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May 10, 2016

To: GS-W-ALL

From: Donna N. Myers, Chief, Office of Water Quality

Subject: Approval of New USGS Methods: Determination of Heat Purgeable (Method O-4437-16) and Ambient Purgeable (Method O-4436-16) Volatile Organic Compounds in Water by Gas Chromatography/Mass Spectrometry

The Office of Water Quality (OWQ) has approved two new whole-water analytical methods, O-4437-16, and O-4436-16, National Water Quality Laboratory (NWQL) schedules (SH) 4437 for the determination of 37 heat purgeable volatile organic compounds (VOCs) and SH 4436 for the determination of 49 ambient purgeable VOCs. See attached tables 1 and 2 for compounds included in the methods. The methods are described in their entirety in a new USGS Techniques and Methods Report (Rose and others, in press).

The U.S. Geological Survey (USGS) developed these methods to support studies of selected VOCs in a variety of whole-water matrices, including groundwater, surface water, and drinking water. The VOCs in the new methods have high priority for method development and future monitoring studies in the USGS, because of their potential for occurrence and persistence in groundwater and surface water, and their toxicity to humans and aquatic organisms (Olsen and others, 2013).

All compounds are determined using purge-and-trap techniques/gas chromatography/mass spectrometry. A 25-milliliter sample is transferred to the purge-and-trap concentrator, via an autosampler. A solution of surrogate/internal standards is added to the sample, and then the sample is purged at 60 degrees Celsius (°C) for Method O-4437-16, and at ambient temperature for Method O-4436-16. The sample is desorbed into the gas chromatograph where the compounds are separated. The sample is determined using electron-impact-ionization mass spectrometry. For Method O-4437-16, the mass spectrometer is operated simultaneously in the full-scan/selected-ion-monitoring mode. For Method O-4436-16, the mass spectrometer is operated in the full-scan mode. The concentration of each identified compound is determined using the internal-standard technique.

Method O-4437-16 has replaced Method O-4179-03 (NWQL SH 4024 and SH 4025) for the determination of methyl acetate, methyl *tert*-butyl ether (MTBE), and *tert*-butyl alcohol. Thirty high-priority heat purgeable VOCs were added to Method O-4437-16, in addition to four fumigant compounds transferred from Method O-4127-96; Method O-4437-16 has replaced Method O-4127-96 (NWQL SH 2020) for the determination of four fumigant compounds; 1,2,3-trichloropropane, 1,2-dibromoethane (EDB), 1,2-dichloropropane, and 1,2-dibromo-3-chloropropane (DBCP). Method O-4437-16 also replaces U.S. Environmental Protection

Agency (EPA) Method 504.1 (NWQL SH 1306) used for the determination of EDB and DBCP. Method O-4437-16 achieves lower reporting levels than previous methods, eliminates a solvent extraction (NWQL SH 1306), and includes an additional fumigant compound, chloropicrin. NWQL SH 4443 (a subset of NWQL SH 4437) determines the five fumigant compounds (Table 1).

Method O-4436-16 has replaced Method O-4127-96 (NWQL SH 2020) for the determination of ambient purgeable VOCS. Thirty-eight of the 85 VOCs were retained from Method O-4127-96 and 11 high-priority VOCs were added to the new method. The function of 1,2-dichloroethane-d_4 was changed from a surrogate standard compound in Method O-4127-96 to an internal standard compound in Method O-4436-16. NWQL SH 4439, a subset of NWQL SH 4436, determines only MTBE, benzene, toluene, ethylbenzene, and xylenes (BTEX) (Table 2).

The Techniques and Method report (Rose and others, 2016) describes the analytical methods and presents characteristics of method validation including bias and variability in different matrices, method detection limits, and holding-time studies. The results provide a characterization of the performance of the new methods during implementation in routine production, including bias and variability of VOCs over a range of environmental matrices and concentrations.

