

Oxygenate Measurements in Groundwater: Do We Need to Worry About MTBE Acid Hydrolysis?

by Bruce Bauman

Is there one clearly superior protocol for analyzing oxygenates in water samples? Of course not. Like many aspects of UST release prevention, detection, or corrective action, there is no single “best” way to get the analytical job done. Rather, decision makers must have a good understanding of the general principles and site-specific variables that can influence the performance of the various approaches commonly used to generate data characterizing groundwater quality.

In this article, I’d like to throw in my two cents on the subject of oxygenate analysis—especially with regard to questions surrounding methyl tertiary-butyl ether (MTBE) transformations to tertiary-butyl alcohol (TBA) via acid hydrolysis. Several articles and conference presentations in the past year, including one in *LUSTLine* #42 (LL#42), “Analytical Methods for Fuel Oxygenates,” discuss approaches to sample handling and analysis and how such approaches may influence the accuracy of results for MTBE, TBA (for more about TBA, see *LUSTLine* #36), and other oxygenates in groundwater. You also may have seen a draft copy of the U.S. EPA Office of Underground Storage Tank’s widely distributed “Environmental Fact Sheet: Analytical Methods for Fuel Oxygenates.”

These discussions have focused on the most popular protocols for oxygenate analysis, EPA SW-846 methods 5030B (purge and trap) and 8260B (gas chromatograph/mass spectrometer [GC-MS]). To somewhat oversimplify those discussions, questions have been raised regarding the ability of these protocols to provide accurate measurements of MTBE, TBA, and other oxygenates in groundwater.

In particular, critics of the protocols question the following: (a) the effectiveness of purge and trap (P&T)

techniques for extracting all oxygenates (especially alcohols such as TBA) from water samples, and (b) the potential for transforming MTBE to TBA by acid hydrolysis.

As these issues can have profound implications on data quality and interpretations for corrective action decisions at any site, they deserve the considerable discussion surrounding them.

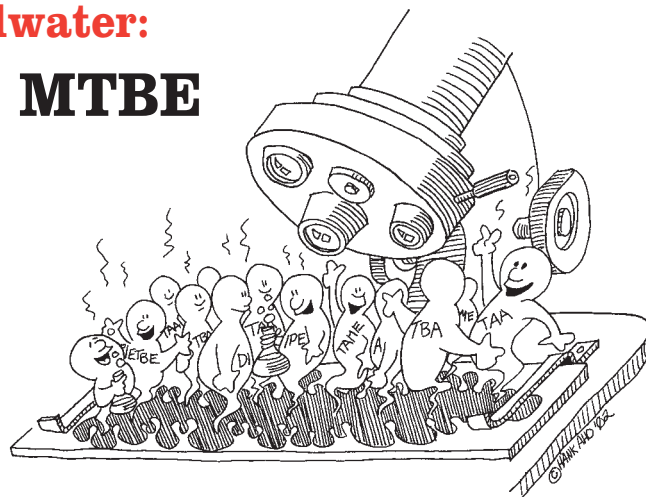
“A tremendous amount of oxygenate data from leaking UST sites have been generated over the past several years, yet there is understandable concern as to whether these data are valid. In general, these concerns are related to two issues: analytical obstacles, and ether hydrolysis (particularly of MTBE to TBA).”

LUSTLine #42
“Analytical Methods for Fuel Oxygenates”

Points of Debate

This discussion will focus on the LL#42 article, as many *LUSTLine* readers are familiar with it. That article did a very good job of addressing a broad variety of complex issues associated with chemical analysis of oxygenates, not just purging efficiency and MTBE hydrolysis. The authors provided a good deal of key information about sampling and analyzing gasoline oxygenates in groundwater. They highlighted some obvious problems with certain analytical methods and addressed the important steps associated with sample preservation before analysis.

The authors also provided a “recommended protocol” that “will greatly improve the quality of the data” by avoiding the some of the perceived problems with existing methods. While the overall guidance



provided in the LL#42 protocol is excellent, I would like to address two of the recommendations that deserve a little more discussion, and, perhaps, debate:

- To ensure good-quality TBA data, P&T extraction procedures used for oxygenates should preferably be heated to 80°C
- To prevent hydrolysis of oxygenates, field preservation of groundwater samples should use a base (trisodium phosphate dodecahydrate [TSP]) instead of hydrochloric acid.

