Supporting Information

Method Development for On-Site Monitoring of Volatile Organic Compounds via Portable TD-GC-MS: Evaluation of the Analytical Performances of HAPSITE® ER Instrumentation and Thermal Desorption Sampling Media

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Table S1. Concentrations of compounds within the 19-compound gas standard. All compounds are balanced in N_2 and have ± 5% analytical uncertainty.

Compound	Concentration in gas standard (ppmv)
Chloroform	1.03
Benzene	1.00
Trichloroethylene	0.97
Heptane	1.02
Toluene	1.00
Tetrachloroethylene	1.00
Ethylbenzene	0.98
p-xylene	0.94
o-xylene	1.02
Mesitylene	0.99
1,2-Dichloroethane	1.05
Benzyl chloride	0.92
Carbon tetrachloride	1.04
Hexane	1.03
Methyl ethyl ketone	1.00
Methyl isobutyl ketone	0.97
Styrene	1.04
1,1,1-Trichloroethane	1.03
Tetrahydrofuran	0.96

Table S2. Volumes and masses of compounds injected onto TD tubes for the MS detector saturation study for analytes collected on Carbopack™ B.

Analyte	Concentration in gas standard (ppmv)	Injection volume (mL)										
		10.0	15.0	20.0	30.0	50.0	60.0	70.0	80.0	90.0	100	150
		Analyte mass (ng)										
Chloroform	1.03	51.1	76.7	102	153	256	307	358	409	460	511	767
Benzene	1.00	32.5	48.7	64.9	97.4	162	195	227	260	292	325	487
Trichloroethylene	0.97	53.0	79.5	106	159	265	318	371	424	477	530	795
Heptane	1.02	42.5	63.7	85.0	127	212	255	297	340	382	425	637
Toluene	1.00	38.3	57.4	76.6	115	191	230	268	306	345	383	574
Tetrachloroethylene	1.00	68.9	103	138	207	345	413	482	551	620	689	1034
Ethylbenzene	0.98	43.3	64.9	86.5	130	216	260	303	346	389	433	649
p-xylene	0.94	41.5	62.2	83.0	124	207	249	290	332	373	415	622
o-xylene	1.02	45.0	67.5	90.0	135	225	270	315	360	405	450	675
Mesitylene	0.99	49.5	74.2	98.9	148	247	297	346	396	445	495	742

All analyte masses were calculated assuming a pressure of 760 torr and temperature of 293.2 K.
The 19-compound gas standard was used for this study.
All compounds are balanced in N_2 and have ± 5% analytical uncertainty.

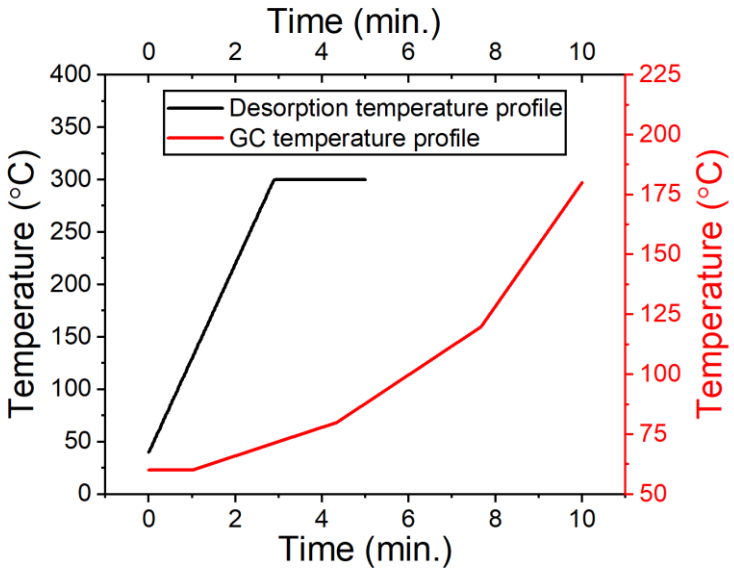


Figure S1. Illustration of the TD tube desorption temperature (black trace, left ordinate y-axis) and GC temperature (red trace, right ordinate y-axis) profiles used for the MS detector saturation study using Carbopack™ B sorbent media. TD tubes were desorbed for a total of 5 minutes from 40 to 300 °C with a ramp rate of 1.5 °C/second. The GC temperature profile started at 60 °C and was held for 1 minute followed by a 6.0 °C/minute ramp for 3 minutes and 20 seconds, a 12.0 °C/min ramp for 3 minutes and 20 seconds, then a 26.0°C/minute ramp for 2 minutes and 20 seconds; constituting a 10-minute gas chromatography – mass spectrometry (GC-MS) run time.

Table S3. Volumes and masses of compounds injected onto TD tubes for the MS detector saturation study for analytes collected on Tenax® TA.

Analyte	Concentration in standard (ppmv)	Injection volume (mL)											
		5.00	7.50	10.0	12.5	15.0	17.5	20.0	22.5	25.0	27.5	30.0	
Chloroform	5.20	129	194	258	323	387	452	516	581	645	710	774	Analyte mass (ng)
Benzene	5.09	82.6	124	165	207	248	289	330	372	413	454	496	
Trichloroethylene	5.19	142	213	283	354	425	496	567	638	709	779	850	
Heptane	5.17	108	161	215	269	323	377	431	484	538	592	646	
Toluene	3.08	59.0	88.4	118	147	177	206	236	265	295	324	354	
Tetrachloroethylene	5.07	175	262	349	437	524	611	699	786	873	961	1048	
Ethylbenzene	1.05	23.2	34.8	46.3	57.9	69.5	81.1	92.7	104	116	127	139	
p-xylene	1.50	33.1	49.7	66.2	82.8	99.3	116	132	149	166	182	199	
o-xylene	1.55	34.2	51.3	68.4	85.5	103	120	137	154	171	188	205	
Mesitylene	1.56	39.0	58.5	77.9	97.4	117	136	156	175	195	214	234	

All analyte masses were calculated assuming a pressure of 760 torr and temperature of 293.2 K.
The 10-compound gas standard was used for this study.
All compounds are balanced in N_2 and have ± 5% analytical uncertainty.

