

A Quick, Sensitive Solution for Meeting Short Holding Times for VOAs in Drinking Water

Key Words

- Environmental
- TRACE DSQ
- VOAs
- EPA 524.2
- Volatiles

Chromatography and Mass Spectrometry GC/MS Application Note #9197

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Overview

Purpose: Shorten the analysis time for volatile organics in drinking water using a 5 mL sample.

Methods: EI Full-Scan GC/MS analysis of volatile organics in drinking water by thermal desorption from a purge and trap concentrator using a 5 mL sample. A split injection was made into a narrow-bore capillary column using a bent-optics quadrupole, the Finnigan™ TRACE DSQ™.

Results: The tuning criteria for EPA Method 524.2 Rev 4 was met using the Classical Autotune and the EPA Tune File. The linear range was established from 0.4 to 40 ppb (injector split 30/1) and 0.4 to 200 ppb (injector split 200/1) with relative percent standard deviations (%RSD) in the single-digit range for most of the analytes except for a few solvent contaminants found in the lab: methylene chloride, acetone and THF. Replicate runs were made at 0.2 ppb, generating ppt-level MDLs for the target compounds listed in EPA Method 524.2 Rev 4.1. The analysis time was 10 minutes, with identification of all target compounds in the method using fast scanning on the TRACE DSQ quadrupole system.

Introduction

The analysis of volatile organics in drinking water has gone through two very significant changes in the last few years: enhanced sensitivity and shorter run times. The increased sensitivity is attributed to the introduction of a new bent-optics quadrupole, the TRACE DSQ (Figure 1). This quadrupole has a pre-filter that bends the ion beam off-axis to reduce the neutral noise that adversely effects sensitivity. Shorter run times are made possible by the faster scanning rate of the DSQ (up to 10,000 scans/sec) coupled

with the higher resolving power of the narrow-bore Restek Rtx®-VMS, 0.18 mm x 20 meter 1.0 micron film volatile analysis capillary column. Using a shorter, smaller i.d. column, with a thinner film enhances sensitivity because the time in the column is shortened, resulting in less peak broadening and sharper peaks. These smaller i.d. columns work best with very sensitive mass specs that are able to operate at high inlet split flows. Water and methanol make up the bulk of the matrix in these samples. If a high split flow, in excess of 20 mL/min is used, most of the methanol and water may be diverted out the split vent to prevent peak distortion. The complete analysis is now performed in 10 minutes using only a 5 mL sample. No cryogenic oven cooling was required for separation of the early eluting gases.

Methods

The instrument system was comprised of the TRACE™ GC Ultra with a split/splitless injector and 1000 KPA electronic digital pressure flow controller (DPFC), and a Silcosteel® interface to the Tekmar 3100 Purge and Trap using a VOCARB 3000 sorbant trap. The DSQ was tuned for Classical Tune and the EPA Tune File was used to meet the tuning criteria for BFB (Figure 2). The oven was programmed from 50 °C to 230 °C. The internal standard was spiked automatically at 5 ppb by the Tekmar Aquatek 70 autosampler. The data was processed using the new EnviroLab™ Forms package. This package includes the following forms for measuring whether the instrument is “in control” and data reporting for high sample throughput:

Initial Calibration Report, Continued Calibration Report, Internal Standard Summary Report, Tune Report, Quantitation Report, Blank Report, Surrogate Recovery Report, Matrix Spike Matrix Spike Duplicate Recovery Report, Method Validation Report, and Method Detection Limit Report.

