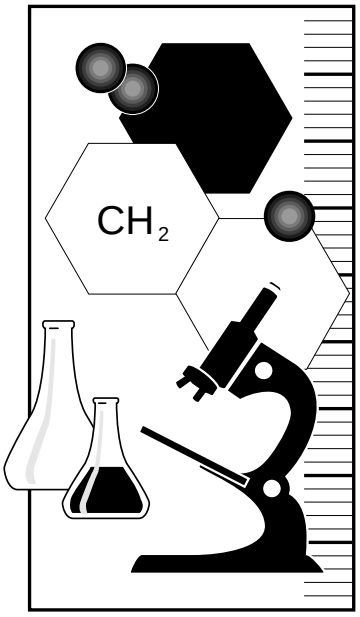
Oxygenates

Analytical Issues for MTBE and Related Oxygenate Compounds

by Deana M. Crumbling and Barry Lesnik



Questions have been raised about which analytical methods for MTBE and related analytes are appropriate within the context of state and federal LUST programs. To help answer some of these questions, we've prepared the following overview of the current status of MTBE analysis from the perspective and experience of EPA's Office of Solid Waste (OSW) Methods Team, the group responsible for developing and maintaining the *SW-846 Methods* manual, and EPA's Technology Innovation Office (TIO).

Because MTBE is not currently a RCRA-regulated analyte, it has not been validated in any SW-846 method at this time. *Neither Method 8021 nor Method 8260 has been validated for MTBE.* As it stands, analyses of a few of the oxygenated analytes that are of more recent interest to LUST program personnel [e.g., tert-butyl alcohol (TBA) and ethanol] have already been validated and published in SW-846 methods several years ago.

"Approved Methods"

Confusion often arises in the search for an "approved method." A common misconception is that when a method is published in SW-846 it becomes an "approved method" and is, therefore, required across the board. This is not true. In fact, any reliable method may be used, whether it is published in an EPA methods manual or suggested as an alternative method. (Note: Some state UST programs require the use of "EPA-approved methods.") Any method used must be able to determine the analytes of concern in the matrix of concern at the action level of concern.

SW-846 Methods

Requirements for using specific "EPA-approved methods" in the context of waste programs are discouraged. The use of prescriptive analytical methods is counterproductive to the generation of reliable data, because samples encountered in waste programs are too varied and complex for any single method to work for all samples all the time. For this reason, the SW-846 manual uses a performance-based approach to analytical methods.

SW-846 is intended to provide general guidance, not prescriptive requirements. There are no "reference methods" in SW-846, in the context that the term is used in the Office of Water Programs. Part of the misunderstanding regarding analytical method requirements stems from the fact that EPA water programs do require "EPA-approved methods" when implementing the Safe Drinking Water Act (SDWA) and the Clean Water Act (CWA). However, meeting SDWA and CWA requirements is not usually the driver for projects within waste programs, and "EPA-approved methods" are not required.

Thus there will never be a prescriptive method for MTBE within OSW programs, even when MTBE is included as a target analyte in published SW-846 methods. However, the growing interest in oxygenates indicates that an SW-846 method that addresses MTBE would be highly valuable to the UST/LUST community.

By the time they are published, SW-846 methods have undergone thorough evaluation and peer review to (1) determine the level of method performance that can be expected under "typical" conditions, and (2) identify what interferences might compromise method performance and what to do when it happens. We believe that some of the existing SW-846 methods are appropriate for the sample preparation (Method 5031) and determination (Methods 8015 and 8260) of MTBE and other related target analytes in aqueous matrices. However, it would take a "demonstration of applicability" to prove it.

In the Meantime

Until MTBE analysis is validated in an SW-846 method, which methods could be used for MTBE and related analytes? The simple answer is that "any method that can be demonstrated to measure the constituent of concern, in the matrix of concern, at the level of concern, and at the degree of accuracy as identified as necessary to address the site decision" can be used. (See http://cluin.org/download/char/article(1).pdf, page 2.) Of course, demonstrating that a method is working as expected on a variety of real-world sample types takes time and technical expertise, and that means that the answer may not be so simple. With this caveat in mind, let's look at oxygenate analysis in relation to existing SW-846 methods.

Method 8015

The chemical and physical properties of the target analytes and the potential for interferences in the samples submitted for oxygenate analyses must be considered when selecting potential sample preparation and determinative methods. SW-846 Method 8015, "Nonhalogenated Organic Compounds Using GC/FID," was developed for the analysis of oxygenates and is expected to be applicable to MTBE and other related compounds. (Note: All SW-846 methods may be accessed on-line at http://www.epa.gov/SW-846/main.htm.)

