Analysis of Volatile Organic Compounds in Seawater by Purge and Trap (P&T) Concentration and Detection by Gas Chromatography/Mass Spectrometry (GC/MS)

Cynthia Elmore, Senior Analyst, Product Management Analytics, cynthia.elmore@xylem.com, OI Analytical, Xylem Lab Solutions
Yina Liu, PhD. Department of Oceanography, Texas A&M University, College Station, Texas 77843
Jakob Woodside, Associate Product Manager, jakob.woodside@xylem.com, OI Analytical, Xylem Lab Solutions

O·I·Analytical
a **xylem** brand

Section 1. Introduction

Volatile organic compounds (VOCs), such as trihalomethanes (THMs), may be found in seawater due to natural processes and man-made sources. THMs include bromodichloromethane, chloroform, chlorodibromomethane, and bromoform. At a global scale, these VOCs are potentially significant contributors to catalytic ozone loss in the troposphere and lower stratosphere. In the open ocean, THMs may be naturally produced from algal sources (Liu et al., 2011; Liu et al., 2013).

Anthropogenic sources of THMs include water treatments. THMs are often disinfection byproducts that are formed by the chlorination process in water sources, including seawater. These contaminants can come from sources such as outfall into the ocean from treatment plants as well as desalination plants (Liu et al., 2011).

In addition to THMs, there are other VOCs of interest. Outfall from various sources mixing with seawater may be monitored to determine the general health of the seawater in regard to plant and animal life. The analysis is also useful in determining the extent of pollution from oil spills and illegal dumping.

The purpose of this poster is to show a method for determining VOCs using Purge and Trap (P&T) concentration and detection by Gas Chromatography/Mass Spectrometry (GC/MS). Also, the effect of salt concentration on recovery of volatile compounds will be explored. A typical compound list for EPA Method 8260 will be analyzed by full scan GC/MS and a subset of THMs will be analyzed by Selective Ion Monitoring (SIM). Seawater samples from the Gulf of Mexico will be analyzed.

Section 2. Instrumentation

Purge and trap (P&T) concentration was performed using an OI Analytical 4760 P&T with an OI Analytical 4100 Soil/Water Sample Processor. An Agilent 7890A/5975C GC/MS was used for chromatographic separation and detection. A column suitable for volatile organic analysis was utilized.

Figure 1. 4100, 4760, GC/MS

Section 3. Experimental

EPA Method 8260D for VOC analysis was used as a guideline for this work.[3] Two instrument methods were used. A representative list of compounds typically analyzed for 8260 were analyzed using full scan GC/MS. THMs were analyzed using SIM. The P&T and 4100 parameters were basically OIA's default which have been found to work well and give consistent results for 8260. All the analyses were carried out using the 4100's soil mode in which the sample is purged in a 40 ml VOA vial rather than using the water mode where sample is transferred to the P&T's frit sparger. Purging in the soil mode is useful for samples that may tend to foam and minimize the amount of salt transferred to the P&T sample pathway. Each vial contained 5ml distilled water plus 5 ml of QC or sample.

To see if the salt content of seawater might affect compound recovery and stability, calibrations were carried out using both distilled water and then salt water to compare. The saltwater contained 32g/liter of NaCl in distilled water and was stored in amber bottles away from light. It was found that purchased distilled water contained low ppt THMs. In order to achieve part per trillion calibrations for SIM, the distilled water was boiled and purged with Nitrogen for at least three hours to remove these.

Table 1. Instrument Parameters

Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator
Trap	#10 trap: Tenax® / Silica gel / CMS
Purge Gas	Zero grade Helium at 40 mL/min
Purge Time	11 min
Sparge Mount Temperature	45 °C
Sample Temperature (purge)	45 °C
Sample Temperature (bake)	55 °C
Desorb Time	0.5 min
Bake Time	5 min
OI #10 Trap Temperature	Ambient during purge / 180 °C during desorb pre-heat / 190 °C during desorb / 210 °C during bake
Water Management	120 °C during purge / Ambient during desorb / 240 °C during bake
Transfer Line Temperature	140 °C
Six-port Valve Temperature	140 °C

Autosampler	4100 Water/Soil Sample Processor
System Gas	Zero grade nitrogen
Purge Gas	Zero grade helium
LV20 Pressure	8.0 psi
Loop-based Time Settings	Default
Mode	Soil
Rinse Water	90 °C
Soil Sample Transfer	150 °C
Soil Oven	150 °C
Soil Lift Station	45 °C

