



# U.S. EPA VOLATILE ORGANICS METHOD 524.2 USING PURGE AND TRAP GC/MS

Cheri Coody, Public Health Laboratory, Mississippi State Health Department, Jackson, MS USA

Michael J. Burke and Elaine A. LeMoine, PerkinElmer Instruments, 761 Main Avenue, Norwalk, CT 06897 USA

## Introduction

Clean drinking water is of worldwide interest. Contaminants can compromise the quality of a water supply and cause short- and long-term health effects. Stringent water quality criteria help to ensure safe drinking water by requiring the detection and quantification of a wide variety of contaminants at extremely low levels. U.S. EPA Method 524.2 (1) provides the guidance necessary for identifying volatile organic pollutants at concentrations consistent with water quality objectives. The equipment and conditions presented here provide data compliant with the rigorous Method 524.2 criteria. It is applicable to a wide range of volatile organic compounds and provides the necessary sensitivity needed to meet drinking water standards. Detection limits, calibration results, precision and accuracy data are presented for the more commonly targeted compounds.

## Method Summary

This is a Gas Chromatography/Mass Spectrometry (GC/MS) method that uses the purge and trap technique for sample introduction. An aliquot of sample is purged of its volatile components by bubbling an inert gas through the sample. These compounds are then trapped on a sorbent material, heated, and backflushed into a gas chromatography (GC) column. Individual analytes are separated using chromatographic temperature programming and eluted to a mass spectrometer (MS) for detection. Identification is performed by comparing retention times and mass spectra to those obtained from known standards under identical conditions. Quantification is performed using the internal standard technique.

## Instrument Conditions

The equipment and conditions for the gas chromatograph, mass spectrometer, and purge and trap unit used to generate the data presented here are listed in Tables 1, 2, and 3. The GC column is connected to the MS transfer line using an open split interface. The interface consists of a 1/16" stainless steel Swagelok® "T" connector. A 0.92 x 0.12 mm i.d. x 0.1 mm 5% phenyl methylsilicone fixed restrictor is inserted into the PerkinElmer TurboMass™ GC/MS with the other end running straight through the connector and out the other end. The chromatography column has the fused silica transfer line at the detector end of the column removed and the "T" is connected directly to the glass column, allowing the fixed restrictor to be inserted directly inside the chromatography column. The restrictor is inserted to a distance equal to 3.5 turns of the glass column and the effluent is vented out the back of the instrument. This configuration is appropriate for low-level drinking water volatile organic analyses.

## Method Performance

### Tuning Criteria

To test instrument performance, a 25-ng (or less) standard solution of 4-bromofluorobenzene (BFB) is analyzed and the spectra compared to the abundance criteria listed in the method. Figure 1 demonstrates a successful BFB analysis to Method 524.2 abundance requirements using the above conditions.

### Calibration

Initially, a method calibration covering the entire analytical range for each target analyte is performed. Specific criteria must be met before samples can be analyzed. A minimum of three standards for a factor of 20 calibration range is required. A factor of 50 range requires at least four and a factor of 100 at least 5. The