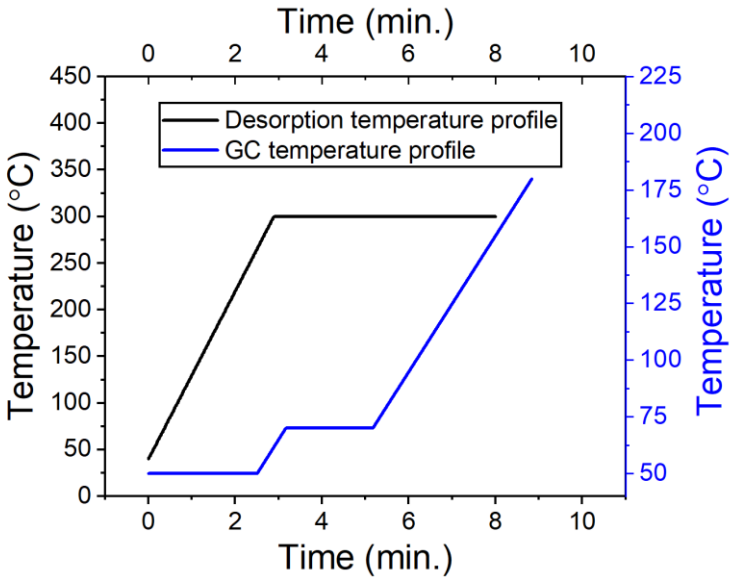
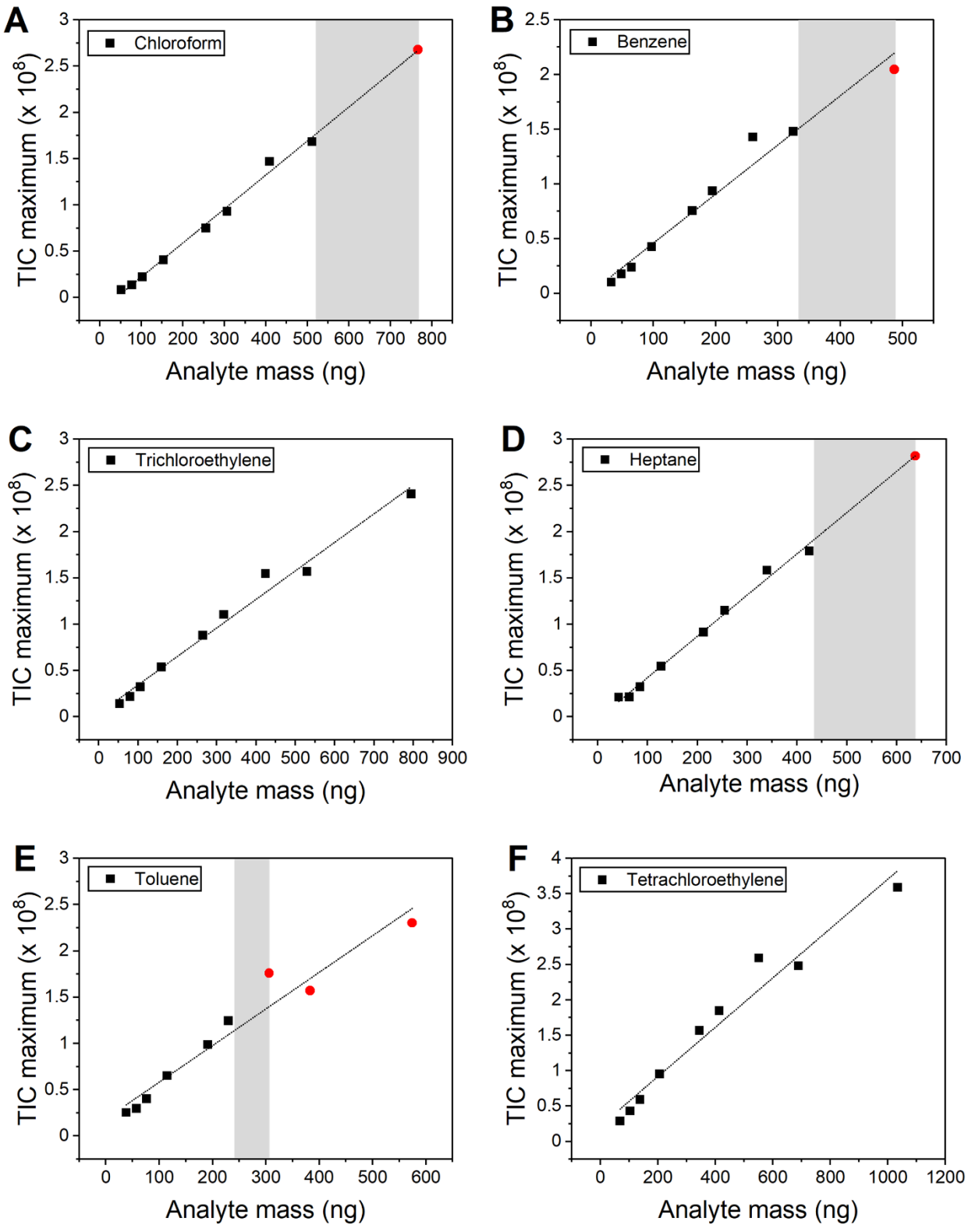


Figure S2. Illustration of the TD tube desorption temperature (black trace, left ordinate y-axis) and GC temperature (blue trace, right ordinate y-axis) profiles used for the various studies on Tenax® TA sorbent media including MS detector saturations, calibration curves, LOD/LOQ studies, carryover, and relative response factor repeatability. TD tubes were desorbed for a total of 8 minutes from 40 to 300 °C with a ramp rate of 1.5 °C/second. The GC temperature profile started at 50 °C and was held for 2.5 minutes followed by a 30.0 °C/minute ramp up to 70 °C with a hold for 2 minutes, then a 30.0 °C/minute ramp up to 180 °C; constituting an 8-minute and 50-second gas chromatography – mass spectrometry (GC-MS) run time.


A
Chloroform
TIC maximum (x 10^8)
Analyte mass (ng)
B
Benzene
TIC maximum (x 10^8)
Analyte mass (ng)
C
Trichloroethylene
TIC maximum (x 10^8)
Analyte mass (ng)
D
Heptane
TIC maximum (x 10^8)
Analyte mass (ng)
E
Toluene
TIC maximum (x 10^8)
Analyte mass (ng)
F
Tetrachloroethylene
TIC maximum (x 10^8)
Analyte mass (ng)

