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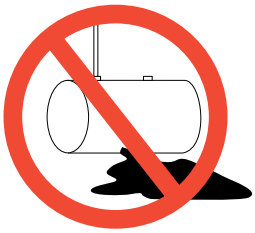
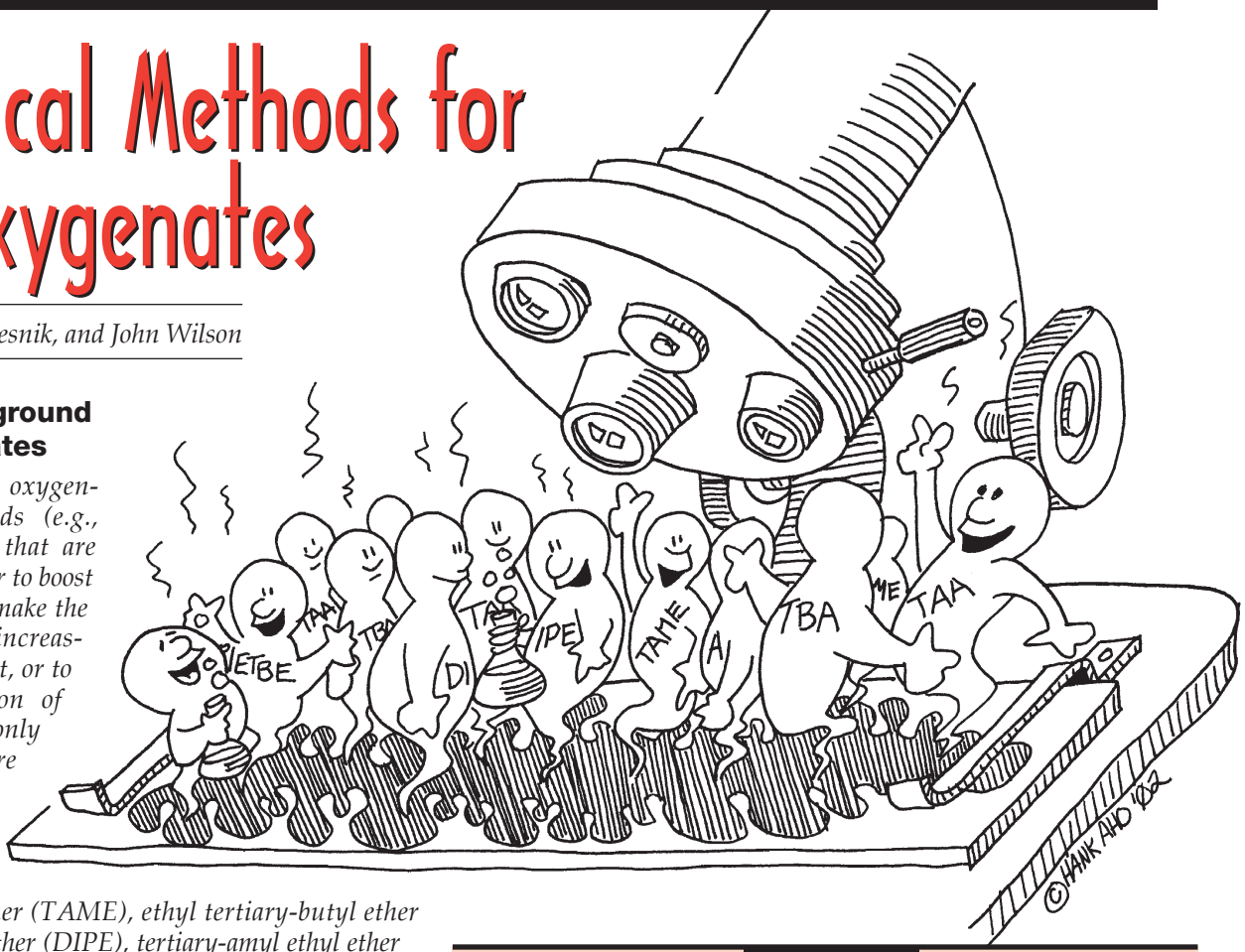


A Report On Federal & State Programs To Control Leaking Underground Storage Tanks

