

Performance Demonstration of a New GC-MS Instrument and Novel BFB Tune for Analysis of Volatile Compounds by EPA Method 524.2

■ Abstract

The US Environmental Protection Agency has published several versions of its method for the analysis of Volatile Organic Compounds (VOCs) in drinking water. Currently, the majority of environmental laboratories analyzing these compounds in drinking water for compliance purposes, use either method 524.2 or 524.3. One of the challenges faced by laboratories performing this analysis is the lack of robustness and stability of BFB tuning required by these methods. The stability and sensitivity of the newly released Shimadzu GCMS-QP2020 NX instrument and novel BFB tuning were evaluated in accordance to method EPA 524.2.

Results demonstrated that BFB tune met EPA method 524.2 criteria for 30 samples over 15 hrs. To assess sensitivity, Method Detection Limits (MDLs) were calculated at two individual concentrations. At 0.25 µg/L the calculated MDL ranged from 0.020 – 0.190 µg/L, while at 0.50 µg/L the calculated MDL ranged from 0.050 to 0.790 µg/L. Overall, the study results illustrate that the GCMS-QP2020 NX passes the EPA detection limits requirement for method 524.2.

■ Introduction

In the pursuit to protect drinking water, in 1974 the United States Environmental Protection Agency (EPA) implemented the Safe Drinking Water Act (SDWA). One of the first analytical methods developed by EPA to analyze Volatile Organic Compounds (VOCs) in drinking water in support of the SDWA was method 524.1. As GC-MS instrumentation advanced, with improvements in sensitivity, reliability, and user experience, method 524.1 has been replaced. Currently, the majority of environmental laboratories analyzing VOCs in drinking water for compliance purposes use either method 524.2 or 524.3.

While many analytical drinking water testing labs have had great success in analyzing drinking water samples according to method 524.2, analysts experience challenges during the implementation and routine performance of the method.

Method 524.2, in comparison to method 524.3 and 524.4, does not allow the modification of purge and trap (P&T) parameters, such as having a shorter desorb timeⁱ. As a result, the performance of some conventional and older GC-MS instruments is impacted by the presence of water from the P&T, resulting in instability during the analysis. The design of the Shimadzu GCMS-QP2020 NX incorporates features for minimizing the inherent challenges of P&T GC-MS instruments required for the analysis of VOCs.

In this study, we demonstrate the performance of the newly released GC-MS and novel BFB tuning algorithmⁱⁱ for the aforementioned methods and determine the Method Detection Limit (MDL) for target compounds.

■ Materials and Methods

Tuning Conditions

A standard autotune was done prior to loading the new BFB tuning algorithm to check the instrument conditions. With satisfactory standard autotuning results, the BFB tune algorithm was then loaded, followed by a BFB autotune. Each of the three days that this study was conducted, a BFB daily spectra check was conducted with respect to EPA tuning criteria. As required by the EPA, the standard tune of the GCMS-QP2020 NX was conducted using an electron emission current of 60 µA as well as standard ionization voltage of 70 eV.

GC-MS and Purge and Trap Conditions

In the study, an EST Analytical Econ Evolution purge and trap concentrator and Centurion WS autosampler were interfaced to the Shimadzu GCMS-QP2020 NX (Figure 1).



Figure 1: Shimadzu GCMS-QP2020 NX

A VOCARB 3000 (k) analytical trap was configured with the P&T unit. A narrow bore inlet liner was used in the GC-MS to improve peak shape and allowed high split injections when transferring sample from the P&T concentrator. Data was acquired in full scan mode from m/z 35 to 330. Prior to the MDL experiment, both the GC-MS and P&T instruments were conditioned. The P&T was conditioned by baking the VOCARB 3000 trap at 260 °C for 8 minutes.

The GC-MS column was conditioned by removing the column from the MS, but it remained connected to the GC inlet; the GC oven temp was ramped from 35 °C to 280 °C and held for 20 mins before returning to the starting method conditions. The experimental parameters for both GC-MS and P&T systems are listed in Table 1.

