

# The Importance of Acid Hydrolysis of MTBE to TBA in Properly Handled Groundwater Samples<sup>1</sup>

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## Abstract

The analysis of gasoline oxygenates in environmental groundwater samples is complicated by a variety of factors including constituent co-elution and the improper selection of surrogates (e.g. Rhodes and Verstuyft 2001; EPA 1997). Misidentification of oxygenate concentrations may lead to erroneous conclusions regarding spill composition and history at gasoline release sites. Recently, several authors have reported the potential for acid-catalyzed hydrolysis of methyl tertiary-butyl ether (MTBE) to tertiary-butyl alcohol (TBA) in environmental groundwater samples (O'Reilly et al. 2001; Pirkle and McLoughlin 2002), a process which could further compromise the validity of oxygenate analytical results. However, the conditions under which the hydrolysis reactions were evaluated included higher temperatures than typically encountered during groundwater sample transport and analysis, as well as higher MTBE concentrations than typically encountered at gasoline spill sites. To empirically evaluate the potential for acid hydrolysis of MTBE to TBA under more typical "field conditions", a series of water samples spiked with 200, 2,000 and 20,000 µg/L MTBE, stored at 4° C, acidified to a pH of ≤ 2, were analyzed for MTBE and TBA via EPA method 624 after various holding times of up to 31 days. Unpreserved control samples were also analyzed. No TBA concentrations were detected above method detection limits in any of the experimental or control samples analyzed and no reductions in MTBE concentrations were noted outside of analytical uncertainty. These data support the contention that acid hydrolysis of MTBE, in properly handled groundwater samples, does not compromise the integrity of dissolved MTBE and TBA analyses.

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<sup>1</sup> 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, NGWA Conference, Petroleum Hydrocarbons and Organic Chemicals in Groundwater: Prevention, Assessment and Remediation, Atlanta, Georgia, Nov. 6 – Nov. 8, 2002.

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## 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. Typically, groundwater samples collected for the analysis of MTBE and TBA are transported from the field to the analytical laboratory in 40 ml Volatile Organic Analysis (VOA) vials, preserved with hydrochloric acid (HCl) to a pH of approximately 2, and packed in ice to maintain a temperature of  $\leq 4^{\circ}$  C. Most analytical methods commonly associated with the analysis of dissolved-phase MTBE and TBA (e.g. EPA 524, EPA 624, EPA 8021, EPA 8260) have holding times of up to 14 days.

The laboratory analysis of TBA in environmental groundwater samples is complicated by various factors including co-elution of TBA with other gasoline constituents, such as MTBE and alkane isomers (e.g. pentane, pentene) and/or the improper selection of surrogates which may not closely mirror TBA's purge characteristics (e.g. Rhodes and Verstuyft, 2001; EPA 1997). Recently, the analysis of TBA in groundwater samples also containing MTBE has come under additional scrutiny due to the reported production of TBA from MTBE through HCl-catalyzed hydrolysis (O'Reilly et al. 2001; Pirkle and McLoughlin 2002). TBA and methanol can be produced from MTBE via 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.

**To test the potential generation of TBA from MTBE via acid hydrolysis under typical “field” conditions, a series of experiments were conducted to empirically measure the generation of TBA from MTBE in acid-preserved VOA vials. A series of MTBE-spiked water samples (200, 2,000 & 20,000 mg/L) were acidified to a pH of  $\approx 2$ , stored at  $4^{\circ}$  C, and analyzed for MTBE and TBA after various holding times up to 31 days. Unpreserved control samples were also analyzed during the experiment.**

## Results

TBA was not generated above method detection limits in any of the MTBE spiked samples, preserved or unpreserved, analyzed during the course of the experiment. Table 1 presents the results of the 200 µg/L MTBE sample analyses, Table 2 presents the results of the 2,000 µg/L MTBE sample analyses and Table 3 presents the results of the 20,000 µg/L MTBE sample analyses. While there was some scatter in the data within expected method analytical uncertainty, there was no apparent reduction in MTBE concentration in the acidified samples relative to the non-acidified samples at any given time interval and at any given MTBE spike concentration. This suggests that the acid preservation methods used were not serving to reduce MTBE concentrations nor were they serving to produce or accumulate TBA concentrations within the sensitivity of the analyses. These data are graphically presented in Figure 1 (200 µg/L), Figure 2 (2,000 µg/L) and Figure 3 (20,000 µg/L).

