Application Note 02032

Evaluation of EPA Method 524.3: A New Draft Method for the Analysis of VOCs in Drinking Water Using GC/MS

Ed George
Varian, Inc.

Introduction

Recently, the U.S. Environmental Protection Agency (EPA) has developed a draft method for the measurement of volatile organic compounds (VOCs) in drinking water [1]. The new method, known as EPA 524.3, is a direct update of the earlier version of EPA Method 524.2. Key differences from 524.2 include the use of solid acid preservatives, a revised target list, an option for use of selected ion monitoring (SIM), and more flexible guidance for optimizing purge-and-trap parameters.

The application lab at Varian, Inc. has elected to participate in what EPA calls a Secondary Laboratory Demonstration study in order to help the Agency evaluate the new method. The study allows commercial laboratories and other stakeholders to provide data and comments to EPA. The study requires participants to:

a) Analyze an acceptable calibration in the range specified in the method

b) Provide precision and accuracy data, known as a Demonstration of Laboratory Capability (DOC)

c) Establish Lowest Concentration Minimum Reporting Levels (LCMRLs) for select regulated compounds

In this application note, data taken for the Secondary Laboratory Demonstration is presented using a Stratum purge-and-trap concentrator with a Varian Archon™ autosampler, and Varian 240-MS GC/MS ion trap mass spectrometer (Figure 1). Commentary is also provided on the proposed changes in EPA 524.3 relative to the existing EPA Method 524.2.

Instrumentation

- Varian 240-MS ion trap mass spectrometer with 431-GC gas chromatograph
- Varian 1177 Split/Splitless injector with 2 mm ID open liner
- Varian Archon purge-and-trap autosampler
- Tekmar Stratum concentrator with #9 StraTrap

Figure 1. Varian Archon purge-and-trap autosampler with Tekmar Stratum concentrator (top) and 240-MS ion trap with 431-GC (bottom).

Purge-and-Trap and GC Conditions

Column:	FactorFour™ VF-624 ms, 20 m x 0.15 mm x 0.84 µm, (Varian Part Number CP9100)
GC Conditions:	35 °C for 2 min, to 200 °C at 10 °C/min, hold 0 min, to 240 °C at 50 °C/min, hold 3 min
Purge Volume:	5 mL at 40 mL/min
Desorb Time:	1 min
Desorb Temp.:	260 °C
Split Ratio:	1:100

General MS Conditions

Scan Range:	*m/z* 35-300 (Gas segment: 47-150)
Scans Averaged:	2 µscans
Max Ion Time:	25,000 µsec
Emission Current:	15-20 µA
Manifold Temp.:	60 °C
Transfer Line Temp.:	220 °C
Ion Trap Temp.:	190 °C

Results and Discussion

Comparison of EPA Method 524.3 to EPA 524.2

The basic differences between the old and new method versions are described in Table 1. In general, there is much greater flexibility in the new method, especially in the purge-and-trap (PAT) concentrator conditions. The new method also mandates the use of a limited sample purge volume of 5.0 mL and currently requires a chilled autosampler system to keep the samples at 10 °C during analysis. (The Archon™ autosampler has a chiller option to meet this requirement).

Table 1. Major differences between the new and old EPA Method 524.

Former EPA Method 524.2 Requirement/Recommendation	New EPA Method 524.3 Requirement/Recommendation
Unrestricted purge volume	Purge volume restricted to 5 mL
No dry purge allowed, desorb time must be 4 minutes	Dry purge allowed, with general flexibility in all PAT concentrator settings
Full scan only method	Selected Ion Monitoring (SIM) allowed for select compounds
HCl used as preservative	Maleic acid and ascorbic acid replace use of HCl
Long capillary column used, typically 60 m and allowed use of cryogenic cooling of GC oven	Short 30 m column recommended, no cryogenics needed
Use of a 3 component sorbent trap of silica gel, charcoal, tenax	Can use Vocarb and other less water adsorbing trap materials
No clear defined calibration procedure	Calibration range recommended with a QC procedure to check calibration curve acceptance
Method contains compounds with poor purge and trap efficiencies	Some poor performing compounds removed from method list, new ethers and other compounds added
Method requires injection of bromofluorobenzene (BFB) tuning compound every 8 hours	BFB requirement only for each new initial calibration or after major maintenance of MS is performed
Method detection limits (MDLs) required based on Student "t" statistical test	MDLs are optional. Must establish a minimum reporting limit (MRL) using a specific procedure
No matrix spikes required in analytical run	Matrix spikes required in QC section of the method
No chilled autosampler compartment required	Chilled autosampler compartment required

