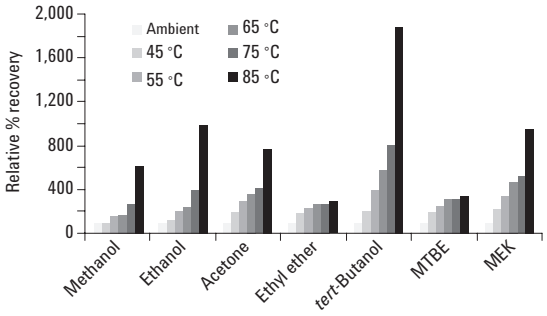


Figure 2. Analyte response vs. sample temperature.

When heating the sample to this degree, the amount of moisture transferred to the sorbent trap is significant. One benefit of the Vocarb™ 3000 trap used in this work is that it is dry-purgeable. Whether or not the water is actually purged from the trap during this step or simply purged completely into an appropriate sorbent was not explored, but a benefit in chromatographic performance is evident (Figure 3).

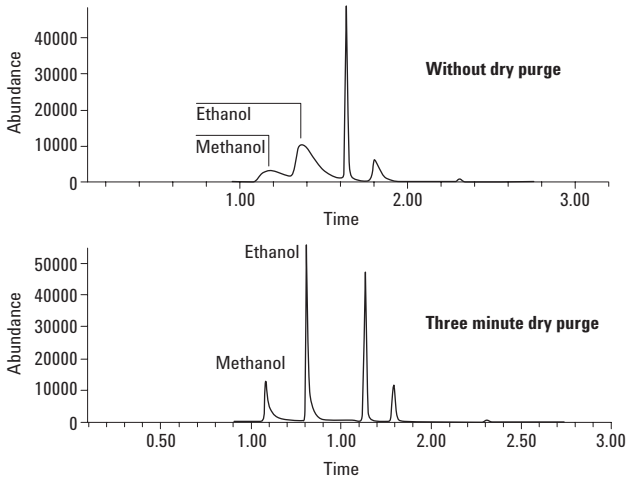


Figure 3. Modifying P&T conditions–secondary effects of increased sample temperature.

Matrix Modification

It is well understood that increasing the ion content of an aqueous solution can lead to improved recovery of non-ionic organic species from that solution. The process of increasing the ion content is generally termed 'Salting'. The primary considerations when salting a solution are what type of salt and how much salt to add. Table 2 refers to the benefits and drawbacks of several common salts. Considering the obvious drawbacks of sodium carbonate and potassium phosphate, this study focused on the use of sodium chloride and sodium sulfate. Figures 4 and 5 show the improved response achieved with different mass additions of both sodium chloride and sodium sulfate, respectively. Figure 6 gives a direct comparison of 'no salt' relative to optimum amounts of sodium chloride and sodium sulfate. It is obvious that sodium sulfate gives superior performance and, as it does not have the same corrosive characteristics as sodium chloride, it was chosen for all further work.

Table 2. The Benefits and Drawbacks of Several Common Salts

Compound	Results
Sodium chloride (NaCl)	Highly soluble in water (~8 g/25 mL), readily available, chlorine ion very reactive
Sodium sulfate (Na_2SO_4)	Highly soluble in water (~6 g/25 mL), neutral pH in solution, 2 sodium ions per molecule of salt
Sodium carbonate (Na_2CO_3)	Highly alkaline in solution
Potassium phosphate dibasic (K_2HPO_4)	Extremely soluble in water (~37 g/25 mL), difficult to work with

Figure 4 shows the effect of sodium chloride salt quantity on response relative to the 'no salt' standard P&T condtions. Above 6 g of NaCl the salt was not dissolving completely into solution and so addition was stopped here.

