Application News

No. GCMS-2003

Gas Chromatography Mass Spectrometry

Performance Demonstration of a Modern GC-MS Instrument and Novel BFB tune for Analysis of Volatile Compounds by EPA Method 624.1 and 8260C

■ Abstract

With global population growth and demand for safe water, there is an increased need for monitoring pollutants in surface and groundwater as well as industrial wastewater discharges. As a result, there is growing demand for high-sensitivity state-of-the art instrumentation to meet and exceed limits set by new environmental regulations. In this study, the latest released Shimadzu GCMS-QP2020 NX is evaluated to demonstrate whether its performance meets the stability and sensitivity criteria from EPA methods 624.1 and 8260C. Results demonstrated that this novel BFB tune met EPA method 624.1 and 8260C criteria for an extended period of operations. To assess sensitivity, MDLs were calculated at two individual concentrations. For method 624.1, MDLs calculated at 0.50 µg/L ranged from 0.07 to 0.40 µg/L, while at 1.00 µg/L they ranged from 0.09 to 0.50 µg/L. Regarding method 8260C, MDLs ranged from 0.07 to 0.40 µg/L and from 0.09 to 0.50 µg/L when standards were spiked at 0.5 and 1.00 µg/L, respectively. Overall, the study results illustrate that the GCMS-QP2020 NX meets the EPA detection limits requirement for both these methods.

■ Introduction

The Clean Water Act of 1972 created the initial pathway for regulating the discharge of pollutants in water bodies in the United States. Since then, the United States Environmental Protection Agency (US EPA) has developed several analytical methods for monitoring Volatile Organic Compounds (VOCs) in water and other environmental matrices. EPA method 8260C is suitable for the analysis of VOCs in solid waste matrices [i]. On the other hand, EPA method 624.1 is approved for analysis of purgeable organics in municipal and industrial wastewater [ii]. The standard operating procedures for both methods are similar, but the list of targeted compounds from each method includes different analytes. Overall, method 8260C is more comprehensive than method 624.1 because of its larger list of VOCs and approved sample types.

While 8260C and 624.1 methods and their use on conventional GCMS have been successful, recent improvements in instrumentation require a reevaluation of the original method on newer instruments to demonstrate that the performance requirements included in these methods are met. This application note is a demonstration study to determine Method Detection Limits (MDLs) for VOCs analysis by both methods 8260C and 624.1 using the newly released Shimadzu GCMS QP2020 NX and novel BFB tuning algorithm [iii].

■ Materials and Methods

Tuning Conditions.

A standard autotune was done prior to loading the new BFB tuning algorithm to verify the instrument operational conditions. With satisfactory standard autotuning results, the BFB tune algorithm was then loaded and followed by a BFB autotune. Unlike the traditional BFB tune, the new tune algorithm makes it easier to set target intensity ratios and keep those conditions longer. Each of the three days that this MDL 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

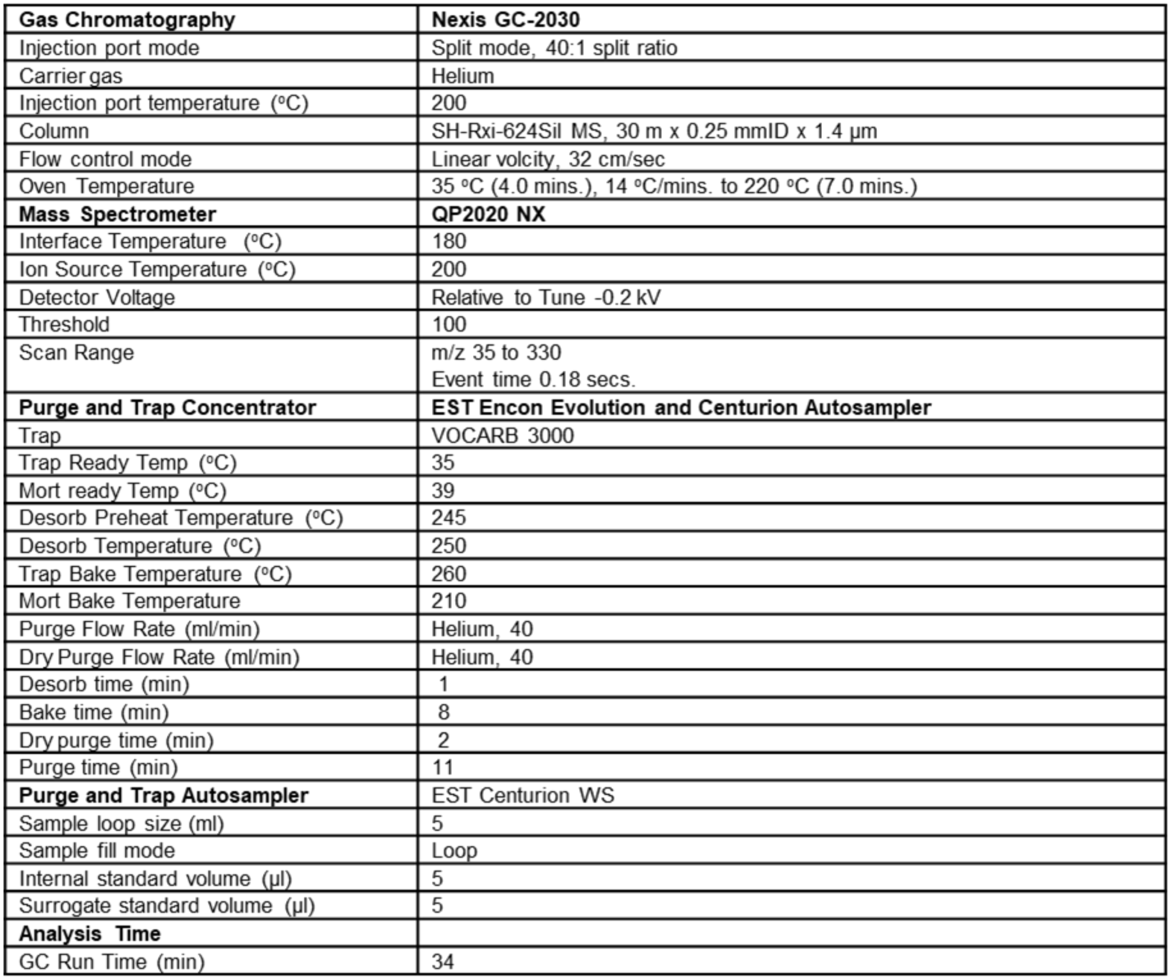
In the study, an EST Analytical Econ Evolution purge and trap concentrator and Centurion WS autosampler were interfaced to the Shimadzu GCMS-QP2020 NX (Figure 1).