Let me begin by summarizing a few key “take-home messages” that readers would have extracted from the LL#42 article and that will serve as the basis for my discussion.

- It is important to analyze for all oxygenates known to be present in gasoline using methods that provide accurate results.
- Standard P&T at ambient temperature does not adequately extract TBA from water samples, so samples should be heated to 80°C.
- Existing conventional approaches to groundwater sample preservation, extraction, and analysis may be prone to the acid hydrolysis of MTBE, which could lead to underestimates of concentrations of MTBE and overestimates of the TBA concentrations.

Do You Need to Analyze for All Oxygenates?

Yes, indeed. Only a few states currently include TBA as a routine target

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analyte for UST sites—this despite numerous recommendations by a wide variety of authorities over the last five years. (See page 21 for a list of reviews and guidance.) Analyzing for all alkyl ethers (e.g., MTBE, TAME, DIPE, ETBE) and alcohols has been widely recommended ever since the first comprehensive evaluation of oxygenate impacts to water quality was published in the National Science and Technology Council's 1997 report *Interagency Assessment of Oxygenated Fuels*. On an annual basis this recommendation has been reiterated by a series of other EPA reports or pronouncements.

So, obviously, every site should be assessed for the potential presence of all oxygenates at some point, preferably early on, as LL#42 suggests. Does this mean you have to analyze every site, for every oxygenate, every time using GC-MS? Of course not, and LL#42 makes that same point, indicating that there will be situations where simple approaches like Method 8015 will work just fine.

Certainly it makes sense to evaluate every site for all oxygenates at some time to make sure you know what's there. Your data needs may be different for any given sampling event during the life cycle of any site, and a careful decision on the appropriate analytical method to use should be made for each round of data collection.

Do You Need to Heat Samples to 80°C to Effectively Extract TBA and Ethers from Water Samples During P&T?

LL#42 states that "if purge and trap is used...it must be modified to increase method sensitivity. One straightforward approach is to heat the sample to 80°C." While it is true that P&T techniques are most effective for nonpolar chemicals like BTEX, there is also good documentation that more polar compounds, such as MTBE and other ethers, can be purged successfully at either ambient room temperature (~25°C) or slightly heated (e.g., <45°C).

EPA's oxygenates method evalu-

ation study (U.S. EPA, 2002) showed good recoveries (>85%) of MTBE and other ethers at ambient temperatures. That same study did show poorer TBA recoveries at ambient temperature and also showed slightly better recoveries of ethers using the 80°C heated purge. It did not evaluate purge recoveries at temperatures between ambient and 80°C.

However, P&T can be an effective TBA extraction method even at ambient temperatures as shown by a Lawrence Livermore National Laboratory study (Halden et al., 2001). These same authors provided similar information several years earlier in a report for California EPA (Happel et al., 1998). Their results showed that gasoline ether oxygenates (i.e., MTBE, TAME, ETBE, and DIPE) and TBA could be effectively measured using P&T/GC-MS at ambient temperatures. They observed that a method detection limit of 35 µg/L could be obtained for TBA but noted that at 40°C, and using a larger sample volume (10 ml versus 5 ml), they were able to reach a detection limit of 4.6 µg/L. So if a heated purge is desirable, a temperature of 45°C should probably be high enough. It should provide acceptable recoveries, and minimize some of the potential problems noted later in this article.

In a very recent paper discussed in more detail later in this article, Evans and Colman (2003) demonstrate another example of effective MTBE and TBA analysis using ambient temperature P&T. In that study, three California labs using Methods 5030/8260 were able to get good MTBE and TBA recoveries, as well as accurate results at low detection levels (~12 µg/L). While their results don't mean that every lab performs as well, they do document that those methods are capable of delivering satisfactory performance.

Purging effectiveness is clearly more important for TBA than for the ethers, but keep in mind that if proper calibration procedures are performed, good results can be obtained, even with lower recoveries. The relative recovery of TBA from a lab's calibration sample should be similar to that from field samples, and so a correction factor can be applied to determine the "correct" concentration. Higher recoveries (i.e., 75 percent and more) are certainly

What's Purge and Trap?

