

A GC–MS Purge-and-Trap Method Comparison Study for MTBE Analysis in Groundwater



The U.S. Environmental Protection Agency has proposed the term *demonstration of method applicability* for the process of analytical method evaluation and selection under a performance-based measurement system approach, wherein methods are selected based on their demonstrated ability to meet project-specified performance criteria in the specific matrices of interest. Such a demonstration recently has been undertaken at the Ventura County Naval Base (Port Hueneme, California). This study supported a treatment technology demonstration for methyl-*tert*-butyl ether (MTBE) in groundwater by assessing the ability of commercially available purge-and-trap gas chromatography–mass spectrometry methods to meet project sensitivity, precision, and accuracy criteria for MTBE and related oxygenate compounds in four groundwater matrices.

The analytical methods used in site and waste characterization historically have been defined by promulgated or other published method protocols such as those included in the U.S. Environmental Protection Agency's (EPA's) *Test Methods for Evaluating Solid Waste*, more commonly called SW-846 (1). Recently, however, performance-based methodology has become a requirement for several EPA programs. As opposed to the default use of published methods as written, 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. To better define a performance-based approach to method selection, the general term *demonstration of method applicability* has been cited by Lesnik (2) and developed in the Resource Conservation and Recovery Act (RCRA) program as a process of validating a method for use in the specific matrices of interest for a given sampling program.

This article describes a study that demonstrated the applicability of purge-and-trap gas chromatography–mass spectrometry (GC–MS) methods for methyl-*tert*-butyl ether (MTBE) determination in specific

groundwater matrices. It demonstrates the importance of laboratory selection for compound analysis based upon technical experience and instrument capabilities. This method study was performed in support of a treatment technology demonstration for MTBE conducted under the EPA Superfund Innovative Technology Evaluation program.

MTBE is an oxygenate added to gasoline for improved combustion performance. Regulatory concern about MTBE is increasing, and the demand is growing for analytical methods for detecting this compound in the environment. Oxygenates such as MTBE have significant water solubility, which can present a particular problem; for example, when MTBE is in groundwater and the sample preparation technique is a purge-and-trap procedure such as SW-846 Method 5030B. The primary concern with this approach is the purging efficiency of MTBE. Because MTBE is highly water soluble, purging this compound to separate it chemically from an aqueous matrix can be less effective than desired, and it could limit method sensitivity and cause low-biased results.

Many researchers, however, have suggested that purge-and-trap methods can pro-

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vide adequate results for oxygenates depending upon the required sensitivity and that method performance in aqueous matrices should be verified by the laboratory performing the analysis (3,4). Halden and co-workers (4) also have suggested that purging this compound using large sample volumes at elevated temperatures (40 °C) could result in method detection limits as low as 1 µg/L.

Our objective in this study was to determine if accurate quantitation of MTBE could be obtained for compound concentrations of less than 5 µg/L, which is the current secondary maximum contaminant level for California. Although Halden and colleagues suggested that *method detection limits* as low as 1 µg/L could be obtained using purge-and-trap methodology, for the purposes of our demonstration it was important to achieve a *practical quantitation limit* of 1 µg/L.

EPA Guidance on Data Quality Indicators (EPA QA/G51) explains in detail the difference between practical quantitation limits and method detection limits (5). Method detection limits are theoretical or statistical lower limits achievable by a particular method and usually represent the minimum concentration of an analyte that can be differentiated from zero with a specified level of confidence. Practical quantitation limits, on the other hand, represent the concentration of an analyte that can be quantified within the precision and accuracy constraints of the analytical method. Many programs and laboratories use the definition of a practical quantitation limit as the lowest quantitation standard used when developing a calibration curve for the specified contaminant. Because the practical quantitation limit incorporates the precision and accuracy requirements of the method, we used it as the basis for method sensitivity requirements in this study. The practical quantitation limit often is 5–10 times higher in concentration than the method detection limit, and detection responses between the practical quantitation limit and the method detection limit often are reported with J qualifiers as estimated concentrations.