The method detection limits were determined in reagent water using the EPA procedure (40 CFR part 136, appendix B). The method detection limits range from 0.002 to 3 micrograms per liter (µg/L) for 37 heat purgeable VOCs (Method O-4437-16) and from 0.005 to 0.06 µg/L for 49 ambient purgeable VOCs (Method O-4436-16). After the methods are implemented into routine production the method detection limits and reporting levels will be updated to reflect long-term method performance. The stability studies in reagent water demonstrated that the majority of the VOC compounds were stable after 14 days of storage at 4 ± 2 °C, so these were selected as the practical holding time and storage temperature for routine sample processing.

Five compounds were tested and subsequently eliminated from the methods. Four semi-volatile compounds; 2-chloronaphthalene, 1,2-dimethylnaphthalene, 1,6-dimethylnaphthalene, and 2,6-di-*tert*-butyl phenol, initially showed acceptable performance. Long-term performance demonstrated these compounds were more suitable for a semi-volatile method. The compounds were eliminated from Method O-4436-16 on May 1, 2014. Acrolein was also tested and subsequently eliminated from Method O-4437-16 on April 1, 2016 due to instability and poor performance.

Field samples for both methods are collected using USGS protocols for collection of VOCs in surface water and groundwater, according to the procedures described in the National Field Manual (USGS, 2006). Samples are collected in 40-mL vials (GCV bottle type, N1560), and are preserved with a 1:1 solution of hydrochloric acid:water (N1140) to a pH of 2. Samples are stored at 4 ± 2 °C during transportation and storage. Three GCV bottles are required for each method. Guidance for neutralization of residual chlorine in finished-water samples by the addition of ascorbic acid is provided in OWQ Water-Quality Information (WaQI) Note 2007.04 accessible at http://water.usgs.gov/usgs/owq/WaQI/WaQI07.04.pdf . Sample vials with ascorbic acid pre-added are available at OneStop (N1160).

This method approval process follows the technical procedures specified in OWQ Technical Memorandum 04.01 and the method is described in a USGS Techniques and Methods Report:

Suggested Citation:

Rose, D.L., Sandstrom, M.W., and Murtagh, L.K., 2016, Determination of heat purgeable and ambient purgeable volatile organic compounds in water by gas chromatography/mass spectrometry: U.S. Geological Survey Techniques and Methods, book 5, chap. B12, 62 p.

The approved report will be release in the near future through the USGS Publications Warehouse.

For questions about the new analytical methods, or a copy of the report, when it is available, please contact Donna Rose (dlrose@usgs.gov, 303-236-3283) or Jeff McCoy (jefmccoy@usgs.gov, 303-236-3940).

For questions about the OWQ-method-approval process, please contact Donna Myers (dnmyers@usgs.gov, 703-648-5012) or Cherie Miller (cvmiller@usgs.gov, 703-648-6866).

References cited:

Olsen, L.D., Valder, J.F., Carter, J.M., and Zogorski, J.S., 2013, Prioritization of constituents for national- and regional-scale ambient monitoring of water and sediment in the United States: U.S. Geological Survey Scientific Investigations Report 2012–5218, 203 p., plus supplemental tables, available at http://pubs.usgs.gov/sir/2012/5218.

U.S. Environmental Protection Agency, 2002, Guidelines for establishing test procedures for the analysis of pollutants (Part 136, Appendix B. Definition and procedure for the determination of the method detection limit-Revision 1.11): U.S. Code of Federal Regulations, Title 40, revised as of July 1, 2002, p. 635-638.

U.S. Geological Survey, 2006, Collection of water samples (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A4, September 2006, accessed [May 29, 2015], available at http://pubs.water.usgs.gov/twri9A4/.

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Attachments:

Table 1. Heat-purgeable volatile organic compounds determined by Method O-4437, simultaneous full scan/selected ion monitoring mass spectrometry.

Table 2. Ambient-purgeable volatile organic compounds determined by Method O-4436, full scan mass spectrometry.