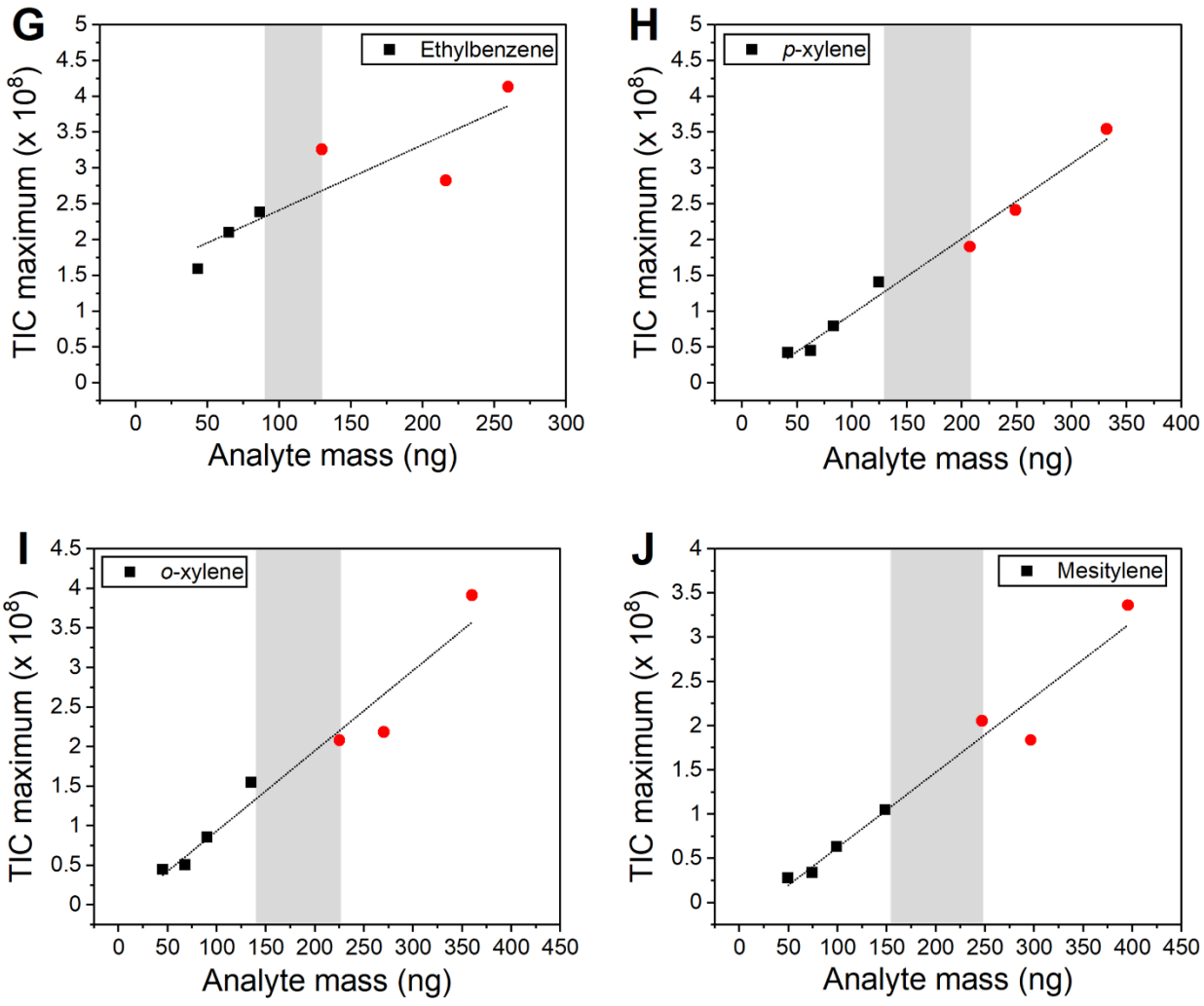
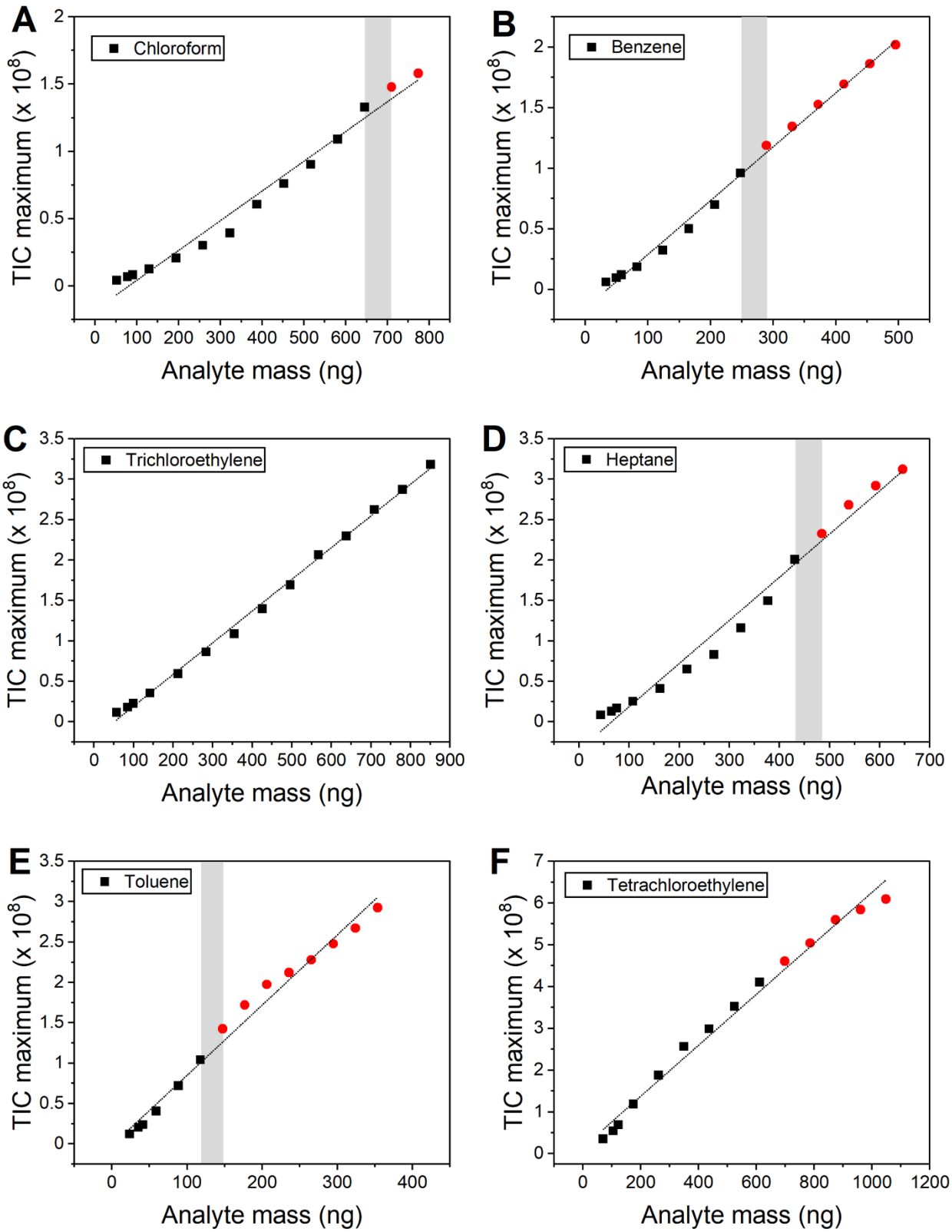


Figure S3. Results of the MS saturation study on Carbopack™ B sorbent (n=1 for each spike level). Plots of TIC maximum vs. analyte mass (ng) for (A) chloroform, (B) benzene, (C) trichloroethylene, (D) heptane, (E) toluene, (F) tetrachloroethylene, (G) ethylbenzene, (H) *p*-xylene, (I) *o*-xylene, (J) mesitylene. Black-square data points indicate signals within the limit of the MS detector range while red-circular data points were instances where ER IQ software reported a saturated MS signal. Linear equations were fit to all data, indicated by black lines. Grey regions indicate the approximate MS detector saturation range.