Another important consideration in method selection for environmental programs is the availability and cost of the methods of interest. Commercial laboratories, for example, work best if they can use automated methods for performing compound analysis. In fact, laboratory automation is one of the major reasons analytical costs have declined significantly during the past 15 years. Because analytical costs always are a significant concern and in particular

because we anticipated our sampling program to require analysis of 1000 or more groundwater samples for MTBE, we chose to use a readily available, automated method. For this reason, we chose to avoid investigating other separation techniques such as azeotropic distillation (EPA Method 5031) or direct aqueous injection (6), two techniques that have shown promise for oxygenate analysis, if purge-and-trap procedures would satisfy our objectives. Of the dozens of laboratories investigated, we found that most claimed they could perform this analysis using purge-and-trap methodology followed by GC–MS (Method SW-846 5030B/8260B). We eliminated GC analysis without MS as an option because of the potential interferences expected in our samples. In addition, many commercial laboratories prefer GC–MS and commercial laboratory GC–MS analysis usually is no more expensive than GC analysis.

For the purposes of our study, we narrowed our choice of laboratories to three, which we chose based upon their ability to accommodate the potential workload, satisfy EPA quality assurance requirements for the Superfund Innovative Technology Evaluation program, and their previous experience in the analysis of MTBE at similar groundwater sites. In addition to MTBE, EPA was interested in analyzing for other compounds at low quantitation limits, including *tert*-butyl alcohol, 2-propanol, and acetone. As potential degradation products of MTBE, each of these compounds presents similar or greater difficulties in terms of purging efficiency; therefore, we included them as part of this study.

The data from this method applicability study indicated that purge-and-trap methods attain acceptable levels of data quality and sensitivity for use in the referenced MTBE demonstration program and should continue to be considered as a method of choice for analyzing MTBE. As described below, specific instrumentation or purge-and-trap techniques used by one laboratory compared with another proved better at obtaining required quantitation limits with acceptable recovery of spiked compounds. As part of the study, we compiled raw analytical data packages from the analytical laboratories for review and validation to identify potential method performance issues.

Study Background

This demonstration of method applicability was conducted in support of the treatment technology demonstration that was initiated under the EPA Superfund Innovative Tech-

nology Evaluation program for MTBE at Port Hueneme CBC (Ventura, California). As explained above, the demonstration of method applicability was designed to assess the proficiency of purge-and-trap GC–MS methods in analyzing groundwater samples from the demonstration site for MTBE and its degradation products — *tert*-butyl alcohol, 2-propanol, and acetone. The method applicability study was designed to demonstrate that purge-and-trap GC–MS methods could generate satisfactory data in the matrix of interest for the treatment technology demonstrations. Based upon discussions with EPA's National Risk Management and Research Laboratory quality assurance and project management staff, we defined the data requirements for the MTBE demonstrations as the ability to meet project accuracy and precision goals of 75–125% recovery and 25% relative percent difference, respectively, at concentrations that were 20–25% of the lowest applicable regulatory level. The action levels and practical quantitation limit requirements for the target compounds are as follows:

- MTBE: 5 µg/L (California secondary maximum contaminant level); target practical quantitation limit: 1–2 µg/L
- *tert*-Butyl alcohol: 12 µg/L (California action level); target practical quantitation limit: 6–8 µg/L
- 2-Propanol: no California regulatory level; target practical quantitation limit: 10 µg/L
- Acetone: no California regulatory level; target practical quantitation limit: 10 µg/L

Of the many potential laboratories investigated, we chose three commercial laboratories for this study through prequalification audits based upon National Risk Management and Research Laboratory quality assurance requirements. For purposes of this article, we will call them laboratory X, laboratory Y, and laboratory Z. Each laboratory conducted the demonstration of method applicability study in accordance with EPA methods with slight variations in the purge-and-trap procedure. Laboratory X used a purge volume of 5 mL and purged at room temperature. (This same laboratory was the only laboratory to use a Varian Archon-EST autosampler [Palo Alto, California], and, as will be explained later, this instrument proved to be an important factor affecting method performance.) Laboratory Y purged at an elevated temperature of 40 °C and used a 10-mL purge volume. Laboratory Z purged at room temperature using a 25-mL purge volume.

