

Selecting Analytical Methods for the Determination of Oxygenates in Environmental Samples and Gasoline

*Demand for analyses is higher,
but are the methods reliable?*

By I.A.L. Rhodes and A.W. Verstuyft

Alcohols and ethers are added to gasoline to comply with air emission regulations in certain parts of the country and as octane enhancers. The most widely used oxygenate is methyl t-butyl ether (MTBE), which accounts for more than 85% of oxygenate usage. Other oxygenates include other ethers and alcohols. Oxygenates have significant water solubility, particularly the alcohols which are infinitely soluble in water. When oxygenated fuels are released to the environment they may pose a threat of groundwater contamination. Some oxygenates are relatively refractory to degradation and are difficult to treat once the aquifer has been impacted. There is a growing regulatory concern about oxygenates, and a growing demand for analytical methods to detect these types of compounds in the environment.

Laboratories have expanded existing U.S. Environmental Protection Agency (EPA) methods used for the determination of benzene, toluene, ethylbenzene and xylenes (BTEX) to include oxygenates. These methods rely on purge-and-trap (P&T) or headspace (HS) gas chromatography (GC) using photoionization (PID) or mass spectrometry (MS) detection. The adequacy of EPA methods for the determination of highly water soluble ethers and infinitely soluble alcohols has come under scrutiny because these EPA methods were not developed and their performance has not been formally validated for the determination of these types of compounds. In addition, no formal assessment has been done related to sample preservation and sample preparation issues.

The critical issue is the potential misidentification of oxygenates in environmental samples containing a gasoline-type matrix. Due to a lack of performance data, the reliability of the methods to accurately measure all oxygenates of interest is in question. Because of the widespread misconceptions associated with referring to the "EPA methods," and the failure to distinguish between preparation methods and determinative methods, the method discussions should be in terms of the analytical techniques used rather than EPA method numbers. The use of EPA method numbers to refer to determinative methods misleads some to think that the use of the method was somehow sanctioned by EPA for these analytes. Neither the EPA 8000 methods nor the 5000 series prep methods have been validated by EPA for application to oxygenates. The analytical process should not simply refer to "8021" (which does not specify the sample prep method). The quality assurance project plan (QAPP) or report should refer to a "5030 purge-and-trap, 8021 GC-PID method" process or sequence.

This article addresses the current status of oxygenate analysis in environmental samples and fuels, including information about the expected performance when using EPA methods, advantages and disadvantages of different methods, and cost-effective recommendations for meeting data quality objectives.

History and Regulations

A brief summary of the history and use of MTBE, regulations pertaining to MTBE as a gasoline oxygenate and proposed health advisory limits for MTBE in groundwater is useful for the environmental laboratory. The primary source of MTBE in the environment is believed

to be transportation, storage and use of oxygenated gasoline. Data on oxygenates other than MTBE is not readily available.

Methyl t-butyl ether, or methyl tert-butyl ether, is a synthetic chemical commonly known as MTBE. MTBE is mixed with gasoline for use in reformulated gasoline (RFG). It is a liquid generally made by combining the chemicals isobutylene and methanol. MTBE was developed in the 1940s; however, it was not commercially produced until the 1970s. MTBE was used commercially for the first time in Europe as a gasoline blending component. It was first introduced in the 1980s in the United States as an octane booster to replace alkyl lead additives. In areas in which there is nonattainment of federal Clean Air Act (CAA) standards for air pollutants such as carbon monoxide, the EPA requires the use of oxygenated additives such as MTBE or ethanol as a cleaner burning oxygenating agent during the winter months. The use of other oxygenates is not as well documented.

Gasoline without deposit control additives (typically proprietary to each major oil company) is exchanged or traded among producers to meet contract and demand requirements, as well as to improve transportation logistics. As a result of exchange agreements, a producer may sell a competitor's gasoline that contains different ethers than the producer would add at its own refinery. Thus, an individual oil company's oxygenate use may not be indicative of the oxygenates present in fuel at that company's station.