Initial Calibration

EPA Method 524.3 recommends the following calibration levels to be used for full scan analysis: 0.5, 1.0, 2.0, 5.0, 10.0, 20.0 and 40.0 ppb. There are no minimum response factors for select compounds in the method. The %RSD (relative standard deviation) of the initial calibration for each analyte is not specified by the method, and in fact, the data presented in the EPA method is calculated using curves with a quadratic fit and weighting at the low end of the calibration curves. The only requirement for acceptance is that each calibration standard point, when calculated against the curve, must have a percent recovery in the range of 70-130%, except for the lowest calibration standard, which must have a recovery between 50-150%.

The method contains approximately 82 compounds with the new surrogate and internal standards. All compounds are included in the calibration mixtures, so it is important for the analyst to ensure that either the column is capable of resolving compounds that have similar quantitation ions, or that there is sufficient sensitivity to choose other quantitation ions of lower intensity.

Figure 2 is a typical chromatogram showing all of the target compounds in the method.

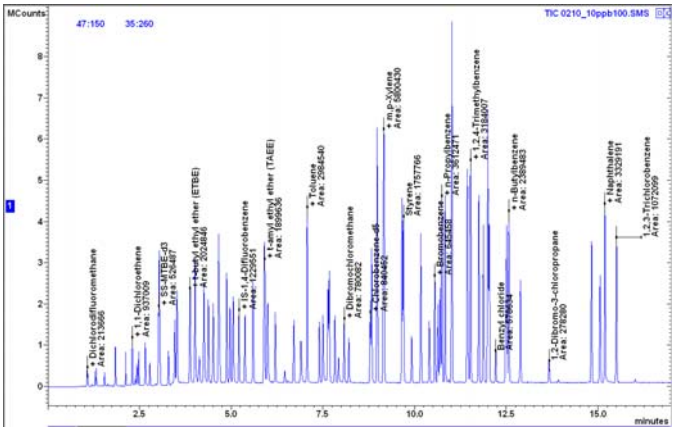

Figure 2. TIC for all target compounds. Excellent peak shape, resolution and sensitivity were easily obtained with the Varian FactorFour™ VF-624ms column and 240-MS GC/MS.

Table 2 contains some general calibration information: correlation coefficient (r^2), relative response factors (RRFs), and %RSD for the full scan analysis. All calibration standards passed the percent recovery quality control check.

All compounds showed excellent calibration coefficient and relative standard deviation at a concentration range from 0.5 to 40 ppb. The average r^2 and %RSD of all compounds are 0.998 and 7.72%, respectively (Table 2). An example calibration curve is displayed in Figure 3 for t-butyl alcohol.

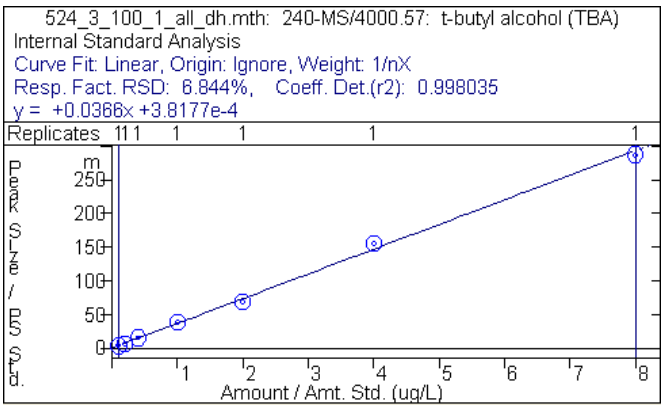

Figure 3. Calibration curve for t-butyl alcohol (TBA) from 0.5 to 40 ppb. Although typically a very poor purge-and-trap compound, it shows excellent response on the 240-MS GC/MS.

Table 2. Calibration data for 524.3 target compounds from 0.5 to 40 ppb, 5 mL purge volume.