A
Chloroform
TIC maximum (x 10^8)
Analyte mass (ng)
B
Benzene
TIC maximum (x 10^8)
Analyte mass (ng)
C
Trichloroethylene
TIC maximum (x 10^8)
Analyte mass (ng)
D
Heptane
TIC maximum (x 10^8)
Analyte mass (ng)
E
Toluene
TIC maximum (x 10^8)
Analyte mass (ng)
F
Tetrachloroethylene
TIC maximum (x 10^8)
Analyte mass (ng)

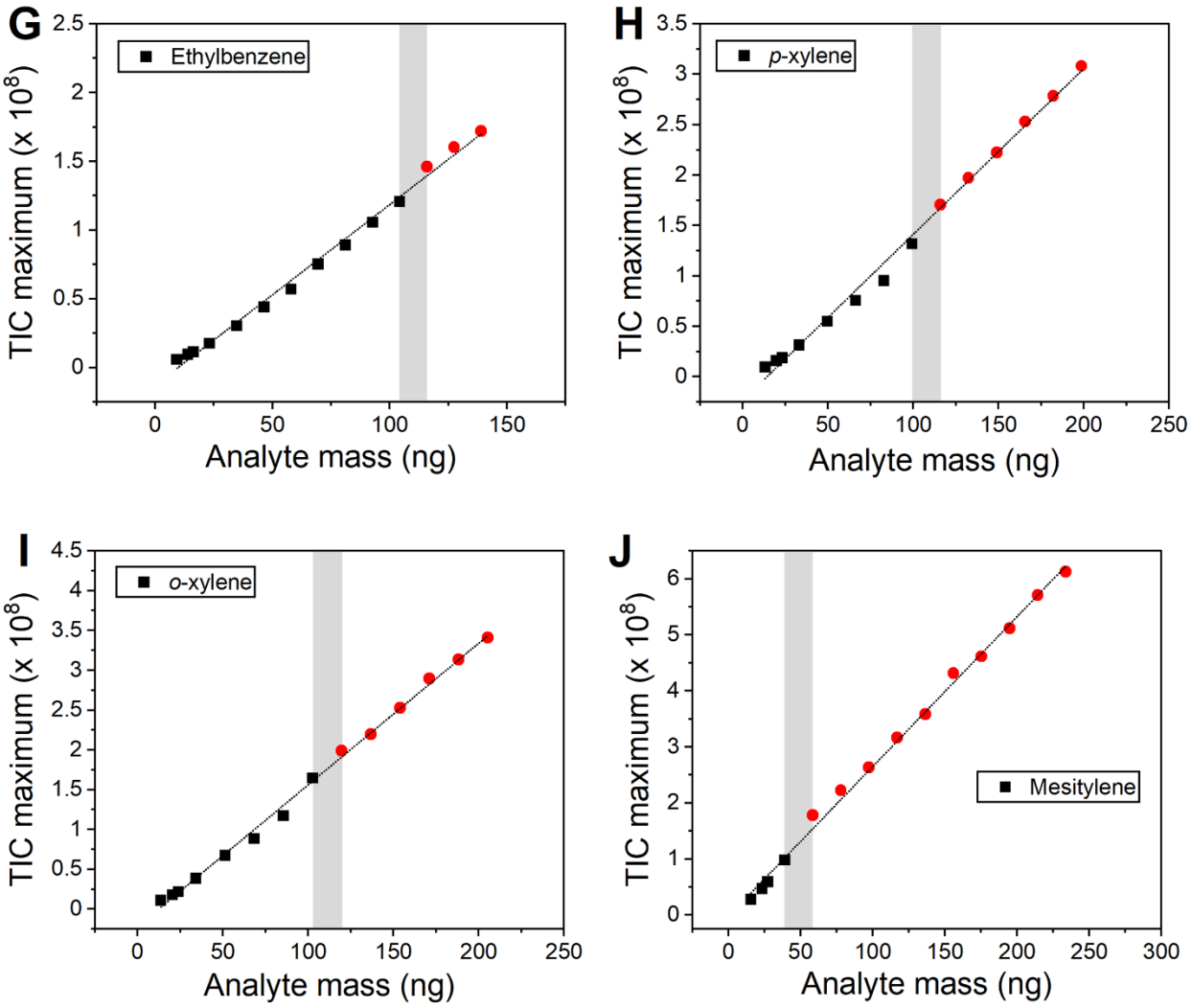


Figure S4. Results of the MS saturation study on Tenax® TA sorbent (n=1 for each spike level). Plots of TIC maximum vs. analyte mass (ng) for (A) chloroform, (B) benzene, (C) trichloroethylene, (D) heptane, (E) toluene, (F) tetrachloroethylene, (G) ethylbenzene, (H) *p*-xylene, (I) *o*-xylene, (J) mesitylene. Black-square data points indicate signals within the limit of the MS detector range while red-circular data points were instances where ER IQ software reported a saturated MS signal. Linear equations were fit to all data, indicated by black lines. Grey regions indicate the approximate MS detector saturation range.

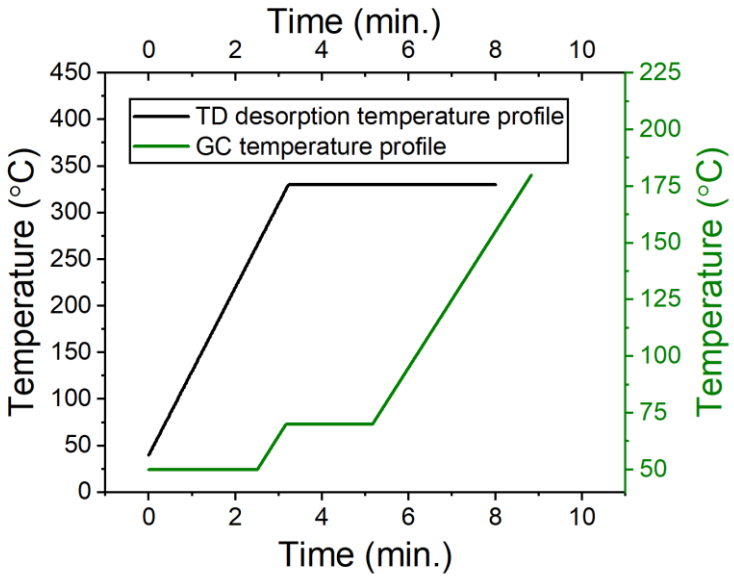


Figure S5. Illustration of the TD tube desorption temperature (black trace, left ordinate y-axis) and GC temperature (green trace, right ordinate y-axis) profiles used for the various studies on Carbopack™ B sorbent media including generation of calibration curves, LOD/LOQ studies, carryover, and relative response factor repeatability studies. TD tubes were desorbed for a total of 8 minutes from 40 to 330 °C with a ramp rate of 1.5 °C/second. The GC temperature profile started at 50 °C and was held for 2.5 minutes followed by a 30.0 °C/minute ramp up to 70 °C with a hold for 2 minutes, then a 30.0 °C/minute ramp up to 180 °C; constituting an 8-minute and 50-second gas chromatography – mass spectrometry (GC-MS) run time.