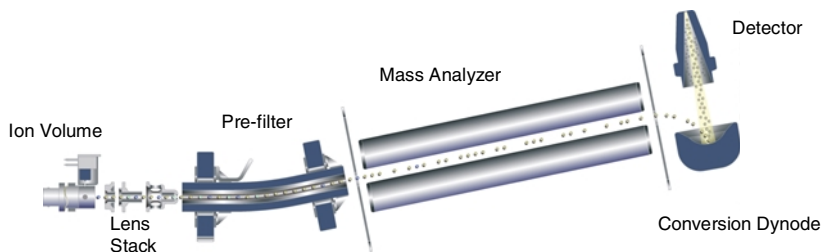


Figure 1: Finnigan TRACE DSQ Bent-Optics Quadrupole

Instrument Parameters:

Finnigan TRACE DSQ Mass Spectrometer:

Tune: Classical Tune
 Lens 1: -25 volts, Lens 2: -6.8 volts, Lens 3: -25 volts, Pre-filter Offset: -4.3
 Electron Lens: 15.0, Electron Energy: -70 volts, Emission Current: 100 microamps
 Resolution Factors:
 1 Start Mass 1.0 Ion Offset: 3.9 Resolution Factor: 1.8
 2 Start Mass 1050 Ion Offset: 3.4 Resolution Factor: 2.8
 Scaling Factors:
 Start Mass: 35 Start Scale: 1000 End Scale: 1000
 Start Mass: 169 Start Scale: 700 End Scale: 700
 Acquisition Time: GC Run Time, Acq Threshold: 0
 Source Temperature: 200 °C
 Segment 1:
 Start Time: 0.0 minutesc
 Detector Gain: 1.0 x 10⁵ (941 volts) Split Flow of 30 mL/min
 Detector Gain: 2.0 x 10⁵ (1000 volts)
 Scan Event 1:
 Scan Rate: 854.2 scans/sec or 0.29 sec/scan, Mass Defect; 0
 Scan Mode: Full Scan First Mass: 35 Last Mass: 260

Results

Since the analysis of volatile organics is time sensitive, the instrument method was designed for high throughput. With the enhanced sensitivity of the TRACE DSQ, the chromatographer can take advantage of the higher theoretical plates available with the Rtx-VMS 0.18 mm i.d. x 20 meter short column with a thinner stationary film (1.0 micron). A 5 mL sample was used instead of 25 mL to provide better partitioning of the polar organics from the liquid to the gas phase during the purge mode. The starting oven temperature was 50 °C for the 30/1 split and 40 °C for the 200/1 split. The actual GC cycle time was 13 minutes. The last analyte eluted at 10 minutes. In order to widen the dynamic range of the method, a higher split flow may be used. The analysis was also performed at a split flow of 200 mL/min with the Detector Gain at 2 (Figure 3 on page 4). The initial oven temperature was lowered to 40°C to sharpen the first six gases (Figure 4).

A 5 mL sample of organic-free water was spiked at various concentrations to show the linear working range of the DSQ, from 0.4 to 40 µg/L (Split 30/1) and 0.4 to 200 ppb (Split 200/1) in Table 1 on page 3. The sensitivity of the instrument was determined by a measurement of the precision, Method Detection Limit (MDL), of nine replicate runs at 0.2 ppb (Split 30/1) as shown in Table 2.

TRACE GC:

Oven: 50 °C, 4 min; 18 °C/min, 100 °C, 0 min, 40 °C/min; 230 °C, 3min. (Split Flow: 30 mL/min)
 Oven: 40 °C, 4 min; 18 °C/min, 100 °C, 0 min, 40 °C/min; 230 °C, 3min. (Split Flow: 200 mL/min)
 Carrier Gas: 25 psi constant pressure
 Split Flow: 30 mL/min (0.4 to 40 ppb) or 200 mL/min (0.4 to 200 ppb)
 Inlet: 150 °C, Transfer line: 230 °C
 Column: Restek Rtx®-VMS 0.18 mm x 20 meter, 1.0 micron film

Tekmar 3100 Purge and Trap Concentrator:

Trap: VOCARB 3000, Sample Size: 5 mL
 Purge Flow: 40 mL/min, Purge 11 min., Dry Purge 2 min.
 Transfer line Temperature: 150 °C, MCS Line Temperature: 40 °C
 GC Start: Start at Desorb, Desorb Preheat Temperature: 245 °C, Desorb: 250 °C, Desorb 4 min.
 Bake: 260 °C, Bake 6 min, MCS Bake Temperature: 300 °C