Compound Name	Correlation Coefficient (r^2)	Average RRF	%RSD	Method Calibration Requirement
Dichlorodifluoromethane	0.9993	0.0826	14.16	PASS
Chlorodifluoromethane	0.9935	0.0657	10.89	PASS
Chloromethane	0.9966	0.0140	20.47	PASS
Vinyl chloride	0.9996	0.0906	17.30	PASS
1,3-Butadiene	0.9854	0.0657	14.79	PASS
Bromomethane	0.9981	0.0480	5.30	PASS
Trichlorofluoromethane	0.9991	0.2755	11.11	PASS
Diethyl ether	0.9998	0.1378	1.87	PASS
1,1-Dichloroethene	1.0000	0.3695	9.62	PASS
Methyl iodide	0.9989	0.1659	19.39	PASS
Carbon disulfide	0.9993	0.3327	6.25	PASS
Allyl chloride	0.9996	0.2561	3.75	PASS
Methylene chloride	0.9984	0.1953	11.79	PASS
t-butyl alcohol (TBA)	0.9943	0.0358	6.59	PASS
SS-MTBE-d_3	0.9964	0.4329	2.29	PASS
trans-1,2-dichloroethene	0.9993	0.4067	3.92	PASS
Methyl acetate	0.9993	0.0179	3.74	PASS
MTBE	0.9999	0.3680	2.03	PASS
1,1-Dichloroethane	0.9992	0.5340	15.98	PASS
Diisopropyl ether (DIPE)	0.9985	0.6685	11.26	PASS
t-butyl ethyl ether (ETBE)	0.9994	0.8996	7.27	PASS
cis-1,2-dichloroethene	0.9999	0.7493	1.90	PASS
Tetrahydrofuran	0.9976	0.0085	8.88	PASS
Bromochloromethane	0.9995	0.2972	1.95	PASS
Chloroform	0.9993	0.4506	4.65	PASS
1,1,1-Trichloroethane	0.9998	0.6684	3.74	PASS
1-Chlorobutane	0.9995	0.3997	5.34	PASS
Carbon Tetrachloride	0.9994	0.3536	7.81	PASS
1,1-Dichloropropene	0.9995	0.1658	7.00	PASS
Benzene	0.9999	0.5661	2.99	PASS
1,2-Dichloroethane	0.9986	0.5679	14.83	PASS
t-amyl methyl ether (TAME)	0.9992	0.3459	13.94	PASS
IS-1,4-Difluorobenzene	NA	NA	NA	PASS
Trichloroethene	0.9999	0.2495	4.37	PASS
1,2-Dichloropropane	0.9994	0.2524	4.30	PASS
t-amyl ethyl ether (TAEE)	0.9980	1.0380	4.80	PASS
Dibromomethane	0.9997	0.3219	2.19	PASS
Bromodichloromethane	0.9999	0.3503	3.54	PASS
cis-1,3-dichloropropene	0.9999	0.2079	5.93	PASS
Toluene	0.9997	1.6637	7.18	PASS
trans-1,3-dichloropropene	0.9997	0.2031	7.19	PASS
Ethyl methacrylate	0.9998	0.4292	6.16	PASS
1,1,2-trichloroethane	0.9988	0.3109	2.62	PASS
Tetrachloroethene	0.9996	0.2983	3.17	PASS
1,3-dichloropropane	0.9999	0.2461	4.34	PASS
Dibromochloromethane	0.9997	0.4468	7.81	PASS
1,2-Dibromoethane	0.9998	0.3767	7.47	PASS
Chlorobenzene-d_5	NA	NA	NA	PASS
Chlorobenzene	0.9996	0.9696	1.73	PASS
1,1,1,2-Tetrachloroethane	0.9999	0.3865	4.65	PASS
Ethylbenzene	0.9997	1.6225	8.17	PASS
m,p-Xylene	0.9984	3.0442	11.68	PASS
o-Xylene	0.9985	1.5195	12.26	PASS
Styrene	0.9999	1.0150	3.95	PASS
Bromoform	1.0000	0.2902	4.90	PASS
Isopropylbenzene	0.9979	1.5110	6.27	PASS
SS-4-Bromofluorobenzene	0.9890	0.8479	4.04	PASS
Bromobenzene	0.9998	0.8290	3.38	PASS
1,1,2,2-Tetrachloroethane	0.9995	0.9228	4.41	PASS
1,2,3-Trichloropropane	1.0000	0.7848	4.61	PASS
n-Propylbenzene	0.9991	4.2451	13.99	PASS
2-Chlorotoluene	0.9998	0.8030	6.77	PASS
4-Chlorotoluene	0.9995	0.7952	5.72	PASS
1,3,5-Trimethylbenzene	0.9995	3.4744	13.75	PASS
tert-Butylbenzene	0.9999	2.9544	14.03	PASS
Pentachloroethane	0.9997	0.6247	7.47	PASS
1,2,4-Trimethylbenzene	0.9993	3.7300	11.49	PASS
sec-Butylbenzene	0.9998	3.6816	18.17	PASS
1,3-Dichlorobenzene	0.9998	1.8824	3.20	PASS
p-Isopropyltoluene	0.9980	3.1720	14.89	PASS
1,4-Dichlorobenzene-d_4	NA	NA	NA	PASS
1,4-Dichlorobenzene	0.9998	1.9685	3.49	PASS
SS-1,2-Dichlorobenzene-d_4	0.9964	0.9356	2.31	PASS
1,2-Dichlorobenzene	0.9999	1.8339	2.72	PASS
n-Butylbenzene	0.9999	2.7767	17.46	PASS
Hexachloroethane	0.9995	0.7008	3.82	PASS
1,2-Dibromo-3-chloropropane	0.9985	0.3456	11.25	PASS
1,2,4-Trichlorobenzene	0.9991	1.2825	7.40	PASS
Hexachlorobutadiene	1.0000	0.8139	4.02	PASS
Naphthalene	0.9995	3.6900	20.60	PASS
1,2,3-Trichlorobenzene	1.0000	1.3324	5.95	PASS
Average	**0.998**		**7.72**	

