

Supplemental to **Internal standards: A source of analytical bias for volatile organic analyte determinations**

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**Biota Methodology Instrumentation.**

**GC/MS:** The vacuum distiller was interfaced to a GC/MS so that the vacuum distillate is transferred directly to the GC/MS. In this study, the GC/MS was a Thermo DSQ mass spectrometer and Trace GC (ThermoElectron Corp., Austin TX). The GC capillary column was a 30 m x 0.25 mm i.d., 1.5 µm film VOCOL (Supelco, Bellefonte, PA). The GC operating conditions were 2.5 min at -20 °C, 40 °C/min ramp to 60 °C, 5 °C/min ramp to 120 °C and held at 120 °C for 1 min, 20 °C/min ramp to 220 °C and held for 12 min resulting in a GC run time of 34 min. The injection was split 60:1 with a constant flow rate of 1.4 ml/min. The mass spectrometer scanned between 35 and 300 amu at 1 scan/sec.

**Vacuum Distiller:** A Cincinnati Analytical Instruments Model VDC1012 vacuum distiller (Indianapolis, IN) performed the distillations in the study. Samples were vacuum distilled for 7.5 min with the condenser at 0 °C and the cryotrap at -150 °C. The distillate was heated to 110 °C during a 2.5 min transfer to the GC/MS through the transfer line held at 200 °C.

**Table S1. Internal Standards used for Method 8261A Quantitation**

Type	Range	Grouping	Value <sup>a</sup>	Amount <sup>b</sup>
Relative volatility	0.62 to 3.72	Internal standards		
		methyl cyclohexane- <i>d</i> <sub>14</sub>	.62	250
		hexafluorobenzene	.86	250
		ethylbenzene- <i>d</i> <sub>10</sub>	3.6	250
	3.72 to 6.20	1,4-difluorobenzene <sup>c</sup>	3.83	250
		ethylbenzene- <i>d</i> <sub>10</sub>	3.6	
		1,4-difluorobenzene	3.83	
		<i>o</i> -xylene- <i>d</i> <sub>10</sub>	6.14	250
	6.2 to 29.2	chlorobenzene- <i>d</i> <sub>5</sub> <sup>c</sup>	6.27	250
		<i>o</i> -xylene- <i>d</i> <sub>10</sub>	6.14	
		chlorobenzene- <i>d</i> <sub>5</sub>	6.27	
		1,2-dibromoethane- <i>d</i> <sub>4</sub>	26.	250
	29.2 to 478	diethyl ether- <i>d</i> <sub>10</sub>	32.5	250
		1,2-dibromoethane- <i>d</i> <sub>4</sub>	26.	
		diethyl ether- <i>d</i> <sub>10</sub>	32.5	
		tetrahydrofuran- <i>d</i> <sub>8</sub>	355	250
	478 to 5800	acetone- <i>d</i> <sub>6</sub>	600	3100
		tetrahydrofuran- <i>d</i> <sub>8</sub>	355	
		acetone- <i>d</i> <sub>6</sub>	600	
		1,4-dioxane- <i>d</i> <sub>8</sub>	5800	2400
5800 to 14400	acetone- <i>d</i> <sub>6</sub>	600		
	1,4-dioxane- <i>d</i> <sub>8</sub>	5800		
	2-chloroethanol- <i>d</i> <sub>4</sub>	13800	120000	
Boiling point	85 to 155 (°C)	pentafluorobenzene	85(°C)	250
		toluene- <i>d</i> <sub>8</sub>	111	250
		bromobenzene- <i>d</i> <sub>5</sub>	155	250
	155 to 181	toluene- <i>d</i> <sub>8</sub>	111	
		bromobenzene- <i>d</i> <sub>5</sub>	155	
		1,2-dichlorobenzene- <i>d</i> <sub>4</sub>	181	250
	181 to 218	1,2-dichlorobenzene- <i>d</i> <sub>4</sub> <sup>c</sup>	181	
		naphthalene- <i>d</i> <sub>8</sub>	217	500
		1,2,3-trichlorobenzene- <i>d</i> <sub>3</sub> <sup>c</sup>	218	500
	218 to 243.5	naphthalene- <i>d</i> <sub>8</sub>	217	
		1,2,3-trichlorobenzene- <i>d</i> <sub>3</sub>	218	
		1-methylnaphthalene- <i>d</i> <sub>10</sub>	241	1050
		3,5-dibromotoluene	246	2200

<sup>a</sup> Values are from references 11.

<sup>b</sup> Amount of internal standard added per sample in ng.

