The Evaluation of a New GC-MS instrument and Novel BFB tune for analysis of EPA Method 524.2.

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1. Introduction

One of the first EPA analytical methods developed to analyze Volatile Organic Compounds (VOCs) in drinking water was method 524.1. As GC-MS instrumentation advanced, with improvements in sensitivity, reliability, and user experience, method 524.1 has either been revised and updated or new methods have been developed. Currently, majority of environmental laboratories analyzing volatile 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. This study has tested the newly released Shimadzu GCMS-QP2020 NX instrument and novel BFB tuning parameter against the aforementioned methods and a study to determine the Method Detection Limit (MDL) of the target compounds was also conducted. In this application, we demonstrate that the performance of the new more sensitive instrument is optimal and traditional issues with methods EPA 524.2/524.3 are overcome.

2. Experimental

In the study, an EST Analytical Econ Evolution purge and trap (P&T) concentrator and Centurion WS autosampler were interfaced to the Shimadzu GCMS-QP2020 NX (Figure 1). A VOCARB 3000 (k) analytical trap was configured with the P&T unit. A narrow bore inlet liner was used 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 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. GC-MS and P&T operating condition

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 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	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

Figure 1. Shimadzu GCMS-QP2020 NX

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 ug/ml. Internal and surrogate standards for purging were prepared at 50 µg/L.

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 outlined in the Federal Register [1] and using the mathematics equation listed below. In brief, 10 sample replicates were made at both 1.0 µg/L and 5.0 µg/L. These samples were analyzed on the GCMS-QP2020 NX and their standard deviation was calculated. To calculate the MDL, the formula listed below was used where the standard deviation was multiplied by the student's t value for a 99% confidence level at n-1 degree of freedom.

$$MDL = T\,(n\text{-}1,\ 1\text{-}x = 99)\ S$$

3. Results and Discussion

A single BFB tune file was used for all the analysis 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).

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

Initial Calibration

In the study, a calibration curve was prepared in the concentration range from 0.25 to 200 µg/L. This linear range was used to estimate MDLs at both the 1.0 and 5.0 µg/L. The calibration curves were evaluated according to method EPA 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 was used as an alternative to the RF criteria. The results, summarized in Table 3, show that most compounds passed the EPA method 524 RF criteria (RF %RSD < 20 %) indicating that the RF can be used for calculating samples concentrations.

Continue Calibration Verification

Continuing calibration verification (CCV) standards were used throughout each of the three sequences for the MDL study. When compared to the initial calibration curve all CCVs passed the EPA requirement (the absolute areas of the internal standard and surrogates quantitation ions should not decrease by more than 50% from areas measured during initial calibration). The CCV recoveries for internal and surrogate standards ranged from 95.32 – 103.17.

Method Detection Limit

Ten 1.0 µg/L and 5.0 µg/L spiked samples were analyzed and the mean accuracy and standard deviation for each analyte was calculated. The mean accuracy for all analytes at 1.0 µg/L ranged from 0.80 to 1.1 µg/L, while at 5.0 µg/L the mean accuracy ranged from 4.2 to 5.7 ppb. Standard deviation at 1.0 µg/L ranged from 0.020 to 0.19, while at 5.0 µg/L, standard deviation ranged from 0.11 to 0.70.

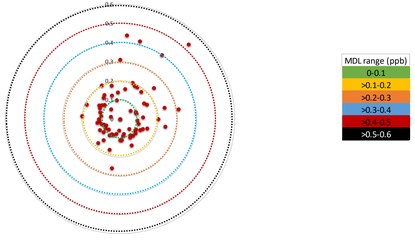
Method Detection Limit (MDL) studies at 1.0 and 5.0 µg/L were estimated using the 10 replicate aliquots mentioned above. MDLs for each standard were able to exceed EPA method 524 criteria. At 1.0 µg/L the MDL ranged from 0.050 to 0.44 µg/L, while at 5.0 µg/L MDL ranged from 0.28 to 3.7 µg/L. Figure 2 illustrates the estimated MDL at 1.0 µg/L for each target compound. Colors used to highlight the compounds in Table 3 correspond to the specific MDL ranges indicated in the legend from Figure 2.

Table 3. Statistical results of initial calibration curve ranging from 0.5 to 200 µg/L