Table 3 is an example of data obtained for 1,2-dibromoethane when the individual calibration points are calculated against the calibration curve. This shows passing data for the curve based on the recovery limits presented in the table.

Table 3. Example results for 1,2-dibromoethane (EDB) where each calibration point is calculated against the calibration curve and compared to recovery criteria in the method.

Compound Name	Target Concentration (ppb)	Results	%Recovery	Limit
1,2-Dibromoethane	0.50	0.56	112	50-100%
1,2-Dibromoethane	1.0	0.95	95	70-130%
1,2-Dibromoethane	2.0	1.952	98	70-130%
1,2-Dibromoethane	5.0	4.801	96	70-130%
1,2-Dibromoethane	10.0	9.767	98	70-130%
1,2-Dibromoethane	20.0	20.166	101	70-130%
1,2-Dibromoethane	40.0	40.304	101	70-130%

Precision and Accuracy

Precision and accuracy are determined after the completion of a valid calibration. Laboratories perform a Demonstration of Capability (DOC), in which a minimum of seven replicates in reagent water are analyzed. Table 4 provides a summary of the results. Note that the limits for the %RSD and %recovery are 20% for each compound. All compounds easily meet the requirements, with an average %recovery of 99.9% and average %RSD of 4.26%.

Table 4. Precision and accuracy data for Method 524.3 compounds.