Analytical Methods for Fuel Oxygenates



by Hal White, Barry Lesnik, and John Wilson

A Concise Background on Fuel Oxygenates

Fuel oxygenates are oxygen-containing compounds (e.g., ethers and alcohols) that are added to gasoline either to boost the octane rating, to make the fuel burn cleaner by increasing the oxygen content, or to achieve a combination of both. The most commonly used oxygenates are methyl tertiary-butyl ether (MTBE) and ethanol. Other oxygenates include tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE), diisopropyl ether (DIPE), tertiary-amyl ethyl ether (TAEE), tertiary-butyl alcohol (TBA), tertiary-amyl alcohol (TAA), and methanol. Some oxygenates have a long history of usage in gasoline. For example, ethanol has been used in automotive fuel blends since the 1930s. Ethers, and primarily MTBE, have been used increasingly since the late 1970s. Initially, MTBE was used to boost the octane rating of mid- and high-grade gasoline and was present at concentrations of about 4 to 8 percent by volume. These fuels were transported, stored, and used nationwide.

Amendments to the Clean Air Act in 1990 led to the implementation of the Oxygenated Fuel (Oxyfuel) and Reformulated Gasoline (RFG) programs in 1992 and 1995, respectively. While these programs stipulated a minimum oxygen content for gasoline sold in specific metropolitan areas to reduce air pollution, the choice of which oxygenate to use was

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left to the discretion of the petroleum refining industry. Primarily for economic and logistical reasons, the industry overwhelmingly opted for MTBE, and it is currently used in approximately 80 percent of oxygenated fuels at concentrations ranging from 11 to 15 percent by volume. Ethanol-containing fuel is used primarily in the midwestern United States and accounts for about 15 percent of the oxygenated fuel supply. The other oxygenates combined account for the remaining 5 percent.

The Down Side of Fuel Oxygenates

Releases of oxygenated fuel into the environment have occurred nationwide from leaking storage tanks and pipelines, transportation accidents, refueling spills, unburned fuel present in the exhaust from watercraft, and/or consumer misuse. Even at very low concentrations, the presence of some of these oxygenates can render water unsuitable for a particular intended purpose (e.g., drinking, cooking, bathing, laundry, watering livestock) because it is either unsafe or unpalatable due to objectionable taste and/or odor.

Remediation of contaminated groundwater and treatment of contaminated drinking water is time-consuming and expensive. Detecting the presence of fuel oxygenates and delineating their extent in the environment is difficult for a variety of reasons. In fact, only a couple of states have even started to investigate the contamination of their groundwater with oxygenates other than MTBE. Thus, the extent and magnitude of oxygenate contamination in the United States is largely unknown.

Oxygenates easily dissolve into water and tend to migrate without significant retardation in flowing groundwater. MTBE plumes in particular may extend farther than is the case for the petroleum hydrocarbons benzene, toluene, ethylbenzene, and the three isomers of xylene (BTEX). Because they spread more extensively, oxygenate plumes are more difficult to detect and delineate. In *LUSTLine* #36 (2000), Jim Weaver and John Wilson discuss the difficulties of characterizing MTBE plumes in their article "Diving Plumes and Vertical Migration at Petroleum Hydrocarbon Release Sites."

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).

In the following sections, we'll discuss these issues and present some new information that may help us in dealing with oxygenates in the environment.

Analytical Obstacles

One of the greatest impediments to understanding the extent of contamination caused by fuel oxygenates is the perceived lack of a single analytical method for the determination of fuel oxygenates as a group. Although the capability to conduct the analyses necessary to determine all of the fuel oxygenates at the concentrations of regulatory concern does exist in the current marketplace, the availability of this service is limited. It simply isn't standard operating procedure to calibrate for all of the oxygenates and, until now, no single method with this capability has undergone a rigorous demonstration of applicability. Conventional analytical procedures designed for petroleum hydrocarbons (i.e., BTEX) can also detect MTBE and the other ethers when properly calibrated for them, but they have very poor sensitivity for TBA and the other alcohols.

Of the several widely used determinative methods published in SW-846 (U.S. EPA, 1997), the two most appropriate for oxygenates are Method 8260 (Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, GC/MS) and Method 8015 (Nonhalogenated Organics Using Gas Chromatography/Flame Ionization Detector, GC/FID). Other GC detectors (e.g., the electrolytic conductivity detector [ELCD] and the photoionization detector [PID]) are not designed to respond well to compounds that do not contain halogens (ELCD) or double bonds (PID). Therefore, methods using either of these detectors are not recommended for the analytical determination of oxygenates.