Method 8015 is a determinative method [gas chromatography/flame ionization detector (GC/FID)] only. As such, it is merely part of the

"analytical method" picture. A "determinative method" applies to the analytical instrumentation used to generate the analytical result. A sample preparation (or sample introduction) method is needed to get the target analytes from the sample matrix into the analytical instrumentation.

An appropriate sample preparation method must be applied to the original sample (such as water or soil) so that the analytes can be transferred from the matrix onto the GC column. If the sample preparative method is not appropriate for the analyte, transfer of the analytes from the original sample into the instrument may be incomplete or unpredictable, and the final results may be erroneous due to low recovery, no matter how good the instrumental determinative method is.

Section 1.1 of Method 8015 covers some of the sample preparative methods that have been shown to be applicable for a variety of oxygenated compounds. Note that Section 1.1 shows that the purge-and-trap technique is rarely successful for highly water-soluble oxygenates. Purge-and-trap works best for analytes that are both volatile *and relatively insoluble* in water (e.g., BTEX compounds).

MTBE, however, is more soluble in water than BTEX compounds, and this characteristic decreases its purging efficiency relative to those compounds, creating the possibility that interferences in complex sample types could render purge-and-trap analyses susceptible to imprecision and poor method sensitivity due to unpredictable sample-specific purging efficiencies. This generalization is even more true for oxygenated analytes that are more water-soluble than MTBE is.

As with *any* preparative or determinative method, evaluation of sample-specific characteristics in relation to expected method performance (to meet project-specific needs) for specific analytes is required to determine whether purge-and-trap or some other sample preparation method can consistently provide the expected data quality.

Section 1.1 of Method 8015 recommends that samples to be analyzed for highly water-soluble oxygenated organic compounds [such as tert-butyl alcohol (TBA) and ethanol] be prepared using direct injection or azeotropic distillation (Method 5031). Direct injection alone (into a GC/FID) has been shown to achieve detection limits in the range of 400–500 ppb for TBA and ethanol.

Azeotropic distillation techniques can be used to concentrate samples for these alcohol analytes. The azeotropic distillation sample preparation/concentration technique has been shown to produce detection limits in the vicinity of 10 ppb when the concentrated samples are analyzed by GC/FID. Vacuum distillation (SW-846 Method 5032) and static headspace (SW-846 Method 5021) could also be considered as potentially viable sample preparative methods. Each of these preparative methods will have its advantages and drawbacks. Additional development work for both preparative and determinative methods will be required to validate routinely applicable methods across the range of oxygenate compounds, sample types, and detection limits that are now of interest.

The selection of any analytical method must always consider the ultimate use of the data. The use of project-specific systematic planning can ensure that data collection methods are cost-effectively matched to the project's decision-making needs.

Method 8021

SW-846 Method 8021—Aromatic and Halogenated Volatiles by GC Using Photoionization (PID) and/or Electroconductivity (ElCD) Detectors—or a similar method that relies on a photoionization detector, is *not recommended* as a determinative method for MTBE and its associated oxygenates. PID is most sensitive to compounds that contain double bonds (which is why this method is a good determinative technique for BTEX compounds).

MTBE and related compounds, however, do not contain double bonds. Although the PID analysis will respond to the oxygen atom in these compounds, the response is weaker than the response for BTEX compounds and, therefore, may be subject to interference and false positives when real-world samples contain significant amounts of other contaminants such as petroleum hydrocarbons. (See pages 9 and 15 of "An Evaluation of MTBE Impacts to California Groundwater Resources," available at http://www-erd.llnl.gov/mtbe/pdf/mtbe.pdf.) The ElCD detector of Method 8021 works only for compounds containing halogen atoms, and MTBE does not possess this characteristic either.