Peak Name	True Value	DOC-A	DOC-B	DOC-C	DOC-D	DOC-E	DOC-F	DOC-G	%RSD	Average %Recovery	PASS/FAIL
Dichlorodifluoromethane	10.0	9.29	8.83	8.05	8.19	9.90	9.19	8.10	8.10	87.9	PASS
Chlorodifluoromethane	10.0	9.71	9.65	9.45	8.53	10.44	9.53	9.99	6.06	96.1	PASS
Chloromethane	10.0	10.95	10.84	10.40	10.24	11.95	11.51	10.21	6.09	108.7	PASS
Vinyl chloride	10.0	9.27	9.69	9.15	9.66	9.46	10.14	9.40	3.46	95.4	PASS
1,3-Butadiene	10.0	8.92	8.44	9.26	7.69	9.58	8.60	9.69	7.91	88.8	PASS
Bromomethane	10.0	10.04	10.20	9.83	9.43	9.85	9.42	9.99	3.05	98.2	PASS
Trichlorofluoromethane	10.0	9.45	9.55	8.73	9.54	10.26	9.86	8.97	5.42	94.8	PASS
Diethyl ether	10.0	10.08	10.16	10.02	10.18	10.32	10.16	10.15	0.92	101.5	PASS
1,1-Dichloroethene	10.0	9.21	9.38	9.02	9.38	9.71	9.71	8.94	3.28	93.4	PASS
Methyl iodide	10.0	10.44	10.82	10.95	11.38	12.23	12.22	11.89	6.25	114.2	PASS
Carbon disulfide	10.0	9.43	9.77	9.33	9.72	9.96	9.78	9.52	2.30	96.4	PASS
Allyl chloride	10.0	9.55	9.42	9.61	9.39	9.61	9.57	9.54	0.93	95.3	PASS
Methylene chloride	10.0	9.94	10.41	10.31	10.15	10.84	10.37	10.78	3.12	104.0	PASS
t-butyl alcohol (TBA)	10.0	10.70	11.57	11.77	11.72	11.56	11.83	12.72	5.05	117.0	PASS
SS-MTBE-d_3	5.0	4.86	5.07	5.14	5.10	4.98	5.03	5.25	2.48	101.2	PASS
trans-1,2-dichloroethene	10.0	9.90	10.51	10.00	10.02	10.34	10.38	9.94	2.42	101.5	PASS
Methyl acetate	10.0	9.18	10.58	9.13	11.06	8.04	10.68	10.33	11.09	98.6	PASS
MTBE	10.0	9.89	10.18	10.08	10.35	9.98	10.29	10.50	2.11	101.8	PASS
1,1-Dichloroethane	10.0	11.36	11.56	11.40	11.37	11.43	11.87	11.43	1.57	114.9	PASS
Diisopropyl ether (DIPE)	10.0	9.78	9.46	10.29	9.67	10.22	9.94	10.52	3.78	99.8	PASS
t-butyl ethyl ether (ETBE)	10.0	9.03	9.21	9.62	9.01	9.46	8.97	9.67	3.21	92.8	PASS
cis-1,2-dichloroethene	10.0	9.94	9.75	10.04	9.88	10.16	10.39	10.24	2.18	100.6	PASS
Tetrahydrofuran	10.0	9.97	8.82	9.23	9.37	10.88	9.26	10.33	7.48	96.9	PASS
Bromochloromethane	10.0	9.76	10.10	10.37	10.14	10.37	10.49	10.37	2.44	102.3	PASS
Chloroform	10.0	9.98	10.21	10.13	10.18	10.73	10.44	10.54	2.54	103.1	PASS
1,1,1-Trichloroethane	10.0	9.73	9.73	9.61	9.97	10.02	10.37	9.58	2.84	98.6	PASS
1-Chlorobutane	10.0	9.23	9.46	9.38	9.57	9.86	9.57	9.11	2.61	94.5	PASS
Carbon Tetrachloride	10.0	9.44	9.78	9.30	9.66	10.32	10.74	8.96	6.25	97.4	PASS
1,1-Dichloropropene	10.0	9.54	9.52	9.36	9.79	10.54	10.13	9.51	4.30	97.7	PASS
Benzene	10.0	9.81	9.95	10.29	10.09	10.44	10.47	10.09	2.42	101.6	PASS
1,2-Dichloroethane	10.0	9.87	10.02	10.00	9.81	9.74	10.08	10.00	1.27	99.3	PASS
t-amyl methyl ether (TAME)	10.0	10.06	10.14	10.37	10.06	10.37	10.03	10.91	3.04	102.8	PASS
Trichloroethene	10.0	9.53	9.56	9.81	9.64	10.05	10.37	10.06	3.19	98.6	PASS
1,2-Dichloropropane	10.0	9.76	10.26	10.25	10.14	10.50	10.80	10.32	3.10	102.9	PASS
t-amyl ethyl ether (TAEE)	10.0	10.22	9.89	10.87	10.18	10.70	10.26	10.83	3.63	104.2	PASS
Dibromomethane	10.0	10.09	10.31	9.95	10.25	10.09	10.40	10.49	1.87	102.3	PASS
Bromodichloromethane	10.0	9.48	10.20	10.12	10.04	9.90	10.19	10.16	2.57	100.1	PASS
cis-1,3-dichloropropene	10.0	9.66	9.82	10.15	9.75	10.11	10.04	9.85	1.92	99.1	PASS
Toluene	10.0	9.91	9.87	9.93	10.01	10.15	10.92	9.70	3.96	100.7	PASS
trans-1,3-dichloropropene	10.0	9.65	9.67	10.05	9.62	9.56	9.71	9.65	1.65	97.0	PASS
Ethyl methacrylate	10.0	9.80	9.71	9.82	9.54	9.79	9.89	9.88	1.25	97.8	PASS
1,1,2-trichloroethane	10.0	10.11	9.71	9.71	9.86	9.99	10.13	10.05	1.81	99.4	PASS