MTBE is regulated under the CAA; the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); and the Emergency Planning and Community Right-to-Know Act. It is regulated by the EPA's Offices of Water, Solid Waste, and Emergency and Remedial Response. It is also regulated by the Consumer Product Safety Commission with consumer product limits. In 1990, Congress passed amendments to the CAA that required gasoline to meet a minimum oxygen content requirement, through the addition of oxygenates such as MTBE or ethanol. This minimum oxygen content requirement was designed to lower exhaust pollutants in the worst ozone- and carbon monoxide-contaminated areas. In 1992, gasoline with up to 15% MTBE content by volume was used nationally to meet the first federally mandated wintertime reduction of carbon monoxide. MTBE is blended at 11% in most gasoline sold in California after October 1992.

The state of California has led the

way in developing regulations related to MTBE. For example, California's Department of Health Services (DOHS) promulgated, based on taste and odor concerns, an enforceable secondary drinking water maximum contaminant level (MCL) of 5 µg/L for MTBE. DOHS will shortly promulgate a primary human-health-based MCL that will likely be close to the California Office of Environmental Health Hazard Assessment's (OEHHA) public health goal of 13 µg/L MTBE. EPA has suggested, based on taste and odor concerns, a consumer acceptance level of 20-40 mg/L, but has set no MCLs. California is also developing a public health goal for tertiary-butyl alcohol (TBA); however, only one health study exists on which to base this goal. An expedited preliminary assessment by OEHHA in June 1999 suggested that this study would result in a public health goal of 12 mg/L. OEHHA is also charged with performing a health risk assessment of using ethanol in gasoline in 1999.

Most recently, California has established a ban on MTBE, which is slated to begin on Dec. 31, 2002. However, since the state regulators did not get former EPA Administrator Carol Browner's signature on the MTBE waiver, it is not clear from a regulatory standpoint whether there now exists an issue between state and federal regulations for oxygenates. This ban reflects a current drive away from MTBE and toward ethanol, although there are still some concerns about ethanol as an oxygenate.

The other regulatory change in California that directly affects the use of analytical methods is that the state's water boards are now requiring that Method 8260 is run on all samples, which is a significant change from a few years ago. It is also a significant change from the American Petroleum Institute (API) recommendation, which had been to run Method 8260 on one sample per set or per site to confirm presence or absence of MTBE. However, this new requirement by California Los Angeles Regional Water Quality Control Board is driving toward using Method 8260 for all MTBE analyses.

What Are MTBE and Other Oxygenates?

Gasoline and other fuels are derived from petroleum and are primarily composed of compounds containing only carbon and hydrogen atoms. Oxygenates are compounds that contain oxygen atoms in addition to carbon and hydrogen. They can be synthesized from petroleum derivatives or plant matter. Oxygenates are added in relatively large concentrations (>5%) and as such are

Alcohol	CAS No.	Molecular Weight, g/Mole	Water Solubility, mg/L	Henry's Law Constant (Dimensionless)
Methanol	67-56-1	32	Infinitely Soluble	~1E-4
Ethanol	64-17-5	46	Infinitely Soluble	~2E-4
t-Butanol (TBA)	75-65-0	74	Infinitely Soluble	~5E-4

Table 1. Alcohols used as blend components.

considered to be *blend components* of gasoline. Oxygenates can be added as a high purity chemical, or as a technical grade chemical with traces of other ethers and alcohols. MTBE is the predominant oxygenate in current use; however, other oxygenates are used to meet reformulated gasoline standards.

Since 1995, federal law requires year round addition of oxygenates to gasoline in nine regions of the nation with the worst ozone conditions. The resulting cleaner-burning "reformulated" gasoline (RFG) may not have less than 2% oxygen by weight. MTBE is blended into gasoline in proportions ranging from 11% in RFG to 15% in oxyfuel. MTBE is blended into 31% of all U.S. gasoline and into every gallon of gasoline sold in major California cities. The relative composition of oxygenate is variable and not indicative of any one refiner or distributor.