Our objective was to let each laboratory select and apply its own preferred method. We chose not to dictate specific method procedures to be followed and instead relied upon the laboratories to apply their experience with oxygenates and their best available purge-and-trap technology to achieve the target practical quantitation limits and the precision and accuracy objectives for the project in samples obtained from the site of concern. In this sense, our study was consistent with the performance-based measurement system approach to method selection currently being established by EPA (see <http://www.epa.gov/epaoswer/hazwaste/test/pbms.htm>). We dictated only quality control requirements and appropriate spiking concentrations and techniques. Our overall objective was to compare interlaboratory results and choose the most suitable laboratory for the demonstration.

Experimental

Samples were collected from four separate well locations at the Port Hueneme site that were of interest for the Superfund Innovative Technology Evaluation program treatment technology demonstration. Sample H-1 was collected near the source of the plume (the NEX gas station) in an area affected by free-phase floating hydrocarbons. Sample GWT was collected downgradient of the source area in the heart of the MTBE plume. Sample 401-3 was collected farther downgradient in the MTBE plume, and sample 401-1 was collected near the plume boundary.

Each sample was composited quickly before being split into three aliquots for submission to the three prequalified laboratories. After receipt, the laboratories each performed the following series of tests on the samples as part of the demonstration of method applicability.

- Each sample was screened to select an appropriate dilution factor for optimal quantitation of the target analytes present. Each sample then was analyzed in triplicate at the selected dilution factor (see Table I).
- Matrix spike–matrix spike duplicate analyses were performed on each of the four samples received to generate matrix-specific precision and accuracy information for all the target analytes. Spike levels were adjusted as deemed appropriate by the laboratories for target analyte concentrations and sample dilution (see Table II).
- Additional samples were collected from Well 401-1 (known to contain very little

Table I: Triplicate analysis*																
Target Analyte	Laboratory X					Laboratory Y					Laboratory Z					
	Replicate 1	Replicate 2	Replicate 3	Mean	RSD (%)	Replicate 1	Replicate 2	Replicate 3	Mean	RSD (%)	Replicate 1	Replicate 2	Replicate 3	Mean	RSD (%)	
Sample 401-1																
MTBE	1.4	1.4	1.4	1.4	0	0.91	0.98	1.0	0.96	4.9	1.0	1.1	1.1	1.1	5.4	
<i>tert</i> -Butyl alcohol	ND†	ND	ND			ND	ND	ND			ND	ND	ND			
2-Propanol	ND	ND	ND			ND	ND	ND			ND	ND	ND			
Acetone	ND	ND	ND			ND	ND	ND			ND	ND	ND			
MTBE- <i>d</i> ₃ (surrogate)‡	107%	112%	112%			NA§	NA	NA			79.9%	90.5%	97.6%			
<i>tert</i> -Butyl alcohol- <i>d</i> ₁₀ (surrogate)‡	118%	118%	117%								73.2%	82.8%	85.4%			
Sample 401-3																
MTBE	491	493	486	490	0.74	510	580	550	547	6.4	470	470	480	473	1.2	
<i>tert</i> -Butyl alcohol	ND	ND	ND			NA#	12#	NA#			20	20	20	20.0	0.0	
2-Propanol	ND	ND	ND			NA#	ND#	NA#			ND	ND	ND			
Acetone	ND	ND	ND			NA#	ND#	NA#			ND	ND	ND			
MTBE- <i>d</i> ₃ (surrogate)‡	97%	97%	97%			NA	NA	NA			160%	168%	149%			
<i>tert</i> -Butyl alcohol- <i>d</i> ₁₀ (surrogate)‡	98%	97%	98%								115%	108%	111%			
Sample GWT																
MTBE	3010	2860	2960	2940	2.6	2500	2800	2900	2730	7.6	2200	2760	2840	2600	13	
<i>tert</i> -Butyl alcohol	12#	NA#	NA#			NA#	69#	NA#			70	80	60	70	14	
2-Propanol	ND#	NA#	NA#			NA#	ND#	NA#			ND	ND	ND			
Acetone	ND#	NA#	NA#			NA#	ND#	NA#			ND	ND	ND			
MTBE- <i>d</i> ₃ (surrogate)‡	110%	103%	102%			NA	NA	NA			91.8%	76.9%	132%			
<i>tert</i> -Butyl alcohol- <i>d</i> ₁₀ (surrogate)‡	95%	93%	92%								142%	119%	120%			
Sample H-1**																
MTBE	740	789	785	771	3.5	780	880	810	823	6.2	690	810	523	674	21	
<i>tert</i> -Butyl alcohol	39	37	38	38.0	2.6	NA#	62#	NA#			50	70	70	63	18	
2-Propanol	ND	ND	ND			NA#	ND#	NA#			ND	ND	ND			
Acetone	ND	ND	ND			NA#	ND#	NA#			ND	ND	ND			
MTBE- <i>d</i> ₃ (surrogate)‡	105%	105%	104%			NA	NA	NA			84.6%	83.6%	82.1%			
<i>tert</i> -Butyl alcohol- <i>d</i> ₁₀ (surrogate)‡	101%	100%	98%								108%	106%	105%			