Table 1: GC-MS and P&T operating conditions

Gas Chromatography	Nexis GC-2030
Injection port mode	Split mode; 40:1 split ratio
Carrier gas	Helium
Injection port temperature (°C)	200
Column	SH-I 624 Sil MS, 30 m x 0.25 mmID x 1.4 um
Flow control mode	Linear velocity, 32 cm/sec
Oven Temperature	35 °C (4.0 minutes), 14 °C/minutes to 220 °C (7minutes)
Mass Spectrometer	QP2020 NX
Interface Temperature (°C)	180
Ion Source Temperature (°C)	200
Detector Voltage	Relative to Tune -0.2 kV
Threshold	100
Scan Range	m/z 35 to 330 Event time 0.18 seconds
Purge and Trap Concentrator	EST Encon Evolution and Centurion Autosampler
Trap	VOCARB 3000
Trap Ready Temp (°C)	35
Mort ready Temp (°C)	39
Desorb Preheat Temperature (°C)	245
Desorb Temperature (°C)	250
Trap Bake Temperature (°C)	260
Mort Bake Temperature (°C)	210
Purge Flow Rate (ml/min)	Helium, 40
Dry Purge Flow Rate (ml/min)	Helium, 40
Desorb time (min)	1
Bake time (min)	8
Dry purge time (min)	2
Purge and Trap Autosampler	EST Centurion WS
Sample loop size (ml)	5
Sample fill mode	Loop
Internal standard volume (ul)	5
Surrogate standard volume (ul)	5
Analysis Time	
GC Run Time	34 min

Sample preparation

All target compounds were purchased from o2si Smart Solutions, while internal and surrogate standards were purchased from Restek Corporation. Individual stock standard solutions of analytes were prepared by dissolving the target compound in methanol, purge and trap grade, at 100 µg/ml. Internal and surrogate standards for purging were prepared at 50 µg/L. All stock standards were placed in Restek micro vials with mini-inert precision sampling valves. Hamilton gas-tight syringes were used to measure various volumes of the analytes from the stock solution. The gas-tight syringe resulted in no to minimal loss of the gaseous portion of the samples, thus allowing accurate measurement during preparation of standards.

For the MDL study that was conducted over three days, 10 replicates of spiked blank water samples were analyzed and the MDL for each compound was estimated according to procedures described in the Federal Registerⁱⁱⁱ. In brief, 10 sample replicates were made at both 0.25 µg/L and 0.50 µg/L. These samples were analyzed on the GCMS-QP2020 NX and the mean accuracy and standard deviation for each analyte were calculated. A laboratory reagent blank was analyzed to ensure that the blank water sample was not contaminated. To calculate the MDL, the mathematical equation 1 was used where the standard deviation was multiplied by the Student's *t* value for a 99% confidence level with n-1 degree of freedom.

$$MDL = T(n-1, 1-\alpha=99) S$$

■ Results and Discussion

BFB tune results

A single BFB tune file was used for all analyses included in this study over the three days. This single BFB file was adequate for meeting criteria outlined by EPA for the analysis of VOCs by method 524.2. Table 2 shows the numeric results for BFB daily spectra check with respect to EPA tuning acceptance criteria from three representative sequences in the study: #1(first day), #2 (second day) and #3 (third day).

Initial Calibration

In the study, a calibration curve was prepared across the range of 0.25 to 200 µg/L. This linear range was used to estimate MDLs at both the 0.25 and 0.50 µg/L concentration. The calibration curve was evaluated according to EPA method 524 criteria using the percent relative standard deviation (%RSD) of the calculated response factors (RF) for each data point in the curve. Also, the coefficients of determination (*r*²) from a linear regression were used as an alternative to the RF criteria. The results listed in Table 3 show that most compounds passed the EPA method 524 RF criteria (RF %RSD ≤ 20 %)ⁱ; hence, the RF can be used for calculating concentrations of target compounds. The RF %RSD for compounds that met the criteria ranged from 4.07 to 19.65%. The compounds with RF %RSD > 20% (with valued from 21 to 32%) were bromomethane, iodomethane, tetrahydrofuran and 1,2-Dichloroethane. The poor purging efficiencies for these compounds may be the reason for method 524.2 RF criteria not being met. Linear calibration curves were found to be suitable for the aforementioned compounds. The *r*² shown in Table 3 for all compounds ranged from 0.9915 to 0.9999.