In particular, Method 8021 (PID detector) cannot be regarded as a consistently reliable analytical tool for the analysis of oxygenates because it is susceptible to both false positives (misidentifying the presence of an oxygenate) and false negatives (failing to identify the presence of an oxygenate). False positives often result in resources being wasted on unnecessary investigation and cleanup efforts. False negatives may result in the exposure of receptors to harmful levels of contaminants. The problems with Method 8021 are due primarily to coelution interferences and to the high ionization energies of many oxygenates.

Method 8021 uses a specialized light bulb (lamp) to ionize analytes of concern. The lamps typically used in a PID for Method 8021 operate at a maximum potential of 10 eV. The ionization potentials of ethanol and TBA are 10.2 eV and 10.25 eV, respec-

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tively. As a result, ethanol and TBA are not ionized and cannot be detected by these lamps. The potential required to ionize MTBE is 10 eV, which is right at the maximum potential of these lamps. Although the PID may respond to MTBE when the lamp is new, the response becomes weaker as the lamp ages with use. If the calibration curve for Method 8021 is not current, the method can return false negatives for MTBE when MTBE is present at concentrations above regulatory action levels.

Method 8021 (PID) may also be subject to coelution interferences and generate false positive results when real-world samples contain significant concentrations of other contaminants such as petroleum hydrocarbons. Halden et al. (2001) found that when a sample contains petroleum contamination (as total petroleum hydrocarbon, TPH) of greater than about 1,000 µg/L (1 part per million), Method 8021 is subject to false positive results for MTBE. He also found that the effect is concentration-dependent (i.e., the effect increases as the concentration of other contaminants in the sample increases). Most laboratory QA/QC procedures for MTBE are not set up to identify circumstances in which coelution and concentration effects compromise the reliability of the method. Without this information the analyst may have the mistaken impression that the analytical results are accurate, when in fact they are erroneous.

A more important concern inolves the unequivocal determination of the presence of oxygenates. Using either GC/MS (Method 8260) or GC/FID (Method 8015) with an appropriate GC column and an appropriate sample-preparation technique, it is possible to detect oxygenates at concentrations of 5 µg/L or less. However, GC/MS provides positive confirmation of the chemical identity of the analyte that is detected, while GC/FID does not.

It is not necessary to modify existing conventional practice for chromatography to obtain data for all of the oxygenates; only the sample preparation and method calibration steps need to be modified. If calibration curves are run for all of the other ethers, then concentrations of all of these oxygenates can be determined for the same samples and in some of the same analytical runs used to determine BTEX and MTBE, provided that the concentrations of all target compounds fall within the operational calibration ranges of the detectors used.

It simply isn't standard operating procedure to calibrate for all of the oxygenates and, until now, no single method with this capability has undergone a rigorous demonstration of applicability. Conventional analytical procedures designed for petroleum hydrocarbons (i.e., BTEX) can also detect MTBE and the other ethers when properly calibrated for them, but they have very poor sensitivity for TBA and the other alcohols.

Another important concern is the method detection limit or the reporting limits of current analytical protocols for the alcohols, and TBA in particular. Analysis of the alcohol oxygenates is a more difficult challenge than analyzing for BTEX (or even MTBE). Many commercial laboratories set reporting limits for TBA that are much higher than reporting limits for BTEX and MTBE. Typical reporting limits for TBA may be as high as 100 or 1,000 µg/L. These reporting limits are higher than the concentrations of TBA that are of regulatory interest to many states.

Overcoming Analytical Obstacles

Methods 8015 (GC/FID) and 8260 (GC/MS) are appropriate for determining the presence and concentration of fuel oxygenates and BTEX. Appropriate sample-preparation methods include Methods 5021 (static headspace), 5030 (purge-and-trap), or 5032 (vacuum distillation). TBA can also be recovered for analysis using the azeotropic distillation technique (Method 5031). If ethers are the only target analytes of interest, then using Method 5030 at ambient temperature (rather than heated) is adequate to determine concentrations of oxygenates that are greater than 5 µg/L. However, if alcohols (or acetone) are analytes of concern, the water sample must be heated to attain adequate recovery of analytes. If the sample is not heated, the effective limit of quantitation for TBA using Method 5030 is near 100 µg/L; when the water sample is heated to 80° C the limit of quantitation is near 10 µg/L.

In response to problems identified with current analytical practice, EPA conducted a study to determine the optimum conditions for purge-and-trap sample preparation of MTBE and the other fuel oxygenates in river water samples both with and without BTEX interferences in the form of gasoline spiked at 600 µg/L. The compounds included in the study were MTBE, TBA, DIPE, ETBE, TAME, TAEE, and acetone. The target sensitivity was 5 µg/L (U.S. EPA, 2002).

