November 5, 2002

To: Water Resources Discipline

From: Peter F. Rogerson, Senior Chemist
Office of Water Quality

For: LeRoy Schroder, Chief
Branch of Quality Systems

Subject: Approval of a Water Quality Analytical Method for the Determination of Gasoline Oxygenates, Degradates, and BTEX in Water by the National Water Quality Laboratory

The Office of Water Quality (OWQ) has approved a Water Quality Analytical Method developed by the National Water Quality Laboratory (NWQL) for the determination of gasoline oxygenates, degradates, and benzene, toluene, ethylbenzene, and xylenes (BTEX) in water samples. This method uses heated purge and trap followed by gas chromatography/mass spectrometry (GC/MS) to determine 4 oxygenates such as tert-butyl methyl ether (MTBE), 4 oxygenate degradates such as tert-butyl alcohol, and 5 BTEX compounds. The new U.S. Geological Survey Method Number is O-4024-03 and is available from the NWQL as Schedule 4024 for un-acidified samples and as Schedule 4025 for acidified (pH 2) samples.

Sample preservation by acidification is required for BTEX compounds which can degrade in un-acidified samples due to bacterial action. However, ethyl acetate, an oxygenate degradation product, is degraded in acidified samples. Therefore, as the following table shows, BTEX is not included in Schedule 4024 (un-acidified samples). Methyl acetate is included in Schedule 4025 (acidified samples), but only with an 'E' (estimated) data qualifier. This is because methyl acetate degrades in acidified samples, with a 7 day holding time. The BTEX compounds are also available from the NWQL in several other volatile organic compound (VOC) Schedules. For information on NWQL Schedules, please follow the NWQL LIMS Catalog link specified below.

Gasoline Oxygenates, Degradates, and BTEX Method (O-1126-02)

Parameter Code (NWIS)	Method Code (Sch. 4024 un-acidified)	Method Code (Sch 4025 acidified)	Analyte Name
50005	C	D	tert-Amyl methyl ether, water, ug/L
50004	C	D	tert-Butyl ethyl ether, water, ug/L
78032	E	F	tert-Butyl methyl ether, water, ug/L
81577	C	D	Diisopropyl ether, water, ug/L
81552	C	D	Acetone, water, ug/L
77073	A	B	tert-Amyl alcohol, water, ug/L
77035	A	B	tert-Butyl alcohol, water, ug/L
77032*	A	B*	Methyl acetate*, water, ug/L
34030	-	F	Benzene, water, ug/L
34010	-	F	Toluene, water, ug/L
34371	-	F	Ethylbenzene, water, ug/L
85795	-	F	meta- and para-Xylene, water, ug/L
77135	-	F	ortho-Xylene, water, ug/L

*Methyl acetate data are reported with the 'E' (estimated) data qualifier in Schedule 4025 due to short holding time (7 days) in acidified samples.

Holding time studies of 45 days were performed for both acidified and un-acidified samples, with average recoveries of acidified samples, not including ethyl acetate, of 99 percent (standard deviation 4 percent). For un-acidified samples, average recoveries were 106 percent (standard deviation 4 percent) not including BTEX. Preliminary laboratory reporting limits vary from about 0.01 ug/L (toluene) to 1.2 ug/L (acetone).

This method approval process follows the technical procedure specified in OWQ Tech Memo 98.05, except that this method is described in a Water Resources Investigations Report instead of an Open File Report. The method performance is described in:

> Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Determination of Gasoline Oxygenates, Selected Degradates, and BTEX in Water by Heated Purge and Trap/ Gas Chromatography/Mass Spectrometry, by Donna L. Rose and Mark W. Sandstrom. U.S. Geological Survey Water Resources Investigations Report 02-XXXX (number to be assigned upon Director's approval).

When approved by the Director, the report will be made available through the NWQL web site at: http://wwwnwql.cr.usgs.gov/USGS/pubs.html .

Information about this method will be available through the NWQL web site http://wwwnwql.cr.usgs.gov/USGS . Please click on LIMS Catalog and request Schedule 4024 (acidified) or 4025 (un-acidified).

If you have questions about the new analytical method, or would like a copy of the report, when it is available, please contact Donna Rose (dlrose@usgs.gov , (303) 236-3499) or Mike Schroeder (schroede@usgs.gov , (303) 236-3270) at the NWQL.

If you have questions about the method approval process, please contact Pete Rogerson (rogerson@usgs.gov , (303) 236-1836).