Figure 1: Shimadzu GCMS-QP2020 NX and EST Econ Evolution Purge and Trap Concentrator.

A VOCARB 3000 (k) analytical trap was configured with the P&T unit. In this method, the P&T desorb time was set to 1 min, which allowed better water management than the conditions required in EPA 524.2, for the analysis of VOCs in drinking water. 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. Quantitation and confirmation of target compounds were conducted using the quantitation ions specified by the EPA for this method.

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 still being 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: GCMS 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-Rxi-624Sil MS, 30 m x 0.25 mmID x 1.4 µm
Flow control mode	Linear volcity, 32 cm/sec
Oven Temperature	35 °C (4.0 mins.), 14 °C/mins. to 220 °C (7.0 mins.)
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 secs.
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	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 time (min)	11
Purge and Trap Autosampler	EST Centurion WS
Sample loop size (ml)	5
Sample fill mode	Loop
Internal standard volume (µl)	5
Surrogate standard volume (µl)	5
Analysis Time	
GC Run Time (min)	34

Sample Preparation

All target compounds were purchased from o2si Smart Solutions, while internal and surrogate standards were purchased from Restek Corporation. Before analysis these chemicals were stored in a refrigerator at –10° C. 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 Code of Federal Regulations [IV]. In brief, 10 sample replicates were made at both 0.5 µg/L and 1.0 µg/L. These samples were analyzed on the GCMS-QP2020 NX and their standard deviation was calculated.

To calculate the MDL, the mathematical equation listed below 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.

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

■ Results and Discussion

BFB Tune Results

A single BFB tune file was used for all the analysis included in this study over the three days. A single BFB file was adequate for meeting criteria outlined by EPA for the analysis of VOCs by method 624.1 and 8260C. 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 from 0.50 to 200 µg/L. This linear range was used to estimate MDLs at both 0.5 and 1.0 µg/L. A total ion chromatogram (TIC) from the 50 µg/L standard illustrating peak resolution is shown in Figure 2.

Table 2: Evaluation of BFB spectra from 3 different injections made prior to method 624.1/8260C MDL study.

m/z	Spectrum Check Criteria	Results		Results		Results	
		Inj. #1	Status	Inj. #12	Status	Inj. #32	Status
50	15 to 40% of mass 95	23.25	Pass	23.59	Pass	24.60	Pass
75	30 to 60% of mass 95	39.24	Pass	39.66	Pass	40.76	Pass
95	Base Peak, 100% Relative Abundance	100.0	Pass	100.0	Pass	100.0	Pass
96	5 to 9% of mass 95	6.43	Pass	6.41	Pass	6.56	Pass
173	< 2% of mass 174	0.55	Pass	0.49	Pass	0.44	Pass
174	> 50% of mass 95	70.90	Pass	72.87	Pass	73.99	Pass
175	5 to 9% of mass 174	7.30	Pass	6.80	Pass	7.01	Pass
176	> 95% but < 101% of mass174	99.12	Pass	100.58	Pass	98.12	Pass
177	5 to 9% of mass 176	6.39	Pass	6.70	Pass	6.65	Pass

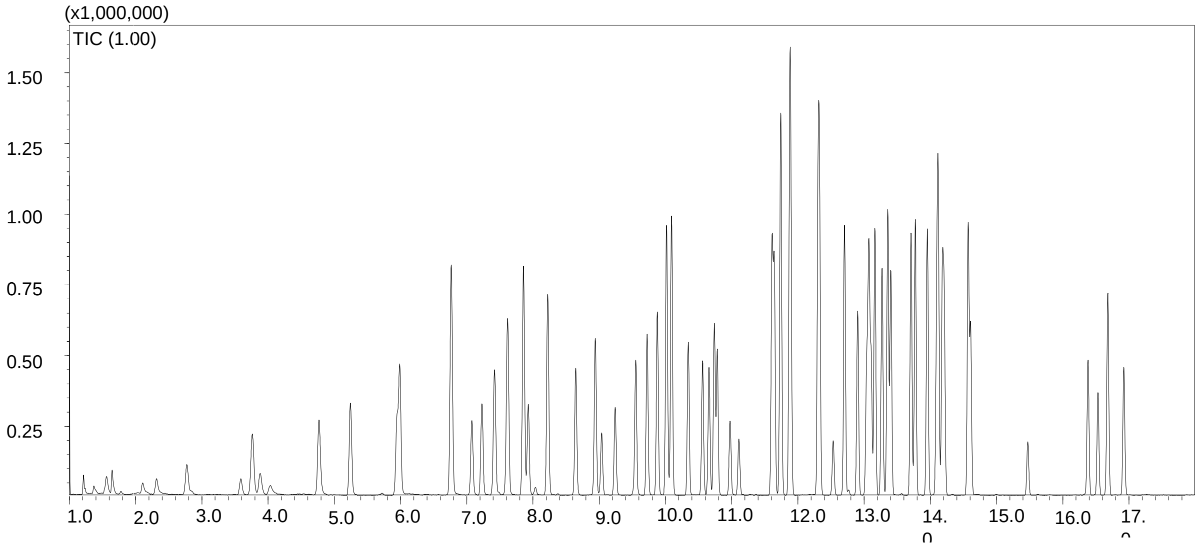


Figure 2: Total Ion Chromatogram from the 50 µg/L Calibration Standard.

The calibration curve was evaluated according to EPA method 8260C criterion (RF %RSD < 20%) using the percent relative standard deviation (%RSD) of the calculated response factors (RF) for each data point in the curve [i]. The method 8260C AVG RF criterion was chosen over method 624.1 criterion for demonstration of initial calibration because its list of target compounds is more comprehensive and covers all compound in this study.

The results listed in Table 3 show that > 90% of the compounds passed the EPA method 8260C RF criteria. The Avg RF calibration was used for calculating most analytes MDL. The RF %RSD for compounds that met the acceptable criterion ranged from 1.92 to 17.27, while for compounds that failed the criterion, RF %RSD ranged from 21.31 to 49.47. The latter group included dichlorodifluoromethane, bromomethane and Iodomethane. These compounds are typically difficult to analyze because of their poor purging efficiency and their background contamination issues in many laboratory environments.