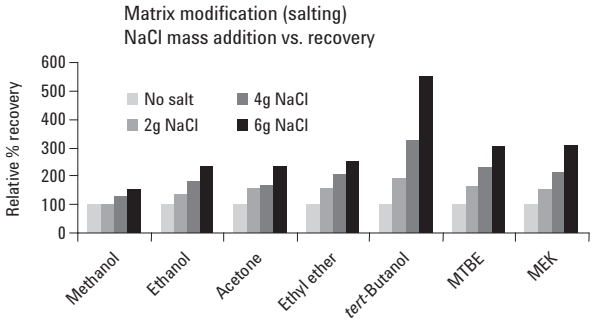


Figure 4. The effect of sodium chloride salt quantity on response relative to the 'no salt' standard P&T condtions.

Figure 5 shows the effect of sodium sulfate salt amount on response relative to the 'no salt' standard P&T conditions. There is a distinct rise in response at 6 g as we approach full saturation of solution.

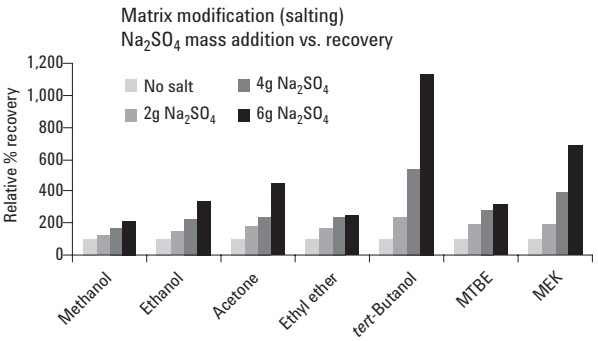


Figure 5. The effect of sodium sulfate salt amount on response relative to the 'no salt' standard P&T conditions.

In Figure 6, this combined bar-graph shows directly the response differences experienced with the two different types of salt (both at 6 g) relative to the 'no salt' standard P&T conditions. It is clear that there is a definite response advantage to using sodium sulfate vs. sodium chloride.

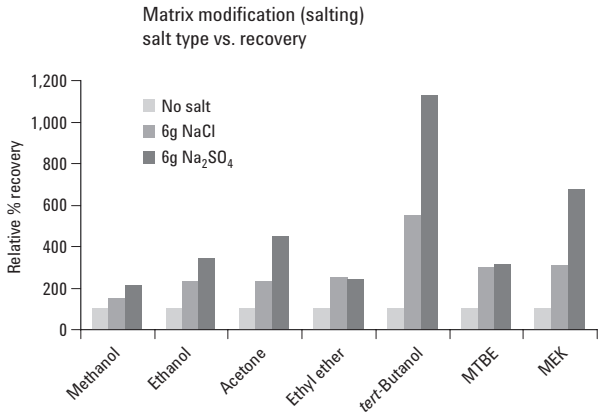


Figure 6. The response differences experienced with the two different types of salt relative to the 'no salt' standard P&T conditions.

Combining Parameters

Figure 7 shows the effect of temperature and salt addition alone, relative to standard conditions, but also shows how much more impact these modifications made once they were combined. For instance, *tert*-Butanol response was increased roughly 20 times using an 85 °C purge temperature and roughly 10 times using the addition of 6 g of sodium sulfate, but when these two modifications were combined it resulted in an overall response increase of over 75 times relative to standard P&T conditions.