Alcohols and ethers are the two classes of oxygenates that may be found in gasoline. Analytical methods for these classes differ because of differences in water solubility and mobility.

Alcohols are a broad class of organic compounds containing a hydroxyl (-OH) functional group. Alcohols can be obtained from plant matter or synthetically from petroleum derivatives. They have many uses, such as in organic synthesis as solvents, and in the manufacturing of detergents, pharmaceuticals, foods, plasticizers and fuels. Alcohols used as blend components are listed in Table 1. These low molecular weight alcohols are highly soluble in water. They cannot be added to gasoline at the refinery because of the potential to be subsequently extracted and phase-separated through water contact in storage tanks and pipelines. Alcohols are typically added at the distribution terminal or truck rack before shipment to the service station by "splash" blending.

Ethers are a class of organic compounds in which an oxygen atom is interposed between two carbon atoms: C-O-C. They can be made from petroleum derivatives and are widely used as industrial solvents. The ethers that have been used as blend components, such as tertiary-amyl methyl ether (TAME), ethyl tertiary-butyl ether (ETBE) and diiso-

propyl ether (DIPE), are listed Table 2. These ethers are partially soluble in water and are added at the refinery.

What Are the Commonly Used Analytical Methods for the Determination of Oxygenates in Gasoline?

Analytical methods for the determination of alcohols and ethers in gasoline include well-established American Society of Testing Materials (ASTM) procedures, as well as adapted EPA methods. While EPA and ASTM methods have not been validated for the determination of oxygenate compounds in environmental samples, the following are methods used to determine oxygenates in gasoline:

- *ASTM D 4815*. A multidimensional GC/FID method for the determination of MTBE, ETBE, TAME, DIPE, TBA, and C₁ to C₆ alcohols in gasoline. The quantification range of this method for individual ethers is 0.1 to 20 mass percent and for individual alcohols is 0.1 to 12 mass percent. This method is the alternative method for oxygenate analysis of federal RFG (40 CFR 80.46), and the designated reference method for California Phase II RFG.

- *ASTM D 5599*. A capillary column GC and oxygen flame ionization detection (OFID) method for the determination of MTBE, ETBE, TAME, DIPE, TBA, and C₁ to C₂ alcohols in gasoline. Only oxygen-containing compounds are detected by OFID. The quantification range of this method for oxygenates is 0.1 to 20 mass percent. Commercial and

refinery laboratories commonly use this ASTM version of the federal RFG method (40 CFR 80.46) to analyze RFG.

- *ASTM D 5769*. A GC/MS method for benzene, toluene and total aromatics in finished gasoline. This is a detailed, interlaboratory-validated version of the EPA method for reformulated gasoline (40 CFR 80.46). This method has been used by the EPA in the ASTM Reformulated Gasoline Interlaboratory Crosscheck Program for oxygenate analysis although it has not been validated for oxygenates.

- *Detailed Hydrocarbon Analysis by GC/FID—ASTM D 5134*. This method uses 30-meter to 60-meter capillary columns to analyze oxygenates in complex gasoline mixtures or naphthas.

- *EPA SW-846 Methods 8240C/8260B*. It is difficult to detect oxygenates directly in a gasoline matrix without dilution. Typically, the best reporting limit is around 0.01 to 1 percent for the ethers and about 0.1 to 20 percent for TBA. This method has not been validated for fuels and its use should be highly discouraged because of the multiple dilutions needed to bring the sample into the calibration range and the complex matrix of the sample.

What Are the Commonly Used Analytical Methods for the Determination of Oxygenates in Environmental Samples?