For those compounds with an RF value outside the acceptable criterion, coefficients of determination (R^2) from linear regression analysis were used as an alternative calibration. The criterion for R^2 is different in method 624.1 and 8260C; hence, regression analysis was evaluated according to both methods. In method 624.1, the regression was weighed inversely proportional to concentration (1/C). There is no required weighting for method 8260C.

All compounds passed method 8260C and 624.1 regression criteria ($R^2 \geq 0.990$) and ($R^2 \geq 0.920$) [i, ii], respectively, including the three compounds that failed the 8260C RF criterion. The R^2 value was used instead of Avg RF for MDL measurements for the three compounds that did not pass the 8260C RF criteria. R^2 calculated according to method 624.1 ranged from 0.9912 to 0.9999, while values according to method 8260C ranged from 0.9945 to 0.9999 (Table 3).

Table 3: Statistical analysis of the initial calibration curve for methods 624.1 and 8260C ranging from 0.5 to 200 µg/L (10-point calibration curve).

Peak #	Compound Name	8260C R^2	624.1 R^2	8260C Avg RF	8260C RF %RSD
1	Dichlorodifluoromethane	0.9989	0.9967	0.042	30.884
2	Chloromethane	0.9983	0.9966	0.148	10.920
3	Vinyl chloride	0.9965	0.9947	0.133	12.957
4	Bromomethane	0.9977	0.9961	0.079	21.311
5	Chloroethane	0.9998	0.9989	0.105	13.975
6	Trichlorofluoromethane	0.9978	0.9973	0.176	11.708
7	Acrolein	0.9997	0.9989	0.112	9.326
8	1,1-Dichloroethene	0.9982	0.9977	0.171	8.892
9	Acetone	0.9997	0.9990	0.064	9.036
10	Iodomethane	0.9984	0.9914	0.088	49.470
11	Methylene chloride	0.9999	0.9999	0.224	6.708
12	trans-1,2-Dichloroethene	0.9989	0.9986	0.233	7.066
13	1,1-Dichloroethane	0.9999	0.9998	0.537	4.849
14	Vinyl acetate	0.9999	0.9997	1.197	6.232
15	2-Butanone	0.9977	0.9959	0.069	7.434
16	cis-1,2-dichloroethene	0.9999	0.9999	0.282	6.424
17	2,2-Dichloropropane	0.9991	0.9968	0.262	10.890
18	Bromochloromethane	0.9985	0.9972	0.110	9.576
19	Chloroform	0.9999	0.9998	0.401	7.306
20	Dibromofluoromethane (SS)	NA	NA	0.197	1.923
21	1,1,1-Trichloroethane	0.9986	0.9982	0.275	8.181
22	Carbon tetrachloride	0.9985	0.9981	0.219	9.778
23	1,1-Dichloropropylene	0.9989	0.9987	0.121	7.566
24	Benzene	0.9998	0.9996	1.394	6.786
25	1,2-Dichloroethane	0.9996	0.9992	0.409	4.453
26	Trichloroethene	0.9983	0.9977	0.289	7.698
27	1,2-Dichloropropane	0.9996	0.9993	0.434	4.606
28	Dibromomethane	0.9999	0.9999	0.178	2.644
29	Bromodichloromethane	0.9997	0.9994	0.400	3.955
30	2-Chloroethylvinylether	0.9994	0.9982	0.375	6.394
31	cis-1,3-Dichloropropene	0.9999	0.9998	0.569	4.178
32	4-Methyl-2-pentanone	0.9999	0.9999	0.100	5.406

Peak #	Compound Name	8260C R^2	624.1 R^2	8260C Avg RF	8260C RF %RSD
33	Toluene-d8 (SS)	NA	NA	1.220	2.859
34	Toluene	0.9999	0.9997	0.898	7.291
35	trans-1,3-Dichloropropene	0.9999	0.9999	0.510	4.991
36	1,1,2-Trichloroethane	0.9999	0.9999	0.271	2.629
37	Tetrachloroethene	0.9972	0.9968	0.222	7.203
38	1,3-Dichloropropane	0.9999	0.9997	0.614	5.350
39	2-Hexanone	0.9999	0.9999	0.699	5.041
40	Dibromochloromethane	0.9999	0.9999	0.275	4.488
41	1,2-Dibromoethane	0.9999	0.9999	0.320	5.702
42	Chlorobenzene	0.9986	0.9996	0.898	8.369
43	Ethylbenzene	0.9988	0.9972	1.465	10.772
44	1,1,1,2-Tetrachloroethane	0.9980	0.9966	0.275	9.390
45	Xylene Total	0.9989	0.9968	0.609	11.233
46	m/p-Xylene	0.9989	0.9971	0.629	10.687
47	o-Xylene	0.9987	0.9970	0.612	9.543
48	Styrene	0.9984	0.9970	1.000	9.891
49	Bromoform	0.9994	0.9994	0.466	6.785
50	Isopropylbenzene	0.9997	0.9991	3.126	8.807
51	4-Bromofluorobenzene (SS)	NA	NA	1.280	1.978
52	1,1,2,2-Tetrachloroethane	0.9985	0.9971	0.478	7.284
53	Bromobenzene	0.9991	0.9990	0.733	5.843
54	trans-1,4-Dichloro-2-butene	0.9945	0.9919	0.493	12.953
55	1,2,3-Trichloropropane	0.9970	0.9959	1.558	6.809
56	n-Propylbenzene	0.9998	0.9993	3.694	9.080
57	2-Chlorotoluene	0.9998	0.9996	2.453	7.784
58	4-Chlorotoluene	0.9997	0.9996	2.593	5.623
59	1,2,4Trimethylbenzene	0.9992	0.9981	2.746	8.358
60	tert-Butylbenzene	0.9997	0.9990	2.240	9.084
61	1,3,5-Trimethylbenzene	0.9995	0.9988	2.716	7.933
62	sec-Butylbenzene	0.9995	0.9987	3.263	8.335
63	1,3-Dichlorobenzene	0.9992	0.9985	1.345	8.567
64	4-Isopropyltoluene	0.9993	0.9979	0.822	6.693
65	1,4-Dichlorobenzene	0.9999	0.9998	1.351	6.853
66	1,2-Dichlorobenzene	0.9999	0.9999	1.262	6.150
67	n-Butylbenzene	0.9995	0.9992	2.421	7.041
68	1,2-Dibromo-3-chloropropane	0.9989	0.9983	0.251	8.116
69	1,2,3-Trichlorobenzene	0.9981	0.9956	0.811	9.966
70	Hexachlorobutadiene	0.9960	0.9912	0.371	17.274
71	Naphthalene	0.9997	0.9990	3.012	5.814
72	1,2,4-Trichlorobenzene	0.9983	0.9957	0.756	9.453

NA: Surrogates were spiked at the same concentration. Therefore, regression analysis was not conducted for these compounds.

