U.S. EPA Method 524.3 – Providing Laboratories Increased Flexibility and Capability in VOC Analysis

Laura Chambers, Senior Product Specialist

September 24, 2009

www.oico.com

Opportunity through Innovation™

Webinar Outline

- Background information
- EPA project objectives
- Changes to the method
  - *Modified target compound list*
  - *New preservation scheme*
  - *QC requirements*
  - *Instrument operating parameters*
- Analytical data

Background

38348 Federal Register / Vol. 74, No. 147 / Monday, August 3, 2009 / Rules and Regulations

impact on a substantial number of small entities under the Regulatory Flexibility Act (5 U.S.C. 601 *et seq.*). Because this rule approves pre-existing requirements under State law and does not impose any additional enforceable duty beyond that required by State law, it does not contain any unfunded mandate or significantly or uniquely affect small governments, as described in the Unfunded Mandates Reform Act of 1995 (Pub. L. 104–4). This rule also does not have Tribal implications because it will not have a substantial direct effect on one or more Indian Tribes, on the relationship between the Federal Government and Indian Tribes, or on the distribution of power and responsibilities between the Federal Government and Indian Tribes, as specified by Executive Order 13175 (65 FR 67249, November 9, 2000). This action also does not have Federalism implications because it does not have substantial direct effects on the States, on the relationship between the national government and the States, or on the distribution of power and responsibilities among the various levels of government, as specified in Executive Order 13132 (64 FR 43255, August 10, 1999). This action merely approves a State rule implementing a Federal requirement, and does not alter the relationship or the distribution of power and responsibilities established in the CAA. This rule also is not subject to Executive Order 13045 "Protection of Children from Environmental Health Risks and Safety Risks" (62 FR 19885, April 23, 1997), because it approves a State rule implementing a Federal standard. In reviewing section 111(d)/129 plan submissions, EPA's role is to approve State choices, provided that they meet the criteria of the CAA. In this context, in the absence of a prior existing requirement for the State to use voluntary consensus standards (VCS), EPA has no authority to disapprove a 111(d)/129 plan submission for failure to use VCS. It would thus be inconsistent with applicable law for EPA, when it reviews a 111(d)/129 plan submission, to use VCS in place of a 111(d)/129 plan submission that otherwise satisfies the provisions of the CAA. Thus, the requirements of section 12(d) of the National Technology Transfer and Advancement Act of 1995 (15 U.S.C. 272 note) do not apply. This rule does not impose an information collection burden under the provisions of the Paperwork Reduction Act of 1995 (44 U.S.C. 3501 *et seq.*).

B. Submission to Congress and the Comptroller General

The Congressional Review Act, 5 U.S.C. 801 *et seq.*, as added by the Small Business Regulatory Enforcement Fairness Act of 1996, generally provides that before a rule may take effect, the agency promulgating the rule must submit a rule report, which includes a copy of the rule, to each House of the Congress and to the Comptroller General of the United States. EPA will submit a report containing this rule and other required information to the U.S. Senate, the U.S. House of Representatives, and the Comptroller General of the United States prior to publication of the rule in the **Federal Register**. This rule is not a "major rule" as defined by 5 U.S.C. 804(2).

C. Petitions for Judicial Review

Under section 307(b)(1) of the Clean Air Act, petitions for judicial review of this action must be filed in the United States Court of Appeals for the appropriate circuit by October 2, 2009. Filing a petition for reconsideration by the Administrator of this final rule does not affect the finality of this rule for the purposes of judicial review nor does it extend the time within which a petition for judicial review may be filed, and shall not postpone the effectiveness of such rule or action. Parties with objections to this direct final rule are encouraged to file a comment in response to the parallel notice of proposed rulemaking for this action published in the proposed rules section of today's **Federal Register**, rather than file an immediate petition for judicial review of this direct final rule, so that EPA can withdraw this direct final rule and address the comment in the proposed rulemaking. This action, approving the submitted West Virginia HMIWI plan revision, may not be challenged later in proceedings to enforce its requirements. (See section 307(b)(2).)