Think of the purge and trap technique as a very small-scale air-sparging application in a closed system in which you are capturing the volatilized gases in a carbon canister. In practice, a small volume of water (usually 5 ml, but sometimes larger volumes are used to improve method performance) is purged with a gas (usually helium) to remove the soluble VOCs from that sample. The sample may be heated (e.g., in the 20° to 45°C range) to enhance the removal process, and the purging time may vary, although 11 minutes is very common. The volatilized chemicals are "trapped" on a sorbent column that is then heated slowly to facilitate the sequential separation of chemicals with varying boiling points in the gas chromatograph (GC). The constituents are then identified in the mass spectrometer (MS).

desirable, but may not always be necessary to document good method performance if recoveries are consistent among all samples.

Finally, there is some anecdotal evidence from lab technicians that when using an 80°C P&T extraction, complicating issues with water management may result in worse recovery of TBA than would be the case at 45°C or lower. The potential problem here is that at this high temperature, some water may also be evaporated, ending up in the instrument's water trap. Some TBA may be in that water and not find its way into the GC, leading to poor recovery. So perhaps 45°C is a good compromise temperature when TBA is a target analyte.

Is Hydrolysis of MTBE to TBA a Concern under Normal Conditions?

The rate of hydrolysis of MTBE to TBA is affected primarily by pH, temperature, concentration, and time. The impact of pH and temperature on the rate of MTBE hydrolysis

“Under normal environmental conditions ethers do not undergo hydrolysis at significant rates without enzyme catalysis; even in acidified (pH < 2) groundwater samples, ethers are generally stable (Church, et al., 1999).”

“Therefore, if water samples are preserved with acid, there is an understandable concern as to whether or not any of these data are valid. . . . If [acidified] groundwater samples are refrigerated before analysis and all the sample preparative methods are carried out at ambient temperature (as opposed to an elevated temperature of 80°C), there is minimal opportunity for hydrolysis of the ether oxygenates.”

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has been well documented (O’Reilly et al., 2001). At very low pH (e.g., below 1.5) and at high temperatures (e.g., 80°C) hydrolysis rates will be relatively fast, but those conditions are unusual except perhaps during the heated P&T or heated headspace extractions.

As shown in LL#42, at 4°C, MTBE hydrolysis is negligible under almost any condition. Even at ambient temperature there is insignificant hydrolysis over the standard holding times of VOC samples (14 days) if the sample pH is 2. (Of course, samples should never be stored this way!)

For example, in a recent paper by Douthit et al. (2002), the calculated pseudo-first-order-rate constant for MTBE hydrolysis for a solution containing 900,000 ppb of MTBE at 26°C and pH 2 is 0.0022 per day—that is, 0.2 percent of the MTBE will be transformed into TBA each day. At 100,000 µg/L MTBE and the same temperature and pH, the calculated rate constant is 50 percent slower (0.0011/day). That same study showed no measurable hydrolysis of MTBE to TBA above detection limits as low as 5 µg/L in samples stored at 4°C for 7 to 31 days and analyzed by P&T/GC-MS. Unpreserved control samples were also analyzed. No TBA was detected at 5 to 20 ppb.

The authors state that their results show that “acid hydrolysis of MTBE, in properly handled groundwater samples, does not compromise the integrity of dissolved MTBE and TBA analyses.” This is very good evidence that hydrolysis should not be a

problem when samples are handled and analyzed according to commonly used standard protocols. Using the method outlined in O’Reilly et al., it is useful to calculate some possible effects of hydrolysis under a variety of typical analytical conditions. Using an upper range of heated purge conditions (45°C), a sample containing 1,000 µg/L of MTBE theoretically will yield 0.7 µg/L of TBA at pH 1. Under the same conditions, a sample containing 10,000 µg/L MTBE will yield 7 µg/L of TBA, and a sample containing 100 µg/L of MTBE will yield 0.1 µg/L of TBA. So even when pH is extreme, if moderate heating is used, hydrolysis should be insignificant.