**Table 1: Chromatographic Conditions**

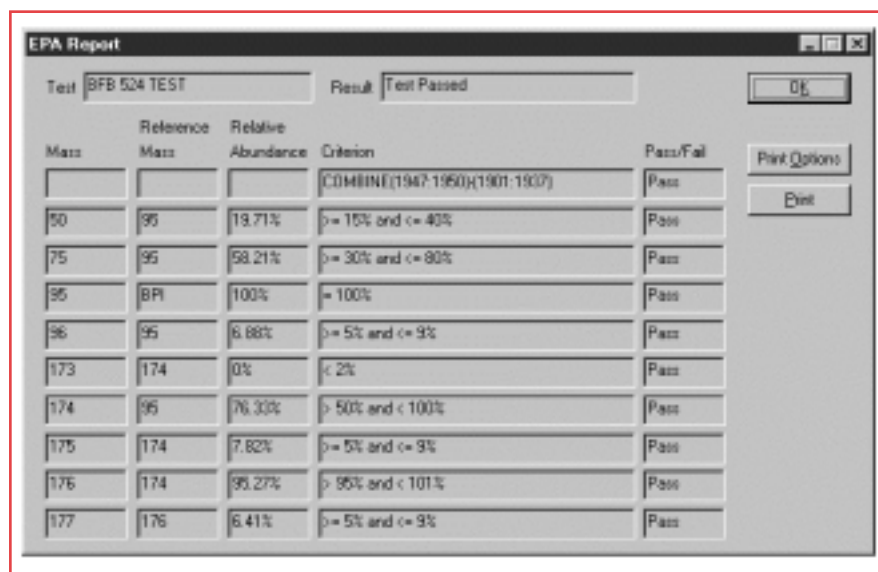
PerkinElmer AutoSystem XL GC	
Column	Vocol 60 m x 0.75 mm, 1.5- $\mu$ m film thickness
Oven Temperature Program	10°C for 5.00 min; 6°C/min to 75°C for 10.00 min; 15°C/min to 145°C for 5.00 min; 15°C/min to 160°C for 5.00 min
Coolant	Liquid CO <sub>2</sub>
Manual Pneumatic Control (PPC)	Helium at 15.0 mL/min
Packed Injector	100°C

**Table 2: Mass Spectrometer Conditions**

PerkinElmer TurboMass Mass Spectrometer	
Mass Scan Range	35-260 m/z
Scan Time	0.5 sec
Inter-scan Delay	0.13 sec
Filament Delay	2 min
Ion Source Temperature	150°C
Transfer Line Temperature	200°C
Ionization Mode	EI

**Table 3: Purge and Trap Conditions**

Tekmar LSC 3000 Sampler	
Purge Flow Gas	He at 40 mL/min
Time and Temperature Settings:	
Purge	11 min ambient
Desorb	4 min at 180°C
Bake	5 min at 220°C
Trap	Vocarb 3000
Sample Size	25 mL



**Figure 1.** Tune report.

calibration data presented here are the results of six standards, specifically 0.5, 1.0, 2.5, 5.0, 10.0, and 20.0 ppb (a factor of 40 range). Every calibration standard contains 10 ppb of the internal standard fluoroben-

zene and 1 ppb of the surrogate standard p-bromofluorobenzene.

Demonstration of initial calibration performance is based on a comparison of the calculated Relative Standard Deviation (RSD) of the

standard's Relative Response Factors (RRF) to a maximum threshold value. Response Factors are calculated using the formula:

$$RF = \frac{(A_x)(Q_{is})}{(A_{is})(Q_x)}$$

where:

RF = Response Factor,

$A_x$  = integrated abundance of the analyte quantitation ion,

$A_{is}$  = integrated abundance of the internal standard quantitation ion,

$Q_x$  = quantity of analyte purged in nanograms or concentration units, and

$Q_{is}$  = quantity of internal standard purged in nanograms concentration units.

The RSD is then calculated using the formula:

$$RSD = 100 (SD/\overline{RF})$$

where:

RSD = Relative Standard Deviation,

SD = Standard Deviation, and

$\overline{RF}$  = average relative Response Factor (of initial calibration standards).

The calculated %RSD for the initial calibration must be less than 20% to be considered compliant. Alternatively, a linear or second order regression calibration curve can be used by plotting:

$$A_x/A_{is} \text{ vs. } Q_x$$

The data presented in Table 4 list the %RSDs for a compliant calibration using the RSD test. Figure 2 exemplifies a compliant linear regression curve where the coefficient of determination is greater than or equal to 0.99.

### Precision and Accuracy

Precision and accuracy must be demonstrated initially by analyzing replicates of each analyte at a concentration of 2 – 5 µg/L. The measured concentrations are calculated and averaged. Accuracy is the percentage of the true value measured as % Recovery and precision is the Relative Standard Deviation of this value. Accordingly, the % Recoveries must comply with the 80-120% accuracy requirements and all