List of Subjects in 40 CFR Part 62

Environmental protection, Administrative practice and procedure, Air pollution control, Aluminum, Fertilizers, Fluorides, Intergovernmental relations, Paper and paper products industry, Phosphate, Reporting and recordkeeping requirements, Sulfur oxides, Sulfuric acid plants, Waste treatment and disposal.

Dated: July 21, 2009.

William C. Early,

Acting Regional Administrator, Region III.

■ 40 CFR Part 62, Subpart XX, is amended as follows:

PART 62—[AMENDED]

■ 1. The authority citation for part 62 continues to read as follows:

Authority: 42 U.S.C. 7401 *et seq.*

Subpart XX—West Virginia

■ 2. Section 62.12150 is amended by designating the existing paragraph as paragraph (a) and adding paragraph (b) to read as follows:

§ 62.12150 Identification of plan.

* * * * *

(b) On May 11, 2009, the West Virginia Department of Environmental Protection submitted a State plan revision (#1) that consolidates all existing section 111(d)/129 incinerator regulatory requirements into one modified rule, WV45CSR38.

■ 3. Section 62.12152 is amended by designating the existing paragraph as paragraph (a) and adding paragraph (b) to read as follows:

§ 62.12152 Effective date.

* * * * *

(b) Plan revision #1 is effective October 2, 2009.

[FR Doc. E9–18482 Filed 7–31–09; 8:45 am]

BILLING CODE 6560–50–P

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 141

[EPA–HQ–OW–2009–0345; FRL–8938–9]

Expedited Approval of Alternative Test Procedures for the Analysis of Contaminants Under the Safe Drinking Water Act; Analysis and Sampling Procedures

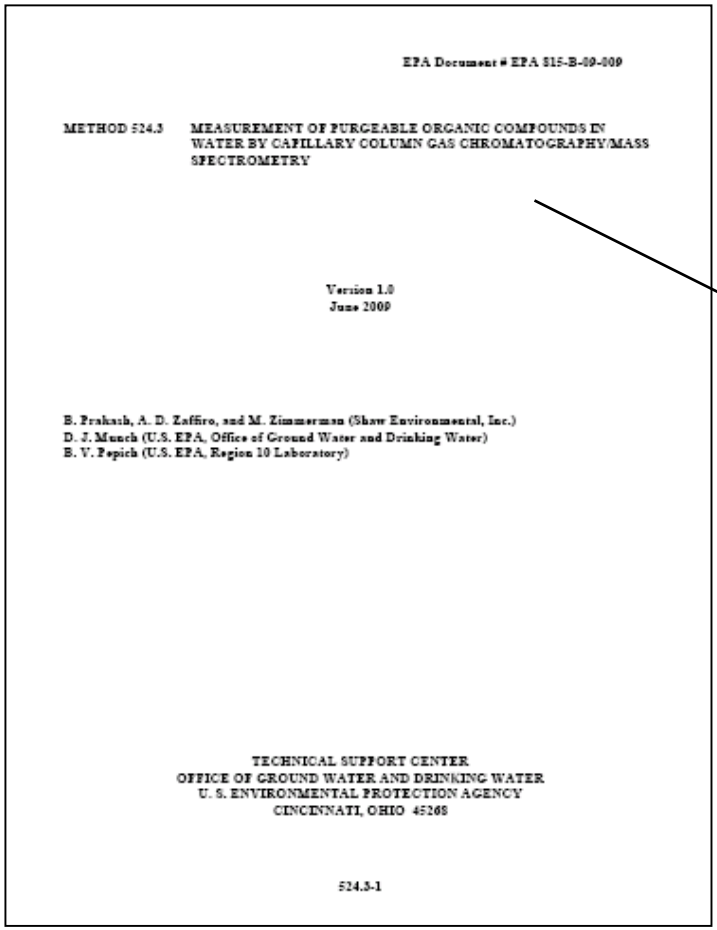
AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This action announces the Environmental Protection Agency's (EPA's) approval of alternative testing methods for use in measuring the levels of contaminants in drinking water and determining compliance with national primary drinking water regulations. The Safe Drinking Water Act (SDWA) authorizes EPA to approve the use of alternative testing methods through publication in the **Federal Register**. EPA is using this streamlined authority to make six additional methods available for analyzing drinking water samples required by regulation. This expedited approach provides public water systems, laboratories, and primacy agencies with more timely access to new