The study was performed over a five-point calibration range of 2 µg/L to 40 µg/L for each target analyte. The analytes were purged at 80° C for seven minutes and trapped on a Supelco H trap[1], held at 35° C, dry purged, desorbed and baked for three minutes each, and analyzed on a standard VOA column and a wax column. Water samples were run both with and without BTEX present in the samples. An additional evaluation using purge-and-trap conditions at ambient temperature (20° C) and the standard VOA column was also performed.

The results of EPA's study demonstrate that the recoveries of low levels of MTBE and related oxygenates can be improved over current practice. The most consistent oxygenate recoveries were obtained using the following combination of methods: sample preparation using Method 5030 with a heated (80° C) purge-and-trap, then analysis by Method 8260 using a DB-Wax capillary column as the determinative method. Use of an RTX-Volatile capillary column with a heated purge did not significantly improve the

[1]Performance with other brands of traps may vary from that of the present study. If a different trap is used, its performance must be demonstrated, not merely assumed to be comparable to the Supelco H trap. Silica gel is needed as a trapping material for the trap to perform properly.

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overall oxygenate recovery compared to the DB-Wax capillary column. In addition, BTEX interferences did not adversely affect the chromatographic separation, quantitation, and recovery of oxygenates.

For samples with high concentrations of hydrocarbons and oxygenates, the samples will have to be diluted so that they are within the operating range of the instrument. As a general rule, analysts dilute and rerun samples when the concentration of any analyte exceeds 0.5 mg/L when using Method 8260 (MS detector) or exceeds 4 mg/L when using Method 8015 (FID). If the concentration of one of the BTEX compounds or oxygenates is much higher than the other analytes, then multiple runs will have to be made using diluted samples.

These methods must only be used by, or under the supervision of, analysts experienced in the use of gas chromatography for measurement of organic compounds at low concentrations (i.e., µg/L) and skilled in the interpretation of gas chromatograms and/or mass spectra. Each analyst must demonstrate the ability to generate acceptable results with these methods. This should be no different than current good laboratory practice.

To demonstrate that these methods work as well with real field samples as they do with laboratory-prepared samples, EPA recently participated in an interlaboratory comparison of the performance of methods for the BTEX compounds and the fuel oxygenates using static headspace as the sample preparation method. Water samples from monitoring wells in two fuel plumes on Long Island were sent to an EPA/ORD lab and two commercial labs. The agreement in the reported concentrations between the three laboratories was expressed as the percent relative standard deviation (%RSD) of the samples.

All three laboratories reported concentrations of MTBE above their detection limit in water from 23 of the 50 wells that were sampled. The %RSD for MTBE was 12.9. All three laboratories detected ETBE in water samples from six wells; the %RSD was 12.3. All three laboratories detected TAME in 12 wells; the %RSD was 5.3.

The EPA laboratory and one of the commercial laboratories detected TBA in 10 wells; the %RSD was 21.4. The method detection limits for TBA in the EPA laboratory and the commercial laboratory were 2.4 and 5 µg/L respectively. The reported concentrations of TBA ranged from 6 to 154 µg/L. The other commercial laboratory had a minimum reporting limit of 100 µg/L and did not detect TBA in any of the water samples analyzed. The agreement between analyses of MTBE, TAME, ETBE, and TBA was good. The other oxygenates were not present in these plumes at concentrations that made it possible to make a comparison.

Ether 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). However, Wade (1998) reported evidence of decreasing MTBE concentrations in 91 acidified groundwater samples collected over a two-year period from a site known to have experienced a release of gasoline that contained MTBE. He postulated that acid-catalyzed hydrolysis of MTBE during sample storage could explain these observations.

Most protocols for the preservation of groundwater samples call for the addition of a sufficient volume of hydrochloric acid to adjust the pH of the sample to < 2. As a practical matter, more acid is added than is needed to preserve the samples. One standard drop of concentrated hydrochloric acid will adjust distilled water in a standard 40 mL VOA vial to pH = 1.8. Most field technicians add two or three drops of acid to each 40 mL VOA vial. Typically, it takes seven drops of acid to adjust a 40 mL VOA vial to pH=1. The majority of groundwater samples that have been preserved with acid probably have a pH of between 1 and 2.

As discussed in the preceding section, if purge-and-trap is used as the sample preparation procedure for TBA and the other alcohols, then it must be modified to increase method sensitivity, or an alternate high-temperature sample preparative procedure must be used. One straightforward approach to increase sensitivity is to heat the water sample to 80° C during sample preparation. However, heating creates a problem with conventional practice for preserving groundwater samples.

