

# Physical and Chemical Properties of the Fuel Oxygenates

**Barry Lesnik**

U.S. Environmental Protection Agency  
Office of Solid Waste – Methods Team (5307 W)  
1200 Pennsylvania Avenue, NW  
Washington, D.C. 20460



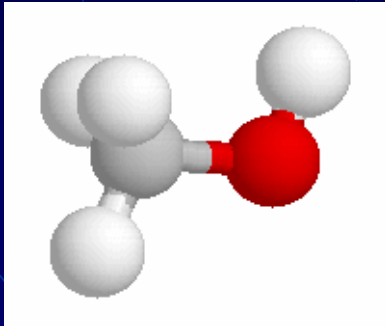
# Topics for Discussion

- Compounds of Concern
- Chemical Structures
- Physical Properties
- Chemical Properties
- Potential Health Effects
- Potential Problems Using Typical Analytical Methods

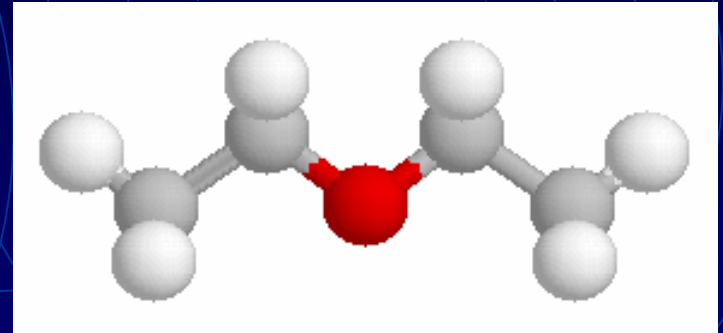


# Compounds of Concern

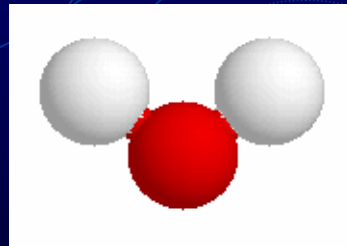
## Compound Classes



Alcohols



Ethers



Water

O – Red  
C – Grey  
H – White



# Compounds of Concern

## Specific Compounds

ETHERS	
Name	CAS No.
methyl- <i>tert</i> -butyl ether (MTBE)	1634-04-4
<i>tert</i> -amyl-methyl ether (TAME)	994-05-8
ethyl- <i>tert</i> -butyl ether (ETBE)	637-92-3
di-isopropyl ether (DIPE)	108-20-3
<i>tert</i> -amyl ethyl ether (TAEE) (4,4-dimethyl-3-oxahexane)	919-94-8



# Compounds of Concern

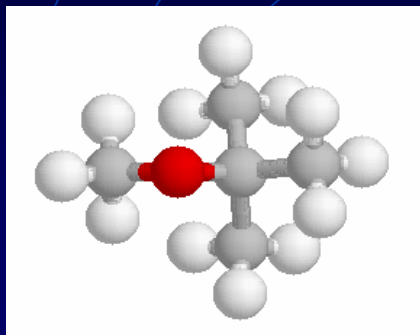
## Specific Compounds (Cont.)

ALCOHOLS	
Name	CAS No.
<i>tert</i> -butyl alcohol (TBA)	75-65-0
<i>tert</i> -amyl alcohol (TAA)	75-85-4
ethanol	64-17-5
methanol	67-56-1