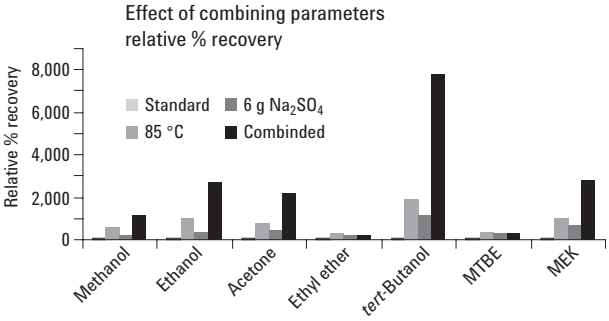


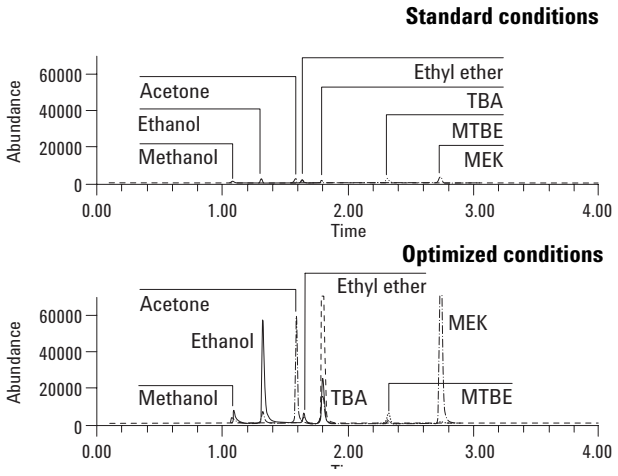
Figure 7. Effect of combining optimized purge and trap parameters.

Table 3 shows the final optimized run conditions for this analysis. Figure 8 is a direct visual comparison of standard vs. optimized P&T conditions. Again, methanol and ethanol are spiked into solution at 500 ppb. Note the much smaller response for ethyl ether and MTBE in the optimized chromatogram. Recall that they are in solution at 5 ppb vs. 50 ppb for acetone, TBA and MEK and 500 ppb for methanol and ethanol.

Table 3. Optimized Run Conditions

Column:	**DB-VRX**
P/N:	**121-1524**
Length:	20 m
Diameter:	0.18 mm
Film thickness:	1.0 µm film
Carrier:	Helium at 45 cm/sec (1.0 mL/min)
Oven:	45 °C for 3.5 minutes
	45–150 °C at 15 °C/min
Injector:	Tekmar 3100 Purge and Trap
Trap:	Vocarb 3000
Sample volume:	25 mL
Sample temp:	85 °C (1 minute preheat)
Purge:	11 Minutes
Dry purge:	3 Minutes
Desorb preheat:	245 °C
Desorb:	1 Minute at 250 °C
Bake:	10 Minutes at 260 °C
Line and valve temp:	125 °C
Interface:	Split injector at 200 °C,
	60:1 Split ratio
Gas saver:	150 mL/min at 1 minute
Agilent 5973 MSD	
Scan range:	29-260 amu
Scan rate:	3.17 scans/sec
Quad temperature:	150 °C
Source temperature:	230 °C
Transfer line temp:	250 °C
Matrix modification:	6 g Sodium sulfate

Figure 8 shows a chromatographic comparison between typical and optimized P&T conditions. The 'Y' scales are normalized for comparative purposes.



Abundance normalized for comparative reasons

Figure 8. A chromatographic comparison between typical and optimized P&T conditions.

Performing a Calibration Curve

Eight points were used with the realistic expectation that not all analytes were going to be linear from 0.5 ppb up to 200 ppb. It was expected that the methanol and ethanol may not achieve single digit ppb levels. As expected, methanol was not able to be calibrated down to 0.5 ppb or even 5 ppb. At these lower concentrations the signal-to-noise ratio was simply too low to be reliable. At 10 ppb it was approaching a more reasonable 10:1 ratio. Figure 9 shows the calibration curve for methanol. Using linear regression per EPA methodology and a calibration range of 10–200 ppb the R-squared value was 0.9987, which is well above the EPA required 0.990 needed for valid quantitative use. Ethanol was calibrated from 0.5–200 ppb with an R-squared value of 0.998 (Figure 10). Both methanol and ethanol calibration ranges could likely be extended to well above 200 ppb.