If the sample is heated, the acid commonly added to preserve the sample can actually cause the hydrolysis of ether bonds. As a consequence, ether concentrations originally present in the sample may be underestimated, and the concentration of the hydrolysis products may be overestimated (e.g., TBA formed from the MTBE hydrolysis).

These analytical errors can cause errors in risk assessment, can lead to the implementation of a remedial technology that is not necessary, and can bias an evaluation of monitored natural attenuation (MNA). For example, the alcohol that corresponds to the ether is often the first product of biotransformation of the ether. Higher concentrations of the alcohol and lower levels of the ether may be interpreted erroneously as evidence for natural biodegradation in the plume. Consequently, the time required for MNA to achieve cleanup goals may be significantly underpredicted.

Recently, O'Reilly et al. (2001) published rate constants that can be used to calculate the effect of temperature on the rate of acid hydrolysis of MTBE in samples of groundwater. They measured the rate of MTBE hydrolysis at 26° and 37° C. As discussed above, a temperature of 80° C is necessary to promote efficient transfer of alcohols to the gas phase for sampling. If the rates published by O'Reilly et al. are extrapolated to 80° C, they predict that MTBE should be rapidly hydrolyzed to TBA during analysis.

EPA/ORD measured the rate of MTBE hydrolysis at 80° C at pH =1 and pH = 2; the results are presented in Table 1. The water samples in the heated headspace sampler are typically heated for 30 minutes before they are analyzed. After 30 minutes of incubation, 6 percent of the MTBE was hydrolyzed to TBA at a pH of 2, and 57 percent of MTBE was hydrolyzed at a pH of 1.

Data documenting the hydrolysis of MTBE during analysis of groundwater samples from an MTBE plume in California are presented in Table 2. The samples were preserved in the field with hydrochloric acid to pH < 2

Table 1 EFFECT OF PH ON THE EXTENT OF HYDROLYSIS OF MTBE* AT 80° C

Preserved with	Time of Incubation (minutes)	MTBE (µg/L)	TBA (µg/L)	Percent MTBE Hydrolyzed
HCL pH = 1	0	536	<3	
	30	196	255	57%
	60	88.5	343	77%
HCl pH = 2	0	495	<3	
	30	401	25.2	6.1%
	60	393	53.8	13%
1% trisodium phosphate pH > 12	0	476	<3	
	30	424	<3	<1%
	60	432	<3	<1%

* The hydrolysis of 1 µg/L of MTBE should yield 0.84 µg/L of TBA.

Table 2 EFFECT OF SAMPLE PRESERVATION WITH HYDROCHLORIC ACID ON THE MEASURED CONCENTRATION OF TBA

Sample ID	Dilution	TBA (µg/L) corrected for dilution	MTBE (µg/L) corrected for dilution	Percent MTBE Hydrolyzed
ML-12-16	none	3,230		89%
	1:10	1,065	2,953	
ML-16-12	none	10,400		83%
	1:10	2,644		5.8%
	1:100	2,006	12,669	
ML-17-12	none	6,170		56%
	1:10	1,483		0.7%
	1:100	1,405	13,273	
ML-19-12	none	4,640		60%
	1:10	1,309		12%
	1:100	591	7,216	
ML-19-16	none	5,100		68%
	1:10	1,222		7.3%
	1:100	740	8,551	
ML-23-16	none	719		22%
	1:10	260	2,550	

and shipped to EPA's R. S. Kerr Environmental Research Center for analysis using a static headspace sampler (Method 5021).

The water samples were brought to 80° C for 30 minutes prior to analysis of the headspace by GC/MS. Replicates of selected groundwater samples were diluted and then analyzed. The concentration of TBA reported for a sample was the sum of the concentration of TBA that was originally present plus the concentration of TBA produced from hydrolysis of MTBE.

For each tenfold dilution, the concentration of acid used as a preservative was diluted tenfold, the rate of acid hydrolysis of MTBE was reduced tenfold, and the concentration of TBA produced from hydrolysis was reduced. The reported concentrations in Table 2 are corrected for dilution of the sample. The reported concentration of TBA in the undiluted samples was much higher than in the diluted samples.

The last column in Table 2 presents the fraction of MTBE that was hydrolyzed during analysis. The fraction was calculated by assuming that the reported concentration of TBA at the highest dilution was the true concentration of TBA that was originally present in the sample and that the higher concentrations of TBA in the undiluted samples were produced by hydrolysis of MTBE.