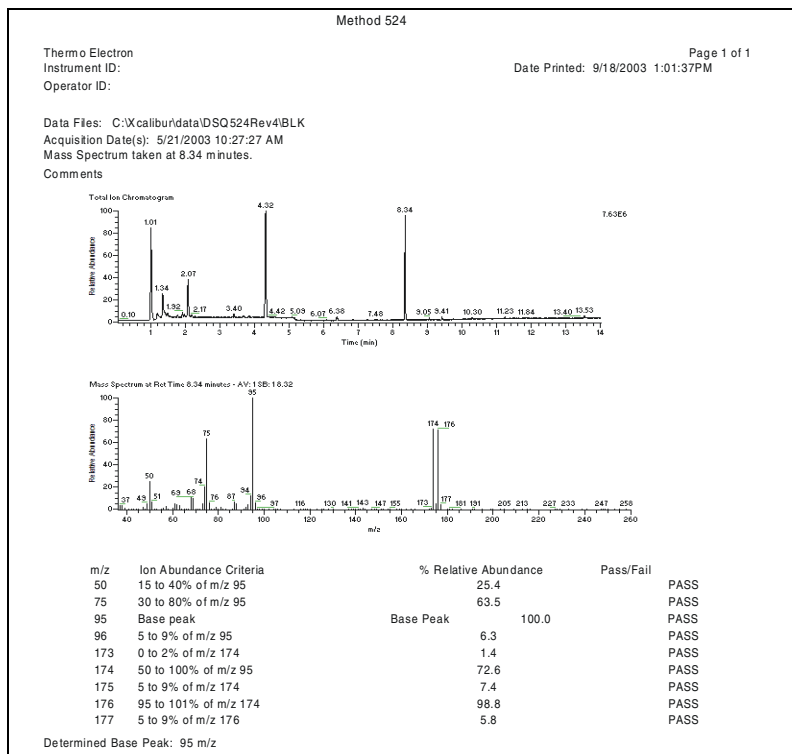
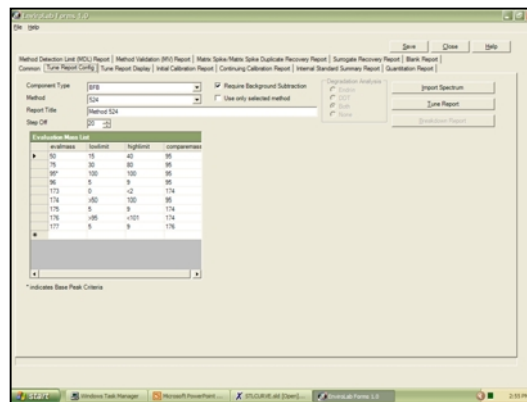


Figure 2: BFB Tune Report from EnviroLab Forms

Table 1: Calibration Curve (0.4-40 ppb) Split 30/1 and (0.4 ppb - 200 ppb) Split 200/1