Figure 1

Theoretical TBA Production from a 500 µg/L Solution of MTBE at pH 1.5

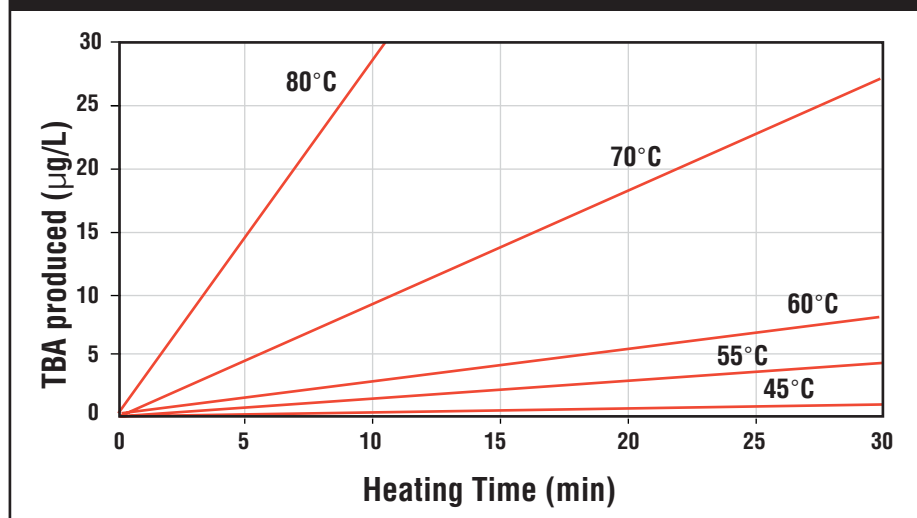
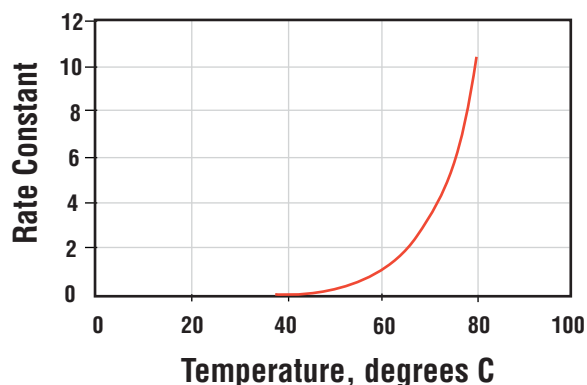


Figure 2

Changes in Hydrolysis Rate Constant with Temperature



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To illustrate this point more rigorously, Figure 1 shows the calculated amount of TBA that can theoretically result from the hydrolysis of a sample containing 500 µg/L

µg/L are diluted prior to analysis. This practice both dilutes the acid, raising the pH, and reduces the MTBE concentration to a point where any resulting TBA concentration is below reporting limits.

To see that temperature effects are of greatest concern above 40°C, look at Figure 2. As temperature increases, the rate constant for hydrolysis increases by nearly an order of magnitude between 45°C and 80°C. Keeping purge temperatures below this range should greatly reduce potential rates of hydrolysis.

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A Multi-Lab Performance Study Validation of Methods 5030/8260

As mentioned earlier, the recent article by Evans and Colman (2003) provides an excellent summary of a study that addresses many of the issues raised about the data quality provided by P&T/GC-MS analysis. The authors note that the U.S. EPA Office of Solid Waste is a strong advocate of performance-based analytical methodology, which is a requirement for several RCRA programs. Briefly defined, "the performance-based approach requires that methods be selected and approved based upon their ability to meet the data quality goals of a given project in the actual matrix to be sampled." (Readers looking for more information this topic are referred to EPA's site at: <http://www.epa.gov/epaoswer/hazwaste/test/pbms.htm>.)

The authors compared the performance of three different California commercial labs for MTBE and TBA that use routine P&T/GC-MS analysis. They wanted to make sure that the data they were collecting for their site (the world-famous Port Hueneme) would be adequate to quantify MTBE at 5 µg/L and TBA at 12 µg/L (2-propanol and acetone were two other target analytes).