Peak Name	True Value	DOC-A	DOC-B	DOC-C	DOC-D	DOC-E	DOC-F	DOC-G	%RSD	Average %Recovery	PASS/FAIL
Tetrachloroethene	10.0	9.67	9.46	9.11	9.23	10.40	10.21	8.92	5.85	95.7	PASS
1,3-dichloropropane	10.0	9.99	9.92	10.13	10.34	10.40	10.29	9.83	2.18	101.3	PASS
Dibromochloromethane	10.0	10.06	9.67	9.73	9.93	10.29	9.93	10.18	2.26	99.7	PASS
1,2-Dibromoethane	10.0	9.89	9.87	9.56	10.13	9.75	10.05	9.85	1.89	98.7	PASS
Chlorobenzene	10.0	10.27	9.94	10.33	9.97	10.63	10.67	10.05	2.92	102.7	PASS
1,1,1,2-Tetrachloroethane	10.0	10.61	10.04	10.07	10.38	10.64	10.29	9.76	3.12	102.6	PASS
Ethylbenzene	10.0	10.00	9.74	9.99	10.14	10.55	10.49	9.53	3.69	100.6	PASS
m,p-Xylene	10.0	10.22	9.69	10.11	10.01	10.73	10.77	9.78	4.19	101.9	PASS
o-Xylene	10.0	10.34	10.47	10.30	10.81	11.27	11.05	10.32	3.69	106.5	PASS
Styrene	10.0	9.91	9.90	10.14	10.18	10.19	10.38	9.96	1.77	101.0	PASS
Bromoform	10.0	9.91	9.54	9.79	9.85	9.94	9.93	9.80	1.41	98.2	PASS
Isopropylbenzene	10.0	9.90	9.55	10.10	10.33	10.74	10.58	9.24	5.42	100.6	PASS
SS-4-Bromofluorobenzene	5.0	4.53	4.61	5.01	4.73	4.82	5.20	4.92	4.83	96.6	PASS
Bromobenzene	10.0	9.75	9.34	10.41	10.16	10.53	10.99	10.24	5.26	102.0	PASS
1,1,2,2-Tetrachloroethane	10.0	10.10	9.86	10.41	10.52	10.51	11.04	10.85	3.86	104.7	PASS
1,2,3-Trichloropropane	10.0	10.13	9.69	10.28	10.15	10.33	10.51	10.57	2.85	102.4	PASS
n-Propylbenzene	10.0	9.77	9.16	9.98	9.97	10.54	10.90	9.94	5.52	100.4	PASS
2-Chlorotoluene	10.0	9.52	8.77	9.92	10.13	10.43	10.89	9.78	6.82	99.2	PASS
4-Chlorotoluene	10.0	9.86	9.30	9.97	10.30	9.98	11.30	9.74	6.18	100.6	PASS
1,3,5-Trimethylbenzene	10.0	9.66	9.08	9.83	10.15	10.39	10.94	9.71	5.97	99.7	PASS
tert-Butylbenzene	10.0	9.82	9.16	10.18	10.29	10.86	11.18	10.01	6.53	102.1	PASS
Pentachloroethane	10.0	9.74	9.34	10.39	9.97	10.67	11.35	9.97	6.49	102.0	PASS
1,2,4-Trimethylbenzene	10.0	9.62	9.03	10.24	10.39	10.69	11.19	10.10	6.90	101.8	PASS
sec-Butylbenzene	10.0	9.75	9.14	9.70	10.21	11.07	11.26	9.58	7.85	101.0	PASS
1,3-Dichlorobenzene	10.0	9.67	9.18	10.05	9.99	10.36	11.00	9.88	5.65	100.2	PASS
p-Isopropyltoluene	10.0	9.82	9.04	9.86	10.11	10.94	11.38	9.89	7.67	101.5	PASS
Benzyl chloride	10.0	9.02	8.12	8.80	8.09	8.24	7.95	8.15	4.85	83.4	PASS
1,4-Dichlorobenzene	10.0	9.75	9.09	10.16	10.05	10.48	10.97	10.13	5.78	100.9	PASS
SS-1,2-Dichlorobenzene-d_4	5.0	4.52	4.32	4.97	4.80	4.76	4.95	4.97	5.27	95.1	PASS
1,2-Dichlorobenzene	10.0	9.95	9.49	10.19	10.07	10.88	11.42	10.36	6.16	103.4	PASS
n-Butylbenzene	10.0	9.74	8.91	9.84	10.18	10.69	11.02	9.41	7.29	99.7	PASS
Hexachloroethane	10.0	8.31	7.89	8.48	8.81	9.20	9.91	8.83	7.44	87.8	PASS
1,2-Dibromo-3-chloropropane	10.0	10.19	9.78	10.34	10.22	10.48	10.92	10.83	3.78	103.9	PASS
1,2,4-Trichlorobenzene	10.0	9.53	8.95	9.86	9.95	10.32	10.48	9.48	5.36	98.0	PASS
Hexachlorobutadiene	10.0	9.75	8.79	9.66	10.69	10.97	11.01	10.09	8.01	101.4	PASS
Naphthalene	10.0	10.13	9.39	10.22	10.31	10.12	11.02	9.95	4.75	101.6	PASS
1,2,3-Trichlorobenzene	10.0	9.49	9.06	10.09	9.96	10.50	10.93	9.88	6.18	99.9	PASS
Average									**4.26**	**99.97**	