4100 Sample Process Methods	
P&T Rinses	3
Rinse Water	Hot
Soil Pre-Heat/Purge Temp °C	45 °C

Gas Chromatograph	Agilent 7890A
Column	Restek Rtx-VMS / 30 meter, 0.25 mm ID, 1.4 µm film
Carrier Gas	Zero grade helium
Inlet Temperature	240 °C
Inlet Liner	Agilent Ultra Inert, 1 mm straight taper
Column Flow Rate	0.8 mL/min
Split Ratio	125 for Full Scan 50 for SIM
Oven Program	Hold at 40 °C for 1.5 min / 16 °C/minute to 180 °C / 40 °C/minute to 220 °C / Hold at 220 °C for 4 min / Total GC Run is 15.25 min

Mass Spectrometer	Agilent 5975C
Mode	Full Scan
Scan Range	35-300 amu
Scans/Second	5.19
Solvent Delay	1.25 min
Mode	Selective Ion Monitoring
Dwell Time	110 msec
Resolution	Low
SIM Compounds	
Group 1 Chloroform	Start 3.50 Mz 83,85
Group 2 Dibromofluoromethane	Start 4.17 Mz 111,113
Group 3 Pentafluorobenzene	Start 4.49 Mz 99,168
Group 4 1,2-Dichloroethane-d4	Start 4.59 Mz 65,102
Group 5 1,4-Difluorobenzene	Start 4.85 Mz 63,114
Group 6 Bromodichloromethane	Start 5.28 Mz 83,85
Group 7 Toluene-d8	Start 5.80 Mz 98,100
Group 8 Chlorodibromomethane	Start 6.50 Mz 127,129
Group 9 Chlorobenzene-d5	Start 7.10 Mz 82,117
Group 10 Bromoform	Start 7.55 Mz 173,175

Transfer Line Temperature(AUX)	240 °C
Source Temperature	230 °C
Quadrupole Temperature	150 °C
Draw Out Plate	6 mm

Calibration

Bromofluorobenzene (BFB) was injected at the beginning of each 12 hour sequence and 8260 acceptance criteria met.

Standards for full scan calibration were prepared at 1, 2, 5, 10, 25, 50, 100, 150, and 200ppb for most compounds. Acrolein and m,p-xylenes were two times and ketones were at five times those concentrations. Internal Standards and Surrogates were added to all analyses by spiking 5ul of 50ppm standard. Initial Demonstrations of Capability (IDOC) were run at 50ppb for most compounds and Method Detection Limit (MDL) studies were run at 0.5ppb for most compounds.

Standards for SIM calibration were prepared at 1, 2, 5, 10, 25, 50, 100, 250, 500, and 1000ppt. The working standard was diluted daily from a 10ppm stock to 0.05ppm. Internal Standards and Surrogates were added to all analyses by spiking 5ul of 0.25ppm standard. IDOCs were run at 250ppt and MDLs were run at 4ppt.

Samples

Samples were collected in 40ml amber VOA vials. Four grab samples were taken along the shore near High Island, Texas. Four grab samples were taken along the shore in the Rockport, Texas area. Two samples were taken by Dr. Liu in Galveston Bay and one in the Houston Ship Channel from aboard Texas A&M's research vessel Trident using a Niskin bottle. Surface waters (within 1 meter) were collected for this study. The samples were stored on ice, in the dark, and were then refrigerated at 4 degrees C upon receipt by the lab. Samples for full scan were analyzed within 6 days of sampling and samples for SIM were analyzed within 12 days. There was an 18 day and 24 day gap between sampling and analysis for the Rockport samples. These samples had to be taken sooner because of logistical reasons and they were useful as experimental samples to validate the method.

Figure 2. Texas A&M R/V Trident

Figure 3. Sampling Aboard the R/V Trident

Section 4. Results and Discussion

Calibration criteria of </= 20% RSD were easily met with the exception of Chlorodibromomethane and Bromoform for SIM in which case linear regression was used. Calibration points for both methods were recalculated using the final calibration curve and compounds passed the refit criteria of +/- 50% for the low level and +/- 30% for other levels. The recalculation of the 100ppt point for the SIM calibration for Chlorodibromomethane and Bromoform had much higher % deviation. Continuing calibration recoveries were well within 20% on days where samples, MDLs, and IDOCs were analyzed. IDOCs had very good recovery and %RSD values. The MDLs were also acceptable. Please see tables 2 and 3.