Table 2: Evaluation of BFB spectra from three different injections made prior to each method 524.2 validation step

m/z	Spectrum Check Criteria	Results		Results		Results	
		Inj. #2; Day1	Status	Inj. #2; Day2	Status	Inj. #3; Day3	Status
50	15 to 40% of mass 95	22.15	Pass	21.90	Pass	22.39	Pass
75	30 to 80% of mass 95	41.49	Pass	41.41	Pass	42.47	Pass
95	Base Peak, 100% Relative Abundance	100.00	Pass	100.00	Pass	100.00	Pass
96	5 to 9% of mass 95	6.64	Pass	6.50	Pass	6.62	Pass
173	< 2% of mass 174	0.579	Pass	0.543	Pass	0.518	Pass
174	> 50% of mass 95	67.09	Pass	65.28	Pass	66.80	Pass
175	5 to 9% of mass 174	6.94	Pass	7.37	Pass	6.86	Pass
176	> 95% but < 101% of mass174	96.82	Pass	100.36	Pass	97.77	Pass
177	5 to 9% of mass 176	6.69	Pass	6.36	Pass	6.65	Pass

Table 3: Statistical analysis of calibration curves ranging from 0.50 to 200 µg/L and CCVs

Peak #	Compound Name	10-Point Calibration		
		0.25 to 200 µg/L		
		R ²	Avg RF	RF % RSD
1	Dichlorodifluoromethane	0.9998	0.05	11.70
2	Chloromethane	0.9988	0.15	7.95
3	Vinyl chloride	0.9999	0.14	5.34
4	Bromomethane	0.9967	0.07	27.96
5	Chloroethane	0.9999	0.14	8.23
6	Trichlorofluoromethane	0.9995	0.20	8.88
7	1,1-Dichloroethene	0.9993	0.17	4.90
8	cis-1,2-dichloroethene	0.9991	0.11	7.69
9	Iodomethane	0.9995	0.10	31.87
10	Carbon disulfide	0.9999	0.55	9.19
11	Allyl chloride	0.9988	0.13	6.72
12	Methylene chloride	0.9999	0.24	19.65
13	Acrylonitrile	0.9999	0.22	11.24
14	trans-1,2-Dichloroethene	0.9999	0.21	6.89
15	Methyl tert-butyl ether	0.9997	0.83	10.87
16	1,1-Dichloroethane	0.9999	0.53	5.83
17	2,2-dichloropropane	0.9987	0.31	9.75
18	Propionitrile	0.9999	0.09	14.40
19	Methyl acrylate	0.9993	0.52	12.64
20	Bromochloromethane	0.9984	0.10	9.45
21	Methyl acrylonitrile	0.9999	0.21	4.07
22	Tetrahydrofuran	0.9999	0.07	20.72
23	Chloroform	0.9997	0.38	6.74
24	1,1,1-Trichloroethane	0.9999	0.27	9.13
25	Carbon tetrachloride	0.9987	0.22	10.85
26	1-chlorobutane	0.9992	0.76	8.32
27	Benzene	0.9985	1.12	9.64
28	1,2-Dichloroethane	0.9999	0.43	21.23
29	Trichloroethene	0.9996	0.24	9.43
30	1,2-Dichloropropane	0.9975	0.33	9.30
31	Dibromomethane	0.9993	0.13	7.03
32	Methyl methacrylate	0.9993	0.29	7.00
33	Bromodichloromethane	0.9997	0.30	4.96
34	2-Nitropropane	0.9999	0.17	14.13
35	cis-1,3-Dichloropropene	0.9990	0.43	7.19
36	Toluene d-8 (SS)	NA	0.91	1.58
37	Toluene	0.9999	0.74	17.44
38	trans-1,3-Dichloropropene	0.9987	0.39	8.20
39	Ethyl methacrylate	0.9996	0.48	6.68
40	1,1,2-Trichloroethane	0.9991	0.21	8.26
41	Tetrachloroethene	0.9995	0.25	10.71
42	1,3-Dichloropropane	0.9985	0.46	8.51
43	Dibromochloromethane	0.9980	0.20	8.56
44	1,2-dibromoethane	0.9987	0.23	8.51
45	Chlorobenzene	0.9972	0.68	12.13
46	Ethylbenzene	0.9929	1.16	14.77
47	1,1,1,2-tetrachloroethane	0.9930	0.21	12.69
48	m/p-Xylene	0.9976	0.50	14.42
49	o-Xylene	0.9933	0.48	14.07
50	Styrene	0.9936	0.77	12.42
51	Bromoform	0.9999	0.16	17.30
52	Isopropylbenzene	0.9980	1.07	14.46
53	4-BromoFluorobenzene (SS)	NA	0.37	4.98
54	1,1,2,2-Tetrachloroethane	0.9954	0.36	9.85
55	Bromobenzene	0.9948	0.24	11.06
56	trans-1,4-dichloro-2-butene	0.9915	0.16	13.11
57	1,2,3-trichloropropane	0.9939	0.50	10.33
58	n-Propylbenzene	0.9952	1.26	14.27
59	2-chlorotoluene	0.9960	0.81	13.85