**Table 4: Compliant Initial Calibration**

Compound	%RSD	Compound	%RSD
Benzene	7.8	1,3-Dichloropropane	10.0
Bromobenzene	11.8	2,2-Dichloropropane	7.7
Bromochloromethane	8.5	1,1-Dichloropropene	3.7
Bromodichloromethane	6.7	cis-1,3-Dichloropropene	5.0
Bromoform	12.9	trans-1,3-Dichloropropene	4.6
Bromomethane	4.9	Ethylbenzene	9.5
n-Butylbenzene	7.9	Hexachlorobutadiene	5.3
sec-Butylbenzene	5.2	Isopropylbenzene	5.6
tert-Butylbenzene	5.0	4-Isopropyltoluene	5.2
Carbon tetrachloride	6.3	Methylene chloride	6.5
Chlorobenzene	10.7	Naphthalene	7.2
Chloroethane	3.0	n-Propylbenzene	8.5
Chloroform	9.2	Styrene	7.8
Chloromethane	15.5	1,1,1,2-Tetrachloroethane	11.1
2-Chlorotoluene	13.3	1,1,2,2-Tetrachloroethane	17.3
4-Chlorotoluene	11.5	Tetrachloroethene	4.2
Dibromochloromethane	9.8	Toluene	8.3
Dibromomethane	6.2	1,2,3-Trichlorobenzene	6.6
1,2-Dichlorobenzene	8.7	1,2,4-Trichlorobenzene	6.4
1,3-Dichlorobenzene	9.1	1,1,1-Trichloroethane	3.3
1,4-Dichlorobenzene	9.8	1,1,2-Trichloroethane	9.8
Dichlorodifluoromethane	11.8	Trichloroethene	5.9
Dichloroethane	9.0	Trichlorofluoromethane	3.3
1,2-Dichloroethane	7.9	1,2,4-Trimethylbenzene	5.8
1,1-Dichloroethene	11.2	1,3,5-Trimethylbenzene	5.6
cis-1,2-Dichloroethene	8.3	Vinyl chloride	4.7
Trans-1,2-Dichloroethene	5.5	o-Xylene	11.1
1,2-Dichloropropane	9.4	m&p-Xylene	9.6
Compliance Limit	< 20%	Compliance Limit	< 20%

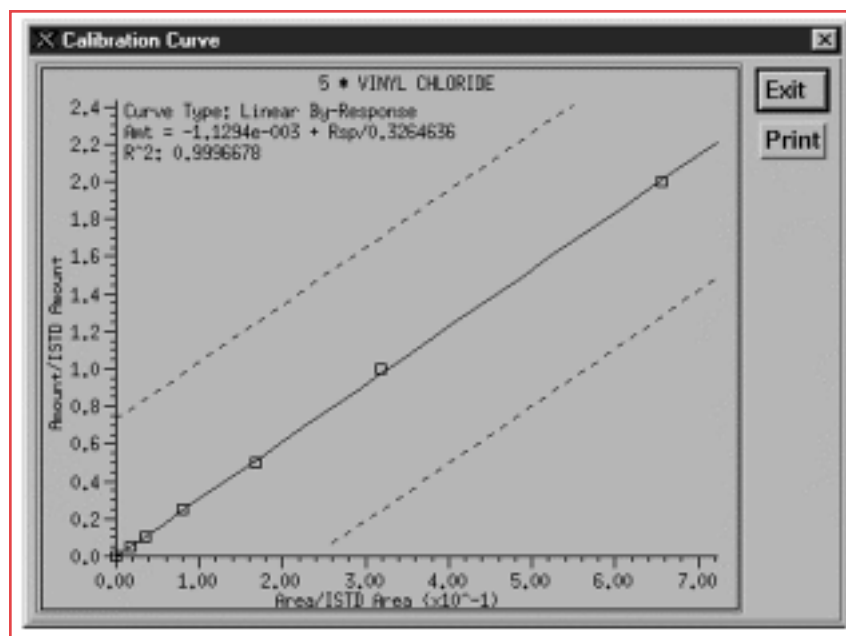


Figure 2. Linear regression curve of vinyl chloride.

the %RSDs must be less than the 20% maximum to demonstrate precision. Table 5 lists the precision and accuracy data for target analytes obtained from eight (8) replicate analyses using 2.5-µg/L standards. All the compounds show compliant precision and accuracy.