Peak #	Compound Name	10-Point Calibration 0.25 to 200 µg/L R2	Avg RF	RF %RSD	Peak #	Compound Name	10-Point Calibration 0.25 to 200 µg/L R2	Avg RF	RF %RSD
1	Dichlorodifluoromethane	0.9998	0.0527	11.694	40	Ethyl methacrylate	0.9996	0.476	6.681
2	Chloromethane	0.9988	0.146	7.953	41	1,1,2-Trichloroethane	0.9991	0.207	8.255
3	Vinyl chloride	0.9999	0.135	5.336	42	Tetrachloroethene	0.9995	0.25	10.713
4	Bromomethane	0.9967	0.0742	27.958	43	1,3-Dichloropropane	0.9985	0.461	8.506
5	Chloroethane	0.9999	0.136	8.234	44	Dibromochloromethane	0.998	0.201	8.56
6	Trichlorofluoromethane	0.9995	0.196	8.884	45	1,2-dibromoethane	0.9987	0.232	8.51
7	1,1-Dichloroethene	0.9993	0.173	4.904	46	Chlorobenzene	0.9972	0.678	12.133
8	cis-1,2-dichloroethene	0.9991	0.105	7.889	47	Ethylbenzene	0.9929	1.162	14.771
9	Iodomethane	0.9995	0.1	31.874	48	1,1,1,2-tetrachloroethane	0.993	0.208	12.693
10	Carbon disulfide	0.9999	0.554	9.188	49	m/p-Xylene	0.9978	0.496	14.42
11	Allyl chloride	0.9988	0.127	6.722	50	o-Xylene	0.9933	0.479	14.072
12	Methylene chloride	0.9999	0.239	19.647	51	Styrene	0.9936	0.766	12.418
13	Acrylonitrile	0.9999	0.222	11.237	52	Bromoform	0.9999	0.161	17.3
14	trans-1,2-Dichloroethene	0.9999	0.209	6.893	53	Isopropylbenzene	0.998	1.069	14.462
15	Methyl tert-butyl ether	0.9997	0.826	10.865	54	4-BromoFluorobenzene (SS)	NA	0.365	4.98
16	1,1-Dichloroethane	0.9999	0.525	5.828	55	1,1,2,2-Tetrachloroethane	0.9954	0.361	9.853
17	2,2-dichloropropane	0.9987	0.306	9.745	56	Bromobenzene	0.9948	0.238	11.062
18	Propionitrile	0.9999	0.089	14.4	57	trans-1,4-dichloro-2-butene	0.9915	0.164	13.109
19	Methyl acrylate	0.9993	0.523	12.64	58	1,2,3-trichloropropane	0.9939	0.496	10.333
20	Bromochloromethane	0.9984	0.099	9.448	59	n-Propylbenzene	0.9952	1.264	14.27
21	Methyl acrylonitrile	0.9999	0.209	4.067	60	2-chlorotoluene	0.996	0.805	13.85
22	Tetrahydrofuran	0.9999	0.0716	20.719	61	4-chlorotoluene	0.9951	0.845	16.315
23	Chloroform	0.9997	0.379	6.736	62	1,2,4-trimethylbenzene	0.9965	0.954	10.796
24	1,1,1-Trichloroethane	0.9999	0.272	9.132	63	tert-butylbenzene	0.9972	0.813	11.686
25	Carbon tetrachloride	0.9987	0.218	10.845	64	1,3,5-trimethylbenzene	0.9961	0.919	10.493
26	1-chlorobutane	0.9992	0.763	8.317	65	Pentachloroethane	0.9947	0.165	15.844
27	Benzene	0.9985	1.117	9.635	66	sec-butylbenzene	0.9971	1.142	11.009
28	1,2-Dichloroethane	0.9999	0.432	21.231	67	1,3-Dichlorobenzene	0.9976	0.439	8.76
29	Trichloroethene	0.9998	0.237	9.428	68	4-isopropyltoluene	0.9979	0.264	12.502
30	1,2-Dichloropropane	0.9975	0.331	9.208	69	1,4-Dichlorobenzene	0.9972	0.44	12.598
31	Dibromomethane	0.9993	0.133	7.028	70	1,2-Dichlorobenzene	0.9983	0.401	9.782
32	Methyl methacrylate	0.9993	0.291	7.002	71	n-butylbenzene	0.9981	0.783	10.658
33	Bromodichloromethane	0.9997	0.296	4.957	72	Hexachloroethane	0.9984	0.1396	7.861
34	2-Nitropropane	0.9999	0.17	14.127	73	1,2-dibromo-3-chloropropane	0.9998	0.0808	4.76
35	Chloroacetonitrile	0.9991	0.1268	14.149	74	Nitrobenzene	0.9999	0.0193	21.896
36	cis-1,3-Dichloropropene	0.999	0.429	7.189	75	1,2,3-trichlorobenzene	0.9993	0.235	9.57
37	Toluene d-8 (SS)	NA	0.914	1.579	76	Hexachlorobutadiene	0.9977	0.111	7.131
38	Toluene	0.9999	0.738	11.44	77	Naphthalene	0.9998	0.918	5.264
39	trans-1,3-Dichloropropene	0.9987	0.387	8.198	78	1,2,4-trichlorobenzene	0.9993	0.219	9.154

Note: Compounds in white in Table 3 are not included in Figure 2

Figure 2. Calculated MDL for each compound highlighted in Table 3.



4. 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 (< 20%), which is the EPA primary initial calibration requirement. Results from the CCV also met the EPA requirements (the absolute areas of the internal standard and surrogates quantitation ions should not decrease by more than 50% from areas measured during initial calibration). All calculated MDL were within the EPA requirement.

Results from a subsequent experiment will be presented in Poster 626-14P. In the subsequent experiment, real world water samples were tested using EPA method 524.2 and BFB tuning outline in this poster.

References:

1. Definition and Procedures for the Determination of the Method Detection Limit. Fed. Regist. 1984. 49 (209), Appendix B to Part 136.

Replacement Consumables

Part Number	Item Name	Item Description
221-75926-30	Capillary Column	SH-Rxi-624 Sil MS, 30m x 0.25 mmID x 1.40 um
220-90784	Inlet Liner	Low-volume liner, 1.0 mmID, Straight, Sr/kg (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)
MXI0482-6	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)
120016-03	Method 8260 Gases	Method 8260 Gases, 2,000 mg/L, 2 x 0.6ml (o2si)
120023-03-02	Method 8260 VOC liquid	8260 VOC Liquids, 54 Compounds, 2,000 mg/L, 2 x 0.6ml (o2si)
123485-02	Methods 8260 VOC solution	Method 8260 VOC Reactive Solution 8-1, 2,000 mg/L, 1ml (o2si)