- U.S. EPA Office of Water in Cincinnati has been working on an update for Method 524.2 for ~ 3 years
- August 3, 2009 approval of the new method was published in 40 CFR Part 141
- "Expedited Approval of Alternative Test Procedures for the Analysis of Contaminants Under the Safe Drinking Water Act; Analysis and Sampling Procedures"

Background (cont.)



EPA Document # EPA 815-B-09-009

METHOD 524.3 MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Version 1.0
June 2009

B. Prakash, A. D. Zaffiro, and M. Zimmerman (Shaw Environmental, Inc.)
D. J. Munch (U.S. EPA, Office of Ground Water and Drinking Water)
B. V. Pepich (U.S. EPA, Region 10 Laboratory)

TECHNICAL SUPPORT CENTER
OFFICE OF GROUND WATER AND DRINKING WATER
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

524.3-1

- Method is available to the public and can be downloaded from the EPA web site
  - *http://epa/gov/safewater/methods/analyticalmethods_ogwdw.html*
- Method 524.3: MEASUREMENT OF PURGEABLE ORGANIC COMPOUNDS IN WATER BY CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY, Version 1.0, June 2009
- Does not replace the existing methods (e.g., 524.2 or 502.2)

EPA Project Objectives

1. Update the target compound list
2. Develop a new preservation system that does not employ hydrochloric acid (HCl)
3. Develop procedures and criteria which will permit additional method flexibility without compromising data quality
   - *Quality Control (QC) criteria*
   - *Instrument operating parameters*

Modified Target Compound List

- Removed 15 compounds that are not regulated, have poor purge efficiency, or are of lesser environmental interest
- Added six fuel oxygenates
- Added two compounds from Rev. 3 of the Contaminant Candidate List (CCL3)
  - *Chlorodifluoromethane*
  - *1,3-butadiene*
- Total of 76 target compounds
- Increased number of IS from 1 to 3
- Increased number of SS from 2 to 3

- **benzene**
- **toluene**
- **xylene**

O·I·Analytical

New Preservation Scheme

- No longer calls for HCl
- Uses ascorbic acid and maleic acid (a common food preservative)
  - *25-mg ascorbic acid and 200-mg maleic acid added to 40-mL VOA vial*
- Requires procedural QC, whereby both of the preservatives must be added to all QC samples

QC: Initial Calibration Criteria

Method 524.2	Method 524.3 (*Section 10.1.10*)
Calibration based on average RRF; linear or second order regression allowed as alternate	Calibration based on linear or quadratic regression; weighting may be used; forcing through zero not recommended
Acceptance criteria: %RSD for RRF must be < 20%	Acceptance criteria: calculate the concentration of the analytes for each of the analyses used to generate the calibration curve. Standards ≤ MRL must be within ± 50% of true value. All other standards must be within ± 30% of true value.

QC

O·I·Analytical

QC: Minimum Reporting Levels

- Minimum Reporting Level (MRL) is the minimum concentration that can be reported by a laboratory as a quantified value for the method analyte. The concentration must be no lower than the concentration of the lowest calibration standard. (*Section 3.16*)
  - *Statistical MDLs are no longer required by the method*
- MRL confirmation (*Section 9.2.4*):
  - *Establish target MRL based on intended use of data*
  - *Run 7 replicates at MRL, calculate mean and standard deviation*
  - *Establish Upper and Lower Prediction Interval of Results (PIR) for each compound*
  - *Upper PIR must be $\leq$ 150%*
  - *Lower PIR must be $\geq$ 50%*

