Analysis of Volatile Organic Compounds (VOCs) by Proposed U.S. EPA Method 524.3

Presented at the 2009 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Chicago, Illinois March 8–March 13, 2009

Introduction

Over the last two years, the U.S. EPA Office of Groundwater and Drinking Water has conducted extensive studies (1) in preparation for release of an updated method for the "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry", U.S. EPA Method 524.3 (2). As a result of their research, the draft method includes several significant changes and improvements over its predecessor, U.S. EPA Method 524.2 (3).

Proposed U.S. EPA Method 524.3 has a modified analyte list. Compounds that are not regulated or that are of lesser environmental interest, and some of the poor performers have been deleted. Fuel oxygenates and several compounds from the Contaminant Candidate List (CCL3) have been added to the method. The revised method includes a new sample-preservation scheme that does not require transporting hazardous materials to the field and does not employ hydrochloric acid. Most importantly, the proposed new method includes criteria that will permit analysts to modify currently prescriptive portions of the method while maintaining data quality. The new method will permit the analyst to select P&T and GC conditions appropriate for their instrumentation, including five key P&T parameters that can be modified within specified ranges: sample temperature (ambient to 60 °C), purge flow rate (20 to 200 mL/minute), total purge volume (240 to 680 mL), desorb time (0.2 to 4 minutes), and total of purge volume plus dry purge volume (240 to 880 mL). The new method will also allow Selected Ion Monitoring (SIM) mode for low-level detection of some compounds.

This paper presents data acquired with optimized P&T operating parameters for use with proposed U.S. EPA Method 524.3.

Experimental

Instrumentation used in this study was an OI Analytical Eclipse 4660 Purge-and-Trap (P&T) Sample Concentrator with the Model 4551A Water Vial Autosampler (Figure 1), and the Agilent 7890/5975 GC/MS.

Figure 1. OI Analytical Eclipse 4660 P&T Sample Concentrator with
Model 4551A Water Vial Autosampler and Standard Addition Module (SAM)

A set of experiments was designed to demonstrate the relative performance of the proposed new method using a 5-mL sample and three different purge gas volumes: 440 mL (40 mL/min for 11 minutes), 280 mL (40 mL/min for 7 minutes), and 300 mL (60 mL/min for 5 minutes). Optimum sample temperature (40 °C) and the benefits of a shortened desorb time (0.5 to 1 minute) have been fully characterized for the Eclipse in previous work (4). Operating conditions for the P&T and the GC/MS are shown in Table 1.

.

Table 1: Instrument Operating Conditions for Proposed U.S. EPA Method 524.3

Purge-and-Trap	**Eclipse 4660 P&T Sample Concentrator**
Sample Size/Temperature	5–mL sample, 40 °C during Purge
Purge Gas	Helium
Purge Conditions	11 minutes at 40 mL/min (440–mL purge volume) 7 minutes at 40 mL/min (280–mL purge volume) 5 minutes at 60 mL/min (300–mL purge volume)
Desorb Preheat	ON, 180 °C
Desorb Conditions	1 minute at 190 °C
Bake Conditions	5 minutes at 210 °C
Six-Port Valve and Transfer Line Temperatures	110 °C
Water Management Temperatures	110 °C during Purge 0 °C (ambient) during Desorb 240 °C during Bake
P&T Cycle Time	12 minutes (with 5–min Purge)
Gas Chromatograph	**Agilent 7890**
Inlet	Split/splitless, 4–mm I.D. glass liner with single gooseneck, 35–to–1 split
Column	Restek Rtx®-624, 30–meter x 0.25–mm I.D. x 1.4 –μm film 0.8 mL/minute He (constant flow mode)
Oven Program	45 °C for 4.5 minutes 12 °C/minute to 100 °C (0 minutes) 25 °C/minute to 240 °C (hold 1.3 minute)
GC Run Time	16 minutes plus cool down
Mass Spectrometer	**Agilent 5975**
Solvent Delay	1.75 minutes
Tune File	bfb.u (not modified)
MS Source Temperature MS Quad Temperature	230 °C 150 °C
MS Mode	Scan (35 to 260)/SIM
SIM Compounds	Chloromethane, m/z 50 and 52 Bromomethane, m/z 94 and 96 *t*-Butyl alcohol, m/z 41 and 59 Trichloroethylene, m/z 95 and 130 1, 2–Dibromo-3-chloropropane, m/z 75 and 155

A complete proficiency study was conducted for each set of operating conditions, including a 7-point calibration curve (0.5 to 100 ppb), an MDL determination, and precision and accuracy tests.