Continuing Calibration Verification

Continuing calibration verification (CCV) standards were used for the three consecutive days of the MDL study. A laboratory control sample (LCS) was prepared and analyzed prior to running the batch on each day. The concentration (A) of each analyte was determined and the percent recovery (Q) was calculated as 100 (A/T) %, where T is the true value of the concentration in the LCS. The Q value of each analyte was compared with its corresponding quality control (QC) acceptance criteria set by the USEPA and shown in table 4 [ii].

When compared to the initial calibration curve, the CCV recoveries for all compounds ranged from 79.83% to 110.57% (Table 4). From the CCV standards, all target compounds fell within their respective QC acceptance criteria and these CCV standards confirmed that the initial calibration (ICAL) curve can be used to calculate MDLs for method 624.1.

Table 4: Method 624.1 CCVs calculated recoveries of analytes during MDL study compared to spiked amount.

Peak #	Compound Name	Range for Q Recovery (%)	CCV #1	CCV #2	CCV #3
1	Dichlorodifluoromethane	60-140	101.31	103.29	110.57
2	Chloromethane	D-205	91.60	96.80	99.63
3	Vinyl chloride	5-195	93.64	97.47	104.70
4	Bromomethane	15-185	87.00	87.91	89.36
5	Chloroethane	40-160	87.17	90.28	95.59
6	Trichlorofluoromethane	50-150	98.59	98.87	109.83
7	Acrolein	60-140	95.06	100.34	100.74
8	1,1-Dichloroethene	50-150	94.57	99.05	105.35
9	Acetone	60-140	94.43	95.81	97.47
10	Iodomethane	60-140	81.21	88.12	93.37
11	Methylene chloride	60-140	87.99	92.00	93.03
12	trans-1,2-Dichloroethene	70-130	86.00	92.20	94.32
13	1,1-Dichloroethane	70-130	87.40	92.24	94.34
14	Vinyl acetate	60-140	96.76	102.55	101.39
15	2-Butanone	60-140	93.68	97.95	96.32
16	cis-1,2-dichloroethene	60-140	90.92	95.76	97.83
17	2,2-dichloropropane	60-140	80.01	97.10	83.57
18	Bromochloromethane	60-140	87.83	89.92	90.75
19	Chloroform	70-135	85.36	90.93	91.74
20	Dibromofluoromethane (SS)	60-140	100.30	100.99	100.00
21	1,1,1-Trichloroethane	70-130	87.82	94.21	97.57
22	Carbon tetrachloride	70-130	88.22	93.64	97.27
23	1,1-dichloropropylene	60-140	87.92	94.34	97.81
24	Benzene	65-135	86.33	91.56	92.88
25	1,2-Dichloroethane	70-130	89.44	94.18	93.92
26	Trichloroethene	65-135	86.45	92.16	94.08
27	1,2-Dichloropropane	35-165	87.64	93.35	93.87
28	Dibromomethane	60-140	89.49	95.45	93.98
29	Bromodichloromethane	65-135	87.82	93.55	93.51
30	2-Chloroethylvinylether	D-225	85.20	94.48	87.40
31	cis-1,3-Dichloropropene	25-175	85.59	93.00	90.69
32	4-methyl-2-pentanone	60-140	95.74	101.41	98.33
33	Toluene-d8 (SS)	60-140	99.88	100.33	100.51
34	Toluene	70-130	85.13	90.87	91.35
35	trans-1,3-Dichloropropene	50-150	85.64	93.99	89.33
36	1,1,2-Trichloroethane	70-130	88.71	94.86	93.19
37	Tetrachloroethene	70-130	86.58	93.26	94.35
38	1,3-Dichloropropane	60-140	88.72	93.61	92.49
39	2-Hexanone	60-140	94.91	99.16	97.94
40	Dibromochloromethane	70-135	89.97	96.17	93.26
41	1,2-dibromoethane	60-140	87.95	94.19	92.28
42	Chlorobenzene	65-135	83.92	89.85	88.34
43	Ethylbenzene	60-140	83.19	90.10	89.75
44	1,1,1,2-tetrachloroethane	60-140	86.73	92.62	91.26
45	Xylene Total	60-140	97.42	103.97	101.36
46	m/p-Xylene	60-140	83.14	90.36	88.92
47	o-Xylene	60-140	84.00	90.16	88.89
48	Styrene	60-140	85.15	91.42	90.06
49	Bromoform	70-130	88.19	96.29	90.53
50	Isopropylbenzene	60-140	84.20	91.05	90.09
51	4-Bromofluorobenzene (SS)	60-140	99.47	99.64	99.98
52	1,1,2,2-Tetrachloroethane	60-140	89.52	95.20	92.15
53	Bromobenzene	60-140	84.63	91.47	89.93
54	trans-1,4-dichloro-2-butene	60-140	82.18	91.74	84.97
55	1,2,3-trichloropropane	60-140	88.91	96.84	91.10
56	n-Propylbenzene	60-140	83.66	91.05	89.54
57	2-chlorotoluene	60-140	83.42	89.89	88.49
58	4-chlorotoluene	60-140	87.50	94.60	83.32
59	1,2,4-trimethylbenzene	60-140	84.60	91.76	90.53
60	tert-butylbenzene	60-140	83.87	92.73	90.33