Table S4. Equations, symbol definitions, and acceptance criteria for parameters from calibration data.[1,2]

Parameter	Equation	Symbol definitions	Acceptance criteria
Relative retention times (RRT)	$RRT = \frac{RT_x}{RT_{IS}}$	RT_x = Analyte retention time (min.) RT_{IS} = Internal standard retention time (min.)	± 0.06 RRT units of the mean RRT for the compound at each calibration level
Area response of internal standard ($\%A_{IS}$)	$\%A_{IS} = \frac{Y}{\bar{Y}} \times 100$	Y = Area response for the quantitative ion for the internal standard $\bar{Y}$ = Mean area response for the quantitative ion for the internal standard	± 40% (for blanks and calibration standards)
Retention time shift of the internal standard (RT_{shift})	$RT_{shift} = RT_{IS} - \overline{RT}_{IS}$	RT_{IS} = Internal standard retention time (min.) $\overline{RT}_{IS}$ = Mean internal standard retention time (min.)	± 20 seconds of the $\overline{RT}_{IS}$ over the initial calibration range for each internal standard

Table S5. Volumes and masses of compounds injected onto TD tubes containing Carbopack™ B sorbent for LOD and LOQ studies.

Analyte	Concentration in standard (ppmv)	Injection volume (µL)			
		50	100	200	
Chloroform	5.20	1.29	2.58	5.16	Analyte mass (ng)
Benzene	5.09	0.83	1.65	3.30	
Trichloroethylene	5.19	1.42	2.83	5.67	
Heptane	5.17	1.08	2.15	4.31	
Toluene	3.08	0.59	1.18	2.36	
Tetrachloroethylene	5.07	1.75	3.49	6.99	

Table S6. Volumes and masses of ethylbenzene injected onto TD tubes containing Carbopack™ B sorbent for LOD and LOQ studies.

Analyte	Concentration in standard (ppmv)	Injection volume (µL)			
		250	500	750	
Ethylbenzene	1.05	1.16	2.32	3.48	Analyte mass (ng)

Table S7. Volumes and masses of compounds injected onto TD tubes containing Tenax® TA sorbent for LOD and LOQ studies.

Analyte	Concentration in standard (ppmv)	Injection volume (µL)			
		50	100	200	
Chloroform	5.20	1.29	2.58	5.16	Analyte mass (ng)
Benzene	5.09	0.83	1.65	3.30	
Trichloroethylene	5.19	1.42	2.83	5.67	
Heptane	5.17	1.08	2.15	4.31	
Toluene	3.08	0.59	1.18	2.36	
Tetrachloroethylene	5.07	1.75	3.49	6.99	
Ethylbenzene	1.05	0.23	0.46	0.93	
p-xylene	1.50	0.33	0.66	1.32	
o-xylene	1.55	0.34	0.68	1.37	
Mesitylene	1.56	0.39	0.78	1.56	

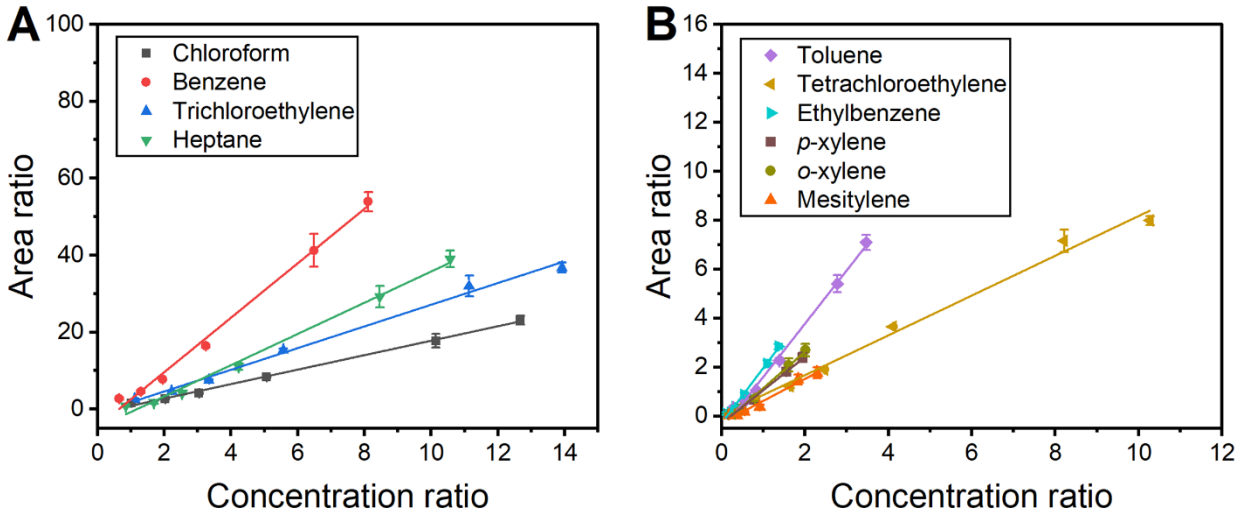


Figure S6. Calibration curves for analytes collected on Carbopack™ B sorbent. TRIS was used an internal standard in plot (A) while BPFB was used as the internal standard in plots (B). These calibration curves were used for the carryover and relative response factor repeatability studies.

Table S8. Summary of the slopes, y-intercepts, $\overline{RRF_x}$, and $\%RSD_{RRF}$ from the analyte calibration data in Figures S6A and S6B using Carbopack™ B sorbent.

Analyte	Slope	y- intercept	$\overline{RRF_x}$	$\%RSD_{RRF_x}$
Chloroform†	1.88 ± 0.03	–1.02 ± 0.20	1.58	12.8
Benzene†	7.08 ± 0.14	–4.53 ± 0.66	4.96	24.8
Trichloroethylene†	2.82 ± 0.07	–1.04 ± 0.55	2.48	12.8
Heptane†	4.06 ± 0.10	–4.79 ± 0.60	2.26	49.5
Toluene‡	2.17 ± 0.05	–0.57 ± 0.09	1.53	25.8
Tetrachloroethylene‡	0.81 ± 0.02	0.05 ± 0.14	0.82	8.65
Ethylbenzene‡	2.26 ± 0.05	–0.29 ± 0.04	1.42	39.2
p-xylene‡	1.36 ± 0.05	–0.29 ± 0.05	0.76	51.8
o-xylene‡	1.49 ± 0.06	–0.35 ± 0.07	0.81	53.7
Mesitylene‡	0.90 ± 0.05	–0.28 ± 0.06	0.43	67.1

† and ‡ represent the use of TRIS or BPFB as the internal standard.
$\%RSD_{RF_{TRIS}} = 12.3$ and $\%RSD_{RF_{BPFB}} = 13.9$.