Peak #	Compound Name	10-Point Calibration		
		0.25 to 200 µg/L		
		R ²	Avg RF	RF % RSD
60	4-chlorotoluene	0.9951	0.85	16.32
61	1,2,4-trimethylbenzene	0.9965	0.95	10.80
62	tert-butylbenzene	0.9972	0.81	11.69
63	1,3,5-trimethylbenzene	0.9961	0.92	10.49
64	Pentachloroethane	0.9947	0.17	15.84
65	sec-butylbenzene	0.9971	1.14	11.01
66	1,3-Dichlorobenzene	0.9976	0.44	8.76
67	4-isopropyltoluene	0.9939	0.26	12.50
68	1,4-Dichlorobenzene	0.9972	0.44	12.57
69	1,2-Dichlorobenzene	0.9983	0.40	9.782
70	n-butylbenzene	0.9981	0.78	10.66
71	Hexachloroethane	0.9984	0.14	7.86
72	1,2-dibromo-3-chloropropane	0.9998	0.08	4.76
73	1,2,3-trichlorobenzene	0.9993	0.24	9.57
74	Hexachlorobutadiene	0.9977	0.11	7.13
75	Naphthalene	0.9998	0.92	5.26
76	1,2,4-trichlorobenzene	0.9993	0.22	9.15

Continuing Calibration Verification

Continuing calibration verification (CCV) standards at 50 parts-per-billion (ppb) were used for the three consecutive days of the MDL study. When compared to the initial calibration curve, all CCV standards passed the EPA requirement from method 524.2 (the absolute areas of the quantitation ions of the IS and SS must not decrease by more than 30% in the most recent continuing calibration check or by more than 50% from areas measured during initial calibration)¹.

The CCV recoveries for internal and surrogate standards ranged from 95.32 – 103.17% (Table 4). CCV standards' recoveries for each analyte concentration were also calculated (Table 5). Although not required by method 524.2 criteria for MDL determination, the above step was taken to further validate the data quality. Table 5 shows %RSD for each analyte in the CCV.

Table 4: CCVs recoveries of IS and SS as compared to initial calibration curve

Peak #	Compound Name	CCV #1	CCV #2	CCV #3
		Calculated Recoveries (%)		
1	Fluorobenzene	98.51	95.32	100.15
2	Toluene-d8	102.52	96.40	101.74
3	4-BromoFluorobenzene	100.92	97.94	103.17

Table 5: CCVs recoveries and %RSD of analytes during MDL study compared to spiked amount

Peak #	Compound Name	CCV #1	CCV #2	CCV #3	% RSD
		Calculated Recoveries			
		%	%	%	
1	Dichlorodifluoromethane	113.14	110.62	107.93	2.36
2	Chloromethane	94.19	93.58	94.63	0.56
3	Vinyl chloride	99.75	98.20	99.50	0.84
4	Bromomethane	100.51	90.61	67.88	19.38
5	Chloroethane	96.44	96.84	96.81	0.23
6	Trichlorofluoromethane	89.03	90.54	91.02	1.15
7	1,1-Dichloroethene	95.76	95.88	98.05	1.33
8	cis-1,2-dichloroethene	94.91	95.24	97.77	1.63
9	Iodomethane	79.85	80.32	79.14	0.74
10	Carbon disulfide	89.94	89.38	88.13	1.04
11	Allyl chloride	97.52	96.88	93.85	2.04
12	Methylene chloride	78.67	82.38	80.28	2.31
13	Acrylonitrile	92.19	96.24	92.03	2.55

