

The Relevance of MTBE Acid Hydrolysis to TBA Under Standard and Heated-Purge Analytical Methods¹

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ABSTRACT

Previously, it has been shown that negligible acid hydrolysis of methyl tertiary-butyl ether (MTBE) to tertiary-butyl alcohol (TBA) occurs in properly handled, acid-preserved environmental groundwater samples, either during sample transport, storage, or analysis (Douthit et al. 2002). However, that study utilized ambient-temperature purging methods during sample analysis. An additional concern has been raised regarding the potential for acid hydrolysis of MTBE if heated-purge analytical methods are used. Heated-purge analytical methods are being proposed by the EPA (EPA 2003) as a means to increase the recovery (and therefore reduce the method detection limits) of certain constituents like TBA, but these methods are also thought to exacerbate the temperature-dependent hydrolysis reactions, artificially increasing TBA concentrations while reducing MTBE concentrations. To evaluate this potential phenomenon, a follow-up study to the Douthit et al. (2002) work was conducted wherein a series of water samples spiked with MTBE ranging in concentrations between 200 and 20,000 ug/L were analyzed via EPA Method 624 using both ambient-temperature (~22° C) purge and heated-purge (80° C) methods. In the ambient purge study, spike concentrations of 2,000 and 20,000 ug/L were analyzed without dilution for the lowest possible TBA detection limit. In the heated purge study, spike concentrations of 200, 2,000 and 20,000 ug/L were analyzed undiluted to minimize the TBA detection limit. Heated-purge diluted analyses of the 2,000 and 20,000 ug/L spikes were also conducted for comparison purposes and to evaluate the effect of pH on acid hydrolysis since the dilution process raises the sample pH. All samples were analyzed in triplicate on the day they were prepared.

TBA was only detected in the samples spiked with 20,000 ug/L MTBE, in both the heated-purge *and* the ambient-temperature purge studies. TBA concentrations in the heated-purge samples averaged approximately 27 ug/L (approximately 0.14% of the original spike concentration), while TBA concentrations in the ambient-temperature samples averaged approximately 36 ug/L (approximately 0.18% of the original spike concentration). These data suggest that the heated purge process did not generate more TBA through acid hydrolysis of MTBE than the ambient-temperature purging method. Furthermore, the presence of equivalent concentrations of TBA in both the heated and ambient-temperature purge samples suggests either temperature-independent TBA generation or impurities in the original MTBE standard.

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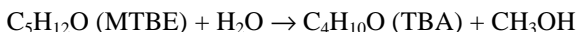
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A negative secondary effect of the 80° C heated purge process was degradation of chromatography resulting in significant TBA peak tailing. This peak tailing is due to the amount of water vapor being trapped and entering the chromatographic system. The main quantitation ion for TBA is 59 amu. MTBE at high concentrations will contribute to the 59 amu quantitation ion of TBA if adequate peak separation is not achieved. At higher heated purge temperatures (above 45° C), the tailing of TBA expanded through and past the later eluting MTBE. If both compounds were present in a heated sample, proper peak integration and quantitation for TBA would become more difficult to attain. An additional study was conducted using increasing purge temperatures in 5-degree increments from 25° to 80° C to evaluate the peak response/peak shape of TBA. It was determined that peak tailing was insignificant at temperatures below 45° C, while maintaining an approximate 400% increase in TBA sensitivity compared to 25° C. However, long-term effects of the heated purge process, even at 45° C, are unknown. Water vapor over time will require more maintenance of detector source components.

Introduction

Methyl tertiary-butyl ether (MTBE) and tertiary-butyl alcohol (TBA) are environmental contaminants frequently analyzed for in groundwater samples collected at fuel spill sites. Recently, both preservation and analysis of groundwater samples containing MTBE have come under increased scrutiny based on the potential for HCl-catalyzed hydrolysis of MTBE to TBA according to the reaction:



The generation of TBA during sample transport and/or analysis could be problematic in that artificially elevated concentrations of TBA and artificially reduced concentrations of MTBE could potentially be generated, leading to misinterpretations regarding spill characteristics, subsurface conditions, remedial strategies and the site's regulatory status. Previous work has documented that the generation of TBA via acid hydrolysis of MTBE is negligible in properly collected, shipped and stored groundwater samples (e.g. Douthit et al. 2002). Additionally, Douthit et al. (2002) demonstrated that the analysis of groundwater samples using ambient-temperature purge methods did not generate TBA concentrations above method detection limits (via EPA 624). However, the acid hydrolysis reaction shown above is temperature-dependent, and recent moves toward heated-purge analytical methods as a means to increase the sensitivity of oxygenate analytical methods, have again raised the question of whether TBA could be inadvertently generated during the analysis of groundwater samples containing MTBE. In the absence of experimental data, it has been suggested that alternative, basic preservatives (e.g. Na_3PO_4 – trisodium phosphate, or TSP) be used to keep the pH of the groundwater sample high enough to avoid acid hydrolysis reactions. However, the effects of basic preservatives on analytical equipment have yet to be investigated. The utilization of both 80° C purging methods and TSP are recommended in the new EPA method 5030C for samples containing oxygenates (EPA 2003).