Peak #	Compound Name	Range for Q Recovery (%)	CCV #1	CCV #2	CCV #3
61	1,3,5-trimethylbenzene	60-140	84.35	92.15	89.42
62	sec-butylbenzene	60-140	84.07	92.90	91.36
63	1,3-Dichlorobenzene	70-130	84.35	90.91	87.80
64	4-isopropyltoluene	60-140	86.31	96.23	92.61
65	1,4-Dichlorobenzene	65-135	85.44	92.87	89.02
66	1,2-Dichlorobenzene	65-135	86.98	94.01	89.40
67	n-butylbenzene	60-140	84.50	95.79	91.74
68	1,2-dibromo-3-chloropropane	60-140	93.51	98.96	94.33
69	1,2,3-trichlorobenzene	60-140	81.92	92.09	86.87
70	Hexachlorobutadiene	60-140	79.83	100.75	91.23
71	Naphthalene	60-140	86.93	95.49	90.54
72	1,2,4-trichlorobenzene	60-140	84.88	95.75	90.74

D = Detected result must be greater than zero

Method 8260C calibration verification has four criteria: Each of the most common target analytes in the calibration verification standard should meet a minimum response factor outlined by the EPA. Secondly, all target compounds of interest must be evaluated using a 20% variability criterion. Thirdly, the retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition and must not vary by more than 10 seconds from that in the mid-point standard level of the most recent initial calibration sequence. Fourthly, the extracted ion current profile (EICP) area for any of the internal standards in the calibration verification standard must not change by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence [i].

1) *Minimum response factor:* Table 5 shows the results from the CCV standards minimum response factor evaluation. Most compounds were able to pass this criterion. The only compounds that did not pass the criterion were dichlorodifluoromethane, bromomethane, acetone, 2-butanone and 4-methyl-2-pentanone. When analyzed by a Purge and Trap and EPA 8260 protocols, all of the above compounds are described by the EPA as analytes that exhibit known difficulties with reproducibility, response, recovery and stability [V].

Table 5: Recommended minimum relative response factor criteria for continuing calibration verification.

Peak #	Compound Name	Minimum Response Factor (RF)	CCV #1 RF	CCV #2 RF	CCV #3 RF
1	Dichlorodifluoromethane	0.100	0.043	0.044	0.047
2	Chloromethane	0.100	0.136	0.143	0.147
3	Vinyl chloride	0.100	0.125	0.130	0.140
4	Bromomethane	0.100	0.068	0.069	0.070
5	Chloroethane	0.100	0.106	0.110	0.117
6	Trichlorofluoromethane	0.100	0.173	0.174	0.193
7	Acrolein*		0.107	0.113	0.113
8	1,1-Dichloroethene	0.100	0.161	0.169	0.180
9	Acetone	0.100	0.061	0.062	0.063
10	Iodomethane*		0.108	0.118	0.125
11	Methylene chloride	0.100	0.197	0.206	0.208
12	trans-1,2-Dichloroethene	0.100	0.201	0.215	0.220
13	1,1-Dichloroethane	0.200	0.469	0.495	0.507
14	Vinyl acetate*		1.158	1.227	1.214
15	2-Butanone	0.100	0.065	0.067	0.066
16	cis-1,2-dichloroethene		0.244	0.257	0.263
17	2,2-dichloropropan*		0.182	0.233	0.201
18	Bromochloromethane*		0.097	0.099	0.100
19	Chloroform	0.200	0.342	0.365	0.368
20	Dibromofluromethane (SS)		0.197	0.198	0.197
21	1,1,1-Trichloroethane	0.100	0.241	0.259	0.268
22	Carbon tetrachloride	0.100	0.193	0.205	0.212
23	1,1-dichloropropylene*		0.107	0.114	0.118

Peak #	Compound Name	Minimum Response Factor (RF)	CCV #1 RF	CCV #2 RF	CCV #3 RF
24	Benzene	0.500	1.203	1.276	1.295
25	1,2-Dichloroethane	0.100	0.366	0.385	0.384
26	Trichloroethene	0.200	0.250	0.267	0.272
27	1,2-Dichloropropane	0.100	0.380	0.405	0.407
28	Dibromomethane*		0.159	0.170	0.167
29	Bromodichloromethane	0.200	0.351	0.374	0.374
30	2-Chloroethylvinylether*		0.319	0.354	0.328
31	cis-1,3-Dichloropropene	0.200	0.487	0.529	0.516
32	4-methyl-2-pentanone	0.100	0.096	0.101	0.098
33	Toluene-d8 (SS)*		1.219	1.224	1.227
34	Toluene	0.400	0.749	0.800	0.804
35	trans-1,3-Dichloropropene	0.100	0.436	0.479	0.455
36	1,1,2-Trichloroethane	0.100	0.240	0.257	0.252
37	Tetrachloroethene	0.200	0.192	0.207	0.209
38	1,3-Dichloropropane*		0.545	0.575	0.568
39	2-Hexanone	0.100	0.663	0.693	0.684
40	Dibromochloromethane	0.100	0.248	0.265	0.257
41	1,2-dibromoethane	0.100	0.281	0.301	0.295
42	Chlorobenzene	0.500	0.754	0.807	0.793
43	Ethylbenzene	0.100	1.219	1.320	1.315
44	1,1,1,2-tetrachloroethane*		0.238	0.254	0.251
45	Xylene Total*		0.520	0.555	0.541
46	m/p-Xylene	0.100	0.523	0.568	0.559
47	o-Xylene	0.300	0.514	0.552	0.544
48	Styrene	0.300	0.852	0.914	0.901
49	Bromoform	0.100	0.411	0.449	0.422
50	Isopropylbenzene	0.100	2.632	2.846	2.816
51	4-Bromofluorobenzene (SS)*		1.273	1.276	1.280
52	1,1,2,2-Tetrachloroethane	0.300	0.428	0.455	0.441
53	Bromobenzene*		0.620	0.670	0.659
54	trans-1,4-dichloro-2-butene*		0.405	0.452	0.419
55	1,2,3-trichloropropane*		1.385	1.509	1.419
56	n-Propylbenzene*		3.090	3.363	3.307
57	2-chlorotoluene*		2.024	2.181	2.147
58	4-chlorotoluene*		2.269	2.453	2.161
59	1,2,4-trimethylbenzene*		2.323	2.520	2.486
60	tert-butylbenzene*		1.879	2.078	2.024
61	1,3,5-trimethylbenzene*		2.291	2.503	2.429
62	sec-butylbenzene*		2.743	3.031	2.981
63	1,3-Dichlorobenzene	0.600	1.134	1.223	1.181
64	4-isopropyltoluene*		0.709	0.791	0.761
65	1,4-Dichlorobenzene	0.500	1.155	1.255	1.203
66	1,2-Dichlorobenzene	0.400	1.098	1.187	1.128
67	n-butylbenzene*		2.046	2.319	2.221
68	1,2-dibromo-3-chloropropane	0.050	0.235	0.248	0.237
69	1,2,3-trichlorobenzene*		0.664	0.747	0.704
70	Hexachlorobutadiene*		0.296	0.374	0.338
71	Naphthalene*		2.618	2.876	2.727
72	1,2,4-trichlorobenzene	0.200	0.641	0.723	0.686

*Data for minimum RF was not provided by EPA method 8260C.