<sup>c</sup> Internal standards from Table 1 of Method 8260C [1]. 1,2-Dichlorobenzene-*d*<sub>4</sub> is a substitute for 1,4-dichlorobenzene-*d*<sub>4</sub>. 1,2,3-Trichlorobenzene-*d*<sub>3</sub> was added as an internal standard for semivolatile analytes.

**Table S2. Surrogate Compounds by Class for Method 8261A**

	Boiling Point	Relative Volatility <sup>a</sup>	Amount <sup>b</sup>
<i>Volatile Class (boiling point less than 159)</i>			
vinyl chloride- <i>d</i> <sub>3</sub>	-13	.48	250
methylene chloride- <i>d</i> <sub>2</sub>	40	11.10	250
benzene- <i>d</i> <sub>6</sub>	79	3.92	250
1,2-dichloropropane- <i>d</i> <sub>6</sub>	95	11.00	200
1,1,2-trichloroethane- <i>d</i> <sub>3</sub>	112	26.6	200
4-bromofluorobenzene	152	8.05	250
<i>Non-Purgeable Class (rel vol&gt;100)</i>			
nitromethane- <sup>13</sup> C	101	510	650
ethylacetate- <sup>13</sup> C	77	150	2500
pyridine- <i>d</i> <sub>5</sub>	115	15000	12500
<i>Semi-Volatile Class (boiling point &gt;= 159)</i>			
decafluorobiphenyl	206	3.03	250
nitrobenzene- <i>d</i> <sub>5</sub>	210	87.5	250
acetophenone- <i>d</i> <sub>5</sub>	202	161	1042
1,2,4-trichlorobenzene- <i>d</i> <sub>3</sub>	213	7.88	250
<i>a,a</i> -dichloro- <i>o</i> -xylene	240	113.5	9800
azulene	242	91	2500
3,5- <i>di-tert</i> -butyltoluene	244	3.61	1000

<sup>a</sup> Values are from reference 11.

<sup>b</sup> Amount of surrogates added per sample in ng.

**Table S3. List of analytes**

Analytes	ln(RV) <sup>a</sup>	bp <sup>b</sup>	Group <sup>c</sup>	ISTD <sup>d</sup>
dichlorodifluoromethane	-2.66	-30	4	1,4-difluorobenzene
chloromethane	0.31	-24	4	1,4-difluorobenzene
vinylchloride	-0.73	-13	4	1,4-difluorobenzene
bromomethane	0.60	4	4	1,4-difluorobenzene
chloroethane	0.01	12	4	1,4-difluorobenzene
trichlorofluoromethane	-1.61	24	4	1,4-difluorobenzene
diethyl ether	3.55	35	4	1,4-difluorobenzene
1,1,2-trichloro-1,2,2-trifluoroethane	-0.92	48	3	1,4-difluorobenzene
acetone	6.40	56	4	1,4-difluorobenzene
1,1-dichloroethene	-0.46	37	4	1,4-difluorobenzene
iodomethane	0.83	42	3	1,4-difluorobenzene
allylchloride	0.29	45	3	1,4-difluorobenzene
acetonitrile	6.30	82	4	1,4-difluorobenzene
methyl acetate	5.40	57	4	1,4-difluorobenzene
carbon disulfide	-1.17	46	3	1,4-difluorobenzene
methylene chloride	2.31	40	3	1,4-difluorobenzene
methyl- <i>tert</i> -butyl ether	3.52	55	3	1,4-difluorobenzene
acrylonitrile	5.08	78	4	1,4-difluorobenzene
<i>trans</i> -1,2-dichloroethene	0.83	48	3	1,4-difluorobenzene
1,1-dichloroethane	1.42	57	3	1,4-difluorobenzene
2,2-dichloropropane	0.31	69	2	1,4-difluorobenzene
propionitrile	7.26	97	4	1,4-difluorobenzene
2-butanone	6.65	80	4	1,4-difluorobenzene
<i>cis</i> -1,2-dichloroethene	1.68	60	3	1,4-difluorobenzene
methacrylonitrile	4.63	90	4	1,4-difluorobenzene
chloroform	1.85	62	3	1,4-difluorobenzene
bromochloromethane	2.73	68	3	1,4-difluorobenzene
cyclohexane	-0.53	80.7	2	1,4-difluorobenzene
1,1,1-trichloroethane	0.27	74	2	1,4-difluorobenzene
1,1-dichloropropene	-0.13	104	2	1,4-difluorobenzene
carbon tetrachloride	-0.45	76.5	2	1,4-difluorobenzene
1,2-dichloroethane	2.93	84	2	1,4-difluorobenzene
benzene	1.27	80	1	1,4-difluorobenzene
trichloroethene	0.85	87	1	1,4-difluorobenzene
methyl cyclohexane	-0.48	101	2	1,4-difluorobenzene
1,2-dichloropropane	2.39	96	2	1,4-difluorobenzene
methylmethacrylate	4.27	101	3	1,4-difluorobenzene
dibromomethane	3.17	97	2	1,4-difluorobenzene
bromodichloromethane	2.51	90	2	1,4-difluorobenzene
1,4-dioxane	8.66	101	4	1,4-difluorobenzene
4-methyl-2-pentanone	4.79	117	4	1,4-difluorobenzene