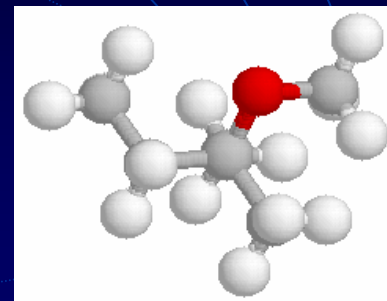


# Chemical Structures

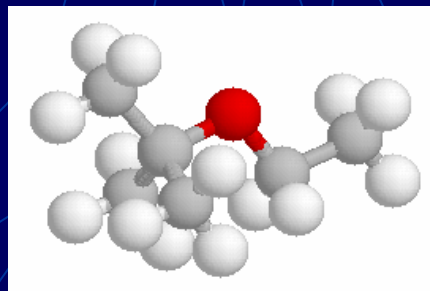
## Ethers



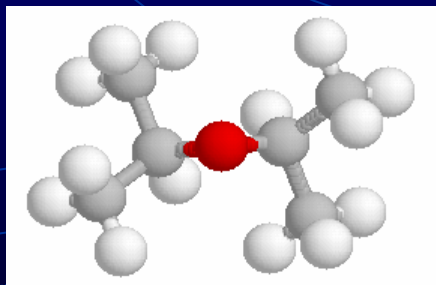
MTBE



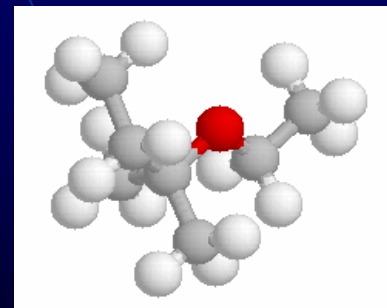
TAME



ETBE



DIPE



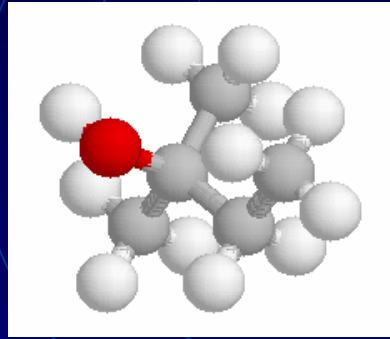
TAEE

O – Red  
C – Grey  
H – White

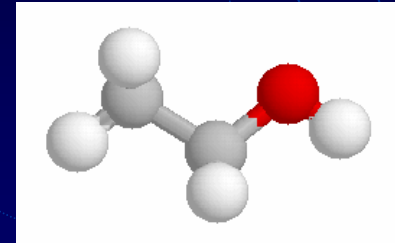


# Chemical Structures

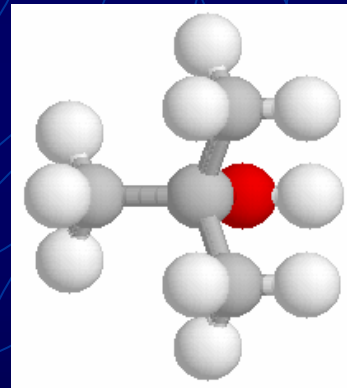
## Alcohols



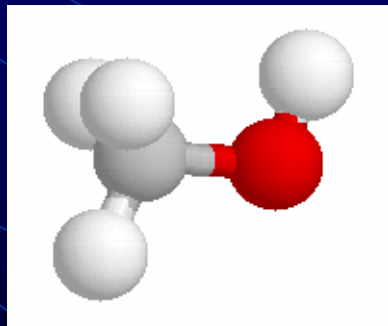
TAA



Ethanol



TBA



Methanol

O – Red  
C – Grey  
H – White



# Physical Properties

- Boiling Point
- Polarity (Dipole Moment)
- Water Solubility



# Physical Properties

Compound	Mol. Wt.	BP(°C)	Density g/mL	Water Solubility
MTBE	88.15	55.2	0.741	5.1g/100 mL
ETBE	102.18	71	0.7519	<0.1g/100 mL (21°C)
TAME	102.18	85-86	0.764	---
DIPE	102.18	68.5	0.724	0.20g/100 mL
TAAE	116.20	---	---	---
TBA	74.12	82.2	0.786	Miscible
TAA	88.15	102	0.805	---
Methanol	32.04	64.6	0.791	Miscible
Ethanol	46.07	78.3	0.789	Miscible
Water	18	100	1.00	NA



# Physical Properties

## Boiling Point

- All of the fuel oxygenate compounds have boiling points well below 150°C which would classify them generally as volatile organic compounds (VOCs)
- Boiling points are higher than would be expected for compounds of these low molecular weights
- These high boiling points are due to chemical structure and “polarity”
- “Hydrogen bonding” is another factor which contributes to the high boiling points of the alcohols