2) *Variability:* more than 95% of the compounds met this condition. The percent difference of the CCV standards was used to evaluate the suitability of average response factor model calibration, while the percent drift was used in the evaluation of the linear calibration (Table 6).

3) *Retention time:* The retention times of the internal standards in the calibration verification standard was evaluated immediately after data acquisition to ensure that they met the method criterion (≤ 10 seconds from that in the mid-point standard level of the most recent initial calibration sequence). All internal standards met this criterion.

4) *EICP:* The EICP of internal standard in the CCV standard was evaluated against the same response in the ICAL curve to ensure that the IS in the CCV met the method criterion (-50% to + 100%relative to the response of that IS in the mid-point of the ICAL). The internal standards were able to pass this criterion.

Results from the CCVs met the QC criteria outlined in Method 8260C and 624.1, hence, the ICAL was used to calculate the MDL for each compound in the methods.

Table 6: Method 8260C % Difference or % Drift of CCVs during MDL study.

Peak #	Compound Name	CCV #1	CCV #2	CCV #3
1	Dichlorodifluoromethane	2.36	4.58	12.83
2	Chloromethane	-8.41	-3.21	-0.39
3	Vinyl chloride	-6.15	-2.31	4.94
4	Bromomethane	-14.11	-13.29	-11.98
5	Chloroethane	1.42	5.03	11.21
6	Trichlorofluoromethane	-1.41	-1.12	9.83
7	Acrolein	-4.96	0.32	0.72
8	1,1-Dichloroethene	-5.43	-0.95	5.35
9	Acetone	-4.67	-3.27	-1.60
10	Iodomethane	23.51	34.42	42.75
11	Methylene chloride	-11.99	-7.98	-6.95
12	trans-1,2-Dichloroethene	-14.02	-7.82	-5.70
13	1,1-Dichloroethane	-12.59	-7.75	-5.65
14	Vinyl acetate	-3.24	2.54	1.39
15	2-Butanone	-6.21	-1.93	-3.57
16	cis-1,2-dichloroethene	-13.49	-8.88	-6.90
17	2,2-dichloropropan	-30.59	-11.16	-23.32
18	Bromochloromethane	-12.17	-10.07	-9.25
19	Chloroform	-14.63	-9.06	-8.25
20	Dibromofluromethane (SS)	0.32	1.01	0.02
21	1,1,1-Trichloroethane	-12.18	-5.79	-2.43
22	Carbon tetrachloride	-11.80	-6.38	-2.75
23	1,1-dichloropropylene	-12.06	-5.64	-2.16
24	Benzene	-13.67	-8.45	-7.12
25	1,2-Dichloroethane	-10.56	-5.82	-6.07
26	Trichloroethene	-13.55	-7.83	-5.92
27	1,2-Dichloropropane	-12.36	-6.66	-6.13
28	Dibromomethane	-10.49	-4.54	-6.00
29	Bromodichloromethane	-12.17	-6.45	-6.48
30	2-Chloroethylvinylether	-14.79	-5.51	-12.59
31	cis-1,3-Dichloropropene	-14.41	-7.00	-9.31
32	4-methyl-2-pentanone	-4.24	1.43	-1.65
33	Toluene-d8 (SS)	-0.11	0.33	0.51
34	Toluene	-16.56	-10.93	-10.46
35	trans-1,3-Dichloropropene	-14.36	-6.01	-10.67
36	1,1,2-Trichloroethane	-11.28	-5.13	-6.80
37	Tetrachloroethene	-13.41	-6.73	-5.64
38	1,3-Dichloropropane	-11.28	-6.38	-7.50
39	2-Hexanone	-5.09	-0.84	-2.06
40	Dibromochloromethane	-10.03	-3.84	-6.74
41	1,2-dibromoethane	-12.04	-5.80	-7.71
42	Chlorobenzene	-16.09	-10.16	-11.67
43	Ethylbenzene	-16.81	-9.90	-10.25

Peak #	Compound Name	CCV #1	CCV #2	CCV #3
44	1,1,1,2-tetrachloroethane	-13.28	-7.39	-8.75
45	Xylene Total	-14.60	-8.86	-11.15
46	m/p-Xylene	-16.86	-9.65	-11.08
47	o-Xylene	-16.00	-9.84	-11.12
48	Styrene	-14.85	-8.58	-9.94
49	Bromoform	-11.80	-3.70	-9.47
50	Isopropylbenzene	-15.80	-8.95	-9.91
51	4-Bromofluorobenzene (SS)	-0.53	-0.36	-0.02
52	1,1,2,2-Tetrachloroethane	-10.48	-4.80	-7.85
53	Bromobenzene	-15.37	-8.53	-10.07
54	trans-1,4-dichloro-2-butene	-17.81	-8.26	-15.02
55	1,2,3-trichloropropane	-11.09	-3.16	-8.90
56	n-Propylbenzene	-16.34	-8.95	-10.46
57	2-chlorotoluene	-17.49	-11.08	-12.47
58	4-chlorotoluene	-12.50	-5.40	-16.68
59	1,2,4-trimethylbenzene	-15.40	-8.24	-9.47
60	tert-butylbenzene	-16.12	-7.27	-9.67
61	1,3,5-trimethylbenzene	-15.65	-7.85	-10.57
62	sec-butylbenzene	-15.93	-7.10	-8.64
63	1,3-Dichlorobenzene	-15.65	-9.09	-12.20
64	4-isopropyltoluene	-13.69	-3.77	-7.39
65	1,4-Dichlorobenzene	-14.56	-7.12	-10.98
66	1,2-Dichlorobenzene	-13.01	-5.99	-10.60
67	n-butylbenzene	-15.50	-4.21	-8.27
68	1,2-dibromo-3-chloropropane	-6.47	-1.02	-5.65
69	1,2,3-trichlorobenzene	-18.08	-7.90	-13.13
70	Hexachlorobutadiene	-20.19	0.74	-8.79
71	Naphthalene	-13.07	-4.51	-9.46
72	1,2,4-trichlorobenzene	-15.12	-4.26	-9.27

Method Detection Limit (MDL)

Ten 0.50 µg/L and 1.00 µg/L spiked samples were analyzed by methods 624.1 and 8260C. The %RSD was calculated by determining the mean accuracy and standard deviation for all analytes at 0.50 µg/L and 1.00 µg/L. The %RSD for all targeted compounds for method 624.1 and 8260C are respectively listed in Table 6 and 7.