Peak #	Compound Name	CCV #1	CCV #2	CCV #3	% RSD
		Calculated Recoveries			
		%	%	%	
14	trans-1,2-Dichloroethene	92.23	94.83	95.22	1.73
15	Methyl tert-butyl ether	79.13	86.13	82.13	4.26
16	1,1-Dichloroethane	88.32	91.35	90.86	1.80
17	2,2-dichloropropane	83.41	71.81	59.65	16.59
18	Propionitrile	89.32	93.01	88.26	2.76
19	Methyl acrylate	90.00	92.43	88.37	2.26
20	Bromochloromethane	83.23	89.20	85.68	3.49
21	Methyl acrylonitrile	88.74	94.45	89.78	3.34
22	Tetrahydrofuran	72.01	74.43	71.04	2.40
23	Chloroform	88.89	91.70	90.72	1.57
24	1,1,1-Trichloroethane	91.70	93.67	93.84	1.27
25	Carbon tetrachloride	91.15	91.96	94.74	2.04
26	1-chlorobutane	87.02	87.19	88.19	0.72
27	Benzene	87.02	89.79	88.77	1.58
28	1,2-Dichloroethane	91.79	98.14	94.58	3.36
29	Trichloroethene	86.39	87.90	87.60	0.92
30	1,2-Dichloropropane	86.40	89.75	87.84	1.91
31	Dibromomethane	83.80	90.58	86.08	3.97
32	Methyl methacrylate	86.50	92.39	87.11	3.65
33	Bromodichloromethane	89.87	93.39	91.29	1.93
34	2-Nitropropane	94.45	98.42	93.20	2.86
35	cis-1,3-Dichloropropene	88.02	89.89	84.06	3.41
36	Toluene	80.04	81.65	80.38	1.05
37	trans-1,3-Dichloropropene	85.88	88.23	81.90	3.75
38	Ethyl methacrylate	86.63	92.26	87.08	3.53
39	1,1,2-Trichloroethane	82.78	88.67	83.59	3.76
40	Tetrachloroethene	87.48	90.28	87.97	1.69
41	1,3-Dichloropropane	83.54	88.67	84.28	3.24
42	Dibromochloromethane	86.80	92.32	87.21	3.46
43	1,2-dibromoethane	82.53	87.46	82.24	3.49
44	Chlorobenzene	84.58	86.83	84.27	1.64
45	Ethylbenzene	83.78	85.52	83.77	1.20
46	1,1,1,2-tetrachloroethane	85.96	89.54	86.88	2.13
47	m/p-Xylene	83.90	84.79	83.19	0.95
48	o-Xylene	84.48	85.84	83.04	1.66
49	Styrene	85.83	87.86	84.97	1.72
50	Bromoform	76.94	81.88	75.50	4.29
51	Isopropylbenzene	83.85	83.95	81.90	1.39
52	1,1,2,2-Tetrachloroethane	83.03	88.60	82.44	4.01
53	Bromobenzene	83.72	86.34	82.55	2.31
54	trans-1,4-dichloro-2-butene	81.72	80.51	70.95	7.59
55	1,2,3-trichloropropane	85.59	88.80	81.00	4.60
56	n-Propylbenzene	83.46	83.65	80.89	1.86
57	2-chlorotoluene	83.35	84.91	81.39	2.12
58	4-chlorotoluene	87.97	89.37	86.11	1.86
59	1,2,4-trimethylbenzene	84.35	84.55	80.70	2.61
60	tert-butylbenzene	81.91	82.76	78.99	2.43
61	1,3,5-trimethylbenzene	84.57	85.34	81.55	2.39
62	Pentachloroethane	93.39	92.90	88.88	2.70
63	sec-butylbenzene	83.49	83.46	79.26	2.97
64	1,3-Dichlorobenzene	86.12	87.21	82.64	2.79
65	4-isopropyltoluene	83.78	83.97	79.62	2.98
66	1,4-Dichlorobenzene	84.22	85.81	80.18	3.48
67	1,2-Dichlorobenzene	83.85	87.78	81.97	3.51
68	n-butylbenzene	86.73	86.85	81.31	3.72
69	Hexachloroethane	93.82	93.66	88.36	3.38
70	1,2-dibromo-3-chloropropane	84.90	89.61	83.15	3.90
71	1,2,3-trichlorobenzene	86.67	93.46	83.35	5.87
72	Hexachlorobutadiene	95.94	96.63	87.44	5.48
73	Naphthalene	82.27	87.07	78.38	5.28
74	1,2,4-trichlorobenzene	87.53	93.50	83.29	5.82

Method Detection Limit (MDL)

Ten 0.25 µg/L and 0.50 µg/L spiked samples were analyzed and the mean accuracy and standard deviation for each analyte was calculated. The %RSD was calculated by determining the mean accuracy and standard deviation for all analytes at the 0.25 µg/L and 0.50 µg/L range.