In 15 undiluted samples, the fraction of MTBE that was hydrolyzed during analysis varied from 22 percent to 89 percent, with a median of 62 percent hydrolyzed. The hydrolysis of MTBE in the undiluted samples increased the reported concentration of TBA by a factor of four to eight. When samples that were diluted 1:10 are compared to samples that were diluted 1:100, the extent of hydrolysis in the samples that were diluted 1:10 varied from 1 percent to 18 percent with an average of about 9 percent.

These data-quality problems associated with the hydrolysis of MTBE to TBA illustrate the importance of a quality assurance/quality control program. Any significant hydrolysis of MTBE can be detected easily if matrix spike samples are included in the analyses. The accuracy of the analysis is determined by measuring the concentration of the target compound present in a sample, then adding a known concentration of the target compound to a replicate sample of the same water (a matrix spike) and again determining the concentration of the target compound. The concentration in the matrix spike sample should equal the sum of the spiked concentration and the original concentration.

Therefore, if water samples are preserved with acid, there is an understandable concern as to whether or not any of these data are valid. Unfortunately, the answer to this can only be determined by reviewing the reports of analytical results from each site of interest. The things to look for are indications of sample-preservation methods, method operating parameters, quality assurance/quality control results, and whether or not confirmatory identification of analytes is provided.

The rate constants published by O'Reilly et al. (2001) can be used to estimate the stability of MTBE in water samples. Figure 1 (page 6) presents predictions for water samples that are preserved at pH=1 and pH=2 and stored before analysis at temperatures of 4° C, 10° C, and 20° C. If the samples were refrigerated at 10° C or lower, less than 5 percent of

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the MTBE would be hydrolyzed in the first 30 days of storage. If samples were acidified to pH=1 and stored at 20° C, as much as 20 percent of the MTBE could be hydrolyzed in 30 days. If groundwater samples are refrigerated before analysis and all the sample preparation 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.

Preventing Ether Hydrolysis Through Improved Sample-Preservation Technique

There are two widely used methods of preservation: refrigeration and chemical preservation (usually acidification). Often both methods are used on the same samples. If acid causes a problem with analysis of MTBE and TBA, one might be tempted to not use acid and rely on refrigeration alone.

It is essential, however, to use both a chemical preservative and refrigeration for groundwater samples, especially if they are to be analyzed for BTEX compounds. Groundwater samples from permanent wells typically contain microorganisms that are capable of degrading BTEX relatively quickly when oxygen is available. Contaminants may persist in groundwater because the plume is devoid of dissolved oxygen, but groundwater samples from wells invariably contain dissolved oxygen, particularly if samples were collected with a bailer. In samples that have not been preserved, BTEX compounds may be completely biodegraded in less than two weeks (Wilson et al. 1994) and MTBE and TBA may be completely degraded within two weeks of storage (Kane et al. 2001).

As good practice, samples should be packed in ice for shipment and refrigerated during storage. The temperature and general condition of the samples upon receipt by the laboratory should be indicated on the chain-of-custody. Samples should be cold (preferably close to 4° C upon arrival at the lab), they should be preserved, and they should be analyzed within prescribed holding times.

If samples arrived at the lab warm, if they weren't preserved, if they were analyzed past their holding time, or if acid-preserved samples were analyzed using a heated preparatory method, then there is a chance that some of the MTBE was hydrolyzed to TBA. If hydrolysis is a possibility, then examine the quality assurance/quality control data provided with the analytical report. If the recovery of MTBE (or other ether oxygenate) from spiked samples is near 100 percent, then hydrolysis of MTBE during analysis was minimal and should not be of concern.