Detection Limits

In EPA Method 524.3, the standard method detection limit (MDL) calculation based on Student's *t* value for the 99% confidence level with n-1 degrees of freedom (Section 9.2 of the method) is now optional. For the Secondary Laboratory Demonstration, the Agency has asked participating labs to perform a Lowest Concentration Minimum Reporting Level (LCMRL) experiment. The LCMRL is described as the true concentration for which future recovery is predicted to fall with high confidence (99%) between 50 and 150% recovery [2].

This gives the user more accurate information on the reporting limit and true detection limit for analytes in the method.

The procedure involves taking multiple concentration replicate data and processing it through a downloadable LCMRL calculator as measured concentrations versus the true concentrations [3]. The LCMRL calculator was developed through a collaboration of Shaw and EPA contract statisticians.

For the experiments on the 240-MS, a special calibration curve was prepared at concentrations of 10, 50, 100, 500, 1000, 2000, 5000, 10,000 and 20,000 ng/L (ppt). Units of ng/L or ppt were required for data entry into the LCMRL calculator. After the calibration curves were completed, four replicates at seven different concentration levels near the low-end of the calibration curves were analyzed. The levels were 10, 25, 50, 100, 200, 500 and 700 ng/L. The calculated results of these replicate injections along with the true or target values were entered into the LCMRL calculator. Figure 4 is an example of the output information generated by the calculator.

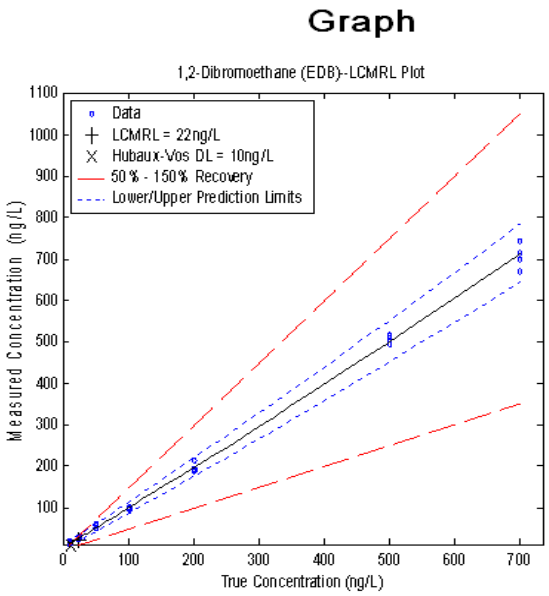

Figure 4a. Calibration curve regression graph for EDB obtained as output from the LCMRL calculator.