In order to evaluate the potential for generation of TBA utilizing heated-purge analytical techniques, a follow-up study to the Douthit et al. (2002) work was conducted wherein a series of water samples spiked with MTBE ranging in concentrations between 200 and 20,000 ug/L were analyzed via EPA Method 624 using both ambient-temperature (~22° C) purge and heated-purge (80° C) methods. Selected samples were analyzed without dilution for the lowest possible TBA detection limit.

Experimental Method

Sample vials were spiked with 200 µg/L, 2,000 µg/L and 20,000 µg/L concentrations of a MTBE standard in HCl-preserved VOA vials. Preserved vials were brought to a pH of ≤ 2. All samples were analyzed in triplicate on the day they were prepared. All analyses were performed via EPA Method 624 at Accutest Analytical Laboratories⁵, Dayton, New Jersey. In the ambient purge study, spike concentrations of 2,000 and 20,000 ug/L

⁵ Methodology: An inert gas is bubbled through a 5 ml sample contained in a specifically designed purging chamber at specific temperatures (ambient through 80° C). The purgeables are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the purgeables are trapped. After purging is completed, the sorbent column is heated and back flushed with the inert gas to desorb the purgeables onto a gas chromatographic (GC) column. The volatile compounds are separated by the temperature programmed GC column and detected using a mass spectrometer, which is used to provide both qualitative and quantitative information. The peaks detected are qualified by comparison to characteristic ions and retention times specific to the known target list of compounds. Once identified the compound is quantitated by comparing the response of major (quantitation) ion relative to an internal standard technique with an average response factor generated from a minimum of 3-point curve.

Accutest has taken steps to mitigate the quantitative variability associated with TBA analysis through the use of a stable labeled analog of TBA (Tertiary Butyl Alcohol - d_9) as an internal standard specifically for the quantitation of TBA. This isotopically labeled compound has similar physical and chemical properties to TBA, has a chromatographic elution time within 5 seconds of unlabeled TBA and can be distinguished from TBA by its mass spectra that reflects a molecular weight difference of nine. Sample matrix variation that affects the purge efficiency of TBA will similarly affect the purge efficiency of TBA - d_9 .

Spiked blank data that has been pooled since the use of TBA - d_9 has begun indicates a considerable decrease in quantitative variability. The 99% confidence interval for spiked blank recovery has improved from 47– 158% to 80– 116% for aqueous samples with the use of TBA - d_9 .

were analyzed without dilution for the lowest possible TBA detection limit. In the heated purge study, spike concentrations of 200, 2,000 and 20,000 ug/L were analyzed undiluted to minimize the TBA detection limit. Heated-purge diluted analyses of the 2,000 and 20,000 ug/L spikes were also conducted for comparison purposes and to evaluate the effect of pH on acid hydrolysis since the dilution process raises the sample pH.

Results

TBA was only detected in the samples spiked with 20,000 ug/L MTBE, in both the heated-purge *and* the ambient-temperature purge studies. TBA concentrations in the heated-purge samples (Table 1) averaged approximately 27 ug/L (approximately 0.14% of the original spike concentration), while TBA concentrations in the ambient-temperature samples (Table 2) averaged approximately 36 ug/L (approximately 0.18% of the original spike concentration). These data suggest that the heated purge process did not generate more TBA through acid hydrolysis of MTBE than the ambient-temperature purging method. Furthermore, the presence of equivalent concentrations of TBA in both the heated and ambient-temperature purge samples suggests either temperature-independent TBA generation or impurities in the original MTBE standard. Note that the poor MTBE recovery in the undiluted 20,000 ug/L runs was due to detector saturation.

TABLE 1
Comparison of MTBE Spike Concentrations and TBA Generation in HCL-Preserved Water Samples Purged at 80° C.