### Detection Limits

Five (5) replicates of a 1.0-µg/L standard solution were analyzed to determine the Method Detection Limits (MDLs). As stated in Method 524.2, the detection limits are calculated using the following formula:

$$MDL = S t_{(n-1, \alpha = 0.99)}$$

where:

$t_{(n-1, \alpha = 0.99)}$  = Student's *t* value for the 99% confidence level with *n*-1 degrees freedom,  
*n* = number of replicates, and  
*S* = the standard deviation of the replicate analyses.

**Table 5: Precision and Accuracy Results from Eight Replicate Analyses of a 2.5 µg/L Standard**

Precision and Accuracy Data			
Compound	Average (µg/L)	%Recovery	%RSD
Benzene	2.26	90.2	3.3
Bromobenzene	2.59	103.4	10.0
Bromochloromethane	2.18	87.3	3.2
Bromodichloromethane	2.31	92.3	3.0
Bromoform	2.20	87.9	7.3
Bromomethane	2.94	117.6	8.9
n-Butylbenzene	2.57	102.7	10.0
sec-Butylbenzene	2.09	83.4	9.6
tert-Butylbenzene	2.57	102.6	4.7
Carbon tetrachloride	2.80	112.1	2.7
Chlorobenzene	2.37	94.8	10.0
Chloroethane	2.74	109.6	5.1
Chloroform	2.45	97.9	1.2
Chloromethane	2.28	91.2	8.3
2-Chlorotoluene	2.39	95.6	10.6
4-Chlorotoluene	2.51	100.4	10.2
Dibromochloromethane	2.57	102.8	8.5
Dibromomethane	2.62	104.6	2.6
1,2-Dichlorobenzene	2.55	102.1	10.7
1,3-Dichlorobenzene	2.58	103.0	10.1
1,4-Dichlorobenzene	2.57	103.0	10.5
Dichlorodifluoromethane	2.32	92.8	10.5
Dichloroethane	2.89	115.6	4.2
1,2-Dichloroethane	2.82	112.6	3.7
1,1-Dichloroethene	2.70	107.8	5.2
cis-1,2-Dichloroethene	2.87	114.7	2.3
Trans-1,2-Dichloroethene	2.45	98.0	1.7
1,2-Dichloropropane	2.98	119.3	3.1
1,3-Dichloropropane	2.23	89.3	3.3
2,2-Dichloropropane	2.36	94.4	8.4
1,1-Dichloropropene	2.31	92.3	2.3
cis-1,3-Dichloropropene	2.11	84.2	5.1
trans-1,3-Dichloropropene	2.18	87.1	4.4
Ethylbenzene	2.55	101.9	7.4
Hexachlorobutadiene	2.57	102.8	14.0
Isopropylbenzene	2.08	83.3	9.6
4-Isopropyltoluene	2.66	106.2	5.9
Methylene chloride	2.26	90.4	3.3
Naphthalene	2.74	109.5	4.0
n-Propylbenzene	2.46	98.4	8.7
Styrene	2.25	89.8	8.7
1,1,1,2-Tetrachloroethane	2.58	103.0	7.1
1,1,2,2-Tetrachloroethane	2.55	102.2	5.0
Tetrachloroethene	2.58	103.3	3.3
Toluene	2.82	112.9	2.5
1,2,3-Trichlorobenzene	2.53	101.3	10.2
1,2,4-Trichlorobenzene	2.69	107.6	9.9
1,1,1-Trichloroethane	2.54	101.7	2.0
1,1,2-Trichloroethane	2.54	101.7	2.7
Trichloroethene	2.57	102.7	1.1
Trichlorofluoromethane	2.67	106.6	8.9
1,2,4-Trimethylbenzene	2.25	90.0	10.6
1,3,5-Trimethylbenzene	2.11	84.5	10.0
Vinyl chloride	2.63	105.2	2.6
o-Xylene	2.51	100.3	6.3
m&p-Xylene*	4.89	97.8	12.5
Compliance Criteria		80 – 120 %	< 20%

\* Total concentration 5.0 µg/L

Table 6 lists MDLs for all the listed target analytes obtained using the same conditions and calculations referenced here. Detection limits obtained using a wide-bore capillary column referenced in Method 524.2, range from 0.019 – 1.6 µg/L. The Maximum Contami-

nant Levels (MCLs) cited in the National Primary Drinking Water Standards (2) are also listed for comparison. The MDLs are well below the MCLs and compare favorably with the guidance limits listed in the U.S. EPA method.

