



**CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD  
CENTRAL VALLEY REGION**

3443 Routier Road, Suite A  
Sacramento, CA 95827-3098  
Phone (916) 255-3000  
FAX (916) 255-3015

Cal/EPA



Pete Wilson, Governor

18 July 1997  
Revised 30 August 1997<sup>2</sup>

To Whom It May Concern

**ANALYSIS REQUIRED FOR OXYGENATE COMPOUNDS USED IN CALIFORNIA  
GASOLINE - EPA METHOD 8260 (8240-B and 8020)**

At a June 1997 meeting at the Department of Health Services in Berkeley, the statewide analytical methods committee for establishing analytical TPH and additive standards, was informed that oxygenate compounds, which may constitute a threat to groundwater, other than MTBE, have been and are being added to gasoline. The list includes, in order of analytical identification:

1. Methanol
2. Ethanol
3. Tertiary Butyl Alcohol (TBA)
4. MTBE
5. Di-isopropyl ether (DIPE)
6. Ethyl Tertiary Butyl Ether (ETBE)
7. Tertiary Amyl Methyl Ether (TAME)

The first three are alcohols and the latter four are ether compounds. Ethanol has been used for several years in California. MTBE, as you know, has been used as an octane enhancer additive since the late 1970s and is now used at a higher percentage as an oxygenate in gasoline. Now we have learned that, TAME has been added to California fuels, since 1995. DIPE has been used on the East Coast, but recently has been found in Southern California ground water (May 1997) and San Joaquin County (August 1997). TBA has been found in ground water at a gasoline service station site in San Joaquin County (1100 ppb, August 1997). To date, we have no information regarding the use of ETBE in California.

The introduction of these additives present analytical problems for laboratories because the multiple analytes can co-elute from the column. For instance, TAME may co-elute with benzene in the EPA-8020 analytical method commonly used today. Therefore, we believe that Mass Spectrometry (MS) is the most definitive procedure to determine oxygenate compounds. MS will likely increase the cost of sample analysis; but, until another comprehensive analytical method is developed that can distinguish between the compounds, we believe that EPA Method 8260 is the most reliable, readily available procedure for laboratories. Completion of proposed studies on analytical procedures for oxygenate compounds by the Lawrence Livermore National Laboratory, under contract to the State Water Resources Control Board, should provide additional guidance by early 1998.

The problem of identifying which oxygenates are present is further compounded because the oil refineries ship gasoline around the state and then trade gasoline between geographic areas. For instance, if gasoline is needed in the San Francisco Bay area by BogCo Oil, BogCo will obtain some gasoline from, say, Generic Oil in the Bay area and, in exchange, Generic will receive some BogCo gasoline in Southern California. The result is that we do not know what oxygenate compound is in the gasoline at a particular gas station. TAME may be used by Generic, but, because of this swapping, TAME, rather than MTBE, will end up in the ground water at a BogCo site.

Research recently completed by DuPont-DOW (<http://www.dupont-dow.com/products/viton/lkprev.html>) show that oxygenates may be incompatible with some elastomer seals used on underground tank piping. One test, using several concentrations of MTBE, was short term (168 hours) and showed swelling could occur with some elastomers at current gasoline mixture levels. Presumably, this will be true, to some extent, for all ether oxygenate additives, and, over a longer time, conceivably cause the failure of the seals; thereby, releasing the oxygenated gasoline into the environment. We are particularly concerned that older tank seals or material used to upgrade tanks may not be compatible with the oxygenates and may fail due to the high concentrations of oxygenates in the alternative fuel sources.

On 14 August 1997, a workshop was conducted at the Sacramento office of this Regional Board, attended by representatives of Regional and State Boards, Local Implementing Agencies, analytical Laboratories and the petroleum industry. The objective was to provide guidance to the regulated community on how and where to analyze for the oxygenated compounds in gasoline until definitive protocol can be established in several months. The goal was to allow closure of underground tank sites with assurances that the interim methodology can detect and quantify oxygenates.

The workshop attendees concurred that the methyl and ethyl alcohols can't be detected by EPA Method 8260 with certainty and that detection limits for methyl and ethyl alcohols are about two orders of magnitude higher than TBA and the ethers. Also, with the exception of one oil company and special, alternative fuel vehicles (including the State of California automobiles), ethanol and methanol are used infrequently in California, and can be isolated by station and the more accurate analytical methods used. Therefore, at this time, unless ethanol or methanol are specifically requested, we are requiring soil and water analysis only for TBA and the ether compounds by EPA Method 8260 in order to determine which oxygenated compound is present.

Presence or absence of the oxygenate must be reported whenever gasoline range hydrocarbons are present. However, because free product or high petroleum concentrations raise the detection limits of the oxygenates, the oxygenates cannot be detected with certainty. Therefore, at this time, we do not recommend sampling where product is present on groundwater.

Quarterly water samples for oxygenate compounds are to be taken from all monitoring wells at sites with 10 or fewer wells (supply wells and surface water may be included in the monitoring program, as appropriate, by the Regional Board or Local Implementing Agency). At sites with more than ten monitoring wells, requests to change the sampling procedure must be approved by the Regional Board or Local Implementing Agency. Soil samples should be analyzed beneath the primary leak source(s) (tank, pipeline, or dispenser) at regular depth intervals to the groundwater interface. If only MTBE is found in the initial sampling/analysis, as confirmed by 8260, the Responsible Party may continue analysis by EPA Method 8020 for the oxygenate. Prior to requesting site closure, a "confirming round" for all oxygenate compounds must be completed.

Laboratories must include all listed oxygenated standards (TBA and Ethers) in their calibration standards and follow the QA/QC protocol detailed in EPA Methods 8000 and 8020, or 8240-B or 8260, and the Code of Federal Regulations (CFR Title 40, parts 136.4 and 136.5).

In addition to the compounds discussed above, we have found that both Tertiary amyl ethyl ether (TAEE) and Isopropyl alcohol (IPA), WSPA, 1997 data, also may be added to gasoline; and PRIST® (ethylene glycol monomethyl ether) is added to aviation fuel and, reportedly, some diesel fuels to prevent clogging of fuel lines by microorganisms. Prist is registered as a pesticide with anti-microbial properties: CAS# 000109864. These compounds may be added to the analysis list as more information becomes available.

If you have any questions, please call John Noonan in Fresno at (209) 445-5550, Karen Clementsen in Redding at (916) 224-4852, or me in Sacramento at (916) 255-3139.



GORDON LEE BOGGS  
Underground Tank  
Program Manager