Oxygenates such as MTBE are primarily regulated by EPA under the Clean Air Act for fuels and modified for specific use by the states. They have not been targets of EPA methods as written, with the exception of MTBE in Method 524.2. However, methods have been expanded to include some of the oxygenates. These include EPA methods using P&T-GC/PID (Methods 8021B/8021A and 602) and EPA methods using P&T-GC/MS (Methods 8260A/8240B, 624, and 524). Although EPA Method 8015 which is based on GC/FID has

Ether	CAS No.	Molecular Weight, g/Mole	Water Solubility, mg/L	Henry's Law Constant (Dimensionless)
Methyl Tertiary-Butyl Ether (MTBE)	1634-04-4	88	~40,000 - 50,000	~2E-2 to 12E-2
Diisopropyl Ether (DIPE)	108-20-3	102	~2,000 - 9,000	~20E-2 to 40E-2
Ethyl Tertiary-Butyl Ether (ETBE)	637-92-3	102	~8,000	~11E-2
Tertiary-Amyl Methyl Ether (TAME)	994-05-8	102	~20,000	~5E-2

Table 2. Ethers used as blend components.

been used for MTBE analysis, it should be noted that the state of California issued a memorandum on Oct. 21, 1999, which stated that analysts cannot use the method to quantitate individual oxygenate compounds. As such, EPA Methods 8260 and 8021 are the preferred methods. The memo stated that on most chromatographic columns MTBE comes off before the volatile range organics and will not be included in the volatile range result. Other oxygenates, such as TAME and DIPE, will coelute with the volatile range organics. Certainly, in California, this will change the approach of conducting a combined 8015/8021 for gasoline BTEX, and will likely result in laboratories solely using Method 8260 as total petroleum hydrocarbons (TPH) volatile and BTEX/MTBE as the standard.

Another related issue is that these methods need to be validated for the oxygenates using SW-846 3rd Edition, Update III, 1296, Method 3600C, Section 8. This is significant for all of us in the regulated community and the commercial laboratories, because we all use these methods as if they were validated and they are not. As it stands now, EPA's position is that methods are for guidance and that it is the user's responsibility, both the commercial laboratory and the customer, to make sure the method results in technically sound data. As such, it is important to remember that the users need to run multiple samples at multiple concentrations, make sure there aren't matrix effects, and use the Update III criteria for validation of methods.

Oxygenates in Environmental Samples: Method Performance

Limited data have been published by EPA and other researchers indicating that oxygenates are potentially measurable by three SW-846 methods: 8015, 8021 or 8260. This discussion addresses the latter two methods from the most recent promulgated version of SW-846, EPA's methods manual for the RCRA program. Table 3 lists other EPA methods that are technologically comparable to the two discussed here.

These two methods are comparable in terms of sensitivity, accuracy and precision. Method 8021, using GC/PID, tends to be lower in price. Method 8260, a GC/MS method, is generally recognized as more selective, but higher in price. Selectivity or specificity is a term used to describe how well a given technique can provide accurate identification; the ability to unequivocally identify the analyte in the presence of other components that may be also expected to be present. A nonselective

Current Promulgated SW-846 Method	Technology Basis	Other Comparable EPA Methods	Selectivity
8015	FID	None	Poor
8021	PID	8020, 602, 502.3	Good
8260	MS	8240, 624, 524.2, 1624	Excellent

Table 3. EPA methods.

method will respond universally to many compounds, and thus is prone to false positive results in the presence of interferences. Method 8021 provides identification based on retention time/elution time, and quantitation is based on signal of standards. The potential problem with the method is that coelutions with hydrocarbons in gasoline may arise. Method 8021 is selective for aromatic compounds but can respond to other compounds, including branched alkanes and olefins. Method 8260 is highly selective, providing a unique identification pattern—the mass spectrum—for virtually any compound (except isomers). It provides identification based on retention time/elution time and qualifying ions. Quantitation is based on a single ion after qualifying criteria are met.

With regard to verifying results for these two methods, the analyst's options are reduced if GC/PID is used. The analyst may reanalyze or resample, or using

Note that the sample preparation methods are not applicable to air samples.