* All results are presented in units of micrograms per liter, except for surrogate recoveries, which are reported in percent.
† ND = not detected.
‡ Surrogate recoveries that do not meet program accuracy criteria (75–125% recovery) are in bold.
§ NA = not analyzed.
|| *tert*-Butyl alcohol-*d*₉ was used as an internal standard by laboratory Y rather than as a surrogate. Bold type indicates samples in which the internal standard recovery was outside of program precision goal of 75–125%.
The laboratory analyzed one of the three replicates at lower dilution to assess lowest possible practical quantitation limits and quantitate analytes other than MTBE.
**High levels of BTEX (greater than 1000 µg/L) were reported by the laboratories for this sample.

if any MTBE but otherwise representative of site conditions) for low-level spiking by each laboratory. The laboratories were asked to perform a minimum of three low-level spike analyses (MTBE, *tert*-butyl alcohol, 2-propanol, and acetone) on this matrix, wherein the spiking concentrations were at or near the desired practical quantitation limit for the technology demonstrations (see Table III).

In association with the above tests, we asked the laboratories to use oxygenated surrogates or internal standards to monitor recovery in each sample and spike analyzed. The laboratories responded by using deuterated analogues of MTBE or *tert*-butyl alcohol in this capacity. The laboratories also were required to ensure that their method calibration curves included their target practical quantitation limit (that is, to

demonstrate that their low-level method reporting limit could be considered a practical quantitation limit rather than a statistical method detection limit). The practical quantitation limit requirements were stated above.

After receipt of the results from the method applicability study, we performed a raw data review of all laboratory data. Included in this review were standard quality control checks for purge-and-trap GC–MS methods, such as holding times, GC–MS instrument tuning and calibration, surrogate compound recoveries, matrix spike–matrix spike duplicate and low-spike recoveries, relative percent differences, triplicate results, target compound identification and quantitation, and method blanks.

Laboratory X: Laboratory X analyzed the proficiency study samples in accordance

with EPA SW-846 Methods 5030B and 8260B. Each sample was purged at room temperature using a 5-mL purge volume. The purge-and-trap device comprised a Varian Archon-EST autosampler and a Tekmar 3000 concentrator (Tekmar-Dohrmann, Mason, Ohio) equipped with a Supelco Vocab K 3000 trap (Carbopack B/Carboxen, Bellefonte, Pennsylvania). A purge time of 11 min was used, followed by a 3-min desorb time (240 °C) and an 8-min bakeout (260 °C). Neither the purge-and-trap nor the analysis method was modified or optimized for analysis of the oxygenated target analytes. Sample analysis was completed using a DB-VRX column on a model 5890 gas chromatograph linked to a model 5971 mass spectrometer (all from Agilent Technologies, Wilmington, Delaware).

Laboratory Y: Laboratory Y performed a modified version of Method 5030B that uses a 10-mL sample purge volume and a 40 °C purge temperature. A purge time of 11 min was used, followed by a 2-min trap desorb time and a 15-min bakeout at 180 °C. As was true for laboratory X, laboratory Y applied its standard method for volatile organic compound analysis of water samples by GC–MS; purge-and-trap protocols and other method parameters were not modified specifically for analysis of oxygenates. The sample analysis system included an OI DPM16 purging autosampler and an OI 4560 preconcentrator (both from OI Analytical, College Station, Texas) with a combination (Tenax–silica gel–CMS) trap. The analysis was performed using a model 6850 gas chromatograph equipped with a DB-VRX column and

linked to a model 5973 mass spectrometer (all from Agilent Technologies).

