

Analytical Methods for Fuel Oxygenates

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Topics for Discussion

- ∩ Nature of the Problem
- ∩ Background
- ∩ Context
- ∩ Analytical Methods
- ∩ Sample Preservation
- ∩ Issues with Existing Data
- ∩ Recommendations



Nature of the Problem

∞ Oxygen-containing compounds (“oxygenates”) that have been added to gasoline include:

methyl <i>tert</i>-butyl ether (MTBE)	<i>tert</i>-butyl alcohol (TBA)
<i>tert</i>-amyl methyl ether (TAME)	<i>tert</i>-amyl alcohol (TAA)
ethyl <i>tertiary</i>-butyl ether (ETBE)	ethanol
di-isopropyl ether (DIPE)	methanol
<i>Tert</i>-amyl ethyl ether (TAEE)	acetone



Nature of the Problem (Contd.)

∞ Conventional analytical procedures, e.g., ambient temperature purge-and-trap followed by GC/FID or GC/MS determination, designed for petroleum hydrocarbons (usually benzene, toluene, ethylbenzene, and the xylenes, or “BTEX”) can also detect MTBE and the other ethers, but they have very poor sensitivity for TBA and the other alcohols



Nature of the Problem (Contd.)


∞ Other GC detectors, e.g., electroconductivity (EICD) and photoionization (PID) have very little, if any sensitivity for fuel oxygenates



Background

∞ Fuel oxygenates are ethers or alcohols added to gasoline to:

 boost the octane content

 make the fuel burn cleaner by increasing the oxygen content

 or combination of both

∞ Ethers, and primarily MTBE, have been used increasingly since the late 1970s

Background (Contd.)

∞ In 1990, Congress passed the Clean Air Act (CAA). Subsequent amendments to the CAA led to the initiation of the Oxygenated Fuel (“Oxyfuel”) and Reformulated Gasoline (“RFG”) programs in 1992 and 1995, respectively.



Background (Contd.)

∞ While these programs stipulated a minimum oxygen content for gasoline sold in specific metropolitan areas to reduce air pollution, the choice of which oxygenate to use was left to the discretion of the petroleum refining industry



Background (Contd.)

∞ Primarily for economic and logistical reasons, industry overwhelmingly opted for MTBE

 currently used in approximately 80% of oxygenated fuels

 concentrations range from 11% to 15% (by volume)

Background (Contd.)

∞ Ethanol






- used primarily in the midwest
- accounts for about 15% of the oxygenated fuel supply

∞ Other oxygenates

- include TAME, ETBE, DIPE, TAEE, TAA and TBA
- account for the remaining 5%

Context

∞ Releases of oxygenated fuel into the environment have occurred Nationwide from:

-  leaking storage tanks and pipelines
-  transportation accidents
-  refueling spills
-  watercraft exhaust
-  consumer misuse

Context (Contd.)

- ∞ Fuel oxygenates, because of their significant water solubility, have significant potential to contaminate groundwater and drinking water sources
- ∞ Fuel oxygenate plumes can separate from the BTEX and travel faster and farther than the hydrocarbon contaminants of groundwater

Context (Contd.)


- ∞ Conventional practice for preserving groundwater samples may also present a problem for the analysis of oxygenates
- ∞ Acid can hydrolyze the ether bonds producing spurious analytical results for both ethers and the alcohols produced by the hydrolysis of the ethers

Context (Contd.)

- ∞ For MTBE this may result in its presence being under-reported and the presence of TBA being over-reported
- ∞ Estimates of the rate of MTBE biodegradation based on erroneous analytical results may in turn be overly optimistic


Analytical Methods

∞ Optimization of Sample Preparative Methods

-  OSW initiated a study to determine the optimum conditions for running the ethers, alcohols and acetone at the lowest regulatory limits of 5 ppb by the commonly-used purge-and-trap technique (Method 5030), the details of which were presented at last year's WTQA Symposium


Analytical Methods (Contd.)

∞ Optimization of Sample Preparative Methods (Contd.)