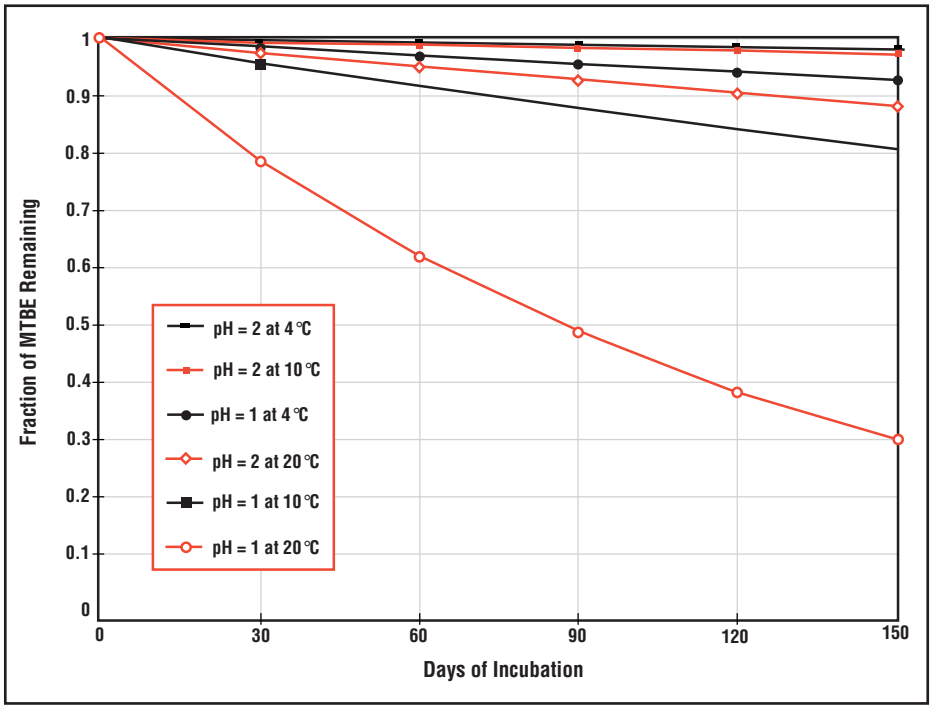

FIGURE 1. *Predicted effect of pH and temperature on the stability of MTBE in samples of groundwater.*

We must reiterate that both a chemical preservative and refrigeration should be used to preserve sample integrity. Refrigeration by itself may slow the rate of biological degradation, but not to a useful extent. A conventional refrigerator is often near 10° C and refrigerated storage for samples is usually near 4° C.

The temperature of groundwater in the northern half of the United States ranges from 10° C to 15° C. As a consequence, the microorganisms collected along with a groundwater sample are already adapted to cold conditions. Storage of samples without a chemical preservative at 10° C to 4° C will only slow the rate of biological degradation of BTEX by a factor of two to four at most. Although refrigeration is only minimally effective in retarding biodegradation of the sample, it is effective at inhibiting the chemical deterioration of the sample.

Kovacs and Kampbell (1999) developed an alternative procedure for chemically preserving groundwater samples that avoids hydrolysis of ether oxygenates. Instead of using an acid to lower the pH, samples are preserved with a base to a pH greater than 11. The elevated pH effectively prevents the biodegradation of organic compounds in the sample. The ethers are not subject to base-catalyzed hydrolysis, and a basic pH has no adverse effect on BTEX or the alcohol oxygenates (O'Reilly et al. 2001). The pH is elevated by adding a salt of a weak acid (trisodium phosphate dodecahydrate, or TSP), instead of a solution of a strong base such as potassium hydroxide. Table 1 compares MTBE hydrolysis in samples that were preserved with acid to samples preserved with TSP. There was no evidence of MTBE hydrolysis to TBA in the samples that were preserved with TSP.

The Kovacs and Kampbell (1999) procedure is safe and convenient. In the laboratory, between 0.40 and 0.44 gram of TSP is added to each 40 mL sample vial. Because it is more convenient to measure the required amount of TSP on a volume basis rather than by weight, staff of the R.S. Kerr Center use a precalibrated

spoon (Hach # 907-00 or equivalent). In the field, each vial is filled with the groundwater sample and sealed without headspace (the same as is done if the sample is preserved with acid).

The salt is added to excess. If a portion of the salt is washed out of the vial as the vial is filled with sample, enough TSP will remain to preserve the sample. As the salt dissolves, it buffers the sample to a pH greater than 11.

No special handling of the samples is required prior to analysis, although they should be stored in a refrigerator at 4° C. Water samples preserved with TSP are 1 percent salt by weight. If purge-and-trap (Method 5030) is used to prepare the water samples, it is particularly important to prevent the transfer of aerosols from the purged water to the trap and GC column. This should be no different than current good laboratory practice.

It is prudent to check the pH of the sample with indicator paper to ensure that the pH is greater than 11 prior to introducing it into the purge vessel or the headspace sampler for analysis. If it is necessary to analyze samples that have already been preserved with acid, the acid can be destroyed with TSP prior to analysis. An amount of TSP sufficient to raise the pH of the sample to greater than 11 is added to the sample vial, which is quickly resealed without headspace and shaken gently to dissolve the salt. Generally, about 0.7 gram of TSP is sufficient for a 40 mL VOA vial, but sometimes (depending upon the pH of the sample) more must be added to elevate the pH to greater than 11.