Laboratory Z: Laboratory Z analyzed the proficiency study samples in accordance with EPA Method 524.2 for drinking water. Each sample was purged at room temperature using a 25-mL purge volume. The purge-and-trap device comprised a Tekmar 2000/2016 autosampler with a Tekmar Purge Trap K (Carbopack B/Carboxen). The purge time was 11 min, followed by a 6-min desorb time (250 °C) and an 8-min bakeout (260 °C). Again, neither the purge-and-trap nor the analysis method was modified or optimized for analysis of the oxygenated target analytes. The sample analysis was completed using an HP-624 column and a model 5890 series II gas chromatograph linked to a model 5971 mass spectrometer (all from Agilent Technologies).

Results and Discussion

Laboratory X: Table IV summarizes the instrument calibration and method performance data for laboratory X. This laboratory's method and instrumentation achieved a mean relative response factor of approximately 0.8 for MTBE, and the mean relative response factors for the other oxygenated target analytes ranged from 0.021 to 0.038. These values compare favorably with the minimum relative response factor requirement of 0.01 specified for many oxygenated compounds in the EPA Contract Laboratory Program Statement of Work for purge-and-trap GC-MS analysis (no minimum relative response factor requirements are established by EPA Method 8260B) (1,7). The relative standard deviations (RSDs) for the mean relative response factors were well within the Method 8260B limit of 15% for linear response (Table IV), and the percent difference values for daily calibration relative response factors relative to the initial mean relative response factors were 25% or less.

The method performance attained by laboratory X in the demonstration site samples generally met program goals for sensitivity, accuracy, and precision. Laboratory practical quantitation limits and calibration curves extended below the program-required thresholds (see Table IV). As measured by RSDs and relative percent differences, the triplicate analyses and matrix spike–matrix spike duplicates were well within the program precision limit of 25%. Although some matrix spike–matrix spike duplicate and low-spike recoveries were outside the project accuracy goals of 75–125%, these exceedances were invariably slight; the lowest reported recovery was 62% (MTBE) and the highest recovery was 136% (2-propanol). Furthermore, recoveries of MTBE-*d*₃ and *tert*-butyl alcohol-*d*₁₀, spiked as oxygenated surrogates into the proficiency samples and matrix spikes, all were within the program accuracy criteria (see Tables I and III). The target analyte identification also was acceptable for the reported detections, as well as the low-concentration spikes at the target practical quantitation limits, because it was consistent with the mass spectral confirmation criteria outlined in Method 8260B.

In addition, we noted that the Varian Archon-EST autosampler provided a clear advantage in the handling and subsequent purging of samples. The primary difference was the ability of this autosampler to process the samples with minimal sample handling and a high degree of reproducibil-

Table II: Matrix spike–matrix spike duplicate results*

Target Analyte	Laboratory X					Laboratory Y					Laboratory Z				
	Spike Concentration	Native Concentration	Matrix Spike Recovery (%)	Matrix Spike Duplicate Recovery (%)	Relative Percent Difference (%)	Spike Concentration	Native Concentration	Matrix Spike Recovery (%)	Matrix Spike Duplicate Recovery (%)	Relative Percent Difference (%)	Spike Concentration	Native Concentration	Matrix Spike Recovery (%)	Matrix Spike Duplicate Recovery (%)	Relative Percent Difference (%)
Sample 401-1															
MTBE	20	1.4	93	93	0	25	0.91	102	105	3.0	10	1.0	88	96.4	8.3
<i>tert</i> -Butyl alcohol	150	ND	129	125	3	125	ND	104	104	0	90	ND	83.2	114	30.9
2-Propanol	100	ND	101	93	8	250	ND	117	132	12	40	ND	110	113	2.7
Acetone	150	ND	77	77	0	25	ND	56.8	58.4	2.8	40	ND	156	116	29
Sample 401-3															
MTBE	200	491	130	118	10	4000	510	98	104	5.1	2000	470	85.9	91.9	5.3
<i>tert</i> -Butyl alcohol	750	ND	118	115	2	5000	ND	105	113	7.9	12,000	20	90.7	103	12.5
2-Propanol	500	ND	88	89	1	10,000	ND	110	109	0.9	2000	ND	162	159	1.3
Acetone	750	ND	74	78	5	1000	ND	44.9	45.9	2.2	2000	ND	110	118	7
Sample GWT															
MTBE	1200	3010	69	62	11	20,000	2500	101	117	13.2	10,000	2200	74.1	74.3	0.2
<i>tert</i> -Butyl alcohol	3000	ND	112	113	1	25,000	ND	98.4	106	7.1	58,000	70	66.6	84.7	23.8
2-Propanol	2000	ND	85	84	1	50,000	ND	99.4	118	16.8	8000	ND	75	93	21
Acetone	3000	ND	77	72	7	5000	ND	48	54.4	12.5	8000	ND	145	124	15.6
Sample H-1															
MTBE	300	740	81	73	10	5000	780	104	107	2.5	2000	690	106	114	5.8
<i>tert</i> -Butyl alcohol	750	ND	121	122	1	6250	ND	93.4	85.1	9.3	18,000	50	86	101	16.1
2-Propanol	500	ND	96	97	1	12,500	ND	93.6	82.4	12.7	8000	ND	104	116	11
Acetone	750	ND	78	78	0	1250	ND	54.5	55.1	1.2	8000	ND	234	194	18.3