 Using Method 5030 at ambient temperature

☺ MTBE and the other ethers could be recovered

☺ The alcohols and acetone were not significantly recovered

 Using Method 5030 at a purge temperature of 80°C



☺ Almost all of the target analytes can be quantitated

☺ Except for ethanol and methanol

☺ Even in the presence of BTEX contamination


Analytical Methods (Contd.)

∞ Optimization of Sample Preparative Methods (Contd.)

-  At 80°C, either a standard VOA column or a wax column can be used to obtain 5 ppb sensitivity for the target analytes. The wax column gives a little better performance, probably because of better peak shape
-  Other sample preparative methods which can be used to quantitate all of the target analytes including methanol and ethanol at 5 ppb are Static Headspace (Method 5021) or Vacuum Distillation (Method 5032)

Analytical Methods (Contd.)

∞ Optimization of Sample Preparative Methods (Contd.)

 A validation study for TBA using Azeotropic Distillation (Method 5031) was performed in the early 1990s


∞ Either GC/FID (Method 8015) or GC/MS (Method 8260) have been demonstrated to be appropriate determinative methods for the target analytes at 5 ppb

Sample Preservation

- ∞ Standard sample preservation procedures, i.e., acid preservation to pH <2 to prevent biological degradation of BTEX, can cause problems with the analysis of the fuel oxygenate ethers
- ∞ At elevated temperatures during the sample preparation procedures, significant hydrolysis of MTBE to TBA has been observed in studies done at the Kerr Laboratory

Sample Preservation (Contd.)

∞ Trisodium phosphate at a pH of >10

 used as an alternative to acid preservation for fuel oxygenates

 prevents the biological degradation of the target analytes

 does not cause hydrolysis of ethers to alcohols

∞ If samples have been acid preserved, they should be neutralized prior to the sample preparation step, particularly if an elevated temperature is necessary to perform the analysis

Issues with Existing Data

- ∞ If MTBE and the other ethers are the only target analytes of concern, there should be no problem with data generated from purge-and-trap procedures performed at ambient temperature
- ∞ If TBA is also a target analyte, the chances of gross underestimation exist, if the data were generated using ambient temperature purge-and-trap procedures



Issues with Existing Data

(Contd.)

∞ If high-temperature sample preparative procedures were used on acidified samples, there is a significant possibility that the MTBE concentrations can be diminished and TBA concentrations increased due to hydrolysis of the sample

Issues with Existing Data (Contd.)

∞ If data for MTBE were generated using a GC/PID method, it may be significantly underestimated if the lamp has been in use and its output diminished below the MTBE ionization level. PID lamps do not respond to TBA at all.

Recommendations

∞ Collection and Storage

DO

- ☺ collect samples in appropriate containers, e.g., 40-mL VOA vials
- ☺ cool samples to 4°C without addition of acid or with addition of trisodium phosphate
- ☺ run samples ASAP after receipt in the laboratory

DO NOT

- ☺ acid preserve samples if they are to be run using an elevated temperature sample preparative method
- ☺ let samples get too warm or hold them too long before analysis because of increased potential for biological degradation of the target analytes

Recommendations (Contd.)

∞ Sample Preparation

DO

- ☺ use an elevated temperature sample preparatory method if TBA and acetone are target analytes
- ☺ select an appropriate sample prep technique
 - ⚙ **purge-and-trap at elevated temperature 80°C (Method 5030)**
 - ⚙ **Static Headspace (Method 5021)**
 - ⚙ **Vacuum Distillation (Method 5032)**

DO NOT

- ☺ purge samples at room temperature if TBA and acetone are target analytes. These analytes will not be recovered well, if at all

Recommendations (Contd.)

∞ Determination

DO

- ☺ select an appropriate determinative procedure
 - ⚙ **GC/FID (Method 8015)**
 - ⚙ **GC/MS (Method 8260)**
- ☺ select an appropriate chromatographic column
 - ⚙ **standard column for volatiles (RTX-Volatile)**
 - ⚙ **wax column (DB-Wax)**

DO NOT

- ☺ use an inappropriate determinative procedure, e.g., GC/PID, which does not pick up TBA and has very poor sensitivity for MTBE

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