EPA has published no validation data except for Method 5031, used in conjunction with Methods 8015 and 8260. Data for methanol using Methods 5031/8260 are summarized in Table 5. The U.S. Geological Survey (USGS), using Methods 5030/8260, has published the data in Table 6.

Emerging Sampling and Analytical Techniques

There are some newer sampling and analytical methods or newer applications of existing methods that are now coming to the fore with regard to MTBE and other oxygenate analyses. These include solid-phase microextraction (SPME), direct aqueous injection (DAI) into the GC/MS, membrane introduction mass spectrometry (MIMS) and cryofocusing.

SPME. While this technique isn't used very often for MTBE analysis in the

EPA Method	Matrices	Technology Basis
5030	Water, Methanol Extracts of Soil	Purge-and-Trap
5031	Water, Aqueous Leachates of Solids	Azeotropic Distillation and Direct Aqueous Injection
5035	Soil	Closed System Purge-and-Trap
5021	Soil or Water	Headspace

Table 4. Sample preparation methods applicable to oxygenates.

a second column confirmation may help. If the GC/MS method is used, the analyst can check the MS, look at ion ratios and, as a last resort, may reanalyze or resample.

Analyses using any of these three methods must be performed in conjunction with proper sample preparation procedures. Table 4 summarizes the sample preparation methods for measuring oxygenates. To fully describe the method used, both the sample preparation and analytical method must be specified. For example, Methods 5035/8260 would be a closed system purge-and-trap with GC/MS detection.

U.S., the Europeans have used it successfully for such analyses in paint industry wastewater samples. The U.S. Coast Guard published a paper in the *Journal of Microcolumn Separations* in 1998, which described a headspace SPME and two-dimensional GC technique as an approach to MTBE analysis. Although there is a potential of loss of sample when using SPME, the argument for using the technique in oxygenate analysis is that for polar materials in water the analyst can easily do SPME followed by GC.

DAI. Directed aqueous injection into the GC/MS is allowed by Method 8015 and has been used to analyze methanol in

Analyte	MDL, mg/L	Accuracy (%) at Spiking Level:		
		25 mg/L	100 mg/L	500 mg/L
Methanol	38	50 ± 36	46 ± 22	49 ± 18

Table 5. Performance of EPA Methods 5031/8260 for oxygenates.

Compound	Detection Limit, mg/L	Accuracy, as Recovery, %	Precision, %
MTBE	0.06	97	2.5
ETBE	0.20	100	1.8
TAME	0.20	97	2.1

Table 6. Performance of EPA Methods 5030/8260 for oxygenates.

aqueous samples. DAI is very effective for polar compounds such as the alcohols.

MIMS. Information on this highly selective, rapid technique has been published in the literature, and although it has not been validated as a method, it may prove to have some interesting applications with regard to the oxygenates. One published paper stated that although MIMS is a rapid, highly selective, solvent-free method, it might be unusable in the direct collection of analytes from complex samples containing solids such as sludge and soil. Since this capability is clearly desirable for analyzing oxygenates, the paper went on to suggest that purging the sample first, followed by MIMS would be a better overall technique.

Cryofocusing. It is a technique that is allowed in Methods 8260 and 624, but other than for air monitoring applications, cryofocusing has not been widely used for many years. However, now that regulators want lower and lower detection limits, the combination of purge-and-trap with cryofocusing will allow a bigger sample to be introduced to the analytical column and detector to drive the detection limits down. Cryofocusing involves freezing the sample in liquid nitrogen, and as the analyst purges, he or she can trap the sample from the typical trapping material and then drive that onto the column by removing the liquid nitrogen cooling. The analyst can heat the entire sample all at once, or either eliminate the trap or add onto the trap and collect all the material in the gas phase in a Thermos bottle that has liquid nitrogen in it. The analyst puts a loop of the column in the container, which allows a further concentration of these molecules into a smaller plug of material thus achieving a higher loading than one can with a purge-and-trap sample preparation. It is a commonly used method in the air methods TO3 and TO14 for volatiles and BTEX, and is currently being applied to water and soils.