	Split 30/1		Split 200/1	
	RRF	%RSD	RRF	%RSD
dichlorodifluoromethane	0.075	6.6	0.395	9.5
chloromethane	0.159	12.2	0.481	11.5
vinylchloride	0.195	7.3	0.561	8.6
bromomethane	0.098	14.8	0.150	12.8
chloroethane	0.140	5.3	0.217	6.3
trichlorofluoromethane	0.264	8.9	0.497	3.4
diethylether	0.241	8.0	0.360	8.0
1,1-dichloroethylene	0.199	7.4	0.367	5.2
carbonylsulfide	1.048	5.1	1.239	6.0
iodomethane	0.235	18.3	0.132	32.4
allyl_chloride	0.153	5.4	0.116	21.3
methylene_chloride	0.324	22.5	1.060	6.5
acetone	1.722	139.6	0.683	143.0
trans 1,2-dichloroethylene	0.238	4.8	1.261	3.8
MTBE	0.922	5.3	1.225	8.5
1,1-dichloroethane	0.476	5.6	0.625	10.5
acrylonitrile	0.096	4.1	0.139	3.8
cis 1,2_dichloroethylene	0.259	5.1	1.290	5.0
2,2-dichloropropane	0.354	5.5	0.625	10.5
bromochloromethane	0.118	4.9	0.141	6.1
chloroform	0.458	5.2	0.718	5.9
methylacrylate	0.223	9.1	0.277	27.0
carbon_tetrachloride	0.287	6.1	0.542	7.2
THF	0.174	85.7	0.133	13.5
1,1,1-trichloroethane	0.305	3.9	1.103	5.7
dibromofluoromethane*			0.418	5.2
2-butanone	0.144	27.0	0.187	9.1
1,1-dichloropropylene	0.379	6.4	0.987	6.5
1-chlorobutane	0.439	5.1	0.839	7.7
benzene	1.252	4.2	1.917	3.1
methacrylonitrile	0.130	5.1	0.263	11.4
1,2-dichloroethane	0.358	6.3	0.372	7.4
trichloroethylene	0.227	5.1	0.476	3.1
dibromomethane	0.147	6.0	0.236	7.7
1,2-dichloropropane	0.283	6.1	0.255	4.4
bromodichloromethane	0.333	3.5	0.317	6.2
methylmethacrylate	0.183	5.9	0.167	12.7
cis-1,3-dichloropropene			0.089	13.0
toluene-d8*			1.035	1.9
toluene	0.588	3.6	1.932	14.7
1,1-dichloropropane			0.034	17.7
2-nitropropane	0.090	7.5		
tetrachloroethylene	0.493	6.9	0.439	6.4
4-methyl-2-pentanone	0.148	3.6	0.137	42.2
trans-1,3-dichloropropene			0.611	15.5
1,1,2-trichloroethane	0.200	4.9	0.57	5.6
ethylmethacrylate	0.335	6.3	0.23	17.5
dibromochloromethane	0.205	7.5	0.25	9.9
1,3-dichloropropane	0.416	4.6	0.53	5.4
1,2-dibromoethane	0.196	4.4	0.2	9.9
2-hexanone	0.126	11.2	0.16	9.8
chlorobenzene	0.632	3.6	0.9	4.3
ethylbenzene	1.023	3.0	1.89	7.4
1,1,1,2-tetrachloroethane	0.227	5.2	0.3	6.4
m + p-xylene	0.788	3.1	1.72	3.8
o-xylene	0.370	3.6	1.68	5.3
styrene	0.626	5.1	0.89	10.9
bromoform	0.122	6.9	0.14	12.3
isopropylbenzene	0.927	2.3	1.8	6.6
BFB*	0.233	4.1	0.47	2.2
bromobenzene	0.263	3.3	0.36	8.1
n-propylbenzene	1.019	3.8	1.58	5.9
1,1,2,2-tetrachloroethane	0.290	4.0	0.33	4.2
2-chlorotoluene	0.666	3.8	0.35	4.5
1,2,3-trichloropropane	0.258	8.2	0.29	4.8
1,3,5-trimethylbenzene	0.671	3.2	1.76	6.4
trans-1,4-dichloro-2-butene	0.070	6.3	0.13	20.5
4-chlorotoluene	0.604	3.6	0.37	5.9
tert-butylbenzene	0.637	4.2	1.06	3.2
1,2,4-trimethylbenzene	0.664	3.7	1.07	6.2
sec-butylbenzene	0.891	3.3	1.49	4.8
p-isopropyltoluene	0.744	4.1	0.39	5.8
1,3-dichlorobenzene	0.505	4.6	2.47	5.4
1,4-dichlorobenzene	0.516	5.0	2.76	13.5
n-butylbenzene	0.652	3.2	3.74	5.8
hexachloroethane	0.149	5.4	0.35	18.7
1,2-dichlorobenzene	0.464	3.8	2.33	4.7
1,2-dibromo-3-chloropropane	0.042	7.5	0.47	10.6
nitrobenzene	0.018	13.5	0.11	4.9
hexachlorobutadiene	0.055	7.9	0.56	16.6
1,2,4-trichlorobenzene	0.147	8.5	1.09	15.6
naphthalene	0.492	5.2	4.27	14.7
1,2,3-trichlorobenzene	0.136	9.0	1.07	19.6
* Surrogate				
Fluorobenzene	9.5 %RSD			
perfluorobenzene			6.7% RSD	
chlorobenzene-d5			5.4 %RSD	
1,4-difluorobenzene			4.0 %RSD	
1,4-difluorobenzene-d4			4.5 %RSD	