**Table 1**  
*200 mg/L MTBE Spike Sample Analytical Results*

DAY	Preserved (pH <2)		Unpreserved (pH = 6)	
	MTBE	TBA	MTBE	TBA
1	228 µg/L	<5 µg/L	225 µg/L	<5 µg/L
2	236 µg/L	<5 µg/L	240 µg/L	<5 µg/L
3	240 µg/L	<5 µg/L	241 µg/L	<5 µg/L
4	249 µg/L	<5 µg/L	251 µg/L	<5 µg/L
5	223 µg/L	<5 µg/L	211 µg/L	<5 µg/L
6	Not run	NA	Not run	NA
7	233 µg/L	<5 µg/L	241 µg/L	<5 µg/L
8	234 µg/L	<5 µg/L	241 µg/L	<5 µg/L
9	249 µg/L	<5 µg/L	251 µg/L	<5 µg/L
10	260 µg/L	<5 µg/L	242 µg/L	<5 µg/L
11	213 µg/L	<5 µg/L	216 µg/L	<5 µg/L
12	186 µg/L	<5 µg/L	186 µg/L	<5 µg/L
13	Not run	NA	Not Run	NA
14	189 µg/L	<5 µg/L	184 µg/L	<5 µg/L
31	197 µg/L	<5 µg/L	204 µg/L	<5 µg/L