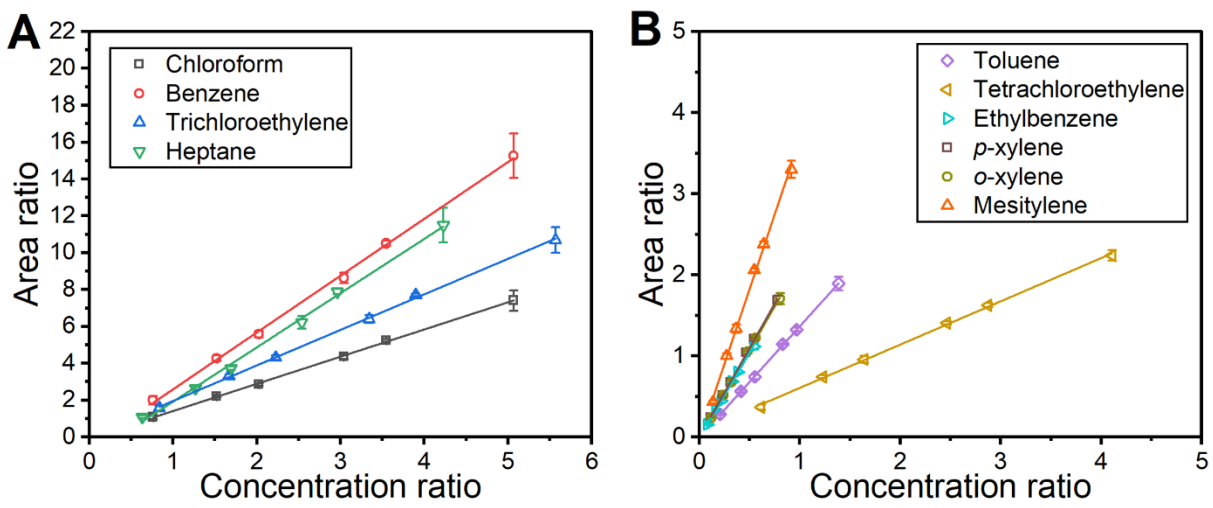


Figure S7. Calibration curves for analytes collected on Tenax® TA sorbent. TRIS was used an internal standard in plot (A) while BPFB was used as the internal standard in plot (B). These calibration curves were used for the LOD and LOQ studies.

Table S9. Summary of the slopes, y-intercepts, $\%RSD_{RF_x}$, and $\%RSD_{RRF}$ from the analyte calibration data in Figures S7A and S7B using Tenax® TA sorbent.

Analyte	**Slope**	**y- intercept**	$\overline{RRF}_x$	$\%RSD_{RRF_x}$
Chloroform†	1.48 ± 0.02	–0.06 ± 0.05	1.44	2.80
Benzene†	4.82 ± 0.06	–0.50 ± 0.12	4.43	5.22
Trichloroethylene†	1.93 ± 0.04	0.03 ± 0.13	1.94	3.67
Heptane†	2.94 ± 0.05	–1.02 ± 0.13	2.30	15.7
Toluene‡	1.37 ± 0.01	–0.01 ± 0.01	1.36	2.80
Tetrachloroethylene‡	0.53 ± 0.01	0.07 ± 0.02	0.58	5.37
Ethylbenzene‡	2.09 ± 0.02	–0.01 ± 0.01	2.05	3.66
p-xylene‡	2.19 ± 0.03	-1.10×10^{-3} ± 0.01	2.18	3.51
o-xylene‡	2.16 ± 0.02	–0.01 ± 0.01	2.12	4.33
Mesitylene‡	3.69 ± 0.05	–0.02 ± 0.03	3.58	5.99

† and ‡ represent the use of TRIS or BPFB as the internal standard.
$\%RSD_{RF_{TRIS}} = 5.01$ and $\%RSD_{RF_{BPFB}} = 4.63$.

Table S10. Summary of CCV data for all experiments using Carbopack™ B sorbent. The acceptance criteria in Table 5 were applied to the data. Instances where the acceptance criteria were not met are indicated by a red box with "FALSE" text. Instances where acceptance criteria were met are indicated by a white box with "TRUE" text. Refer to the excel file titled "Table S10 - CCV summaries". See electronic file for data.

Table S11. Summary of CCV data for all experiments using Tenax® TA sorbent. The acceptance criteria in Table 5 were applied to the data. Instances where the acceptance criteria were not met are indicated by a red box with "FALSE" text. Instances where acceptance criteria were met are indicated by a white box with "TRUE" text. Refer to the excel file titled "Table S11 - CCV summaries". See electronic file for data.