Detection limits can vary tremendously depending on a number of factors such as the exact analytical conditions employed, the technique of the analyst, and the concentration of the standard used to make the determinations.

**Table 6: Method Detection Limits and U.S Maximum Contaminant Levels**

Method Detection Limits and Drinking Water Maximum Contaminant Limits					
Analyte	MDL (ppb)	MCL (ppb)	Analyte	MDL (ppb)	MDL (ppb)
Benzene	0.21	5.	1,3-Dichloropropane	0.20	
Bromobenzene	0.35		2,2-Dichloropropane	0.43	
Bromochloromethane	0.29		1,1-Dichloropropene	0.21	
Bromodichloromethane*	0.24	100.	cis-1,3-Dichloropropene	0.13	
Bromoform*	0.59	100.	trans-1,3-Dichloropropene	0.16	
Bromomethane	0.49		Ethylbenzene	0.34	700.
n-Butylbenzene	0.29		Hexachlorobutadiene	0.38	
sec-Butylbenzene	0.44		Isopropylbenzene	0.47	
tert-Butylbenzene	0.33		4-Isopropyltoluene	0.27	
Carbon tetrachloride	0.37	5.	Methylene chloride	0.23	5.
Chlorobenzene	0.44	100.	Naphthalene	0.39	
Chloroethane	0.28		n-Propylbenzene	0.32	
Chloroform*	0.19	100.	Styrene	0.43	100.
Chloromethane	0.50		1,1,1,2-Tetrachloroethane	0.41	
2-Chlorotoluene	0.62		1,1,2,2-Tetrachloroethane	0.57	
4-Chlorotoluene	0.41		Tetrachloroethene	0.20	5.
Dibromochloromethane*	0.53	100.	Toluene	0.10	100.
Dibromomethane	0.36		1,2,3-Trichlorobenzene	0.40	
1,2-Dichlorobenzene	0.31	600.	1,2,4-Trichlorobenzene	0.38	70.
1,3-Dichlorobenzene	0.29		1,1,1-Trichloroethane	0.25	200.
1,4-Dichlorobenzene	0.30	75.	1,1,2-Trichloroethane	0.33	5.
Dichlorodifluoromethane	0.77		Trichloroethene	0.22	5.
Dichloroethane	0.23	5.	Trichlorofluoromethane	0.35	
1,2-Dichloroethane	0.19		1,2,4-Trimethylbenzene	0.55	
1,1-Dichloroethene	0.41	7.	1,3,5-Trimethylbenzene	0.51	
cis-1,2-Dichloroethene	0.28	70.	Vinyl chloride	0.50	2.
Trans-1,2-Dichloroethene	0.14	100.	o-Xylene	0.37	
1,2-Dichloropropane	0.20	5.	m&p-Xylene	0.66	

\* Total Trihalomethanes must be less than 100 ppb.

## Conclusion

The accurate determination of volatile organic compounds in drinking water is important for the health and safety of the population. The analysis can be challenging and requires a rugged method for optimum results. Tuning, calibra-

tion, method detection limits, precision, and accuracy data presented here are compliant with those listed in the U.S. EPA method and serve to highlight some of the more critical criteria for method validation using the TurboMass GC/MS system.

## References

1. "Measurement of Purgeable Organic Compounds in Water By Capillary Column Gas Chromatography/Mass Spectrometry," Method # 524.2, Revision 4.1, Methods for the Determination of Organic Compounds in Drinking Water, Supplement III, EPA-600/R-95/131, August 1995.
2. "Maximum Contaminant Levels for Organic Contaminants," Code of Federal Regulations, 40 CFR Ch. I (7-1-98 Edition), Part 141.61.

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**PerkinElmer Instruments**  
761 Main Avenue  
Norwalk, CT 06859-0010 USA  
Tel: 800-762-4000 or  
(+1) 203-762-4000  
Fax: (+1) 203-762-4228

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