Results and Discussion

The initial series of tests was designed to determine the relative response of all compounds in the modified 524.3 analyte list using different purge gas volumes. Compound responses from MS scan mode using 280 mL and 300 mL of purge gas are compared to responses using a 440 mL and normalized to 100% (Figure 2). Most compounds displayed slightly improved response using the 300–mL purge volume (60 mL/minute for 5 minutes). Several compounds (e.g. *t*-butyl alcohol) had reduced response and were selected for analysis using MS, SIM mode in the subsequent proficiency studies. A Total Ion Chromatogram (TIC) of a mid-point calibration standard is shown in Figure 3 with an insert highlighting the chromatography of the first six, early-eluting compounds.

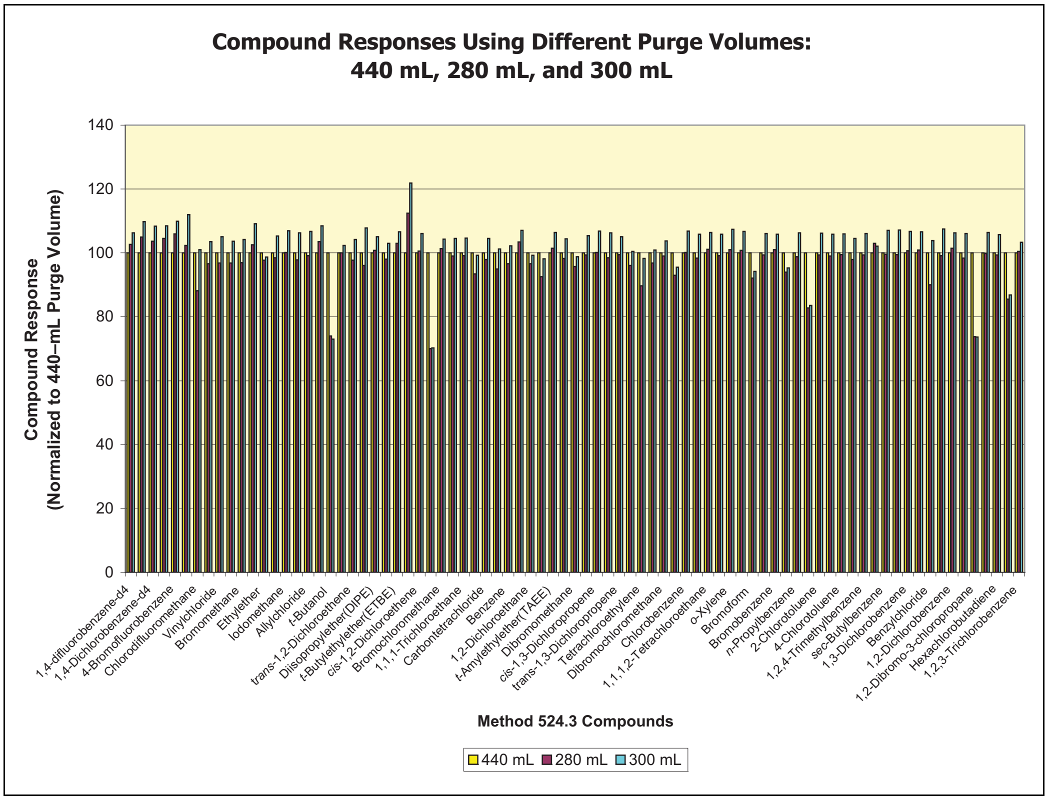

Figure 2. Compound responses using different purge gas volumes: 440 mL (normalized to 100%), 280 mL, and 300 mL.

