Application Note

Analysis of Trihalomethanes (THMs) in drinking water

Purge and Trap (P&T) concentration with separation by Gas Chromatography (GC) and detection by Surface Acoustic Wave (SAW) sensor

Introduction

During water treatment, organic compounds react with free chlorine to form trihalomethanes (THMs). THMs are part of a group of compounds known as disinfection by-products (DBPs) and include chloroform, dichlorobromomethane, dibromochloromethane, and bromoform. These are considered a health risk when elevated levels are present. Formation of these compounds can vary by such factors as the water source, pH, temperature, coagulant treatment, and disinfectant dose. THMs are regulated by the Safe Drinking Water Act (SDWA) under the Environmental Protection Agency (EPA). The SDWA contains National Primary Drinking Water Regulations where maximum contaminant levels are set. The limit for total trihalomethanes is 80 ppb.

Water treatment plants and distribution systems are required to monitor THMs at various monitoring sites to ensure compliance and keep the treatment process optimized. Plant operators need real time data to adjust treatment processes, especially the impact of disinfectant dosage, that affect THM formation.

The classic way to determine THMs typically includes concentration by purge and trap (P&T) with separation by gas chromatography and detection by mass spectrometry (GC/MS). A common solution for testing THMs includes the collection of a sample and sending it to a commercial laboratory for testing. This process may take days to weeks to obtain the results. This delay in reporting is not practical since a THM event may have occurred, and no proper mitigation strategies could be implemented. Bringing P&T-GC/MS testing to the municipal lab bench has been cost prohibitive and a very complex technique to learn and maintain.

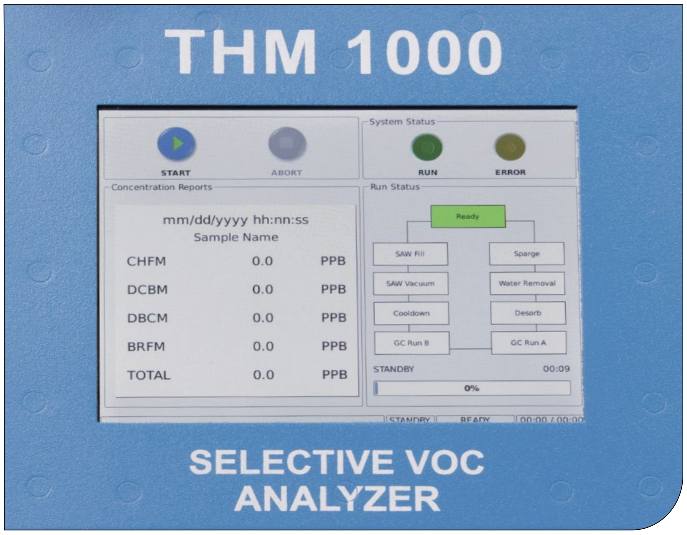
A new solution for effective monitoring of THMs now exists that is fast, simple, and reliable. The THM 1000 Selective VOC Analyzer has combined the P&T, GC, and detector into one simple analyzer. The innovative portion of this solution is the SAW (surface acoustic wave) detector. This unique monolithic detector is coated with a nonporous carbon layer and provides almost instant and extremely sensitive responses. Developed in conjunction with Sandia National Labs, this technology has simplified the detector portion to ensure routine and maintenance free operation.

This application note demonstrates calibration, linearity, reproducibility, and method detection limit results using this new instrument, the THM 1000. Spiked tap water samples from College Station, Texas will be analyzed by both the THM 1000 and GC/MS volatile system for comparison. Samples from sample points which Jefferson Parish Water Quality Lab monitors were also analyzed by both methods.

The THM 1000 can help operators optimize water treatment at the plant and evaluate water age in the distribution system for improved monitoring of the formation of THMs, an EPA-regulated disinfection by-product.

Instrumentation

One of the instruments used for analysis was the THM 1000 Selective VOC Analyzer. The other system included sample concentration using an OI Analytical P&T with an OI Analytical 4100 sample processor. An Agilent 7890A/5975C GC/MS was used for chromatographic separation and detection.



Methodology

EPA Method 501 was used as guidance for the THM 1000 analysis. All QC and samples were analyzed using a 40 ml purge. A system monitoring compound, difluorobenzene, at 20 ppb was added to all samples to monitor purging efficiency.