MTBE Spike Concentration (µg/L)	Dilution	MTBE Recovered Concentration (µg/L)	TBA Detected Concentration (µg/L)	Measured pH
200 (rep. #1)	None	207	<5.0	1.5
200 (rep. #2)	None	208	<5.0	1.5
200 (rep. #3)	None	209	<5.0	1.5
2,000 (rep. #1)	1:4	2,150	<20	2.5
2,000 (rep. #2)	1:4	2,229	<20	2.5
2,000 (rep. #3)	1:4	2,201	<20	2.5
2,000 (rep. #1)	None	2,863	<5.0	1.5
2,000 (rep. #2)	None	2,769	<5.0	1.5
2,000 (rep. #3)	None	2,932	<5.0	1.5
20,000 (rep. #1)	1:50	23,241	<250	3.0
20,000 (rep. #2)	1:50	23,173	<250	3.0
20,000 (rep. #3)	1:50	22,690	<250	3.0
20,000 (rep. #1)	None	7,012	27	1.5
20,000 (rep. #2)	None	8,600	24	1.5
20,000 (rep. #3)	None	8,663	31	1.5

TABLE 2

Comparison of MTBE Spike Concentrations and TBA Generation in HCL-Preserved Water Samples Purged at Ambient Temperatures

MTBE Spike Concentration (µg/L)	Dilution	MTBE Recovered Concentration (µg/L)	TBA Detected Concentration (µg/L)	Measured pH
2,000 (rep. #1)	None	1,940	<5.0	1.3
2,000 (rep. #2)	None	1,890	<5.0	1.3
2,000 (rep. #3)	None	1,915	<5.0	1.3
20,000 (rep. #1)	None	4,290	32.5	1.6
20,000 (rep. #2)	None	4,174	36.6	1.6
20,000 (rep. #3)	None	4,197	38.8	1.6

A negative secondary effect of the 80° C heated purge process was degradation of chromatography resulting in significant TBA peak tailing. Substantial peak tailing occurred resulting in a TBA peak width of 1 minute compared to a normal peak width of 0.2 minutes. This peak tailing is due to the amount of water vapor being trapped and entering the chromatographic system. Several attempts in modifying the water management system and sample split were made to no avail. One of the keys to MTBE and TBA analysis is the peak resolution or peak separation of the two compounds. The main quantitation ion for TBA is 59 amu. MTBE at high enough concentrations will contribute to the 59 amu quantitation ion of TBA if peak separation is not achieved. The heated purge not only tailed the TBA peak but also tailed it to the extreme of stretching it through and past MTBE. If both compounds were present in a heated sample (above 45° C), proper peak integration and quantitation would be very difficult to achieve for TBA. An additional study was conducted using increasing purge temperatures in 5-degree increments from 25° to 80° C to evaluate the peak response/peak shape of TBA. It was determined that peak tailing is insignificant at temperatures below 45° C, while maintaining an approximate 400% increase in TBA sensitivity compared to 25° C. The 45° C limit is supported by other recent work as discussed in Bauman (2003). However, long-term effects of the heated purge process, even at 45° C, is unknown. It is expected that at a minimum, water vapor influx over time will require more maintenance of detector source components.

Discussion

Previous work has indicated that acid hydrolysis of MTBE to TBA in properly handled groundwater samples is negligible during sample collection and transport (Douthit et al. 2002). The data presented above suggest that this reaction is also negligible during the analytical process, even when using heated-purge methods. While TBA was detected in the 20,000 µg/L MTBE spikes, concentrations were very low (<0.2% of the initial MTBE concentration), independent of purge temperature, and only detectable in undiluted samples. The presence of these low levels of TBA may have been due to impurities in the MTBE standard rather than being the result of acid hydrolysis. Furthermore, for samples with high MTBE concentrations, where the potential for acid hydrolysis effects would be greatest, sample dilution prior to analysis would raise the pH. In the experiments conducted in this study, resultant pH values were all above 2.5 in diluted samples. O'Reilly et al. (2001) showed that rate constants for this reaction drop significantly as the pH increases from 2 to 3, and become negligible at pH values of 4 or above⁶, further reducing concern that significant concentrations of TBA will be generated via hydrolysis in highly-concentrated samples requiring dilution.

Increased analytical sensitivity was achieved using heated-purge methods during this study. However, using purge temperatures above 45° C adversely affected heated peak tailing of TBA and degraded the peak separation between TBA and MTBE. Therefore, purge temperatures in the range of 80° C as outlined in EPA method 5030C (EPA 2003) are not recommended if both MTBE and TBA are present in the sample. Furthermore, while purge temperatures of 45° C did increase TBA sensitivity dramatically (~400%) over purging at ambient

⁶ Reported rate constants measured at 26°C were: 7.52 x 10⁻³ mM/h at a pH of 2.01, 2.29 x 10⁻³ mM/h at a pH of 2.5, and 5.42 x 10⁻⁵ mM/h at a pH of 3.01, and a negligible rate at a pH of 4 or above.

temperatures, the long-term effects on analytical equipment of even this relatively low purge temperature is unknown. Additional testing will be required to adequately assess potential increases in machine maintenance and repair.