Method 8260

GC with a mass spectrometer (MS) detector is also appropriate as a determinative method for oxygenates, as long as a sample preparative method appropriate to the sample has been used. MS offers the advantage of unambiguous identification of target compounds. It is a good idea to keep a few things in mind if a GC-MS method for MTBE and other oxygenates is discussed in terms of SW-846 Method 8260:

- Method 8260 has *not* been validated by EPA for use with MTBE.
- Method 8260 is a GC-MS *determinative* method only—the sample preparation method is separate. Purge-and-trap is not specified by Method 8260 and, in fact, is not recommended for the few alcohol analytes that have been validated in Method 8260 (e.g., ethanol and TBA). (See the Appropriate Preparation Technique table in Section 1.1 and Section 1.2.)
- Improved performance of Method 8260 for MTBE and other oxygenates can be expected if instrument operating conditions are modified to accommodate that particular analyte group (rather than trying to generalize operating conditions to accommodate the entire range of 100-plus validated analytes in the Method 8260 list).

■ *continued on page 18*

■ **Analytical Issues for MTBE**
from page 17

Field Methods

In addition to their analysis by GC-MS in the fixed laboratory, MTBE, ethyl t-butyl ether (ETBE), and TBA have been successfully analyzed in the field by using a field-portable GC/MS and heated (at 60˚C) static (i.e., equilibrium) headspace. Method performance information (provided by Field-Portable Analytical, Inc.) shows detection limits in the range of 4–5 ppb when the MS is operated in full-scan mode. When operated in selective ion monitoring (SIM) mode, detection limits down to 0.2 ppb are possible with full positive identification of the analytes. As samples are analyzed in the field at the time of collection, issues regarding sample preservation are avoided.

Depending on the nature of the project, field analysis can significantly decrease costs by supporting real-time decision making according to an Expedited Site Assessment approach. (See EPA 510-B-97-001, "Expedited Site Assessment for Underground Storage Tank Sites: A Guide for Regulators," available on OUST's Web site at http://www.epa.gov/swerust1/pubs/index.htm#sam.)

The Decision-Making Factor

Above all, the selection of any analytical method must always consider the ultimate use of the data. Data for risk assessment purposes typically need lower detection/quantitation limits than when data are used to delineate a plume or to place monitoring wells. The use of project-specific systematic planning can ensure that data collection methods are cost-effectively matched to the project's decision-making needs.

The flexibility inherent in SW-846 methods permits "mixing and matching" of sample preparation and determinative methods so that the needed method sensitivity and accuracy can be achieved. As long as data are of known quality, and that quality has been matched to the decision-making needs of the project, any reliable method can be used.

Although we have discussed in general terms the various analytical method options for oxygenates that might be explored, a more specific answer to the question, "What method should be used for MTBE and/or oxygenates for this particular project?", first requires that the project manager clearly specify the intended use of the data. When this use is known, the required detection limits can be determined, the desired turnaround time for the data results can be estimated, and the most cost-effective option for generating the data (i.e., the sampling program and the analytical methods) can be deduced.

For More Information

Information about SW-846 and the selection of analytical methods can be found through the Clean-Up Information Web page of the Technology Innovation Office at http://cluin.org/char1.htm and the OSW Methods Team home page at http://www.epa.gov/SW-846/. More information about how site characterization and cleanup can be made more cost-effective can be found at http://www.clu-in.org/products/failsafe.htm. ■

Deana Crumbling is an analytical chemist with EPA's Technology Innovation Office, and works on improving the accessibility and application of site characterization tools to waste site cleanups. She can be reached at Crumbling.Deana@epamail.epa.gov. Barry Lesnik is the Organic Methods Manager with EPA's Office of Solid Waste Methods Team and is responsible for the organic methods included in SW-846 and regulatory issues dealing with chemical analysis. He can be reached at lesnik.barry@epa.gov.

Results of NEIWPCC Survey of State Experiences with MTBE to Be Posted on Web

In August, the New England Interstate Water Pollution Control Commission (NEIWPCC) conducted a survey of all 50 state LUST programs to ascertain their experiences with monitoring for and cleaning up MTBE releases from USTs. The survey, funded by the EPA Office of Underground Storage Tanks, was undertaken to provide the states with a better picture of how each state program is currently dealing with MTBE and other oxygenates. This very comprehensive survey consists of 34 questions and numerous subquestions. NEIWPCC received responses from all 50 states.

After sending the compiled results to all states for a final review, NEIWPCC plans to post the results with an executive summary on its *LUSTLine* Web site (lustline@neiwpcc.org) on December 15, 2000. NEIWPCC will encourage states to update their information periodically and will present the information in the next issue of *LUSTLine* and at the national UST/LUST conference in Albuquerque, New Mexico, in March. You will also find issue-specific summaries in this issue of *LUSTLine* with relevant articles. Look for the "What Our Survey Shows" boxes. ■