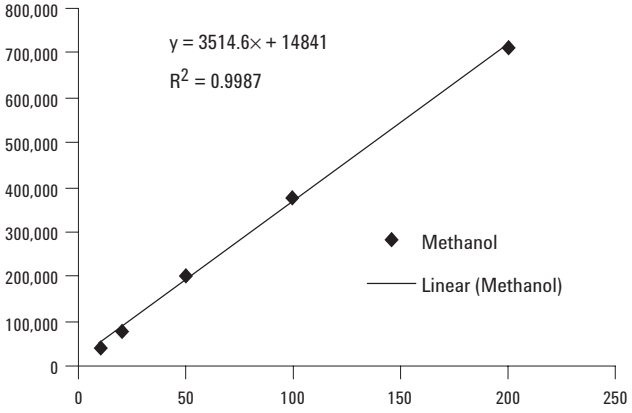


Figure 9. Calibration curve for methanol with a calibration range of 10–200 ppb

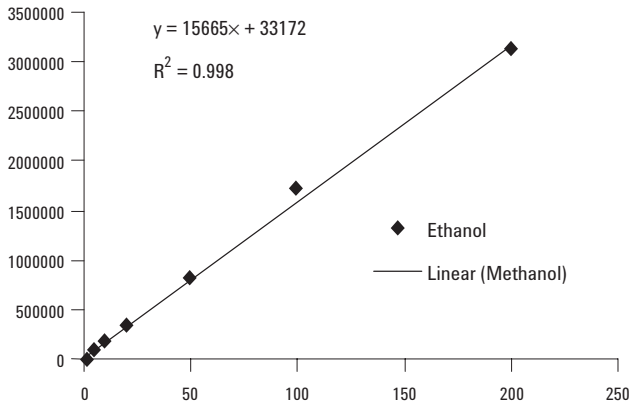


Figure 10. Calibration curve for ethanol with a calibration range of 0.5–200 ppb.

For all components, except methanol, a calibration range of 0.5–200 ppb was achieved with R-squared values ranging from 0.990–0.998 (Table 4), all at or above the Environmental Protective Agency (EPA) requirements for valid quantitation. Methanol as stated earlier was calibrated over a range of 10–200 ppb with an R-squared value of 0.9987.

Table 4. Calibration Curve Summary Using Optimized Analysis Conditions

Compound	Calibration range (ppb)	R^2 Value
Methanol	10–200	0.999
Ethanol	0.5–200	0.998
Acetone	0.5–200	0.993
Ethyl ether	0.5–200	0.994
TBA	0.5–200	0.990
MTBE	0.5–200	0.995
MEK	0.5–200	0.994

USEPA requires R^2 value of 0.990 or greater for quantitative use

Additional Considerations

Automated sampler systems, that accept full VOA vials to reduce sample handling, may require some special approaches to facilitate salt addition. It may be necessary to contact the manufacturer of the autosampler to find out the feasibility of salt addition.

Many laboratories attempt to run the low level oxygenates in conjunction with their 8260 or 524.2 methods. The conditions presented in this work likely will not work well with these standardized EPA methods, but this has not yet been confirmed. If it is desired to run the oxygenates together with the full VOC list these analysis conditions may need to be pared back somewhat, though this will reduce the sensitivity for methanol and ethanol. For example, heating the sample to 65 °C with no salt addition may work for full VOCs and will likely allow for calibration down to around 100 ppb for methanol and ethanol. If the selected ion monitoring (SIM) mode of the MSD is used, per EPA method 8260B section 7.5.12, increased sensitivity will be gained. This may allow for less aggressive conditions than those used in Table 3 while still achieving low ppb quantitation levels.

Salt should be baked to remove moisture and any possible contaminants.

Dry blanks should be run often and line/valve temperatures kept hot (125–150 °C) to reduce water build-up and carryover problems. If a single purge vessel is used for all samples it should be rinsed and/or baked thoroughly after every run.

Conclusion

With optimized P&T conditions it is possible to detect and accurately quantitate low ppb levels of oxygenated contaminants in aqueous sample matrices. This application note provides some of the tools needed if this type of work is to be considered.

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