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

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1. 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. On the other hand, EPA method 624.1 is approved for analysis of purgeable organics in municipal and industrial wastewater. 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 of instrumentation require a reevaluation of the original method on newer instruments to demonstrate that the performance requirements included in these methods are met. This poster presents results from 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 .

2. Experimental

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 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). The experimental parameters for both GC-MS and P&T systems are listed in Table 1.

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

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 (ºC)	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 ºC (4.0 mins.), 14 ºC/mins. to 220 ºC (7.0 mins.)
Mass Spectrometer	**QP2020 NX**
Interface Temperature (ºC)	180
Ion Source Temperature (ºC)	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 (ºC)	35
Mort ready Temp (ºC)	39
Desorb Preheat Temperature (ºC)	245
Desorb Temperature (ºC)	250
Trap Bake Temperature (ºC)	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. 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.

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 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.

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

3. 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), #12 (second day) and #32 (third day).

Table 2. Evaluation of BFB spectra from 3 different injections made throughout 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

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. Figure 2. shows calibration curves for selected compounds in the study.

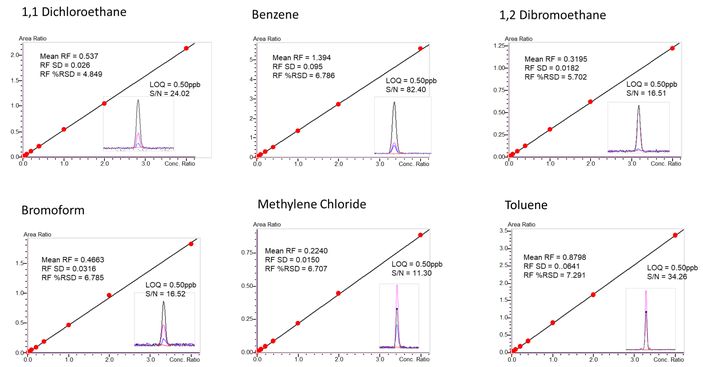

Figure 2. Calibration curves for selected compounds.

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. 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. Greater than 90% of the compounds passed the EPA method 8260C RF criteria.

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 was analyzed prior to running the batch on each day.

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. A list of all targeted compounds is shown in Table 3.

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. Figure 3A illustrates MDL study results for compound listed in EPA method 8260C, while Figure 3B shows the %RSD for each compounds at the two individual spiking concentration.

Table 3. Targeted compounds analyzed in the study.

Peak #	Compound Name	Peak #	Compound Name	Peak #	Compound Name	Peak #	Compound Name
1	Dichlorodifluoromethane	19	Chloroform	37	2-Hexanone	55	4-Chlorotoluene
2	Chloromethane	20	1,1,1-Trichloroethane	38	Dibromochloromethane	56	1,2,4-Trimethylbenzene
3	Vinyl chloride	21	Carbon tetrachloride	39	1,2-Dibromoethane	57	tert-Butylbenzene
4	Bromomethane	22	1,1-Dichloropropylene	40	Chlorobenzene	58	1,3,5-Trimethylbenzene
5	Chloroethane	23	Benzene	41	Ethylbenzene	59	sec-Butylbenzene
6	Trichlorofluoromethane	24	1,2-Dichloroethane	42	1,1,1,2-Tetrachloroethane	60	1,3-Dichlorobenzene
7	Acrolein	25	Trichloroethene	43	Xylene Total	61	4-Isopropyltoluene
8	1,1-Dichloroethene	26	1,2-Dichloropropane	44	m/p-Xylene	62	1,4-Dichlorobenzene
9	Acetone	27	Dibromomethane	45	o-Xylene	63	1,2-Dichlorobenzene
10	Iodomethane	28	Bromodichloromethane	46	Styrene	64	n-Butylbenzene
11	Methylene chloride	29	2-Chloroethylvinylether	47	Bromoform	65	1,2-Dibromo-3-chloropropane
12	trans-1,2-Dichloroethene	30	cis-1,3-Dichloropropene	48	Isopropylbenzene	66	1,2,3-Trichlorobenzene
13	1,1-Dichloroethane	31	4-Methyl-2-pentanone	49	1,1,2,2-Tetrachloroethane	67	Hexachlorobutadiene
14	Vinyl acetate	32	Toluene	50	Bromobenzene	68	Naphthalene
15	2-Butanone	33	trans-1,3-Dichloropropene	51	trans-1,4-Dichloro-2-butene	69	1,2,4-Trichlorobenzene
16	cis-1,2-dichloroethene	34	1,1,2-Trichloroethane	52	1,2,3-Trichloropropane		
17	2,2-Dichloropropane	35	Tetrachloroethene	53	n-Propylbenzene		
18	Bromochloromethane	36	1,3-Dichloropropane	54	2-Chlorotoluene		

Figure 3. 8260C Method Detection Limits (MDL) (Figure3A, Top) and %RSD (Figure 3B, Bottom) study results for compounds listed in Table 3

4. Conclusion

The study demonstrates the satisfactory performance of the Shimadzu GCMS-QP2020 NX in the analysis of VOCs by EPA method 624.1/8260C. 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 %). MDLs were calculated for both methods., but only MDLS for EPA 82060C is shown in this poster. Regarding method 8260C, at 0.50 µg/L the MDL ranged from 0.07 to 0.43, while at 1.00 µg/L MDL ranged from 0.09 to 0.50 µg/L.