Method Detection and Reporting Limits

The issue of method detection limits (MDLs) deserves more attention. The MDL as defined in 40 *CFR* Part 136, Appendix B, states that it is determined by analyzing a minimum of seven replicates of a single low level lab spike by a single analyst. Multiplication of the standard deviation by the Student's t-value

at 99% confidence level (statistically derived parameter from analyses of spiked clean water). The concept of the method detection limit has been challenged by the Inter Industry Analytical Group (IIAG) and will be modified by EPA as part of a Consent Agreement.

Reporting limits for MTBE can differ from .5 ppb up to 5 ppb, depending on the lab's sample treatment (cryofocusing vs. traditional P&T), and the lab's application of the 40 *CFR* 136, Appendix B MDL protocol.

There are newer method detection limit tables published in a Lawrence Livermore National Lab Global Geochemistry Study which show how selected methods perform and some of the issues with method detection limits and practical quantitation limits for oxygenates in groundwater samples (Tables 7 and 8).

Performance-Based Methods

The key issue for EPA SW-846 methods is that *any* method selected for use be able to produce data of known quality that is consistent with the needs of the project driving its collection. Therefore, whether an SW-846 method (or a non-EPA method) is selected for application, whether the method is used as written in an existing, established laboratory standard operating procedure (SOP), or if the existing SOP is modified, the method should undergo a "demonstration of applicability." This demonstration should address any uncertainties that could arise from the interaction of analytes, analytical techniques and

matrix effects in the context of the decisions the data are intended to support. The greater the impact of those uncertainties on the ability to make defensible decisions, the more work has to be done to control for those uncertainties as part of the demonstration of applicability. Assumptions should be documented and questioned as necessary.

Selecting a Method: Ethers and TBA

Extensive work by the USGS, Lawrence Livermore and many laboratories indicate that the ethers and TBA are measurable using purge-and-trap GC in conjunction with any of the determinative methods (EPA SW-846 Methods 8015, 8021 or 8260). Based on studies of the most widely used oxygenate, MTBE, potential analytical problems exist with Methods 8015 and 8021. Misidentification of MTBE can be caused when other gasoline components are present, due to coelution of MTBE with these components. This misidentification is most pronounced with Method 8015, but is also apparent with Method 8021, which makes it an unreliable method for TBA. Method 8260 is considered adequate.

Thus, while Method 8021 may be cost-effective, the analyst should verify results by Method 8260. As an example, the approach shown in the Figure 1 flow-chart for ethers (MTBE, DIPE, ETBE, TAME) may be used for water samples. This approach may be used for soil and air samples with strict QA/QC.

The conclusions drawn from the Lawrence Livermore National Lab Global Geochemistry Study relative to TBA and ethanol analyses are as follows:

- Method 8021: TBA and ethanol are not recommended as analytes. False positives are common at high TPH concentrations. False positive ether concentrations are typically less than 200 ppb. The method "works" when the ratio of TPH

Analyte [ppb]	8020/21 (5 mL/20C)	8260/60 (5 mL/20C)	D4815a (5 mL/20C)
TBA	13.9	34.9	27.4
MTBE	0.2	1	1.1

Table 7. Method detection limits in groundwater samples.

Analyte [ppb]	8020/21 (5 mL/20C)	8260/60 (10 mL/40C)	D4815 (direct injection-ppm)
TBA	195.5	4.6	40.8
MTBE	0.2	1	43.6
DIPE	1.6	0.3	22.6
ETBE	5.5	0.3	10.2
TAME	1.2	0.2	16.1

Table 8. Method detection limits in groundwater samples (5 ppm gasoline matrix). The typical reporting limit is 0.1% per oxygenate in the NAPL.