MDLs for each of the analytes met both EPA method 624.1 and 8260C detection limit criteria. For method 624.1, at 0.50 µg/L the MDLs ranged from 0.07 to 0.40, while at 1.00 µg/L MDLs ranged from 0.09 to 0.50 µg/L. Regarding method 8260C, at 0.50 µg/L the MDLs ranged from 0.07 to 0.40, while at 1.00 µg/L MDLs ranged from 0.09 to 0.50 µg/L. Table 6 and 7 list the MDL study results.

Table 6: 624.1: %RSD and Method Detection Limit (MDL) Study Results.

Peak #	Compound Name	0.50 µg/L; n=10		1.00 µg/L; n=10	
		%RSD	MDL	%RSD	MDL
1	Chloromethane	11.80	0.13	8.17	0.20
2	Vinyl chloride	15.58	0.17	9.57	0.23
3	Bromomethane	14.14	0.20	13.49	0.36
4	Chloroethane	16.38	0.15	10.59	0.23
5	Acrolein	12.02	0.14	9.87	0.22
6	1,1-Dichloroethene	16.91	0.20	9.92	0.24
7	Iodomethane	ND	ND	22.77	0.44
8	Methylene chloride	11.40	0.13	5.36	0.13
9	trans-1,2-Dichloroethene	10.65	0.12	6.84	0.17
10	cis-1,2-Dichloroethene	10.42	0.13	5.04	0.13
11	1,1-Dichloroethane	10.20	0.13	5.47	0.15
12	Chloroform	6.30	0.08	4.77	0.12
13	1,1,1-Trichloroethane	13.43	0.16	8.12	0.21
14	Carbon tetrachloride	12.45	0.16	8.75	0.23
15	Benzene	9.92	0.12	5.39	0.14
16	1,2-Dichloroethane	6.87	0.09	4.03	0.10
17	Trichloroethene	10.47	0.13	6.33	0.16

Peak #	Compound Name	0.50 µg/L; n=10		1.00 µg/L; n=10	
		%RSD	MDL	%RSD	MDL
18	1,2-Dichloropropane	7.34	0.09	4.31	0.11
19	Bromodichloromethane	6.86	0.08	4.51	0.11
20	2-Chloroethylvinylether	7.13	0.08	4.78	0.12
21	cis-1,3-Dichloropropene	7.47	0.08	4.96	0.12
22	Toluene	8.10	0.10	5.49	0.14
23	trans-1,3-Dichloropropene	6.17	0.07	4.83	0.12
24	1,1,2-Trichloroethane	7.95	0.10	4.69	0.11
25	Tetrachloroethene	13.22	0.16	7.20	0.19
26	Dibromochloromethane	6.97	0.08	6.04	0.15
27	Chlorobenzene	7.69	0.10	5.10	0.13
28	Ethylbenzene	9.10	0.12	5.68	0.15
29	Xylene Total	8.86	0.40	5.32	0.50
30	m/p-Xylene	9.29	0.24	5.45	0.29
31	o-Xylene	7.97	0.10	5.20	0.13
32	Bromoform	7.36	0.09	4.30	0.10
33	1,1,2,2-Tetrachloroethane	7.92	0.10	3.76	0.09
34	1,3-Dichlorobenzene	6.14	0.08	5.05	0.13
35	1,4-Dichlorobenzene	6.65	0.09	5.41	0.14
36	1,2-Dichlorobenzene	6.03	0.07	5.21	0.13

Table 7: 8260C: %RSD and Method Detection Limit (MDL) Study Results.

Peak #	Compound Name	0.50 µg/L; n=10		1.00 µg/L; n=10	
		%RSD	MDL	%RSD	MDL
1	Dichlorodifluoromethane	NA	NA	12.04	0.28
2	Chloromethane	11.80	0.13	8.17	0.20
3	Vinyl chloride	15.58	0.17	9.57	0.23
4	Bromomethane	14.14	0.19	13.49	0.34
5	Chloroethane	16.39	0.15	10.61	0.23
6	Trichlorofluoromethane	16.33	0.20	10.55	0.29
7	Acrolein	12.02	0.14	9.87	0.22
8	1,1-Dichloroethene	16.91	0.20	9.92	0.24
9	Acetone	16.89	0.33	12.24	0.36
10	Iodomethane	NA	NA	22.80	0.36
11	Methylene chloride	11.40	0.13	5.34	0.13
12	trans-1,2-Dichloroethene	10.65	0.12	6.83	0.17
13	1,1-Dichloroethane	10.42	0.13	5.02	0.13
14	Vinyl acetate	7.45	0.08	4.84	0.11
15	2-Butanone	13.57	0.17	11.48	0.28
16	cis-1,2-dichloroethene	10.20	0.13	5.47	0.15
17	2,2-Dichloropropane	19.99	0.26	14.87	0.47
18	Bromochloromethane	12.33	0.14	5.41	0.14
19	Chloroform	6.30	0.08	4.78	0.13
20	1,1,1-Trichloroethane	13.43	0.16	8.32	0.22
21	Carbon tetrachloride	12.45	0.16	8.74	0.23
22	1,1-Dichloropropylene	15.00	0.18	7.75	0.21
23	Benzene	9.92	0.12	5.39	0.14
24	1,2-Dichloroethane	6.87	0.09	4.02	0.10
25	Trichloroethene	10.47	0.13	6.47	0.16
26	1,2-Dichloropropane	7.34	0.09	4.31	0.11
27	Dibromomethane	8.95	0.10	5.24	0.13
28	Bromodichloromethane	6.86	0.08	4.52	0.11
29	2-Chloroethylvinylether	7.13	0.08	4.78	0.12
30	cis-1,3-Dichloropropene	7.47	0.08	4.96	0.12
31	4-Methyl-2-pentanone	11.83	0.14	8.01	0.19
32	Toluene	8.10	0.10	5.61	0.15
33	trans-1,3-Dichloropropene	6.17	0.07	4.82	0.12
34	1,1,2-Trichloroethane	7.95	0.10	4.67	0.12
35	Tetrachloroethene	13.22	0.16	7.21	0.19
36	1,3-Dichloropropane	7.05	0.09	3.37	0.09
37	2-Hexanone	8.95	0.10	4.46	0.11
38	Dibromochloromethane	6.97	0.08	6.04	0.14