<i>trans</i> -1,3-dichloropropene	2.65	112	3	1,4-difluorobenzene
toluene	1.36	111	3	1,4-difluorobenzene
<i>cis</i> -1,3-dichloropropene	2.98	104	3	chlorobenzene-d5
2-hexanone	4.88	128	4	chlorobenzene-d5
1,1,2-trichloroethane	3.27	114	2	chlorobenzene-d5
1,3-dichloropropane	3.21	120	2	chlorobenzene-d5
tetrachloroethene	0.36	121	2	chlorobenzene-d5
dibromochloromethane	2.95	120	2	chlorobenzene-d5
1,2-dibromoethane	3.28	132	2	chlorobenzene-d5
chlorobenzene	1.80	132	1	chlorobenzene-d5
1,1,1,2-tetrachloroethane	2.45	130.5	1	chlorobenzene-d5
ethylbenzene	1.28	136	1	chlorobenzene-d5
<i>m,p</i> -xylenes	1.36	138	1	chlorobenzene-d5
<i>o</i> -xylene	1.71	144	2	chlorobenzene-d5
styrene	1.93	145	2	chlorobenzene-d5
isopropylbenzene	1.01	152	3	chlorobenzene-d5
bromoform	3.15	150	2	chlorobenzene-d5
<i>cis</i> -1,4-dichloro-2-butene	3.51	152	3	chlorobenzene-d5
1,1,2,2-tetrachloroethane	3.41	146	2	chlorobenzene-d5
1,2,3-trichloropropane	3.51	157	3	1,2-dichlorobenzene-d4
propylbenzene	0.89	159	3	1,2-dichlorobenzene-d4
bromobenzene	2.07	156	3	1,2-dichlorobenzene-d4
<i>trans</i> -1,4-dichloro-2-butene	3.52	156	3	1,2-dichlorobenzene-d4
1,3,5-trimethylbenzene	1.32	165	2	1,2-dichlorobenzene-d4
2-chlorotoluene	1.40	159	3	1,2-dichlorobenzene-d4
4-chlorotoluene	1.56	162	2	1,2-dichlorobenzene-d4
<i>tert</i> -butylbenzene	1.00	169	2	1,2-dichlorobenzene-d4
<i>sec</i> -butylbenzene	0.65	173	2	1,2-dichlorobenzene-d4
pentachloroethane	2.58	162	2	1,2-dichlorobenzene-d4
1,2,4-trimethylbenzene	1.50	169	2	1,2-dichlorobenzene-d4
<i>p</i> -isopropyltoluene	0.92	183	2	1,2-dichlorobenzene-d4
1,3-dichlorobenzene	1.74	173	1	1,2-dichlorobenzene-d4
1,4-dichlorobenzene	1.81	174	1	1,2-dichlorobenzene-d4
<i>n</i> -butylbenzene	0.63	183	2	1,2-dichlorobenzene-d4
1,2-dichlorobenzene	2.06	180	1	1,2-dichlorobenzene-d4
1,2-dibromo-3-chloropropane	3.66	196	2	1,2,4-trichlorobenzene-d3
1,2,4-trichlorobenzene	2.05	214	1	1,2,4-trichlorobenzene-d3
hexachlorobutadiene	0.73	215	2	1,2,4-trichlorobenzene-d3
naphthalene	2.82	218	1	1,2,4-trichlorobenzene-d3
1,2,3-trichlorobenzene	2.42	218	1	1,2,4-trichlorobenzene-d3
2-methylnaphthalene	4.20	245	3	1,2,4-trichlorobenzene-d3
1-methylnaphthalene	4.20	245	3	1,2,4-trichlorobenzene-d3

<sup>a</sup> The natural logarithm of its relative volatility.

<sup>b</sup> The boiling point.

<sup>c</sup> The grouping that the analyte was a member where Group 1 includes all analytes that have boiling points within 10 °C and within 1 of the lnRV of the Method 8260C internal standard (ISTDs). Group 2 includes all analytes that have boiling points within 20 °C and within 2 lnRV of the ISTDs, Group 3 includes analytes that have boiling points within 50 °C and within 3 lnRV of the ISTDs, and Group 4 includes the remaining compounds.

<sup>d</sup> Internal standard assignments of analytes for Method 8260C determinations.