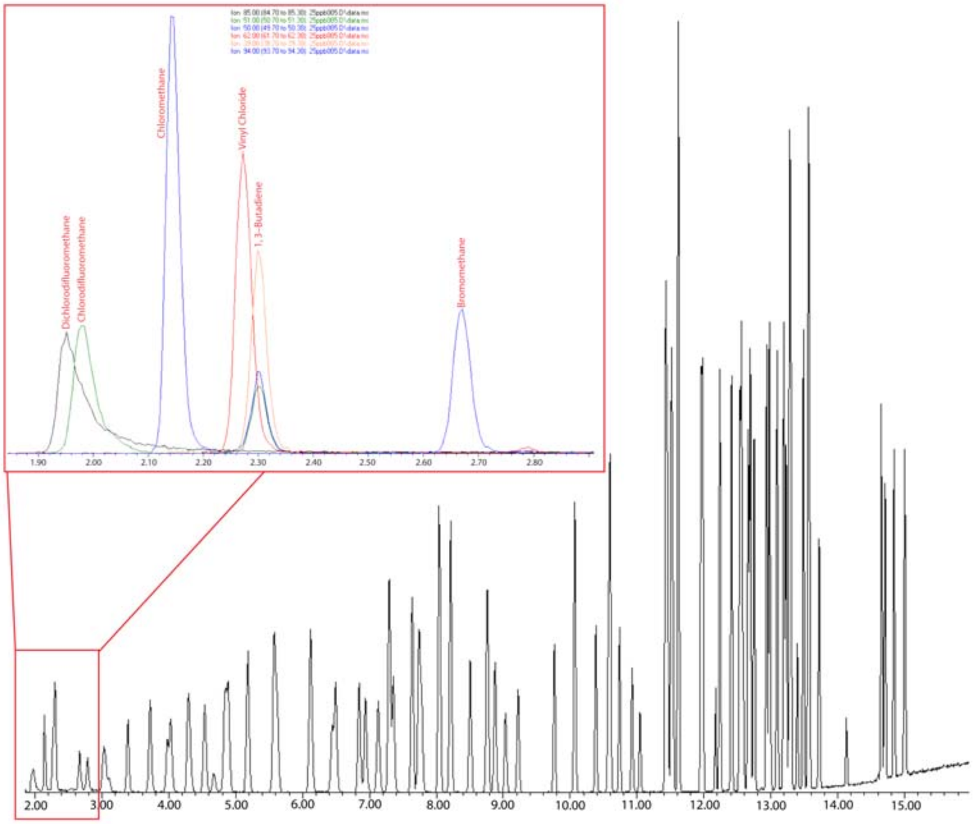

Figure 3. TIC of a mid-point calibration standard including the six new fuel oxygenates and the four new CCL3 compounds. The insert shows the Extracted Ion Current Profiles (EICPs) of the early-eluting compounds.

Selected data from the proficiency studies are shown in Table 2. Two internal standards (IS), 1, 4-difluorobenzene and chlorobenzene-d_5, were used for generating response factors (RF). A third IS suggested by the proposed method, 1, 4-dichlorobenzene-d_4, was not used because it co-eluted with one of the target analytes on the chosen column. Two of the three suggested surrogates were included in the study; the third surrogate on the chosen column, MTBE-d_3, could not be found commercially. The required MDL study was performed using the method described in Appendix B to Part 136 in the Federal Register (5).

Table 2: Partial performance statistics for proposed U.S. EPA Method 524.3 using two different purge gas volumes. Average Response Factors (RF) and percent Relative Standard Deviations (%RSD) are for 7-point calibration curves from 0.5 to 100 ppb; compounds new to the method are shown in red.
(See pages 6 and 7)