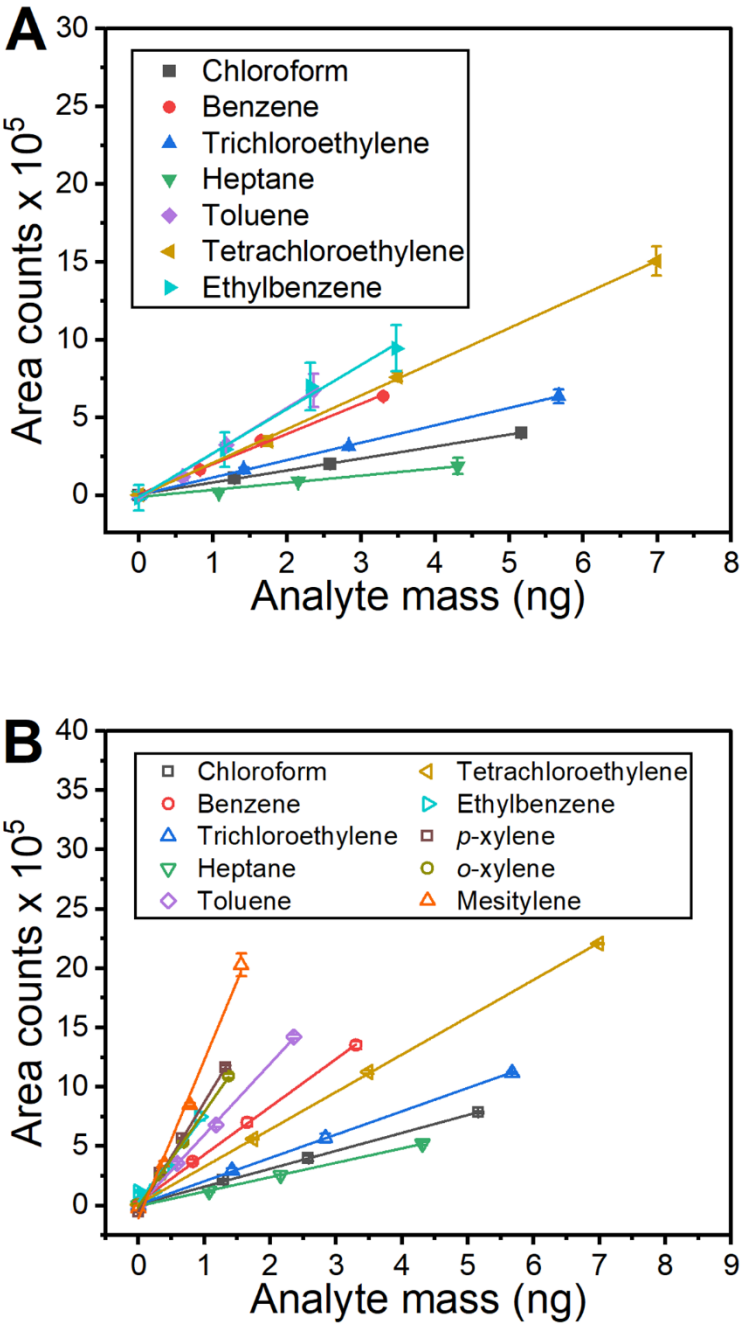


Figure S8. Plots of area counts vs analyte mass (ng) for the LOD/LOQ studies using (A) Carbopack™ B, and (B) Tenax® TA sorbents.

Table S12. Summary of the slopes, y-intercepts, and values of $SE(y)$, and $\%RSD_{RF_x}$ from the LOD/LOQ data in Figure S8A using Carbopack™ B sorbent.

Analyte	**Slope**	**y-intercept**	**SE(y)**	$\%\boldsymbol{RSD_{RF_x}}$
Chloroform	$7.70 \times 10^4 \pm 1.18 \times 10^3$	$5.27 \times 10^3 \pm 3.49 \times 10^3$	6.37×10^3	6.05
Benzene	$1.95 \times 10^5 \pm 5.39 \times 10^3$	$7.99 \times 10^3 \pm 1.02 \times 10^4$	1.86×10^4	5.49
Trichloroethylene	$1.12 \times 10^5 \pm 3.16 \times 10^3$	$2.23 \times 10^3 \pm 1.03 \times 10^4$	1.87×10^4	5.34
Heptane	$4.56 \times 10^4 \pm 5.58 \times 10^3$	$-1.13 \times 10^4 \pm 1.38 \times 10^4$	2.51×10^4	40.2
Toluene	$2.92 \times 10^5 \pm 2.04 \times 10^4$	$-2.24 \times 10^4 \pm 2.75 \times 10^4$	5.03×10^4	19.5
Tetrachloroethylene	$2.16 \times 10^5 \pm 6.18 \times 10^3$	$-8.63 \times 10^3 \pm 2.48 \times 10^4$	4.52×10^4	6.72
Ethylbenzene	$2.88 \times 10^5 \pm 3.01 \times 10^4$	$-7.45 \times 10^3 \pm 6.53 \times 10^4$	1.10×10^5	20.5

Table S13. Summary of the slopes, y-intercepts, and values of $SE(y)$, and $\%RSD_{RF_x}$ from the LOD/LOQ data in Figure S8B using Tenax® TA sorbent.

Analyte	Slope	y-intercept	SE(y)	$\%\boldsymbol{RSD}_{\boldsymbol{RF_x}}$
Chloroform	1.51×10^5 ± 2.55×10^3	7.86×10^3 ± 7.53×10^3	1.37×10^4	5.49
Benzene	4.04×10^5 ± 7.04×10^5	2.58×10^4 ± 1.33×10^4	2.43×10^4	5.16
Trichloroethylene	1.97×10^5 ± 3.38×10^3	8.49×10^3 ± 1.10×10^4	2.00×10^4	5.20
Heptane	1.22×10^5 ± 1.82×10^3	-4.67×10^3 ± 4.48×10^3	8.19×10^3	4.43
Toluene	6.00×10^5 ± 8.33×10^3	-3.39×10^3 ± 1.12×10^4	2.05×10^4	3.36
Tetrachloroethylene	3.15×10^5 ± 1.38×10^3	1.19×10^4 ± 5.51×10^3	1.01×10^4	1.13
Ethylbenzene	7.27×10^5 ± 8.10×10^4	3.36×10^4 ± 4.30×10^4	7.86×10^4	20.5
p-xylene	9.16×10^5 ± 1.00×10^4	-4.46×10^4 ± 7.59×10^3	1.39×10^4	4.09
o-xylene	7.96×10^5 ± 1.20×10^4	-4.44×10^3 ± 9.43×10^3	1.72×10^4	4.45
Mesitylene	1.34×10^6 ± 5.70×10^4	-1.08×10^5 ± 5.09×10^4	9.29×10^4	16.4