References

- Bauman, B. 2003. Do We Need to Worry About MTBE Acid Hydrolysis? New England Interstate Water Pollution Control Commission (NEIWPCC) L.U.S.T.Line Bulletin 43, pp 17-21.
- Douthit T.L., Kramer W.H. and Marr T.J. 2002. The Importance of Acid Hydrolysis of MTBE to TBA in Properly Handled Groundwater Samples. Proceedings, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Assessment, and Remediation. November 6-8, Atlanta, GA
- Environmental Protection Agency 2003. Method 5030C Purge-And-Trap For Aqueous Samples. OSW Methods Team, Washington DC. www.epa.gov/epaoswer/hazwaste/test/pdfs/5030c.pdf Rev. May, 2003.
- O'Reilly K.T., Moir M.E., Taylor C.D. Smith C. A., and Hyman M.R. 2001. Hydrolysis of tert-Butyl Ether (MTBE) in Dilute Aqueous Acid. Environ. Sci. Technol. Vol. 35 pp 3954 – 3961.

Biographical Sketches

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Mr. Sherding is responsible for day-to-day laboratory operations at Accutest's Corporate Headquarters in Dayton, NJ. He has supervisory responsibility for all technical personnel. This includes responsibility for all operational department managers, who report directly to Mr. Sherding regarding production, capacity, and technical issues. He initiates all equipment purchases and executes facility design to accommodate growth in targeted business sectors. Mr. Sherding led the design effort for the expansions of the New Jersey, Massachusetts, Florida, and Houston facilities. Mr. Sherding's tenure at Accutest has included "hands on" experience for the majority of the testing programs used by the organization. This includes method development, laboratory implementation, and sample analysis. He also provides technical support to all Accutest facilities on method development, equipment troubleshooting, and production efficiency. Mr. Sherding's method implementation credits include analytical programs for organic compounds by GC and GC/MS techniques using EPA 500, 600, 8000, and CLP methods. He has also designed and implemented an air toxics program for the analysis of ambient air using EPA Methods TO-3/EPA18 and TO-14/15. He has researched, designed, developed, and implemented methodology for the analysis of dissolved gases to monitor the metabolites of natural attenuation.

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Mr. Marr is a Vice President with Handex Environmental, Inc. and has 19 years of experience in water resource, contaminant hydrogeology, innovative environmental strategies and computer data management systems. Mr. Marr manages Handex's Corporate Technical Services Group (TSG) and Cone Penetrometer Technology (CPT) divisions. Handex' TSG offers environmental training, project and customer support services that seek to improve the knowledge and understanding of environmental work practices. Recent TSG work includes CPT enhancements for 3D geo-technical and contaminant assessments, gasoline/water mixing experiments to determine the presence and sources of various ether and alcohol oxygenate compounds and alternative strategies and published work on oxygenate remediation. TSG employees have also partnered with Handex' IT department in the development of a proprietary computer environmental database and project management system (Site ExplorerTM), which imbeds training, work practice standards and quality control systems aligned with ISO 9000/14000. Mr. Marr's interests include emergency chemical spill incident response management, exposure pathway identification and risk abatement, remediation alternatives selection, implementation and optimization, and the use of innovative approaches for rapid closure during compliance monitoring programs in order to expedite case closure.

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As manager of Land Tech Remedial, Inc.'s Farmingdale, New York office since December, 1993, and as Director of Applied Sciences with Handex since their acquisition of Land Tech Remedial, Inc. in September, 1998, Mr. Douthit has been directly involved in all aspects of petrochemical release management, including assessment, remediation system feasibility testing and implementation, regulatory negotiation and closure. Mr. Douthit's primary interests include the understanding, development and ultimate implementation of innovative and alternative remedial approaches. Recent projects include the regulatory advocacy and application of risk-based corrective action (RBCA), refinement of air sparging techniques, risk assessment utilizing computer-based dissolved-phase contaminant fate, transport and 3-D visualization modeling, co-producing guidance documents on field analytical methods for the American Petroleum Institute (API), and protocol development for field documentation of in-situ, intrinsic bioremediation at petrochemical release sites. Additional activities include the development, calibration and implementation of proprietary computer software for the application of Domenico (1987), Baetsle (1969) and Johnson and Ettinger (1991) contaminant fate-and-transport equations. A primary focus of these applications is the better understanding and quantification of indoor air exposure scenarios. Mr. Douthit served as a member of the American Society for Testing and Materials (ASTM) Task Group on Remediation by Natural Attenuation (RNA), and was a co-author of the ASTM Standard Guide for Remediation by Natural Attenuation at Petroleum Release Sites (E-1943).