Compound Name	280 mL Purge Volume Calibration		300 mL Purge Volume Calibration		Proficiency Study		
	Avg RF	%RSD	Avg RF	%RSD	MDL (ppb)	Precision (%RSD, n = 8)	Accuracy (%Recy, 10 ppb)
Dichlorodifluomethane	0.27	9.9	0.26	9.6	0.17	4.2	104
Chlorodifluoromethane	0.22	9.0	0.25	9.9	0.28	5.7	91
Chloromethane†	0.69	9.8	0.66	9.1	0.15	2.6	112
Vinyl chloride	0.63	8.9	0.64	7.9	0.25	3.2	97
1,3-Butadiene	0.41	10.3	0.39	7.0	0.20	2.7	99
Bromomethane†	0.26	8.7	0.25	5.9	0.11	2.2	118
Trichloromonofluoromethane	0.65	5.9	0.60	4.1	0.11	1.4	110
Ethyl ether	0.56	9.5	0.52	6.6	0.13	1.9	101
1,1-Dichloroethane	0.36	7.3	0.36	5.3	0.12	1.9	94
Iodomethane	0.70	5.1	0.69	2.2	0.13	1.5	103
Carbon disulfide	1.25	7.6	1.23	3.9	0.09	2.3	96
Allyl chloride	0.23	7.9	0.23	4.9	0.11	2.4	97
Methyl acetate	0.46	4.4	0.45	7.5	0.15	8.8	106
Methylene chloride	0.49	5.7	0.47	5.7	0.09	1.6	97
t-Butyl alcohol (TBA)*†	0.08	5.6	0.08	10.2	0.12	4.9	94
Methyl-*t*-butyl ether (MTBE)	1.33	2.6	1.29	2.9	0.19	1.4	109
trans-1,2-Dichloroethene	0.41	6.6	0.41	8.1	0.11	1.7	98
n-Hexane	0.89	14.5	0.99	12.7	0.05	2.2	73
Diisopropyl ether (DIPE)	1.91	1.6	1.84	3.1	0.07	0.9	121
1,1-Dichloroethane	0.99	4.9	0.97	3.2	0.08	1.5	105
t-Butyl ethyl ether (ETBE)	1.89	1.7	1.82	2.9	0.06	1.0	114
2,2-Dichloropropane	0.50	11.9	0.50	10.4	0.16	2.6	117
cis-1,2-Dichloroethene	0.46	6.8	0.46	5.5	0.28	1.8	98
Tetrahydrofuran	0.06	11.6	0.05	4.6	0.10	3.6	92
Bromochloromethane	0.24	5.7	0.23	3.8	0.20	1.8	102
Chloroform	0.79	5.3	0.76	3.2	0.06	1.0	106
1,1,1-Trichlorethane	0.71	4.9	0.68	3.6	0.12	2.2	111
1-Chlorobutane	1.19	4.7	1.17	3.3	0.10	1.9	104
Carbon tetrachloride	0.64	4.8	0.61	2.7	0.08	2.0	111
1,1-Dichloropropane	0.55	6.1	0.55	4.3	0.08	2.8	96
Benzene	1.51	4.2	1.52	2.7	0.04	1.3	96
t-Amyl methyl ether (TAME)	1.21	2.2	1.19	3.4	0.06	1.2	107
1,2-Dichloroethane	0.76	4.2	0.72	2.9	0.10	1.4	114
Trichloroethylene†	0.46	9.3	0.43	5.0	0.09	1.8	99
t-Amyl ethyl ether (TAEE)	1.45	2.8	1.41	2.6	0.10	1.0	113
1,2-Dichloropropane	0.52	3.8	0.52	2.0	0.10	1.7	98
Dibromomethane	0.28	4.2	0.27	2.6	0.15	2.5	100
Bromodichloromethane	0.62	3.1	0.61	2.3	0.09	1.5	102
cis-1,3-Dichloropropene	0.65	2.6	0.67	3.4	0.10	1.6	92
Toluene	0.97	4.4	0.98	3.0	0.11	1.9	95
trans-1,3-Dichloropropene	0.66	3.9	0.68	2.5	0.11	1.7	93