QC

O·I·Analytical

QC: The “12-Hour Rule”

- The “12-hour rule” has been eliminated
- MS must be tuned to meet specified BFB tune criteria before the initial calibration, but is no longer required every 12 hours (*Section 10.1.1*)
- On-going acceptance criteria are based on Continuing Calibration Check (CCC) samples *(Section 10.2)*
  - *Analyze a CCC at the beginning of each analysis batch; at or below the MRL; criteria ± 50% of true value*
  - *Analyze a CCC after every 10th field sample; alternate between remaining calibration levels; criteria ± 30% of true value*
  - *Analyze a CCC at the end of each analysis batch; alternate between remaining calibration levels; criteria ± 30% of true value*

QC

O·I·Analytical

QC: Initial Demonstration of Capability

Section	Requirement	Acceptance Criteria
9.2.1	Low system background	Run LRB; concentration of all compounds must be < ½ MRL
9.2.1	Carryover	LRB after high standard; all compounds < ½ MRL
9.2.2	Precision	7 replicate mid-range LFBs; standard deviation ≤ 20%
9.2.3	Accuracy	7 replicate mid-range LFBs; mean recovery ± 20% of true value
9.2.4	MRL confirmation	Upper PIR ≤ 150% Lower PIR ≥ 50%
9.2.5	QC sample	Concentrations must be within ± 30% of true value

QC

Summarized from Table 15 in Method 524.3

QC: Ongoing Requirements

Section	Requirement	Acceptance Criteria
10.1	Initial calibration	Each standard calculated as an unknown. Standard at MRL ± 50% of true value; others ± 30% of true value
9.3.1	LRB	All compounds < ½ MRL
10.2	CCCs	Initial CCC at MRL ± 50% of true value, others ± 30% of true value
9.3.5	IS	Area counts within ± 30% of most recent CCC and ± 50% of ICAL
9.3.6	SS	70% to 130% recovery
9.3.7 9.3.8	LFSM and Duplicate	± 50% at 2 x MRL ± 30% all others
9.3.9	FRB	Report results
9.3.10	QC sample	Concentrations ± 30% of true value

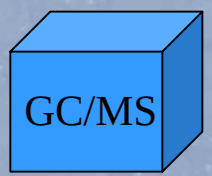
Summarized from Table 16 in Method 524.3

QC

O·I·Analytical

Instrument Operating Parameters

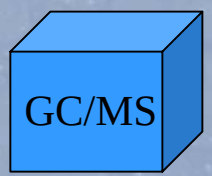
- Allows P&T operating conditions recommended by the instrument manufacturer, with five parameters restricted to prescribed ranges
  - *If instrument operated outside the "Recommended" ranges additional method modification QC required*
- Sample size may NOT vary from 5 mL
- All other parameters, including the remaining concentrator conditions and GC/ MS conditions, may be varied without restriction
- SIM allowed for selected compounds
- Dual P&T configurations allowed
  - *Requires separate QC for each concentrator*



Purge-and-Trap Variables

Parameter	Recommended		Allowable	
	Minimum	Maximum	Minimum	Maximum
Sample Temp	Ambient	40 °C	Ambient	60 °C
Purge Flow Rate	40 mL/min	80 mL/min	20 mL/min	200 mL/min
Purge Volume	360 mL	520 mL	240 mL	680 mL
Desorb Time	1 min	2 min	0.5 min	4 min
Purge + Dry Purge Volume	360 mL	720 mL	240 mL	880 mL

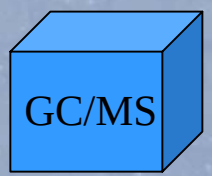
From Section 9.1 of Method 524.3



O·I·Analytical

Trap Requirements

- Any trap design is acceptable provided the data acquired meet all QC acceptance criteria (*Section 6.8.2*)
- OI has a new, proprietary trap for running EPA Method 524.3 on the OI Eclipse P&T
  - *Trap 524.3*
  - *PN 326720*
- Used for the published application note and meets all method QC requirements