Table 2. 8260 QA/QC for Full Scan

Analyte	Compound	Distilled Water Avg RF	Distilled Water %RSD	Salt Water Avg RF	Salt Water %RSD	Salt Water MDL	Salt Water IDOC % Recovery	Salt Water IDOC %RSD
1	Pentafluorobenzene (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2	Dichlorodifluoromethane	0.366	5.09	0.324	8.52	0.25	90.6	4.13
3	Chloromethane	0.697	9.05	0.696	6.95	0.17	93.0	2.55
4	Vinyl chloride	0.387	7.45	0.369	6.30	0.14	97.0	4.77
5	Bromomethane	0.252	13.53	0.237	10.20	0.24	93.5	4.86
6	Chloroethane	0.290	14.53	0.266	8.69	0.15	94.8	6.13
7	Trichlorofluoromethane	0.608	8.30	0.614	8.81	0.14	97.1	5.71
8	Ethyl ether	0.248	5.02	0.268	4.78	0.22	96.5	1.85
9	1,1-Dichloroethene	0.379	12.93	0.342	8.45	0.13	101	7.06
10	Carbon disulfide	0.978	10.54	0.905	6.88	0.20	100	3.99
11	1,1,2-Trichloro-1,2,2-trifluoroethane	0.359	4.96	0.338	8.87	0.19	95.6	5.80
12	Methyl iodide	0.771	8.02	0.725	6.31	0.18	97.7	2.76
13	Acrolein(2x)	0.105	6.52	0.110	11.10	0.71	94.2	3.19
14	Allyl chloride	0.249	5.13	0.244	7.11	0.21	96.3	2.58
15	Methylene chloride	0.456*	8.08	0.456*	11.61	0.64	96.3	2.29
16	Acetone(5x)	0.062*	8.42	0.071*	6.38	4.73	94.7	3.14
17	trans-1,2-Dichloroethene	0.488	9.19	0.482	8.17	0.31	95.4	1.69
18	Methyl tert-butyl ether	1.308	5.53	1.394	3.81	0.12	97.9	2.29
19	Chloroprene	1.216	4.18	1.208	4.10	0.080	99.8	1.14
20	1,1-Dichloroethane	1.060	5.69	1.051	3.89	0.12	98.4	1.54
21	Acrylonitrile	0.215	6.60	0.233	8.34	0.21	99.4	3.56
22	2,2-Dichloropropane	0.528	6.00	0.520	3.89	0.15	98.1	2.18
23	cis-1,3-Dichloropropene	0.537	8.53	0.499	10.45	0.18	98.0	2.26
24	Bromochloromethane	0.293	5.45	0.303	5.13	0.15	97.9	1.71
25	Chloroform	0.910	4.25	0.913	6.53	0.11	97.3	1.60
26	Methyl acrylate	0.549	7.10	0.622	7.88	0.14	104	1.90
27	Carbon tetrachloride	0.784	6.73	0.750	5.03	0.16	99.2	2.02
28	Tetrahydrofuran	0.236	4.23	0.287	13.60	0.16	97.1	4.87
29	Dibromofluoromethane (SS)	0.684	1.88	0.709	2.68	5.13	98.3	1.78
30	1,1,1-Trichloroethane	0.785	6.35	0.762	8.87	0.16	97.6	1.53
31	2-Butanone(5x)	0.050	8.12	0.058	11.22	1.31	95.9	3.64
32	1,1-Dichloropropene	0.615	4.76	0.595	4.41	0.20	100	1.55
33	1,4-Difluorobenzene (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
34	Benzene	0.879	3.98	0.862	4.08	0.10	98.2	1.63
35	Methacrylonitrile	0.236	5.16	0.264	6.00	0.15	99.9	1.52
36	1,2-Dichloroethane-d4 (SS)	0.070	2.59	0.072	2.62	4.34	100	1.53
37	1,2-Dichloroethane	0.425	6.39	0.446	4.78	0.10	97.6	1.40
38	Trichloroethene	0.312	6.15	0.306	5.61	0.14	97.4	1.38
39	Dibromomethane	0.162	3.43	0.172	3.67	0.21	98.6	1.39
40	1,2-Dichloropropane	0.282	3.89	0.282	4.66	0.12	100	1.87
41	Bromodichloromethane	0.339	4.85	0.350	4.07	0.17	100	1.63
42	Methyl methacrylate	0.136	9.12	0.154	7.49	0.14	104	3.20
43	2-Chloroethyl-vinyl-ether	0.104	13.29	0.119	11.09	0.20	109	3.27