Compound Name	280 mL Purge Volume		300 mL Purge Volume				
	Calibration		Calibration		Proficiency Study		
	Avg RF	%RSD	Avg RF	%RSD	MDL (ppb)	Precision (%RSD, n = 8)	Accuracy (%Recy, 10 ppb)
1,1,2-Trichloroethane	0.33	4.8	0.33	3.7	0.12	1.8	90
Tetrachloroethylene	0.83	19.3	0.71	15.0	0.07	2.8	67
1,3-Dichloropropane	0.64	3.1	0.63	3.6	0.11	1.2	93
Dibromochloromethane	0.51	2.4	0.50	1.6	0.11	1.2	100
1,2-Dibromoethane	0.43	2.7	0.42	2.6	0.17	2.0	97
Chlorobenzene	1.21	3.8	1.22	4.0	0.10	1.3	95
Ethylbenzene	2.02	2.8	2.05	2.8	0.07	1.4	96
1,1,1,2-Tetrachloroethane	0.46	3.2	0.46	1.7	0.10	1.1	105
m/p-Xylene	1.56	3.2	1.56	2.7	0.09	2.1	98
o-Xylene	0.77	2.6	0.76	2.5	0.06	1.7	100
Styrene	1.34	1.3	1.33	3.7	0.06	1.7	100
Bromoform	0.40	4.0	0.38	4.3	0.10	1.2	105
1,2-Dichlorobenzene (SS)	0.49	0.8	0.48	1.3	0.05	3.2	105
Isopropylbenzene	2.06	2.9	2.07	3.4	0.06	1.6	100
4-Bromofluorobenzene (SS)	0.50	1.6	0.50	0.6	0.04	3.5	106
Bromobenzene	0.60	4.5	0.58	4.0	0.06	1.3	104
1,1,2,2-Tetrachloroethane	0.49	4.9	0.52	4.8	0.11	1.4	99
n-Propylbenzene	2.41	4.1	2.41	3.0	0.06	1.6	102
1,2,3-Trichloropropane	0.44	2.9	0.43	4.6	0.13	1.4	104
2-Chlorotoluene	1.66	3.1	1.66	4.1	0.08	2.0	104
1,3,5-Trimethylbenzene	1.74	3.5	1.76	3.4	0.05	1.2	104
4-Chlorotoluene	1.55	3.8	1.53	3.8	0.09	1.0	104
tert-Butylbenzene	1.51	3.1	1.50	3.8	0.07	1.7	106
1,2,4-Trimethylbenzene	1.80	2.8	1.77	2.5	0.09	1.4	105
Pentachloroethane	0.07	14.3	0.15	13.2	0.22	2.3	99
sec-Butylbenzene	2.21	3.6	2.22	3.5	0.06	1.9	101
p-Isopropyltoluene	1.93	4.0	1.93	3.0	0.07	2.1	103
1,3-Dichlorobenzene	1.04	8.1	1.00	3.4	0.10	1.7	105
1,4-Dichlorobenzene	1.08	8.2	1.06	5.6	0.08	1.5	100
Benzyl chloride	0.58	7.1	0.72	5.9	0.15	3.9	98
n-Butylbenzene	1.73	4.8	1.75	4.3	0.06	2.1	100
1,2-Dichlorobenzene	0.99	3.8	0.99	6.4	0.08	1.3	100
Hexachloroethane	0.37	3.6	0.38	4.4	0.09	2.1	99
1,2-Dibromo-3-chloropropane†	0.13	14.7	0.12	9.9	0.06	1.4	104
1,2,4-Trichlorobenzene	0.90	7.5	0.87	4.2	0.11	1.5	103
Hexachlorobutadiene	0.46	8.1	0.46	6.0	0.12	2.5	103
Naphthalene	1.91	2.7	1.85	3.6	0.08	1.5	99
1,2,3-Trichlorobenzene	0.82	5.9	0.80	4.9	0.11	1.0	102

† Compounds acquired and quantified in the MS SIM mode.

* *t*-Butyl alcohol was present in the mix at a concentration 5 times higher than the other compounds.

All compounds on the list for Method 524.3 including the ten new compounds, six fuel oxygenates, and four CLL3 compounds easily passed the calibration and proficiency study criteria established for the proposed method using all three sets of P&T conditions. Five compounds were considered good candidates for SIM mode because they had poor response in scan mode and were baseline separated from close eluters in the chromatogram. Tetrahydrofuran also had a low response, but was not analyzed using SIM mode because of close eluting compounds. Using a different column or slightly different GC conditions may allow the analyst to add compounds to the SIM list.

Summary and Conclusions

Proposed U.S. EPA Method 524.3 allows significant changes which will improve the performance of the method while providing the user latitude to optimize instrument parameters. The data shown here demonstrate that using a reduced purge volume of 300 mL (60 mL/minute for 5 minutes) produces data that exceeds all performance criteria for the proposed method and reduces the P&T cycle time by 6 minutes. Using the SIM mode improves response and lowers the detectable limits for some compounds that have historically challenged VOC chemists. Reducing the Purge, Desorb, and Bake times, and eliminating the Dry Purge step will shorten overall cycle time and improve method performance. They also have the added advantage of minimizing the amount of helium required by the method, reducing laboratory operating cost.

References

1. Munch, D.; Pepich, B. *In Validation of Proposed EPA Method 524.3 for the Determination of Volatile Organic Compounds in Drinking Water,* AWWA WQTC, Cincinnati, OH, 2008.

2. Prakash, B; Munch, D.J.; Pepich, B.V. Method 524.3, Draft Version 1.0, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry.* U.S. Environmental Protection Agency. Cincinnati, OH, January 2009

3. Method 524.2, Revision 4.0, *Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry.* U.S. Environmental Protection Agency. Cincinnati, OH, 1992.

4. OI Analytical Application Note, *Techniques for Reducing Purge and Trap Cycle Times in VOC Analysis*, Publication #3012

5. Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11. Federal Register, 49, 198–199 (1984).

Acknowledgements

The analytical standards and capillary column used for this project were provided by Restek Corporation.

O·I·Analytical
P.O. Box 9010
College Station, TX 77842-9010
Tel: (979) 690-1711 • Fax: (979) 690-0440 • www.oico.com