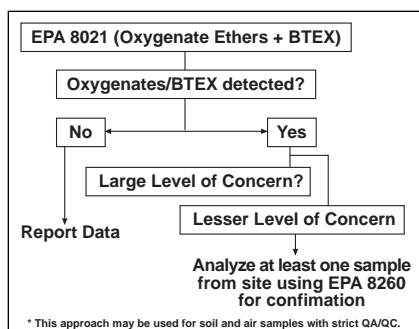


Figure 1. Choosing an approach to ethers in water samples.

to analyte is less than 15.

- Method 8260 is capable of quantifying all fuel oxygenates tested. TBA sensitivity may be increased by heating purge at 40°C. Ethanol is trickier and thus is best analyzed by direct injection, not P&T. The detection limit for oxygenates in NAPL is approximately 2,000 ppm.

- Modified ASTM D4815/D5599 provide excellent overall analysis of oxygenates, but the drawback is that it is a highly customized method that does not address BTEX or TPH. Only one laboratory is known to provide this analysis for environmental samples. It is the method of choice for NAPL and products with a reporting limit of 0.1%.

The most commonly encountered oxygenates in groundwater appear to be MTBE and TBA. According to a report by Kramer & Douhit (Handex, NJ) presented at the November 2000 Petroleum Hydrocarbons and Organic Chemicals in Groundwater Conference, Anaheim, CA, field experience in New Jersey shows widespread occurrence of TBA with MTBE in groundwater at concentrations that are equal to, or in some cases, exceed the MTBE concentrations. They state that it is not unusual to detect TBA alone in a well (without BTEX or MTBE); however, the opposite is also common.

Selecting a Method: Methanol and Ethanol

Ethanol and methanol, two low-molecular weight, water-soluble alcohols, present even more of an analytical challenge than other oxygenates because they are difficult to analyze at low concentrations. The compounds are not measurable using P&T. Direct aqueous injection by Method 8260, provides ppm-level sensitivity. EPA Method 5031 can be used with Method 8260 to improve sensitivity, but this method shows poor accuracy and is in limited use by laboratories.

In July 2000, the California Regional Water Quality Control Board, Central Valley Region, issued a memo entitled, "Ethanol in Groundwater from Bento-

nite Pellets," which noted that 21 out of 23 samples taken from newly constructed wells were contaminated with ethanol with a maximum concentration of 1,200,000 µg/L. The contamination was caused by the bentonite pellets used in well construction materials. The pellets are coated with ethanol to slow the rate of hydration when dropped into deep water columns. This problem is a good example of the problems that can be encountered when alcohols, which are present in many types of products, are put in gasoline and their presence in groundwater is automatically (and erroneously in this case) linked to gasoline.

Conclusions and Recommendations

EPA methods have not been validated for the routine measurement of oxygenates in environmental samples. Existing EPA methods are potentially useful for this purpose, and many laboratories have generated internal validation data. Some of the methods in routine use can result in oxygenate misidentification due to interferences from coeluting gasoline components.

The purge-and-trap methods (5030, 5035) can be used for ethers and TBA in soil or water samples. If Method 8015 or 8021 is used, at least one sample per site should be analyzed by Method 8260 to confirm any detectable amounts. Because of the general lack of EPA validation data, laboratories should be requested to provide evidence of their capability to measure oxygenates using any method. Information on detection limits and recoveries should be provided.

The analysis of environmental samples for methanol and ethanol is more difficult. These compounds cannot be measured using routine EPA methods. Any analysis requests for these compounds should be carefully considered, and laboratories should provide proof of any stated capabilities.

What should the data user do? First, test the labs from time to time with performance evaluation samples. Then, send at least one or two sets of blind duplicates with each batch. Third, if no historical data exists and you are using Method 8021, confirm at least one MTBE or any other oxygenate hit per site by GC/MS. Finally, for critical data, go straight to GC/MS.

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