Recommended Protocol

The protocol described in this article enables us to determine the presence and concentration of all of the common oxygenates and BTEX at levels of regulatory interest. Routine use of this protocol will greatly improve the quality of the data that are reported, which in turn will enable us to make better decisions, which will ultimately result in more effective utilization of available resources.

Because MTBE (and potentially any other oxygenate) may be present at any petroleum UST site, whether the release is new or old, virtually anywhere in the United States, it is also important to respond promptly to any petroleum release. The sooner all of the contaminants in a plume are identified and their subsurface extent determined, the sooner a remedy can be selected and implemented. Because a contaminant plume is smaller and more easily managed early on, the magnitude of the impact and the overall cost of the cleanup should be less than if the plume is allowed to expand.

The protocol described in this article enables us to determine the presence and concentration of all of the common oxygenates and BTEX at levels of regulatory interest. Routine use of this protocol will greatly improve the quality of the data that are reported, which in turn will enable us to make better decisions, which will ultimately result in more effective utilization of available resources.

Consequently, it is prudent to analyze samples for the entire suite of oxygenates as identified in this protocol (i.e., MTBE, TAME, ETBE, DIPE, TAEE, TAA, and TBA). Samples should be prepared for analysis, preferably using EPA Method 5030 heated to 80° C (although either Method 5021 or Method 5032 may be used if the laboratory can demonstrate appropriate performance with these methods).

The determinative method (e.g., Method 8260, 8015, or other appropriate method) should be calibrated for the entire suite of oxygenates, and these analytes should be reported for every sample analyzed. With the understanding that ethanol and methanol are potentially present at fuel release sites, it is also advisable to have samples analyzed for these alcohol oxygenates using appropriate preparative and determinative methods.

EPA Method 8260 (or another method that provides *confirmatory identification* of all of the fuel oxygenates and can be demonstrated to meet project data quality objectives) is the preferred determinative analytical method for fuel oxygenates (and other contaminants of concern) when the analyses will be used to (1) characterize the three-dimensional extent of a contaminant plume, (2) determine whether a site requires active remediation, (3) select an active remedy, (4) design an active remedy, (5) determine whether a site has met site-specific cleanup objectives, or (6) determine if it is no longer necessary to continue monitoring a site.

After all of the oxygenates (and other contaminants of concern) present at a site have been identified and their concentration and extent determined, future analyses might then be conducted using a less expensive determinative method (e.g., 8015). Situations that might not require confirmatory analysis would include routine long-term performance monitoring as part of a MNA remedy or exposure management strategy.

To properly implement this protocol, groundwater samples should be collected from locations where oxygenates are most likely to occur, based on their chemical and physical behavior. Because oxygenates are more soluble than petroleum hydrocarbons and can be more recalcitrant, oxygenate plumes may be longer than typical BTEX plumes.

Oxygenate plumes may also "dive" beneath conventional monitoring wells and migrate undetected until a drinking water source is impacted. (See Weaver and Wilson's article in *LUSTLine* #36.) To ensure that such plumes aren't migrating undetected, samples should be collected from a series of discrete sampling points that draw in groundwater only over short vertical intervals. There should be a sufficient number of sampling points to cover the entire vertical distance over which an oxygenate plume may migrate. Generally this means that additional sampling points are required at progressively greater depths below the water table as the downgradient distance from the source increases. Increasing the length of monitoring well screens is not appropriate as this will only dilute the concentration of contaminants in the sample and mask the true concentration in the plume.

To prevent constituents in the samples from being biodegraded

■ *continued on page 8*

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during storage and transport, samples should be preserved. To prevent chemical hydrolysis of the ether oxygenates during storage, the samples should be preserved with a base delivered as a salt (TSP), rather than as a strong acid, and also refrigerated. Preservation with TSP will also eliminate the possibility that ethers will be hydrolyzed during sample preparation. Stored samples should be refrigerated at 4° C and analyzed within the holding period. ■

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For More Information

***For additional information about analytical methods, call the Methods Information Communication Exchange (MICE) hotline at 703-676-4690, or visit the MICE web site at* http://www.epa.gov/SW_846/mice.htm. *For information about the Underground Storage Tank program, visit* http://www.epa.gov/oust. *For information about either this article or the soon-to-be-released EPA Fact Sheet, e-mail Hal White (EPA/OUST) at* white.hal@epa.gov.**

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