*Results that do not meet program accuracy and precision criteria (75–125% recovery and 25% RSD or relative percent difference) are in bold.

Table III: Low-spike recovery results*

Sample 401-1	Laboratory X					Laboratory Y					Laboratory Z				
	Spike Concentration	Native Concentration	Low Spike 1 Recovery (%)	Low Spike 2 Recovery (%)	Low Spike 3 Recovery (%)	Spike Concentration	Native Concentration	Low Spike 1 Recovery (%)	Low Spike 2 Recovery (%)	Low Spike 3 Recovery (%)	Spike Concentration	Native Concentration	Low Spike 1 Recovery (%)	Low Spike 2 Recovery (%)	Low Spike 3 Recovery (%)
MTBE	1	1.4	90	100	100	2	1	83.5	95	100	1	1.1	130	90	140
<i>tert</i> -Butyl alcohol	10	ND	110	112	111	8	ND	59.5	63.7	65.2	5	ND	100	100	100
2-Propanol	5	ND	110	136	130	80	ND	77.5	89.1	94.4	8	ND	62.5	112.5	75.0
Acetone	7.5	ND	93	84	100	8	ND	48.6	61.5	57.5	8	ND	125	ND	100
MTBE- <i>d</i> ₃			109	111	109								106	93.4	118
<i>tert</i> -Butyl alcohol- <i>d</i> ₁₀			114	116	114								92.5	84	107

*Results that do not meet program accuracy and precision criteria (75–125% recovery and 25% RSD or relative percent difference) are in bold.

ity, which resulted in greater precision and lower opportunity for analyte loss.

Although not required to do so by the scope of the method proficiency study, laboratory X provided method performance data for *tert*-butyl formate, another degradation product of MTBE. Low recoveries of *tert*-butyl formate (9–30%) observed for some matrix spike–matrix spike duplicates and low spikes could be ascribed to acid hydrolysis of *tert*-butyl formate in the proficiency study samples, which were preserved with hydrochloric acid. The laboratory also suspected degradation of *tert*-butyl formate in some calibration standards and spiking solutions. A study of the hydrolysis of *tert*-butyl formate reports a half-life of five days

for this compound under neutral pH conditions and a half-life of 6 h at pH 2 (8). Because of the short apparent half-life of *tert*-butyl formate and uncertainties in proper preservation techniques and holding times for this compound, we had excluded *tert*-butyl formate as a target analyte for the treatment technology demonstrations.

Laboratory Y: Table IV summarizes the instrument calibration and method performance data for laboratory Y. The laboratory attained mean relative response factors of 0.023 and 0.013 for *tert*-butyl alcohol and 2-propanol, respectively, which were greater than the EPA Contract Laboratory Program minimum value of 0.01 for *tert*-butyl alcohol and 2-propanol. Laboratory Y obtained

higher values for acetone and MTBE. RSD values for the mean relative response factors were less than the Method 8260B criterion of 15%, with the exception of acetone, for which the laboratory reported an RSD of 21%. A sample daily calibration provided by the laboratory reported percent difference values of less than 15% for all four target analytes.