Analytical Data

- OI Analytical Application Note 3500 was published in August 2009 and provides
  - *Summary of noteworthy changes to QC reporting requirements*
  - *Optimized instrument operating parameters for the P&T, GC, and MS*
  - *Complete set of method validation data in both scan and SIM modes*
  - *Analysis of real-world samples*

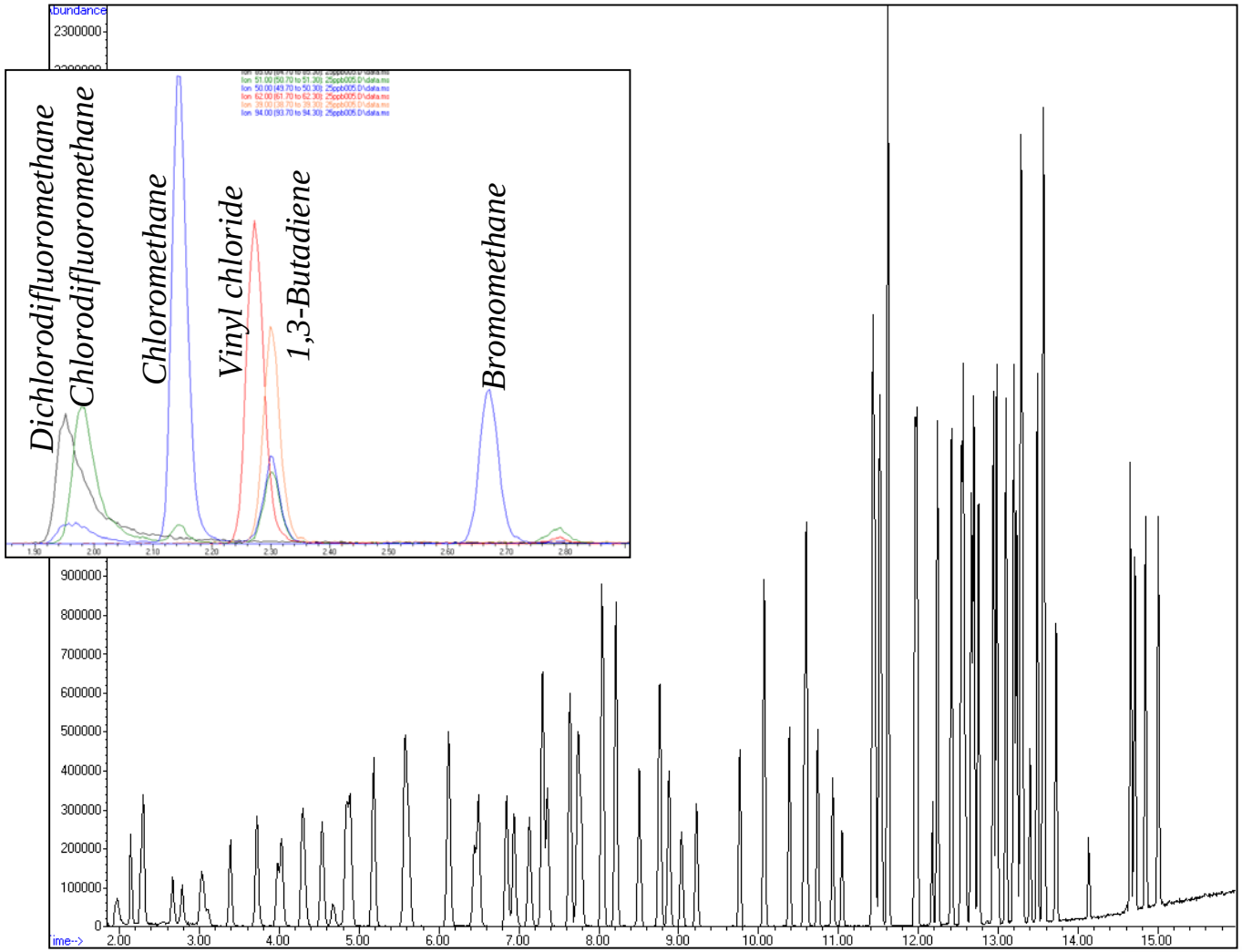
O·I·Analytical

Recommended P&T Conditions

Parameter	Recommended		Recommended conditions for OI Eclipse P&T
	Minimum	Maximum	
Sample Temp	Ambient	40 °C	40 °C
Purge Flow Rate	40 mL/min	80 mL/min	60 mL/min (for 6 minutes)
Purge Volume	360 mL	520 mL	360 mL
Desorb Time	1 min	2 min	1 min
Purge + Dry Purge Volume	360 mL	720 mL	360 mL (no dry purge)

O·I·Analytical

Representative Chromatogram



O·I·Analytical

Method Validation Data

- 7-point calibration curve from 0.5 to 40 ppb
  - *Procedural calibration*
  - *Quadratic regression with inverse concentration weighting, not forced through zero*
  - *Evaluated using the new acceptance criteria*
- Average percent deviation from expected true value ranged from –10.4% to +10.9%

O·I·Analytical

Method Validation Data (cont.)

- Minimum Reporting Level (MRL) confirmation
  - *Lowest calibration standard at 0.5 ppb was established as the MRL*
  - *All compounds fell within the Upper and Lower Prediction Interval of Results*
- Determination of Method Detection Limits (MDL)
  - *Not required by the method, but may be required by monitoring agencies*
  - *Statistical MDLs calculated for all target compounds and reported in the application note*
- Lowest Concentration Minimum Reporting Level (LCMRL)
  - *Secondary laboratory validation data shown in application note*

