Reformulated Gasoline Analysis Method

Determination of Fuel Oxygenates

Microseeps' methods have become official promulgated USEPA Methods SW846 5021A and 8015D

Most gasoline plumes today also contain fuel oxygenates. Initially it was thought that unlike the hydrocarbons, fuel oxygenates didn't biodegrade. However, modern research has revealed that both the ethers and alcohols degrade in all redox processes, either aerobic or anaerobic.

The problems stem from the fact that the ethers don't biodegrade as fast as the hydrocarbons and they are not retarded in the soil matrix as are the hydrocarbons. As a result, there are many hydrocarbon/fuel oxygenate plumes where the hydrocarbon portion of the plume is relatively short and the fuel oxygenate portion of the plume is relatively long—several are a mile in length.

The analytical problems are two fold. First the ethers and alcohols are very soluble if not miscible in groundwater. Thus they are extremely difficult to separate from the water for analysis. Second, the traditional methodology for analysis of hydrocarbons was used without modification for several years which mandated that such groundwater samples be preserved with acid to a pH of 2 or less. The effect of the acid inhibits the microbial degradation of the hydrocarbons and the fuel oxygenates as well. This is the intended purpose of the preservative.

Reformulated Gasoline Analysis Method

Microseeps' Reformulated Gasoline Analysis has significant benefits over traditional analytical methods.

- Reliably measures BTEX, ethers and alcohols in the same run
- Reduces uncertainty
- Supports the understanding of component biodegradation
- Eliminates the potential for acid hydrolysis.
- Meets or exceeds PQL's for fuel oxygenate ethers and alcohols.
- Superior PQL for ethanol (10 ug/l)

However we have known for several decades that organic ethers hydrolyze in acidic aqueous solutions to form alcohols. Such hydrolysis, if it occurs in the vial during the time between sampling and analysis could lead to misleading results since TBA, the hydrolysis product of MTBE, is also the primary product of biodegradation of MTBE. Thus significant levels of TBA in a groundwater sample that result from acid hydrolysis after sampling, could be misinterpreted as resulting from biodegradation.

As demand for ever lower detection levels has continued throughout the last few years, some laboratories heated the samples to facilitate more efficient removal of FO's, particularly the alcohols like TBA, from the water during analysis. Since that efficient removal translated into lower detection limits, heating was a logical response to that pressure. Unfortunately, the acid hydrolysis problem is exacerbated by heating.

At the request of the USEPA, Microseeps developed a new analytical method based on the use of the headspace method SW846 5021 and the FID analytical method SW846 8015. These methods lend themselves more readily to the use of trisodium phosphate (TSP) as the preservative rather than an acid such as HCl. The effect of TSP is to raise the pH to about 12, thus precluding the acid hydrolysis problem. This method then can be applied at elevated temperatures and with the addition of a matrix modifier (salt) to reduce the solubility of the fuel oxygenates. The result is a method that achieves and exceeds the detection levels required and eliminates the potential for acid hydrolysis. Microseeps wrote draft revised methods for both USEPA Methods 5021 and 8015. These revised methods have now become official promulgated USEPA Methods SW846 5021A and 8015D.

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