The %RSD for all targeted compounds is listed in Table 6.

MDLs for each of the above standards were able to pass EPA method 524 detection limit criteria and are within the same order of magnitude as listed by an EPA validation study¹. At 0.25 µg/L, the MDL ranged from 0.020 to 0.190 µg/L, while at 0.50 µg/L, the MDL ranged from 0.050 to 0.790 µg/L. Figure 2 illustrates a comparison of the calculated MDL at 0.25 µg/L and 0.50 µg/L for each target compound. This figure shows the spatial distribution of the MDL for each compound, where most compounds at 0.25 µg/L have an MDL less than 0.1 and at 0.50 µg/L most compounds have an MDL less than 0.2. Table 6 lists the details of the MDL study results.

Table 6: Method Detection Limit (MDL) Study Results

Peak #	Compound Name	0.25 µg/L; n=10		0.50 µg/L; n=10	
		%RSD	MDL	%RSD	MDL
1	Dichlorodifluoromethane	NA	NA	9.51	0.17
2	Chloromethane	17.39	0.15	12.91	0.20
3	Vinyl chloride	8.64	0.07	10.36	0.15
4	Bromomethane	NA	NA	5.67	0.23
5	Chloroethane	18.82	0.14	11.65	0.16
6	Trichlorofluoromethane	14.60	0.11	10.64	0.17
7	1,1-Dichloroethene	22.53	0.19	10.09	0.16
8	cis-1,2-dichloroethene	14.58	0.15	24.29	0.34
9	Iodomethane	NA	NA	6.95	0.44
10	Carbon disulfide	11.10	0.11	5.56	0.10
11	Allyl chloride	9.25	0.08	17.59	0.26
12	Methylene chloride	11.88	0.09	12.73	0.17
13	Acrylonitrile	15.19	0.12	5.68	0.09
14	trans-1,2-Dichloroethene	14.81	0.12	9.86	0.16
15	Methyl tert-butyl ether	5.13	0.04	3.67	0.06
16	1,1-Dichloroethane	10.15	0.08	3.76	0.06
17	2,2-dichloropropane	25.26	0.15	19.08	0.26
18	Propionitrile	NA	NA	12.05	0.17
19	Methyl acrylate	8.00	0.06	4.02	0.06
20	Bromochloromethane	12.71	0.14	11.64	0.21
21	Methyl acrylonitrile	10.43	0.08	17.33	0.13
22	Tetrahydrofuran	13.33	0.19	33.69	0.79
23	Chloroform	5.19	0.05	4.58	0.08
24	1,1,1-Trichloroethane	9.02	0.07	5.62	0.10
25	Carbon tetrachloride	16.16	0.14	8.08	0.15
26	1-chlorobutane	8.70	0.07	6.42	0.11
27	Benzene	4.74	0.04	3.87	0.07
28	1,2-Dichloroethane	3.55	0.03	20.54	0.07
29	Trichloroethene	8.08	0.07	6.77	0.11
30	1,2-Dichloropropane	6.24	0.05	4.04	0.07
31	Dibromomethane	10.04	0.08	5.74	0.10
32	Methyl methacrylate	8.79	0.07	4.09	0.07
33	Bromodichloromethane	7.15	0.06	3.32	0.06
34	2-Nitropropane	12.76	0.09	7.40	0.11
35	cis-1,3-Dichloropropene	9.95	0.08	3.68	0.06
36	Toluene	5.67	0.05	3.78	0.07
37	trans-1,3-Dichloropropene	6.95	0.06	3.17	0.05
38	Ethyl methacrylate	7.16	0.06	2.87	0.05
39	1,1,2-Trichloroethane	8.99	0.08	4.04	0.07
40	Tetrachloroethene	12.12	0.10	6.96	0.12
41	1,3-Dichloropropane	6.58	0.06	3.16	0.06
42	Dibromochloromethane	5.84	0.05	4.74	0.08
43	1,2-dibromoethane	7.41	0.06	3.68	0.07
44	Chlorobenzene	4.16	0.04	4.61	0.09
45	Ethylbenzene	6.64	0.06	3.79	0.07
46	1,1,1,2-tetrachloroethane	16.41	0.12	6.83	0.12
47	m/p-Xylene	5.37	0.10	4.07	0.15
48	o-Xylene	4.05	0.04	3.65	0.07