The authors do not indicate that they had concerns regarding possible hydrolysis of MTBE to TBA, but they do note that some critics question the purging efficiency of these methods for nonpolar compounds like MTBE and especially TBA.

They submitted a variety of Port Hueneme groundwater samples to the three labs (concentrations ranged from 1 µg/L to about 3,000 µg/L in the samples submitted to each lab) and asked them to run their standard method. Two labs used EPA 5030 / 8260 and one used EPA 5242, a similar P&T/GC-MS method. All three labs used a purge cycle of 11 minutes. Two labs purged at ambient temperature, and the other used 40°C. A variety of quality assurance and quality control procedures were also employed to confirm method performance.

To very briefly summarize their results, using the standards of U.S. EPA's performance evaluation protocol criteria, all three labs performed within acceptable limits of accuracy and precision for all four compounds for the entire range of concentrations studies (i.e., 1 to 3,000 µg/L). MTBE and TBA recoveries were almost always within the acceptable range (i.e., between 75 and 125 percent recovery). In all cases, the desired low ppb detection limits were reached.

The authors conclude that the results reflect a successful demonstration of method applicability (P&T/GC-MS) for the compounds studied. This single study of three labs does not, of course, mean that each and every one of the almost 1,000 environmental labs nationwide routinely performs as well. However, the authors conclude, "The results...appear to be a successful demonstration...that...purge-and-trap GC-MS is an acceptable technology for the analysis of MTBE and its oxygenated breakdown products."

There is a lot of other good information and discussion in that well-written article, and I strongly encourage you to take a closer look for yourself. It provides a good template for the kind of information you should be able to obtain from your laboratory regarding the quality of its analytical performance.

With Good Data and Attention to Protocol...

We know a lot more today than we did a few years back about the proper approaches for oxygenate analysis. We also know a lot about MTBE acid hydrolysis and its potential effects on groundwater analysis, but that's not to say we know it all. I suspect that this topic will continue to be of high interest and that we will learn a lot more in the coming year.

The studies cited in this article and in LL#42 collectively provide a lot of interesting information, but more information will be required to conclusively document the performance of the analytical methods currently in common use. To be sure, following the recommended protocol provided in LL#42 would help you become more aware of the quality of the data for the sites you manage,

and any potential limitations to that data. That information should serve you well, and your corrective action decision-making should improve.

However, at most sites you probably do not need to use a heated P&T extraction to generate good data for MTBE and TBA. If heating is shown to improve method performance, then temperatures of 40° to 45°C are likely to be sufficient, and at these temperatures, MTBE hydrolysis should not compromise data quality. Purge-and-trap extraction of water samples at ambient or slightly elevated temperatures (combined with good calibration procedures) should adequately recover any TBA present in samples.

Furthermore, it is probably unnecessary in most situations to use TSP as your field preservative, instead of acid. While both low acidity (pH) and high temperature are known to enhance the rates of MTBE hydrolysis, an evaluation of these factors and a review of the standard analytical procedures employed at many commercial laboratories indicate that it is unlikely that significant MTBE hydrolysis occurs. For conditions used at most UST release sites—using standard acid preservation of samples, followed by P&T/GC-MS extraction and analysis—hydrolysis of MTBE to TBA will be very limited and will not significantly influence data quality. Hydrolysis of MTBE to TBA should not be a concern during storage and analysis of acid-preserved samples.

Data users should have a good understanding of the basic performance of the sampling and analytical procedures they use to generate oxygenate data. If they have concerns about data quality for ongoing evaluations of corrective action at UST sites where gasoline oxygenates are present in groundwater, they should review the protocols in use, the list of target oxygenate analytes, and their performance criteria (e.g., recoveries and detection limits) to determine if any changes might improve performance. I would also recommend that you talk about these issues with some of the commercial labs in your area to determine what they think are the best approaches to maintaining or improving data quality. ■

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[Note from Bruce: Everything I've needed to know about oxygenate analysis I've learned from: Ileana Rhodes (Shell Global Solutions); Mike Miller (ExxonMobil); and Kirk O'Reilly, Michael Moir, and Al Verstuyft (ChevronTexaco). Their substantial contributions to this article are most gratefully acknowledged. I assume sole responsibility for any errors and misstatements.]

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