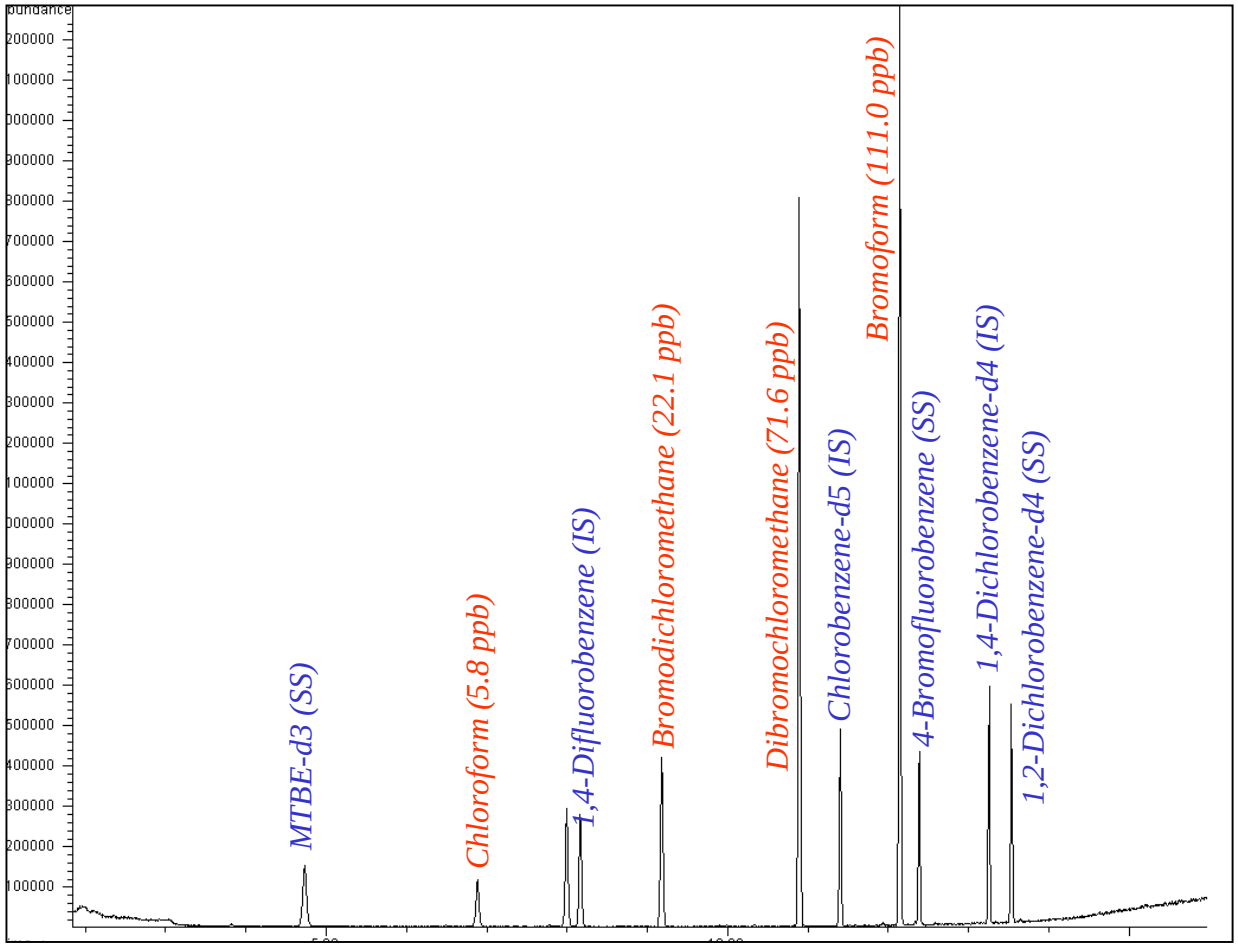
O·I·Analytical

Method Validation Data (cont.)

- Accuracy and precision data sets
  - *Two matrices tested*
  - *Three concentrations with each matrix*
- Laboratory reagent blanks to demonstrate low system background following calibration
- Continuing calibration check samples during IDC sequence
- SIM mode
  - *All validation steps were repeated in SIM mode for six selected compounds*
  - *All scan and SIM data reported in application note*

O·I·Analytical

Analysis of Real-World Samples



Drinking water from Wellborn, TX

O·I·Analytical

Analysis of Real-World Samples (cont.)

Compound	Bryan, TX	College Station, TX	Wellborn, TX	Bottled Water Facility
Surrogate Standard % Recovery				
MTBE-d3	102	104	104	104
4-Bromofluorobenzene	97	98	98	99
1,2-Dichlorobenzene-d4	101	102	102	104
Target Compound Concentration Detected Above the MRL (ppb)				
Tetrahydrofuran	< MRL	92.7	< MRL	< MRL
Chloroform	1.2	1.0	5.8	< MRL
Bromodichloromethane	4.4	5.6	22.1	< MRL
Dibromochloromethane	14.2	16.1	71.6	< MRL
Bromoform	20.7	17.0	111.0	< MRL

Results from analysis of four different samples of finished drinking water, full scan mode. Only compounds with concentrations above the MRL of 0.5 ppb are listed.

O·I·Analytical

Supporting Materials From OI

- Copies of the final method and the Federal Register are available from our sales department
- Application note 3500
  - *Description of some of the key changes*
  - *Recommended operating conditions*
  - *Full set of supporting data*
- New trap specific for method 524.3
  - *PN 326720*
- New standard kit, five vials plus MSDS
  - *PN 326721*
  - *Five vials: three Internal Standards, three Surrogate Standards, six gases, 1,3-butadiene, 69 target compounds*

O·I·Analytical

Next at the EPA

- The next VOC method to be developed by the U.S. EPA Office of Water will be Method 524.4
- They will develop the requirements for using nitrogen as a purge gas in place of helium for VOC methods

Thank you.
Q&A

Publication Number: 35420909 (PDF)
Recorded Webinar: 3544 (WMV)

Opportunity through Innovation™