44	cis-1,3-Dichloropropene	0.358	6.29	0.358	5.54	0.09	104	2.36
45	Chlorobenzene-d5 (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
46	Toluene-d8(SS)	1.175	1.27	1.148	1.09	0.94	99.0	0.55
47	Toluene	0.689	8.47	0.653	11.47	0.11	95.8	2.47
48	2-Nitropropane	0.130	12.61	0.139	10.67	0.21	96.2	0.80
49	4-Methyl-2-pentanone(5x)	0.038	5.90	0.042	7.71	0.90	102	1.91
50	Tetrachloroethene	0.228	2.74	0.215	7.70	0.16	99.5	2.90
51	trans-1,3-Dichloropropene	0.357	6.85	0.359	6.61	0.04	104	1.70
52	Ethyl methacrylate	0.271	7.19	0.290	7.94	0.15	105	3.03
53	1,1,2-Trichloroethane	0.334	5.18	0.335	5.79	0.11	102	2.03
54	Chlorodibromomethane	0.334	5.18	0.335	5.79	0.11	102	2.03
55	1,3-Dichloropropane	0.345	3.41	0.350	5.95	0.09	102	2.47
56	1,2-Dibromoethane	0.243	5.38	0.246	8.06	0.17	103	1.88
57	2-Hexanone(5x)	0.072	5.96	0.317	8.03	0.42	105	2.49
58	Chlorobenzene	0.834	2.65	0.805	4.73	0.13	99.5	1.92
59	Ethylbenzene	1.280	4.06	1.213	6.21	0.20	99.4	2.52
60	1,1,1,2-Tetrachloroethane	0.332	4.72	0.319	4.84	0.12	99.9	1.25
61	o-Xylene	0.499	3.16	0.467	4.62	0.22	101	2.49
62	m-Xylenes(2x)	0.507	4.54	0.476	6.50	0.14	99.0	1.76
63	Styrene	0.791	3.26	0.754	4.89	0.10	103	2.49
64	Bromoform	0.182	6.61	0.189	7.98	0.10	103	2.44
65	Isopropylbenzene	1.285	4.03	1.196	5.01	0.08	102	2.25
66								
67	cis-1,4-Dichloro-2-butene	0.141	16.11	0.162	6.14	0.18	104	3.14
68	1,4-Dichlorobenzene-d4 (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
69	4-Bromofluorobenzene (SS)	0.880	3.06	0.877	2.88	4.41	101	0.72
70	n-Propylbenzene	2.963	3.24	2.757	5.84	0.08	102	2.14
71	Bromobenzene	0.675	4.54	0.652	5.93	0.14	99.8	1.50
72	1,1,2,2-Tetrachloroethane	0.590	3.39	0.611	5.79	0.18	99.5	0.99
73	2-Chlorotoluene	1.988	3.48	1.834	4.99	0.09	102	1.87
74	1,3,5-Trimethylbenzene	2.106	3.45	1.944	4.44	0.14	103	1.84
75	1,2,3-Trichloropropane	0.184	3.32	0.194	6.59	0.32	98.8	3.13
76	trans-1,4-Dichloro-2-butene	0.270	6.44	0.291	11.99	0.28	105	2.72
77	4-Chlorotoluene	2.349	3.47	1.707	5.77	0.16	99.9	2.09
78	tert-Butylbenzene	1.854	3.74	1.698	5.00	0.08	103	1.82
79	1,2,4-Trimethylbenzene	2.145	3.24	1.977	5.15	0.06	102	1.77
80	sec-Butylbenzene	2.635	3.53	2.429	4.30	0.13	102	1.88
81	p-Isopropyltoluene	2.331	2.81	2.132	4.69	0.08	102	2.30
82	1,3-Dichlorobenzene	1.303	3.20	1.242	7.05	0.13	96.8	1.91
83	1,4-Dichlorobenzene	1.389	12.29	1.305	12.67	0.20	93.8	1.73
84	n-Butylbenzene	2.053	3.39	1.898	6.28	0.12	101	2.64
85	1,2-Dichlorobenzene	1.216	6.59	1.165	5.54	0.14	97.5	1.88
86	1,2-Dibromo-3-chloropropane	0.124	10.78	0.138	6.27	0.26	98.0	4.09
87	Hexachlorobutadiene	0.278	6.59	0.250	8.18	0.21	97.4	2.18
88	1,2,4-Trichlorobenzene	0.614	7.09	0.579	9.01	0.18	94.7	3.18
89	Naphthalene	1.658	7.93	1.713	7.04	0.18	95.5	3.08
90	1,2,3-Trichlorobenzene	0.535	6.80	0.512	5.14	0.19	99.8	8.29