Peak #	Compound Name	0.25 µg/L; n=10		0.50 µg/L; n=10	
		%RSD	MDL	%RSD	MDL
49	Styrene	6.15	0.06	4.45	0.08
50	Bromoform	14.06	0.11	4.70	0.08
51	Isopropylbenzene	6.49	0.06	4.95	0.09
52	1,1,2,2-Tetrachloroethane	5.86	0.05	3.15	0.06
53	Bromobenzene	6.17	0.05	4.83	0.09
54	trans-1,4-dichloro-2-butene	14.18	0.10	10.70	0.19
55	1,2,3-trichloropropane	4.67	0.04	2.55	0.05
56	n-Propylbenzene	7.58	0.07	4.68	0.09
57	2-chlorotoluene	6.53	0.06	3.31	0.06
58	4-chlorotoluene	13.50	0.12	7.74	0.14
59	1,2,4-trimethylbenzene	5.88	0.05	4.38	0.08
60	tert-butylbenzene	11.16	0.02	27.14	0.46
61	1,3,5-trimethylbenzene	5.37	0.05	3.83	0.07
62	Pentachloroethane	8.30	0.06	10.13	0.14
63	sec-butylbenzene	8.32	0.08	6.50	0.12
64	1,3-Dichlorobenzene	8.08	0.07	3.81	0.07
65	4-isopropyltoluene	9.32	0.08	4.21	0.08
66	1,4-Dichlorobenzene	4.50	0.04	2.93	0.06
67	1,2-Dichlorobenzene	6.09	0.06	4.58	0.09
68	n-butylbenzene	7.80	0.07	6.05	0.11
69	Hexachloroethane	7.88	0.07	9.34	0.16
70	1,2-dibromo-3-chloropropane	11.05	0.10	9.97	0.16
71	1,2,3-trichlorobenzene	12.00	0.11	8.26	0.15
72	Hexachlorobutadiene	11.45	0.11	12.63	0.20
73	Naphthalene	4.51	0.04	3.85	0.07
74	1,2,4-trichlorobenzene	4.82	0.04	5.68	0.10

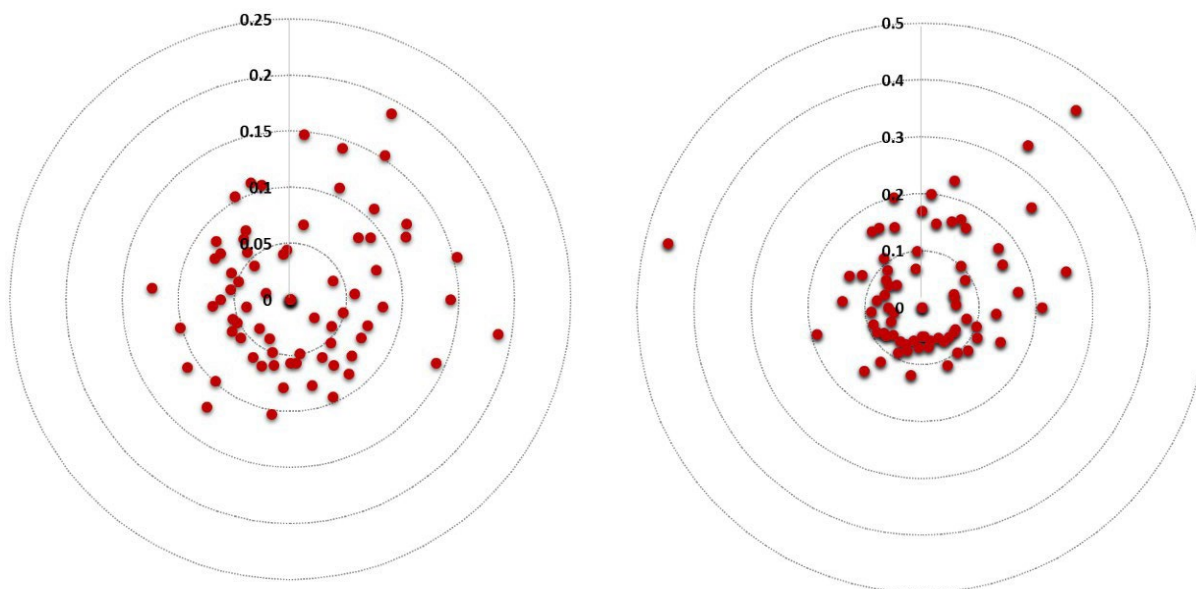


Figure 2: Calculated MDL at 0.25 ug/L (left) and 0.50 ug/L (right) for each compound highlighted in Table 6. Note that scales are different.