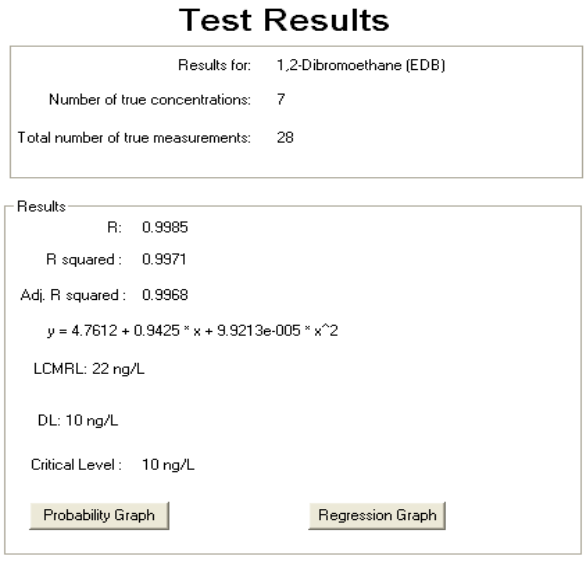

Figure 4b. Results for EDB. LCMRL is calculated to be 22 ng/L, with a predicted detection limit (DL) of 10 ng/L.

The information from the calculator provides improved statistical significance of the reporting limits. Table 5 lists the LCMRLs and Detection Limits (DLs) for the regulated compounds (and some new target analytes as requested by the EPA study).

Table 5. LCMRLs and DLs from the EPA calculator based on test data form the 240-MS.

Peak Name	LCMRL (ng/L)	DL (ng/L)
Chlorodifluoromethane**	NC*	27
Vinyl chloride	177	32
1,3-Butadiene**	NC*	32
1,1-Dichloroethene	44	15
Methylene chloride	209	126
trans-1,2-dichloroethene	64	20
cis-1,2-dichloroethene	15	8.8
Chloroform	24	11
1,1,1-Trichloroethane	13	9.2
Carbon tetrachloride	41	19
Benzene	27	3.3
1,2-Dichloroethane	18	2.7
Trichloroethene	59	19
1,2-Dichloropropane	38	4.6
Bromodichloromethane	42	25
Toluene	27	5
1,1,2-trichloroethane	30	13
Tetrachloroethene	63	1.2
Dibromochloromethane	NC*	7.6
1,2-Dibromoethane (EDB)	22	10
Chlorobenzene	17	6
Ethylbenzene	30	13
m,p-Xylene	13	3.8
o-Xylene	15	6.2
Styrene	14	5.3
Bromoform	83	32
1,4-Dichlorobenzene	47	13
1,2-Dichlorobenzene	38	13
1,2-Dibromo-3-chloropropane (DBCP)	47	31
1,2,4-Trichlorobenzene	49	17

*NC = not calculated. **Indicate new analyte added to EPA Method 524.3.

Three of the compounds register as not calculated (NC) for the LCMRL result: 1,3-butadiene, chlorodifluoromethane, and dibromochloromethane. The LCMRL calculator requires the proper selection of calibration levels and replicates in order to obtain valid results. Therefore, it is often required to repeat the analysis for some compounds since analytes will have different responses in the GC/MS.

Conclusion

The Varian 240-MS GC/MS with Archon™ autosampler and Stratum purge-and-trap concentrator provided excellent results for the new EPA 524.3 draft method. The FactorFour™ VF-624ms column demonstrated excellent peak shape and resolution for the method analytes. All quality control criteria for initial calibration, as well as accuracy and precision were easily met.

The new method has improved procedures for determining the detection and reporting limits for the target compounds. Calculated LCMRLs were the same or lower than data presented in the new draft method.

Data from this study along with comments on the method procedures will be submitted to the EPAs Second Laboratory Demonstration study. The Varian 240-MS GC/MS system will also be used to gather low-level full scan data on the select SIM target analytes in EPA 524.3. This data will be presented in a future application note.

References

1. Method 524.3: Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry , Version 1.0, January 2009, B. Prakash et al.
2. Guidance Document for Determining Lowest Concentration Minimum Reporting Levels (LCMRLs), Document No. TSC-3-0344, Rev 2.0, Stephen Winslow.
3. Downloadable LCMRL calculator available at: http://www.cadmusweb.com/LCMRL/Beta.htm.

These data represent typical results.
For further information, contact your local Varian Sales Office.

Varian, Inc.
www.varianinc.com
North America: 800.926.3000 – 925.939.2400
Europe *The Netherlands*: 31.118.67.1000
Asia Pacific *Australia*: 613.9560.7133
Latin America *Brazil*: 55.11.3238.0400