Table 3. 8260 QA/QC for Sim

Analyte	Compound	Distilled Water Avg RF	Distilled Water %RSD	Salt Water Avg RF	Salt Water %RSD	Salt Water MDL	Walt Water (IDOC % Recovery)	Salt Water IDOC %RSD
1	Pentafluorobenzene (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2	Chloroform	1.021	13.18	0.997	11.24	1.89	92.8	2.87
3	Dibromofluoromethane (SS)	0.540	4.31	0.539	2.46	20.2	102	3.20
4	1,4-Difluorobenzene (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
5	1,2-Dichloroethane-d4 (SS)	0.329	1.73	0.337	1.86	11.8	101	1.49
6	Bromodichloromethane	0.433	12.69	0.429	12.56	1.08	95.2	1.95
7	Chlorobenzene-d5 (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A
8	Toluene-d8(SS)	1.055	0.60	1.045	0.69	3.67	99.6	0.63
9	Chlorodibromomethane	0.444	18.63	0.429	21.12 R²=0.995	1.10	104	4.96
10	Bromoform	0.262	18.79	0.251	23.33 R²=0.994	1.18	108	7.08

BFB and Continuing Calibration Verifications were analyzed before field and QC samples and met BFB tune criteria and the +/- 20% recovery criteria for targets. Internal Standard criteria of 50-200% of the mid-point of the initial calibration and a default surrogate recovery of 70-130% were met for all samples and associated QC. As a precaution, a distilled water blank was run after two analytical runs in order to minimize salt build up. Running several clean up blanks at the end of the sequence is recommended.

Figure 4. 50ppb Standard – Full Scan Chromatogram

Figure 5. 250ppt Standard – SIM Chromatogram

There were no significant findings for the full scan samples. All had approximately 1ppb Methylene Chloride and 3ppb Acetone due to lab contamination. The A&M samples also had Tetrahydrofuran at low levels:

Station 11 = 1.15ppb   Station 13 = 0.25ppm   Station 20 = 0.22ppb

Results for THMs by SIM made sense considering the sample locations. Please see Table 4. The A&M sample at Station 20 had significantly higher results than other samples. This sample was taken in a highly urbanized location in the Houston Ship Channel so higher results were not unexpected.

Table 4. 8260 Results for THMs by SIM

Sample	Chloroform (ppt)	Bromodichloromethane (ppt)	Chlorodibromomethane (ppt)	Bromoform (ppt)
1. A&M Station 11 - Galveston Bay	3.54*	1.76*	3.24*	8.02
2. A&M Station 13 - Galveston Bay	4.34*	1.82*	1.88*	5.54
3. A&M Station 20 - Ship Channel	187	50.2	35.5	205
4. Rockport Area - Little Bay	5.24	3.58*	4.64*	8.04
5. Rockport Area - Aransas Bay	<5	<5	1.40*	5.59
6. Rockport Area - St. Charles Bay	2.57*	<5	1.78*	24.9
7. Rockport Area - Capano Bridge	2.68*	1.29*	2.50*	17.2
8. High Island	<5	<5	<5	7.28
9. High Island	<5	<5	1.50*	7.88
10. High Island	<5	<5	1.82*	7.59
11. High Island	2.32*	<5	1.63*	7.83

* The value reported is between the MDL and the reporting limit.

Figure 6. A&M Station 20 – Full Scan Chromatogram

Figure 7. A&M Station 20 – SIM Chromatogram

Section 5. Conclusions

The two methods have demonstrated the ability to monitor seawater on a regular basis. Since the P&T and GC parameters are the same, the lab can easily switch from full scan to SIM. Cleaning blanks should be added throughout the sequence and at the end to minimize salt build-up.

Section 6. References

1. Liu, Y., Yvon Y., Yvon-Lewis, S. A., Hu, L., Salisbury, J. E., & O'Hern, J. E. (2011). CHBr₃, CH2Br₂, and CHClBr₂ in U.S. coastal waters during the Gulf of Mexico and East Coast Carbon cruise. Journal of Geophysical Research: Oceans, 116(C10). https://doi.org/10.1029/2010JC006729. doi:https://doi.org/10.1029/2010JC006729

2. Liu, Y., Yvon-Lewis, S. A., Thornton, D. C. O., Butler, J. H., Bianchi, T. S.,   Campbell, L., et al. (2013). Spatial and temporal distributions of bromoform and dibromomethane in the Atlantic Ocean and their relationship with photosynthetic biomass. Journal of Geophysical Research: Oceans, 118(8), 3950-3965. doi:doi:10.1002/jgrc.2029

3. USEPA Method 8260D: Volatile Organic Compounds by Gas Chromatography / Mass Spectrometry (GC/MS) Rev. 4 June 2018

Section 7. Acknowledgements