The method performance attained by laboratory Y in the demonstration site samples generally met program goals for MTBE and *tert*-butyl alcohol; however, quantitation limits and low-spike levels for 2-propanol were above the program goals, and acetone recoveries were consistently low in the matrix spike–matrix spike duplicates

and low spikes, ranging from 45 to 61% (see Table II). We also observed slightly low recoveries for *tert*-butyl alcohol in the low spikes performed on sample 401-1, ranging from 60 to 65% (see Table III). We found no basis for the low recoveries of acetone and *tert*-butyl alcohol during the raw data review, which also noted consistently low recoveries for acetone in the laboratory control sample (45–50%).

Although laboratory Y's method did not include the use of oxygenated surrogates, the laboratory used *tert*-butyl alcohol-*d*₉ as an internal standard. Reviews of raw data enabled other method quality control checks — instrument tuning and method blanks — which indicated that method per-

formance criteria were not exceeded, and mass spectral confirmation of target analyte detections again was considered acceptable relative to the guidelines in Method 8260B. As was observed for laboratory X, the retention times of 2-propanol and acetone were approximately 0.1 min apart, and a potential for interference was noted between these two compounds.

Laboratory Z: Table IV summarizes the instrument calibration and method performance data for laboratory Z. Low relative mean relative response factors of 0.008 and 0.006 were reported for *tert*-butyl alcohol and 2-propanol, respectively. The daily calibration check performance was monitored in terms of percent recovery rather than per-

Table IV: Instrument calibration and performance data

Method Parameter	Target Analytes				Surrogate Compounds	
	MTBE	<i>tert</i> -Butyl Alcohol	2-Propanol	Acetone	MTBE- <i>d</i> ₃	<i>tert</i> -Butyl Alcohol- <i>d</i> ₁₀
Laboratory X						
Method detection limit (μg/L)	0.27	0.73	4.57*	4.25*	ND	ND
Practical quantitation limit (μg/L)	1	4	4	4	1	ND
Initial calibration						
Concentration range (μg/L)	1–200	4–400	4–400	4–400	1–200	
Mean relative response factor	0.803	0.023	0.021	0.038	0.74	0.021
RSD (%)	3.4	8.6	4.8	7.2	1.6	2.1
Laboratory Y						
Method detection limit (μg/L)	0.28	5	7.3	5	N/A†	N/A
Practical quantitation limit (μg/L)	5	10	20	10	N/A	N/A
Initial calibration						
Concentration range (μg/L)‡	0.5–200	10–1000	20–2000	5–200	N/A	N/A
Mean relative response factor	1.039	0.023	0.013	0.162	N/A	N/A
RSD (%)	8.55	11.1	3.47	21.4	N/A	N/A
Laboratory Z						
Method detection limit (μg/L)	0.24	2	ND	1.7	ND	ND
Practical quantitation limit (μg/L)	0.5	10	10	10	0.5	10
Initial calibration						
Concentration range (μg/L)‡	0.5–100	2.5–500	4–240	4–240	0.5–100	2.5–500
Mean relative response factor	0.436	0.0083	0.0059	0.044	0.455	0.0074
RSD (%)	19.1	7.13	0.998§	19.6	13.2	9.26

*Method detection limits are greater than the practical quantitation limit. Recalculated method detection limits, using lower standards, likely would result in much lower detection limits.

†N/A = Not applicable. This laboratory did not use MTBE-*d*₃ and *tert*-butyl alcohol-*d*₁₀ as surrogates; instead it used *tert*-butyl alcohol-*d*₉ as an internal standard.

‡In some instances, the concentration range of the compound of interest in the initial calibration curve was less than the practical quantitation limit reported by the laboratory. The laboratory attempted to quantitate sample in this range but could not reliably meet accuracy and precision requirements for the low standard. Practical quantitation limits therefore were adjusted accordingly.

§This value is not an RSD but rather a correlation coefficient for a linear fit with non-zero intercept.

cent difference. Recoveries of the daily standards ranged from 84% to 125%, with the greatest variability observed for 2-propanol.