Table 2: MDLs (µg/L) at 0.2 ppb Split 30/1

Split 30/1	MDL
dichlorodifluoromethane	0.049
chloromethane	0.033
vinylchloride	0.045
bromomethane	0.116
chloroethane	0.057
trichlorofluoromethane	0.084
diethylether	0.046
1,1-dichloroethylene	0.055
carbonylsulfide	0.055
iodomethane	0.071
allyl_chloride	0.070
methylene_chloride	0.092
acetone	0.864
trans 1,2-dichloroethylene	0.082
MTBE	0.045
1,1-dichloroethane	0.047
acrylonitrile	0.105
2,2-dichloropropane	0.198
bromochloromethane	0.064
chloroform	0.053
methylacrylate	0.068
carbon_tetrachloride	0.040
THF	0.751
1,1,1-trichloroethane	0.059
2-butanone	0.360
1,1-dichloropropylene	0.103
1-chlorobutane	0.049
benzene	0.050
methacrylonitrile	0.143
1,2-dichloroethane	0.029
fluorobenzene	6.35%RSD
trichloroethylene	0.070
dibromomethane	0.065
1,2-dichloropropane	0.194
bromodichloromethane	0.048
methylmethacrylate	0.038
toluene	0.039
2-nitropropane	0.073
tetrachloroethylene	0.041
4-methyl-2-pentanone	0.136
1,1,2-trichloroethane	0.036
ethylmethacrylate	0.031
dibromochloromethane	0.034
1,3-dichloropropane	0.037
1,2-dibromoethane	0.034
2-hexanone	0.116
chlorobenzene	0.034
ethylbenzene	0.035
1,1,1,2-tetrachloroethane	0.045
m + p-xylene	0.038
o-xylene	0.046
styrene	0.033
bromoform	0.043
isopropylbenzene	0.037
BFB	0.368
bromobenzene	0.031
n-propylbenzene	0.039
1,1,2,2-tetrachloroethane	0.027
2-chlorotoluene	0.049
1,3,5-trimethylbenzene	0.037
1,2,3-trichloropropane	0.028
trans-1,4-dichloro-2-butene	0.033
4-chlorotoluene	0.047
tert-butylbenzene	0.039
1,2,4-trimethylbenzene	0.033
sec-butylbenzene	0.040
p-isopropyltoluene	0.039
1,3-dichlorobenzene	0.033
1,4-dichlorobenzene	0.038
n-butylbenzene	0.049
hexachloroethane	0.035
1,2-dichlorobenzene	0.034
1,2-dibromo-3-chloropropane	0.046
nitrobenzene	0.193
hexachlorobutadiene	0.050
1,2,4-trichlorobenzene	0.054
naphthalene	0.042
1,2,3-trichlorobenzene	0.040

