Method compliance: **ASTM D4815 and ASTM D7423.**

What is the oxygenates?

Oxygenates are just preused hydrocarbons :-). They contain oxygen, which can not provide energy, but their structure provides a reasonable antiknock value, thus they are good substitutes for aromatics, and they may also reduce the smog-forming tendencies of the exhaust gases [15]. Most oxygenates used in gasolines are either alcohols (Cx-O-H) or ethers (Cx-O-Cy), and contain 1 to 6 carbons. Alcohols have been used in gasolines since the 1930s, and MTBE was first used in commercial gasolines in Italy in 1973, and was first used in the US by ARCO in 1979. The relative advantages of aromatics and oxygenates as environmentally-friendly and low toxicity octane-enhancers are still being researched.

Oxygenates are added to gasolines to reduce the reactivity of emissions,but they are only effective if the hydrocarbon fractions are carefully modified to utilise the octane and volatility properties of the oxygenates.If the hydrocarbon fraction is not correctly modified, oxygenates can increase the undesirable smog-forming and toxic emissions. Oxygenates do not necessarily reduce all exhaust toxins, nor are they intended to.

Oxygenates that are added to gasoline function in two ways. Firstly theyhave high blending octane, and so can replace high octane aromaticsin the fuel. These aromatics are responsible for disproportionate amountsof CO and HC exhaust emissions. This is called the "aromatic substitution effect". Oxygenates also cause engines without sophisticated engine management systems to move to the lean side of stoichiometry, thus reducing emissions of CO (2% oxygen can reduce CO by 16%) and HC (2% oxygen can reduce HC by 10%) [17], and other researchers have observed similar reductions also occur when oxygenates are added to reformulated gasolines on older and newer vehicles, but have also shown that NOx levels may increase, as also may some regulated toxins.

However, on vehicles with engine management systems, the fuel volume will be increased to bring the stoichiometry back to the preferred optimum setting. Oxygen in the fuel can not contribute energy, consequently the fuel has less energy content. For the same efficiency and power output, more fuel has to be burnt, and the slight improvements in combustion efficiency that oxygenates provide on some engines usually do not completely compensate for
the oxygen.

Scope *D4815*	• This test method is designed for the determination of ethers and alcohols in gasolines by gas chromatography, Specific compounds determined are: methyl tert-butylether (MTBE), ethyl tert-butylether (ETBE), tert-amylmethylether (TAME), diisopropylether (DIPE), methanol, ethanol, isopropanol, n-propanol, isobutanol, tert-butanol, sec-butanol, n-butanol, and tert-pentanol (tert-amylalcol). • Individula ethers are determination from 0,1 to 20,0 mass percent. Individual alcohols are determined from 0,1 to 12,0 mass percent. Equations used to convert to mass percent oxygen and to volume % of individual compounds are provided. • Alcohol-based fuels such as M-85 and E-85, MTBE product, ethanol and denatured alcohol are specifically excluded from this method. The methanol content of M-85 fuel is considered beyond the operating range of the system.
Significance and Use	• Ethers, alcohols, and other oxygenates can be added to gasoline to increase octane number and to reduce emissions. Type and concentration of various oxygenates are specified and regulated to ensure acceptable commercial gasoline quality. Drivability, vapor pressure, phase separation, exhaust and evaporative emissions are some of the concerns associated with oxygenates fuels.
Scope *D7423*	• This test method covers the gas chromatographic procedure for the quantitative determination of organic oxygenates in C2, C3, C4, and C5 matrices by multidimensional gas chromatography and flame ionization detection. This test method is applicable when the hydrocarbon matrices have a final boiling point not greater than 200 °C. Oxygenate compounds include, but are not limited to, those listed in Table 1. The linear working range for oxygenates is 0.50 mg/kg to 100 mg/kg..
Significance and Use	• The determination of oxygenates is important in the manufacture of ethene, propene, 1-3 butadiene, C4 hydrocarbons, and C5 hydrocarbons. Alcohols, ethers, aldehydes,

and ketones are trace impurities in these hydrocarbons. Oxygenates decrease catalyst activity in downstream polymerization processes.

Equipment specification

Performance Specifications

Oxygenate compounds:

- Dimethyl ether
- Diethyl ether
- Acetaldehyde
- Ethyl tert-butyl ether
- Methyl tert-butyl ether (MTBE)
- Diisopropyl ether
- Propionaldehyde (Propanal)
- Tertiary amyl methyl ether (TAME)
- Propyl ether
- Isobutylaldehyde
- Butylaldehyde
- Methanol
- Acetone
- Isovaleraldehyde
- Valeraldehyde
- 2-Butanone (MEK)
- Ethanol
- N-propyl alcohol and isopropanol (co-elution)
- Allyl Alcohol
- Isobutanol + Tert-butyl alcohol + Sec-Butanol (co-elution)
- N-butanol
- Other oxygenates upon request

The linear working range for oxygenates is at least 0.50 mg/kg to 100 mg/kg.

Hardware description

The DVLS Oxygenates Analyzer is based upon the Agilent 7890B series gas chromatograph and consists of:

- The ultra-modern Agilent 7890B series gas chromatrograph with gas savong made and EPC controlled flow and detector
- Flame ionization detector (FID) with high scanning rate
- A second flame ionization detector (FID) for application control
- DVLS PTI inlet or Split/Splitless injection port to accommodate (liquefied) gases
- Capillary columns
- Deans switching CFT valve
- Liquid sampling valve and / or Gas Sample valve
- DVLS liqiud gas injector (LGI)
- DVLS pressure station
- Agilent Autoinjector
- Second FID detector