A calibration was run using 5, 10, 20, 40, 60, 80, and 100 ppb THM standards. External standard calibration using peak height and linear regression was performed. A limit for correlation coefficient of >/= 0.995 was used for calibration. Initial demonstration of capability (IDC) was performed by analyzing six replicates at 40 ppb. The method detection limit (MDL) study was performed by analyzing nine replicates at 2 ppb over a three-day period. Please see Table 1 for THM 1000 method parameters.

EPA Method 524.3 was used for the GCMS analysis. All samples were spiked with internal standards and surrogates at 5 ppb. A 5 ml purge was used. A calibration was run using 0.5 ,1 ,2 ,5, 10, 20, and 40 ppb. Internal standard calibration was used where the limit for correlation coefficient of >/= 0.990 was used. Calibration was verified by re-calculating each calibration point with the new calibration.

A tap water sample was obtained and five replicates for each instrument were spiked with 20 ppb THMs. These were analyzed using the THM 1000 and P&T with GC/MS to compare performance between the two applications.

Table 1. THM 1000 Method Parameters

Parameter	Setting
PCT	Tenax®
Purge gas	Zero grade Helium at 60 mL/min
Safety vent 1	25 seconds
Sparge/purge time	600 seconds
Water removal time	150 seconds
Safety vent 2	5 seconds
Desorb time	100 seconds
Bake time	655 seconds
PCT Temperature	Ambient during purge 35 ˚C during water removal 240 ˚C during desorb 150 ˚C during bake
Column	Agilent LTM DB-624 30 meter, 0.32 mm ID, 1.8 µm film
Carrier gas	Zero grade nitrogen
Column flow rate	1 mL/min
GC oven program	Oven before desorb 30 ˚C Hold at 30 ˚C for 200 seconds 160 ˚C/minute to 100 ˚C 40 ˚C/minute 200 ˚C hold 180 seconds 160 ˚C/minute 75 ˚C hold 150 seconds 160 ˚C/minute to 30 ˚C hold 250 seconds

Note: GC default parameters for method THM

Table 2. Instrument Parameters GC/MS

Purge-and-Trap	Eclipse 4760 P&T Sample Concentrator
Trap	#10 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

Methodology

Continued.

Table 2. Instrument Parameters GC/MS (continued)

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	Water
Rinse water	90 ˚C
4100 Sample Process Methods	
P&T Rinses	3
Rinse water	Hot
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	50
Oven Program	Hold at 40˚C for 2.0 min 12 ˚C/minute to 170 ˚C 40 ˚C/minute to 220 ˚C Hold at 220 ˚C for 3 min Total GC Run is 17.1 min
Autosampler	**4100 Water/Soil Sample Processor**
Mode	Full scan
Scan range	35 - 300 amu
Scans/second	5.19
Solvent delay	1.46 min
Transfer line temperature (AUX)	240 ˚C
Source temperature	230 ˚C
Quadrupole temperature	150 ˚C
Draw out plate	6 mm

Results

Calibration criteria, precision and accuracy of IDCs, and MDL criteria were easily met using both methods. Please see Table 3 for THM 1000 QC. The % difference was calculated for THM 1000 and GC/MS results of spiked samples. There was excellent correlation between the two methods. Calibration criteria was also met on the GC/MS system. Please see Table 4 for GC/MS calibration results. The % difference was calculated for THM 1000 and GC/MS results of spiked samples. There was excellent correlation between the two methods. Please see Table 5 for spiked sample results when using tap water as the sample matrix. Please see Table 6 comparison results when using Jefferson Parish samples. There were high % differences for Bromoform since the THM 1000 results were less than the instrument's reporting limit.