As demonstrated by its quantitation limits and calibration curves, this method met program sensitivity goals. As measured by RSDs, the triplicate analyses also were within the program precision goal of 25% (see Table I). However, some matrix spike–matrix spike duplicate and low-spike results exceeded program accuracy and precision goals (see Tables II and III). Acetone was recovered high (145–234%) in four of the eight matrix spike–matrix spike duplicate spikes, and it was undetected in one of the low spikes. We also observed erratic recoveries for the other target analytes; multiple recoveries were observed both above and below the accuracy limits (75–125%) for each compound. Laboratory Z reported relative percent differences that exceeded the precision limit of 25% for *tert*-butyl alcohol and acetone in the matrix spike–matrix spike duplicates. The recoveries of MTBE-*d*₃ and *tert*-butyl alcohol-*d*₁₀, used as surrogate compounds, were outside of the program accuracy goals in multiple sample analyses (see Table I).

Our reviews of raw data allowed other method quality control checks — instrument tuning, internal standards, and method blanks — which indicated that method performance criteria were not exceeded. The target analyte identification also was acceptable for the detections reported in the demonstration site samples. A retention time difference of approximately 0.1 min was observed again for 2-propanol and acetone.

Overall Evaluation of Results

Taken as a whole, the triplicate analytical results presented in Table I show an acceptable level of intra- and interlaboratory precision for the method applicability study. The differences between the laboratory methods did not produce significant biases in the results, although MTBE and *tert*-butyl alcohol precision (RSD) appeared slightly more variable for laboratory Z's method in the higher concentration samples (GWT and H-1).

Our review of the spike recovery data in Tables II and III indicates that laboratory X's method was slightly more successful in meeting program data quality goals, in terms of both the number and magnitude of

outliers reported. The surrogate recoveries, RSDs, and relative percent differences reported by laboratory X for the demonstration site samples were within the program goals. The number and magnitude of exceedances was greater for the other laboratories, with the poorest performance observed for acetone; laboratory Y reported a consistently low bias for this compound, whereas laboratory Z reported high and erratic recoveries. Overall, laboratory Z's Method 524.2 analysis, with its 25-mL purge volume, produced the greatest variations in analytical results and data quality for the four target analytes.

Conclusions and Recommendations

The results presented in this article appear to be a successful demonstration of method applicability, which indicates that purge-and-trap GC–MS is an acceptable technology for the analysis of MTBE and its oxygenated breakdown products, at least in the matrices of interest for our Superfund Innovative Technology Evaluation program treatment technology demonstration. The laboratories generally were able to meet program sensitivity requirements and data

quality goals by using their best available purge-and-trap method without additional optimization for oxygenated compounds. Specified requirements of 25% precision and 75–125% recovery for demonstration samples appear to be achievable.

The method performance was similar between the laboratories, and the overall differences in results were slight. Comparisons between the laboratories and methods lead to the following conclusions:

- Relative to the other laboratories, laboratory X's method exhibited slightly better sensitivity and performance relative to program data quality goals. The precision and stability of this method could relate to the autosampler, which used a single purge port. By comparison, the autosamplers of the other laboratories had as many as 16 purging vessels (one for each sample injected during a given run), each of which might have had a slightly different age, condition, or performance characteristics. The Archon autosampler therefore could have produced more-uniform purging efficiencies between the different sample analyses. The Archon autosampler also required less sample handling before instrument analysis.

- The 25-mL purge volume required by Method 524.2 could be slightly less preferable because of the low calibration response and more-erratic results for some of the target analytes.

- The 40 °C purge temperature used by laboratory Y appeared to provide no advantage.

Based upon the data provided, however, the differences in method performance were slight enough that we could not ascribe clear advantages or disadvantages to specific equipment or method operating parameters, as opposed to other factors that might have affected laboratory performance. Other factors might include the level of analyst experience and care, as well as the equipment condition and maintenance at the time of sample analysis.

A more clear delineation of factors affecting method performance for oxygenates requires more-detailed, comprehensive method development and validation programs that were beyond the scope of this method applicability study. This being said, however, the results of the present study are consistent in demonstrating that purge-and-trap GC–MS methods were appropriate for their intended use in our demonstra-

tion program, and they remain valid options for the analysis of MTBE, *tert*-butyl alcohol, and related oxygenated volatile organic compounds.

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