Peak #	Compound Name	0.50 µg/L; n=10		1.00 µg/L; n=10	
		%RSD	MDL	%RSD	MDL
39	1,2-Dibromoethane	7.78	0.10	5.15	0.13
40	Chlorobenzene	7.69	0.10	5.23	0.14
41	Ethylbenzene	9.10	0.12	5.67	0.15
42	1,1,1,2-Tetrachloroethane	7.66	0.09	4.24	0.11
43	Xylene Total	8.86	0.40	5.32	0.50
44	m/p-Xylene	9.29	0.24	5.45	0.29
45	o-Xylene	7.97	0.10	5.21	0.14
46	Styrene	8.94	0.11	4.67	0.12
47	Bromoform	7.36	0.09	4.30	0.10
48	Isopropylbenzene	10.74	0.14	6.07	0.16
49	1,1,2,2-Tetrachloroethane	7.92	0.10	3.76	0.09
50	Bromobenzene	7.69	0.10	5.32	0.14
51	trans-1,4-Dichloro-2-butene	14.92	0.17	6.15	0.16
52	1,2,3-Trichloropropane	8.42	0.10	4.24	0.10
53	n-Propylbenzene	10.99	0.14	5.54	0.15
54	2-Chlorotoluene	9.02	0.12	4.67	0.12
55	4-Chlorotoluene	22.34	0.27	6.03	0.16
56	1,2,4-Trimethylbenzene	8.62	0.11	5.22	0.14
57	tert-Butylbenzene	10.23	0.13	5.82	0.16
58	1,3,5-Trimethylbenzene	8.80	0.11	4.81	0.13
59	sec-Butylbenzene	10.70	0.14	6.20	0.17
60	1,3-Dichlorobenzene	6.14	0.08	5.04	0.13
61	4-Isopropyltoluene	10.44	0.13	5.79	0.15
62	1,4-Dichlorobenzene	6.65	0.09	5.42	0.14
63	1,2-Dichlorobenzene	6.03	0.07	5.21	0.13
64	n-Butylbenzene	10.82	0.13	6.31	0.16
65	1,2-Dibromo-3-chloropropane	13.52	0.15	9.91	0.22
66	1,2,3-Trichlorobenzene	7.65	0.09	12.30	0.30
67	Hexachlorobutadiene	16.12	0.15	8.86	0.20
68	Naphthalene	6.18	0.07	7.50	0.18
69	1,2,4-Trichlorobenzene	7.05	0.08	9.89	0.23

NA = Target compound was not detected.

■ Conclusions

The study demonstrates the satisfactory performance of the Shimadzu GCMS-QP2020 NX in the analysis of VOCs by EPA method 624.1/8260C. Since the target list in method 624.1 is a partial list of the compounds in method 8260C, both methods were combined and evaluated using the same calibration curve. The suitability of the initial calibration curve was evaluated according to EPA method 8260C criteria using the percent %RSD of the calculated RFs for each data point in the curve; results from most of the targeted compounds met the 8260C method's %RF RSD requirements (RF %RSD < 20 %). The RF %RSD for these compounds ranged from 1.92 to 17.27. The r^2 for all compounds in method 8260C ranged from 0.9945 to 0.9999, while for compounds in method 624.1 the r^2 ranged from 0.9912 to 0.9999.

The MDL experiments were conducted over a three-day period; CCV standards were analyzed during the study and met the EPA requirements. When compared to the initial calibration curve, all CCVs recoveries for all compounds, based on method 624.1, ranged from 62.30 to 111.74%.

From the CCV standards, all target compounds were within their respective QC acceptance criteria and these CCVs determined that the ICAL can be used to calculate MDLs for method 624.1. More than 95% of the target compounds and all the internal standards met the QC criterion required in method 8260C for calculating MDLs for this method.

Using 10 replicates of standards at two individual concentrations, the estimated MDLs met USEPA Method 624.1 and 8260C requirements for detection limits. For method 624.1, at 0.50 µg/L, the MDL ranged from 0.07 to 0.40, while at 1.00 µg/L, the MDL ranged from 0.09 to 0.50 µg/L. Regarding method 8260C, at 0.50 µg/L, the MDL ranged from 0.07 to 0.43, while at 1.00 µg/L, the MDL ranged from 0.09 to 0.50 µg/L.

In this study, we demonstrated that the performance of the new and more sensitive instrument is optimal. The robust operation of the newly released GCMS QP2020 NX results in this instrument being one of the best available technologies for analysis of EPA methods 624.1 and 8260C.

■ References

I. United States Environmental Protection Agency Method 8260C, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 3, August 2006.
II. United States Environmental Protection Agency Method 624.1: Purgeables by GC/MS, EPA Document #EPA 821-R-16-008.
III. 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.
IV. Definition and Procedures for the Determination of the Method Detection Limit. Fed. Regist. 1984. 49 (209), Appendix B to Part 136.
V. United States Environmental Protection Agency Method 8260D, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 4, June 2018.

■ Consumables

Table 7: Consumables used in this application.

Part Number	Item Name	Item Description
221-75926-30	Capillary Column	SH-Rxi-624.1 Sil MS, 30m x 0.25 mmID x 1.40 um
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	8260C Internal Standard Mix (4 components) (Restek)
30073	Surrogate Mix	8260C Surrogate Standard Mix (3 components) (Restek)
120016-03	Method 8260C Gases	Methods 8260C Gas Mix, 2,000 mg/L, 2 x 0.6 ml (o2si)
123485-02	Method 8260C VOC Reactive Solution	Method 8260C VOC Reactive Solution 8-1, 2,000 mg/L, 1ml (o2si)
120023-03-02	8260C VOC Liquids	8260C VOC Liquids, 54 Compounds, 2,000 mg/L, 2 x 0.6ml (o2si)
0202203-02	Iodomethane Solution	Iodomethane Solution, 2,000 mg/L, 1ml (o2si)

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SHIMADZU Corporation
www.shimadzu.com/an/

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com