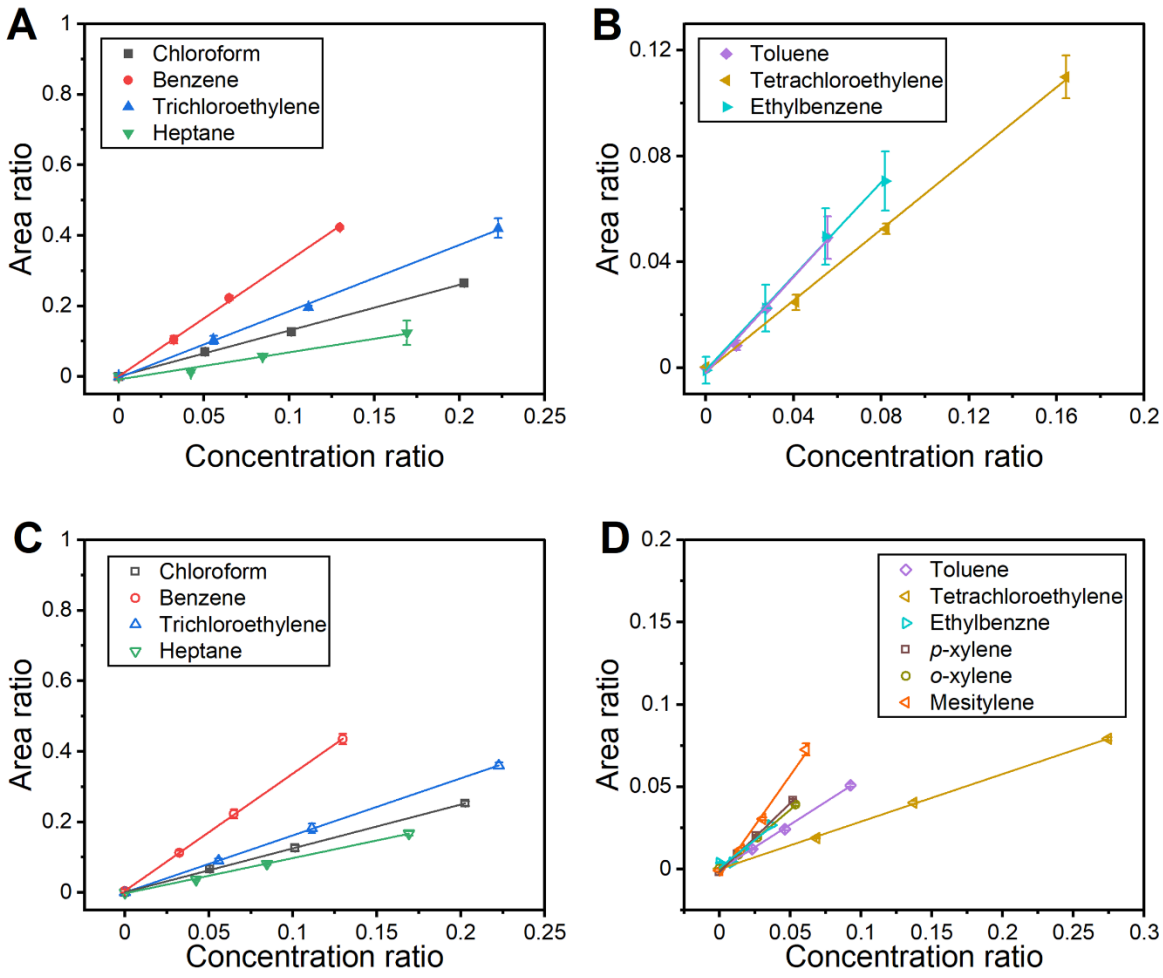


Figure S9. LOD/LOQ study. Plots of area ratio vs concentration for analytes using (A and B) Carbopack™ B, and (C, and D) Tenax® TA sorbents. Plots (A) and (B) represent the use of TRIS as the internal standard while plots (C) and (D) represent use of BPFB as the internal standard.

Table S14. Average percent recoveries for analytes desorbed from Carbopack™ B and Tenax® TA sorbents during the LOD/LOQ study (n=2 at each spike level).

Analyte	Percent Recovery on Carbopack™ B			Percent Recovery on Tenax® TA		
	Low level spike	**Mid level spike**	**High level spike**	**Low level spike**	**Mid level spike**	**High level spike**
Chloroform	106 ± 11.8	94.9 ± 0.06	99.4 ± 13.0	102 ± 5.65	98.9 ± 2.27	98.6 ± 0.85
Benzene	97.5 ± 13.0	104 ± 1.96	98.6 ± 0.98	101 ± 6.41	101 ± 1.90	98.1 ± 0.32
Trichloroethylene	101 ± 16.4	96.0 ± 1.39	103 ± 5.98	99.7 ± 8.86	101 ± 3.80	99.7 ± 2.87
Heptane	51.2 ± 2.80	119 ± 7.14	130 ± 37.5	92.1 ± 5.95	103 ± 4.25	105 ± 5.47
Toluene	79.0 ± 8.91	106 ± 4.10	115 ± 13.9	97.8 ± 5.27	98.9 ± 4.58	103 ± 0.08
Tetrachloroethylene	94.6 ± 1.11	100 ± 2.45	105 ± 2.54	96.6 ± 2.07	103 ± 0.76	101 ± 0.94
Ethylbenzene	95.5 ± 40.6	105 ± 21.2	99.5 ± 19.1	72.2 ± 6.09	106 ± 4.87	121 ± 4.07
p-xylene	--	--	--	92.6 ± 6.28	102 ± 1.01	105 ± 0.26
o-xylene	--	--	--	93.0 ± 5.96	102 ± 3.98%	105 ± 3.26
Mesitylene	--	--	--	79.3 ± 6.07	101 ± 0.00	120 ± 4.35

Table S15. Summary of the instances in which CCV data either met, indicated by "Y", or failed, indicated by "N "the acceptance criteria in which $-40\% < \%D_{RRF} < 40\%$, $-40\% < \%B < 40\%$, and $-30\% < \%P < 30\%$.

Analyte	Carbopack™ B						Tenax® TA					
	LOD/LOQ study			Carryover and relative response factor repeatability			LOD/LOQ study			Carryover and relative response factor repeatability study		
	$\%D_{RRF}$	$\%B$	$\%P$	$\%D_{RRF}$	$\%B$	$\%P$	$\%D_{RRF}$	$\%B$	$\%P$	$\%D_{RRF}$	$\%B$	$\%P$
Chloroform	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Benzene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Trichloroethylene	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Heptane	Y	Y	Y	--	--	--	Y	Y	Y	Y	Y	Y
Toluene	Y	Y	Y	--	--	--	Y	Y	Y	Y	Y	Y
Tetrachloroethylene	N	N	Y	N	N	Y	Y	Y	Y	Y	Y	Y
Ethylbenzene	Y	Y	Y	--	--	--	Y	Y	Y	Y	Y	Y
p-xylene	--	--	--	--	--	--	Y	Y	Y	Y	Y	Y
o-xylene	--	--	--	--	--	--	Y	Y	Y	Y	Y	Y
Mesitylene	--	--	--	--	--	--	Y	Y	Y	Y	Y	Y

"--" Denotes instances where the calibration curve was unacceptable.

Table S16. Summary of CCV data for all experiments using Carbopack™ B sorbent. The acceptance criteria in which $-40\% < \%D_{RRF} < 40\%$, $-40\% < \%B < 40\%$, and $-30\% < \%P < 30\%$ were applied to the data. Instances where the acceptance criteria were not met are indicated by a red box with "FALSE" text. Instances where acceptance criteria were met are indicated by a white box with "TRUE" text. Refer to the excel file titled "Carbopack B CCV summaries – extended criteria". See electronic file for data.

Table S17. Summary of CCV data for all experiments using Tenax® TA sorbent. The acceptance criteria in which $-40\% < \%D_{RRF} < 40\%$, $-40\% < \%B < 40\%$, and $-30\% < \%P < 30\%$ were applied to the data. Instances where the acceptance criteria were not met are indicated by a red box with "FALSE" text. Instances where acceptance criteria were met are indicated by a white box with "TRUE" text. Refer to the excel file titled "Tenax CCV summaries – extended criteria". See electronic file for data.

REFERENCES

(1) United States Environmental Protection Agency (U.S. EPA): Method 325B - Volatile Organic Compounds from Fugitive and Area Sources: Sampler Preparation and Analysis https://www.epa.gov/emc/method-325b-volatile-organic-compounds-fugitive-and-area-sources-sampler-preparation-and (accessed Feb 18, 2020).

(2) McClenny, W. A.; Holdren, M. W. *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air Compendium Method TO-15*; Cincinnati, OH; U.S. Environmental Protection Agency (EPA); Report No.: EPA/625/R-96/010b: 1-32, 1999.