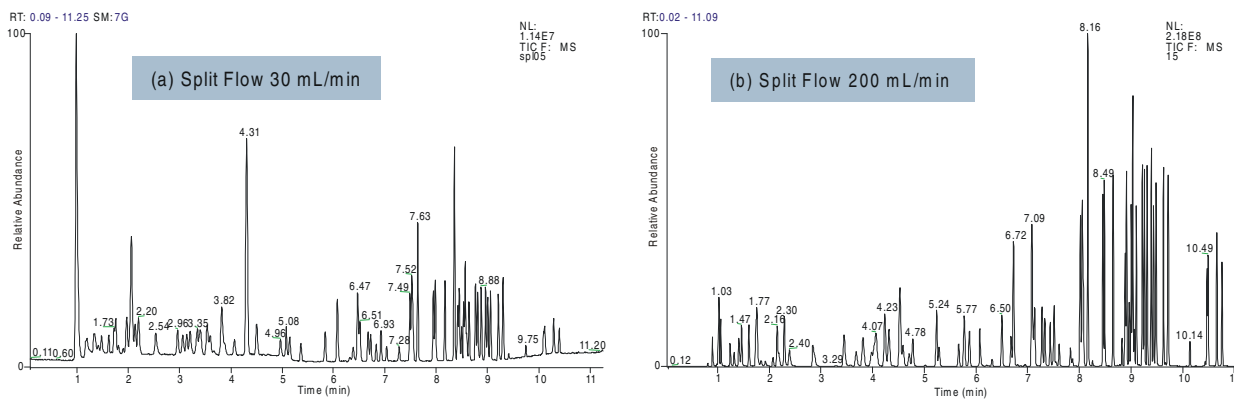


Figure 3: Total Ion Chromatogram for (a) 1.0 ppb and (b) 200 ppb

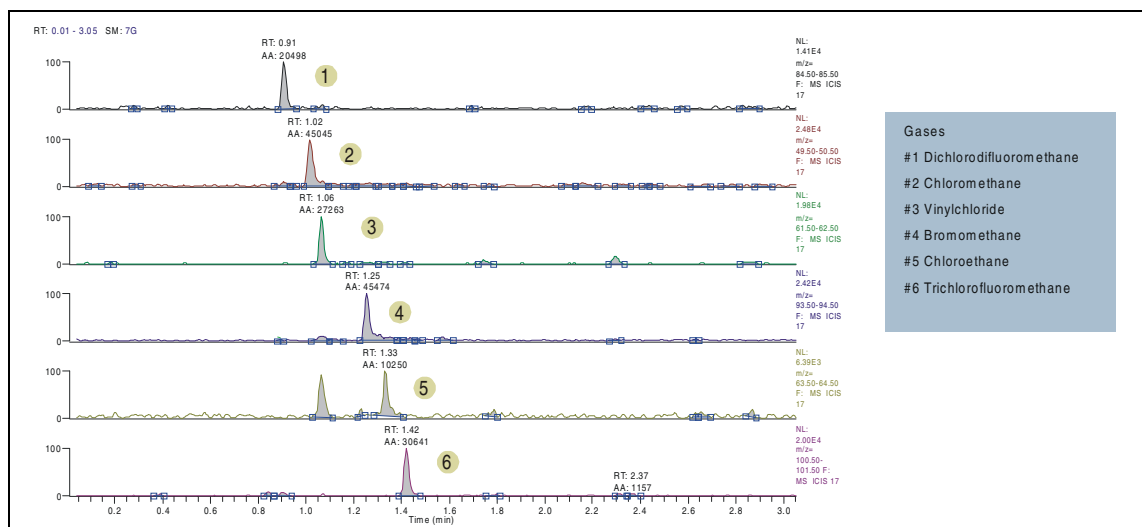


Figure 4: Extracted Ion Profile for first six gases (0.4 ppb) Split Flow 200 mL/min

Conclusions

A 5 mL sample provides sufficient sample volume for the MDL limits for EPA Method 524 Rev 4. The sensitivity of the new Finnigan TRACE DSQ opens the door to a new level of detection for volatile organics in drinking water. Replicates at 0.2 ppb were used to determine the MDLs for all compounds. The linear fit was from 0.4 to 40 ppb at a split of 30/1 and 0.4 to 200 ppb at a split of 200/1. The new EnviroLab Forms provided the complete package of quality control (QC) forms for rapid QC checks to facilitate data review for high sample throughput.

References

EPA Method 524.2 Rev 4.1 "Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry", National Exposure Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268

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