**Table 2**  
*2,000 mg/L MTBE Spike Sample Analytical Results*

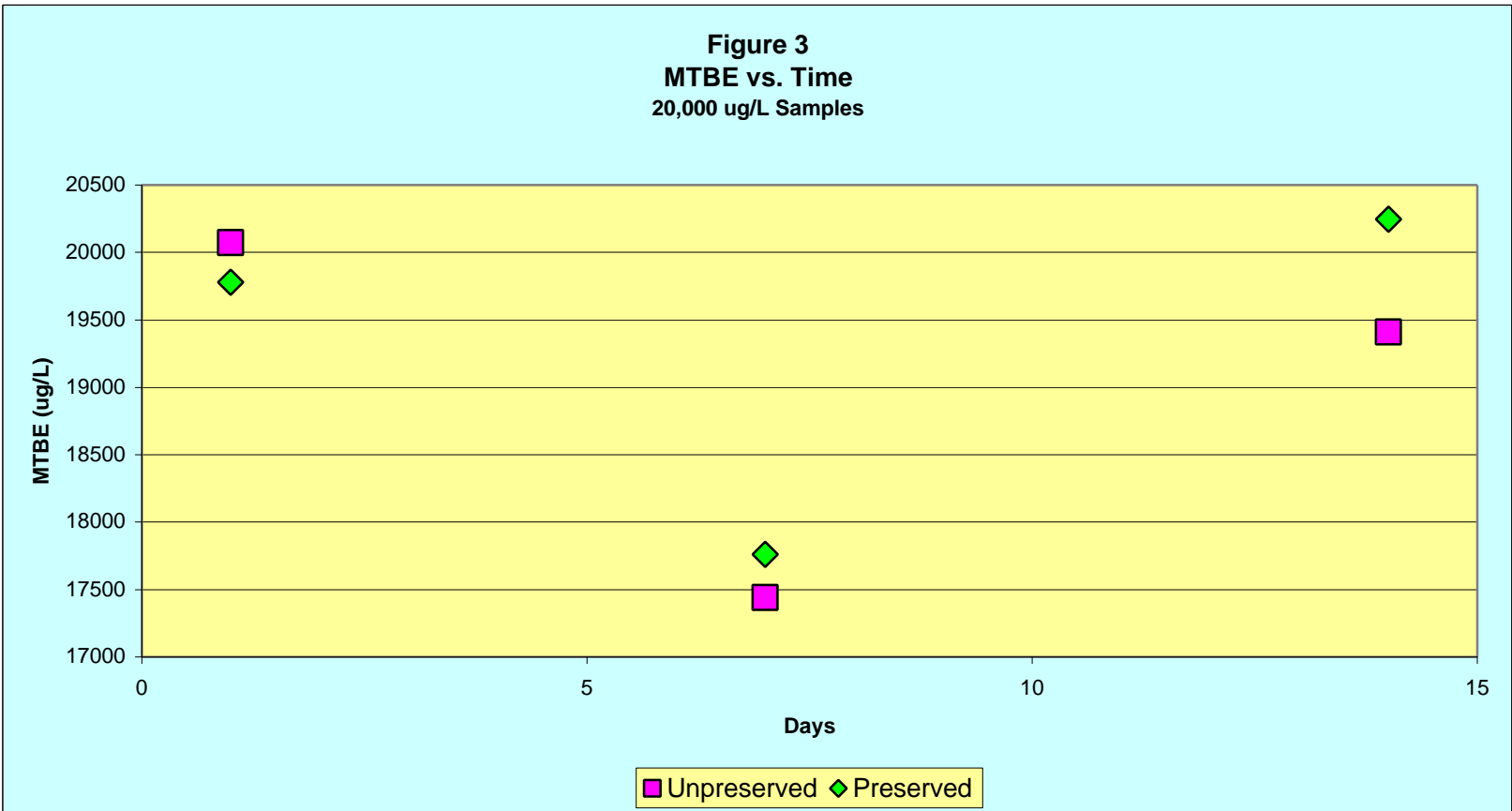
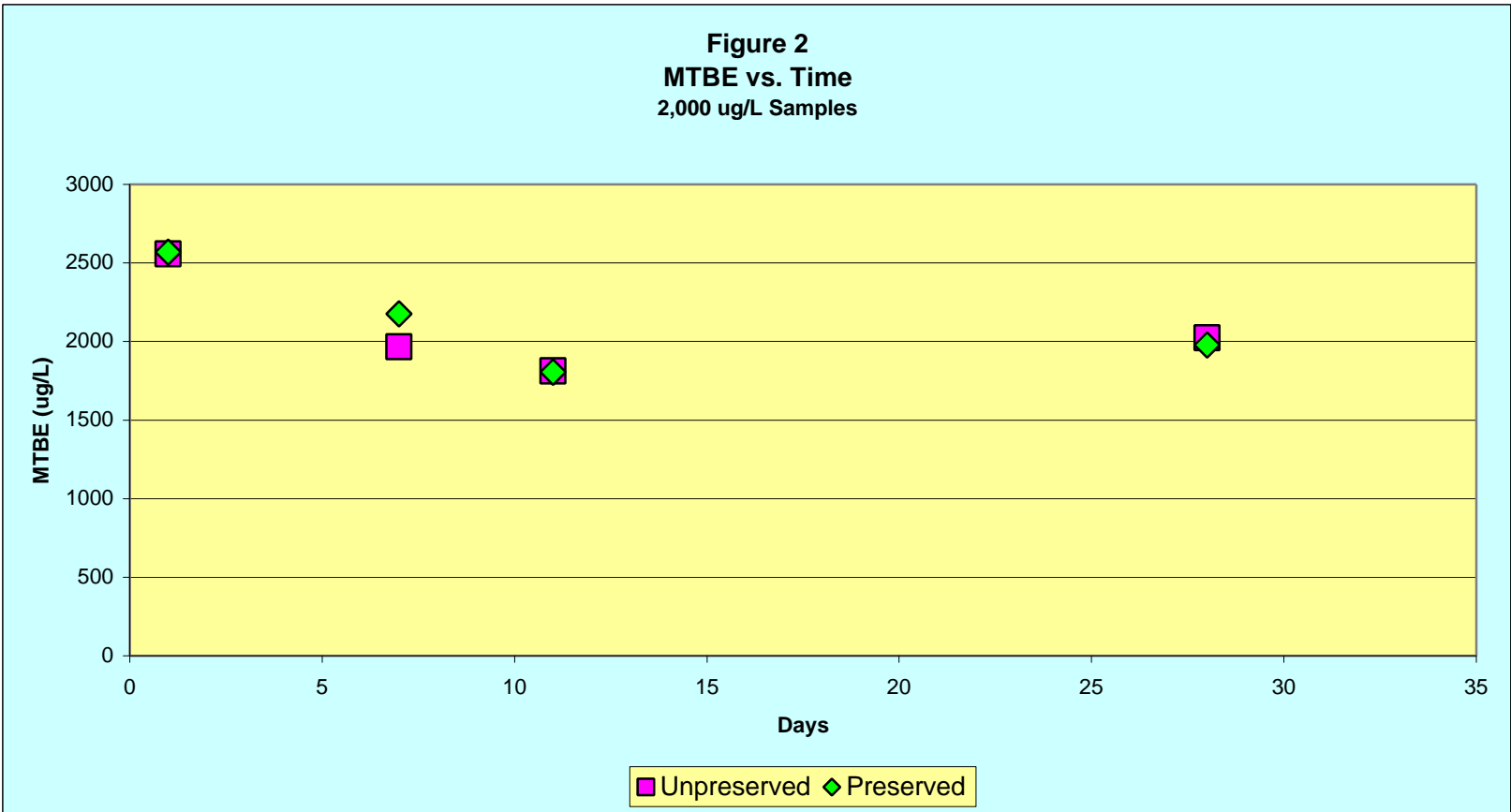
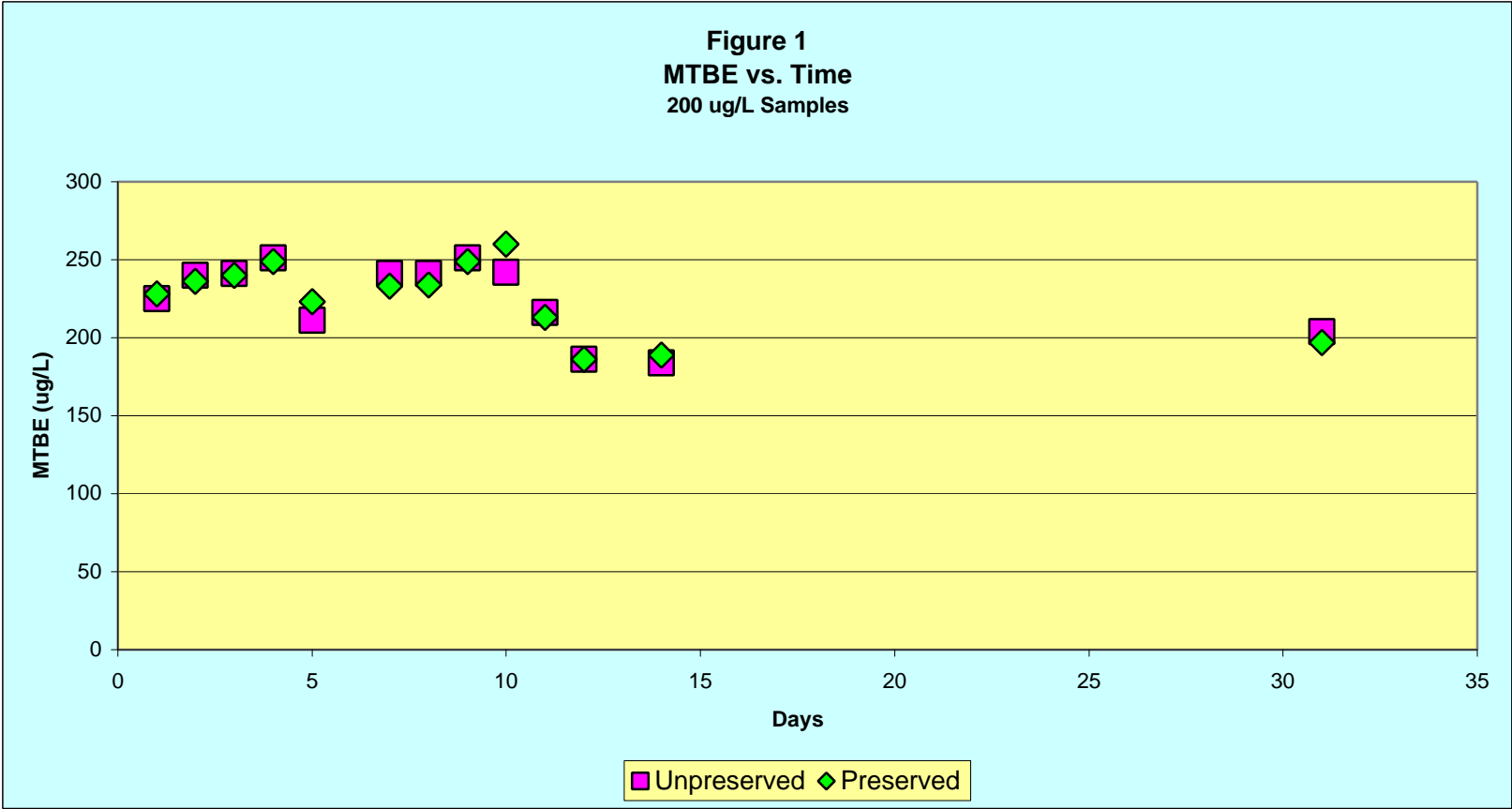
DAY	Preserved (pH <2)		Unreserved (pH =6)	
	MTBE	TBA	MTBE	TBA
1	2,567 µg/L	<20 µg/L	2,558 µg/L	<20 µg/L
2	Not run	NA	Not run	NA
3	Not run	NA	Not run	NA
4	Not run	NA	Not run	NA
5	Not run	NA	Not run	NA
6	Not run	NA	Not run	NA
7	2,177 µg/L	<20 µg/L	1,964 µg/L	<20 µg/L
8	Not run	NA	Not run	NA
9	Not run	NA	Not run	NA
10	Not run	NA	Not run	NA
11	1,806 µg/L	<20 µg/L	1,813 µg/L	<20 µg/L
12	Not run	NA	Not run	NA
13	Not run	NA	Not run	NA
14	Not run	NA	Not run	NA
28	1,979 µg/L	<20 µg/L	2,024 µg/L	<20 µg/L