# Physical Properties

## Solubility

- Chemical structure affects solubility, i.e., “like dissolves like”
- Fuel oxygenates are “polar” compounds to varying degrees which causes them to have significant solubility in water
- All of the fuel oxygenates are less dense than water causing the less soluble ones to form an organic layer on the surface of the water in a plume



# Physical Properties

## Solubility (Cont.)

- The alcohols TBA, ethanol, methanol and most probably TAA, are miscible, i.e., infinitely soluble in, with water
- MTBE is considered soluble in water, while the other ethers would be considered slightly soluble
- MTBE can be mobilized in a plume by dissolution in water as well as floating on the surface



# Physical Properties

## Solubility (Cont.)

- The presence of significant concentrations of the “miscible oxygenates,” i.e., methanol, ethanol, TBA, in a plume increases the water solubility of the esters, therefore increasing their mobility
- Also, the miscibility of alcohols with water causes poor recoveries when purge-and-trap sample preparative procedures are employed at ambient temperatures for analysis



# Physical Properties

## Polarity (Dipole Moment)

- A polar molecule is one in which the positive and negative electrical charges are permanently separated
  - e.g., water
- as opposed to non-polar molecules in which the charges coincide
  - e.g., methane



# Physical Properties

## Polarity (Dipole Moment) (Cont.)

- In many molecules, the atoms and their electrons and nuclei are arranged so that one part of the molecule has a positive electrical charge while the other part is negatively charged. Such a molecule, therefore becomes a small magnet or dipole.



# Physical Properties

## Polarity (Dipole Moment) (Cont.)

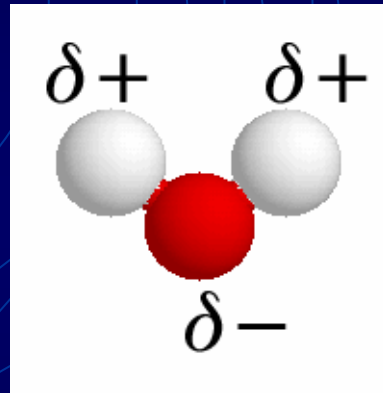
- Changing electric or magnetic fields causes the molecule to turn or rotate in one direction or another, depending on the charge of the field
- The “dipole moment” ( $\delta$ ) is the distance between the charges multiplied by the quantity of charge in electrostatic units



# Physical Properties

## Polarity (Dipole Moment) (Cont.)

- Dipole moment of water is 1.84D



- Dipole moment of alcohols is greater than that of ethers which results in greater water solubility or miscibility for alcohols



# Chemical Properties

- Both ethers and alcohols burn hot and clean because of their internal oxygen content, which makes them appropriate for adding to gasoline to improve octane rating or to cause it to burn cleaner. Combustion products are carbon dioxide and water.
- Ethers are manufactured by acid-catalyzed dehydration of alcohols.



# Chemical Properties (Cont.)

- Ethers can hydrolyze back to the alcohol form under appropriate conditions, e.g., exposure to acids, which increases their water solubility and mobility in plumes