■ Conclusion

The study results demonstrate the high performance of the Shimadzu GCMS-QP2020 NX in the analysis of EPA method 524.2. The initial calibration curve showed that most of the targeted compounds were able to meet the method's RF %RSD requirement (RF %RSD ≤ 20 %), which is the EPA's primary initial calibration requirement. The RF %RSD for compounds that met the criteria ranged from 4.07 to 19.65%. Compounds that did not meet the method's RF criteria were able to meet the r^2 criteria and these analytes' MDLs were determined using concentrations calculated by regression analysis. The r^2 for all compounds ranged from 0.9915 to 0.9999. The experiments were conducted over a three-day time period; CCV standards were analyzed during the study and met the EPA requirements. The CCV standards' recoveries for internal and surrogate standards ranged from 95.32 – 103.17%.

Using 10 replicates of standards at two individual concentrations, the estimated MDLs passed US EPA Method 524.2 requirements for detection limits. Using 0.25 µg/L replicate samples, the calculated MDL ranged from 0.020 – 0.190 µg/L, while at 0.50 µg/L the calculated MDL ranged from 0.050 to 0.790µg/L. In this experiment, we demonstrated that the performance of the new and more sensitive instrument is optimal. The robust operation of the newly released Shimadzu GCMS QP2020 NX results in this instrument being one of the best available technologies for analysis according to EPA method 524.2.

■ References

- i. United States Environmental Protection Agency Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Revision 4.1 June 2009.
- ii. A Guide to the Novel GC-MS BFB Tuning for the analysis of Volatile Organic Compounds in environmental samples, GCMS Application News No. GCMS-2001.
- iii. Definition and Procedures for the Determination of the Method Detection Limit. Fed. Regist. 1984. 49 (209), Appendix B to Part 136.

■ Consumables

Part Number	Item Name	Item Description
221-75926-30	Capillary Column	SH-I-624SiI MS, 30m x 0.25 mmID x 1.40 µm
220-90784	Inlet Liner	Low-volume liner, 1.0 mmID, Straight, 5/pkg (Restek)
84890	Gas tight syringes	Hamilton 1800 series gas tight syringes (Hamilton)
21051	Micro vials	3.0 ml Micro vial with screw thread (Restek)
24903	Sampling valves	Mininert precision sampling valves for micro vials (Restek)
89091-302	Volumetric flask	Pyrex 2 ml class A volumetric flask with stopper (VWR)
80070-360	Volumetric flask	Chemglass 500 ml class A volumetric flask with stopper (VWR)
10124-072	Volumetric flask	Vwr 100ml class A Heavy Duty volumetric flask with stopper (VWR)
21797	Sampling vials	40 ml Volatile Organic Analyte sampling vials (Restek)
MX0482-6	Methanol	Omnisolv methanol for purge and trap (VWR)
30074	Internal Standards Mix	8260 Internal Standard Mix (4 components) (Restek)
30073	Surrogate Mix	8260 Surrogate Standard Mix (3 components) (Restek)
121950-02	Custom 8260 Gas Mix	Custom 8260 Gas Mix, 8-142, 2,000 mg/L, 1ml (o2si)
120730-02	Method 524.2 Drinkwater VOA Mix	Method 524.2 Drinking Water VOA Mix, 2,000 mg/L, 1ml (o2si)
120486-02	Method 524 Oxygenates Standard	Method 524 Oxygenates Standard, 5-486, 2,000 mg/L, 1ml (o2si)
020439-02	Methyl Acetate Solution	Methyl Acetate Solution, 2,000 mg/L, 1ml (o2si)
0202203-02	Iodomethane Solution	Iodomethane Solution, 2,000 mg/L, 1ml (o2si)



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