Samples diluted 1:4

**Table 3**  
*20,000 mg/L MTBE Spike Sample Analytical Results*

DAY	Preserved (pH <2)		Unpreserved (pH = 6)	
	MTBE	TBA	MTBE	TBA
1	19,779 µg/L	<250 µg/L	20,073 µg/L	<250 µg/L
2	Not run	NA	Not run	NA
3	Not run	NA	Not run	NA
4	Not run	NA	Not run	NA
5	Not run	NA	Not run	NA
6	Not run	NA	Not run	NA
7	17,763 µg/L	<250 µg/L	17,440 µg/L	<250 µg/L
8	Not run	NA	Not run	NA
9	Not run	NA	Not run	NA
10	Not run	NA	Not run	NA
11	Not run	NA	Not run	NA
12	Not run	NA	Not run	NA
13	Not run	NA	Not run	NA
14	20,248 µg/L	<250 µg/L	19,407 µg/L	<250 µg/L

Samples diluted 1:50



## Discussion

On the basis of these results, it appears that if samples are properly preserved and properly shipped and stored (i.e. at  $\leq 4^{\circ}\text{C}$ ), then the generation and accumulation of TBA through acid hydrolysis of MTBE will be of minimal concern relative to the method detection limits of TBA. Similarly, reductions in MTBE concentrations via acid hydrolysis, if any, appear to be within analytical uncertainty. Based on the rate constant reported in O'Reilly et al. (2001) for the acid hydrolysis of MTBE at a pH of 2 and a temperature of  $26^{\circ}\text{C}$ , using a holding time of 30 days, approximately 11, 107, and 1,073  $\mu\text{g/L}$  TBA should have been generated for the 200, 2,000 and 20,000  $\mu\text{g/L}$  sample spikes, respectively. These theoretical values all exceed the detection limits for the respective experimental concentrations. However, possibly due to the storage of samples at  $\leq 4^{\circ}\text{C}$ , these rates of reaction were not realized in these experiments, and therefore, TBA generation, if present, remained below detection limits.

Since the hydrolysis of MTBE to TBA appears unimportant in solutions with  $\text{pH} \geq 4$  (O'Reilly et al. 2001, Pirkle and McLoughlin 2002), the preservation of environmental groundwater samples using a base such as  $\text{Na}_3\text{PO}_4$  has been suggested (Pirkle and McLoughlin 2002). While this study does not seek to dissuade groundwater sampling technicians from using basic preservatives in the future (especially if heated-purge analytical methods are adopted), this study does support the contention that samples, which had been properly handled in the past, were probably not compromised with respect to MTBE or TBA concentrations through the use of acidic preservation methodologies. In properly handled environmental groundwater samples containing MTBE, the detection of TBA is more likely a function of its actual presence in the original groundwater sample or alternatively, a function of inadequate care in analytical method selection or application.

## References

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