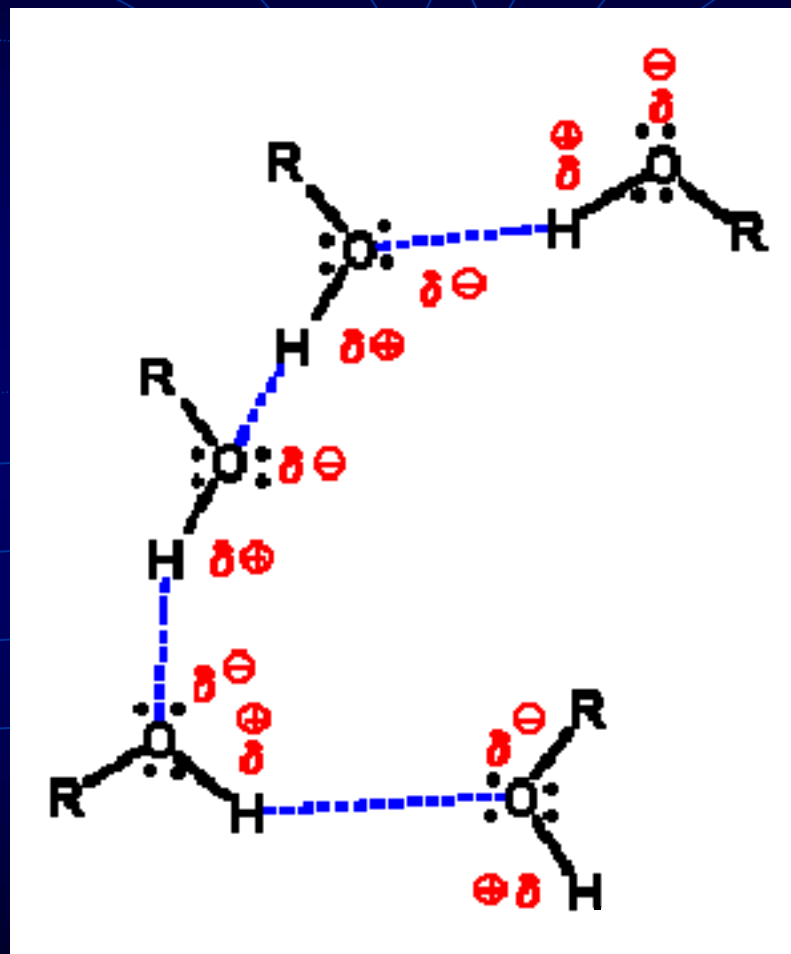


# Chemical Properties (Cont.)

- Alcohols can exhibit hydrogen bonding, a semi-ionic attraction between the hydrogen of the alcohol with the oxygen of water and vice versa
- This effect both enhances the solubility of the alcohols and increases the boiling point, since more energy is needed to break the additional hydrogen bonds to vaporize the compounds



# Chemical Properties (Cont.)



Graphic courtesy of: University of Illinois, Springfield  
Chemistry Program

<http://www.uis.edu/~trammell/organic/alcohols/alcohols.htm>

ASTSWMO State Symposium on Fuel Oxygenates - October 21, 2002



# Potential Health Effects

- Ethers may be inhaled or absorbed through the skin and can cause irritation to the eyes, skin, nose and throat
- Ether exposure can cause difficulty in concentrating and thinking
- Higher levels can cause
  - Headache
  - Nausea
  - Dizziness
  - Weakness
  - Lightheadedness
  - Damage to the kidneys



# Potential Health Effects (Cont.)

- All fuel oxygenate compounds exhibit the characteristic of ignitability, i.e., they all have flash points  $<40^{\circ}\text{C}$  ( $140^{\circ}\text{F}$ )
- Potential for contamination of drinking water supplies by leaching into ground water



# Potential Problems Using Standard Analytical Methods

- Extreme solubility of the alcohols in water results in very poor recoveries from the aqueous matrix using standard ambient temperature purge-and-trap technique (Method 5030)



# Potential Problems Using Standard Analytical Methods (Cont.)

- Fuel oxygenates by their chemical nature do not contain multiple bonds and therefore will not give a signal response in the photoionization detector (PID) using Method 8021 for BTEX (MTBE will give a minimal response when a brand new lamp is used, but the signal response disappears rapidly after repeated use of the lamp)



# Potential Problems Using Standard Analytical Methods (Cont.)

- Acid preservation of samples can cause hydrolysis of MTBE to TBA when high temperature sample preparative methods are used
  - static headspace (Method 5021)
  - vacuum distillation (Method 5032)
  - heated purge-and-trap (Method 5030)
- Resolution of these problems will be covered in the next presentation



# Contact Information

- Methods Team Homepage:  
[www.epa.gov/SW-846](http://www.epa.gov/SW-846)
- Methods Information Communication Exchange (MICE)
  - Phone: (703) 676-4690
  - Email: [mice@saic.com](mailto:mice@saic.com)
- Barry Lesnik
  - Phone: (703) 308-0476
  - Email: [lesnik.barry@epa.gov](mailto:lesnik.barry@epa.gov)



# Acknowledgement

Chemical structures courtesy of:

U.S. National Library of Medicine  
Specialized Information Services

<http://chem.sis.nlm.nih.gov/chemidplus>

University of Illinois, Springfield  
Chemistry Program

<http://www.uis.edu/~trammell/organic/alcohols/alcohols.htm>