Table 3. THM 1000 QC

Compound	Calibration Correlation	MDL Spike (ppb)	MDL % Recovery	MDL (ppb)	IDC Spike (ppb)	IDC % Recovery	IDC % RSD
Chloroform	0.998	2	82.2	0.33	40	100	2.48
Dichlorobromomethane	0.997	2	91.1	0.32	40	99.8	3.66
Dibromochloromethane	0.996	2	96.1	0.28	40	101	4.61
Bromoform	0.997	2	78.3	0.29	40	99.9	4.34

Table 4. GC/MS /QC

Compound	Calibration Coefficient (R^2)	AVG. Response Factor	Cal 0.5 ppb % Recovery	Cal 1 ppb % Recovery	Cal 2 ppb % Recovery	Cal 5 ppb % Recovery	Cal 10 ppb % Recovery	Cal 20 ppb % Recovery	Cal 40 ppb % recovery
1,4-Difluorobenzene (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Methyl tert-butyl ether-d3(SS)	% RSD = 5.49	0.994	108	99.9	101	100	101	100	89.6
Chloroform	0.998	0.648	109	109	107	107	105	108	97.7
Dichlorobromomethane	1.00	0.416	108	87.7	100	99.4	99.4	99.8	100
Chlorobenzene-d5 (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Dibromochloromethane	1.00	0.407	97.2	110	96.3	96.2	92.4	98.4	101
Bromoform	0.999	0.305	95.4	84.7	86.2	89.1	90.7	97.4	98.6
1,4-Dichlorobenzene-d4 (IS)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
4-Bromofluorobenzene (SS)	%RSD = 3.31	0.737	99.5	98.3	102	96.3	101	97.0	106
1,2-Dichlorobenzene-d4 (SS)	%RSD = 3.17	0.972	99.3	101	110	102	104	101	93.8

Note : Surrogates were run at the same concentration on all calibration levels so average response was used.

Table 5. THM 1000 Results Compared to GC/MS Results for Tap Water

Sample		Chloroform ppb	Dichlorobromomethane ppb	Dibromochlormethane ppb	Bromoform ppb
Tap	THM 1000	0.2*	1.5**	5.4	6.4
Tap	GC/MS	0.52	2.00	5.64	6.30
% Difference		88.9	28.6	4.35	1.58
Tap MS1	THM 1000	20.7	21.9	25.7	26.5
Tap MS1	GC/MS	19.9	21.3	24.8	24.7
% Difference		3.94	2.78	3.56	7.03
Tap MS2	THM 1000	21.6	22.9	27.0	28.0
Tap MS2	GC/MS	19.4	21.2	25.3	25.0
% Difference		10.7	7.71	6.50	11.3
Tap MS3	THM 1000	20.9	21.8	25.9	27.0
Tap MS3	GC/MS	20.0	21.5	24.5	24.4
% Difference		4.40	1.39	5.56	10.1
Tap MS4	THM 1000	20.5	21.1	24.7	24.9
Tap MS4	GC/MS	21.9	21.4	25.1	24.7
% Difference		6.60	1.41	1.60	0.81
Tap MS5	THM 1000	20.0	20.9	24.6	24.8
Tap MS5	GC/MS	21.4	21.2	24.2	23.6
% Difference		6.76	1.42	1.64	4.96
2nd Source Calibration Verification at 40 ppb	THM 1000	41.9	42.5	42.7	41.9
2nd Source Calibration Verification at 40 ppb	GC/MS	38.3	39.4	40.8	38.2
% Difference		8.98	7.57	4.55	1.82

Tap water spiked with 20 ppb THMs.

Reporting level for THM 1000 is 5 ppb.

Reporting level for GC/MS is 0.5 ppb

* Value is less than MDL.

** Value is between the MDL and reporting level.

Table 6. THM 1000 Results Compared to GC/MS Results for Jefferson Parish Samples

Sample		Chloroform ppb	Dichlorobromomethane ppb	Dibromochlormethane ppb	Bromoform ppb
POE-New	THM 1000	31.2	20.1	8.6	0.4*
	GC/MS	40.2	25.6	10.6	0.74
% Difference		25.2	24.1	20.8	59.6
POE-LTM1	THM 1000	22.7	15.7	7.6	0.4*
	GC/MS	27.2	16.6	8.38	0.68
% Difference		18.0	5.57	9.76	51.8
POE-LTM2	THM 1000	26.0	20.6	10.6	0.6*
	GC/MS	26.9	18.6	9.44	0.82
% Difference		3.40	10.2	11.6	31.0

Sample		Chloroform ppb	Dichlorobromomethane ppb	Dibromochlormethane ppb	Bromoform ppb
POE-LTM3	THM 1000	21.3	16.1	8.7	0.7*
	GC/MS	23.8	15.7	8.41	0.86
% Difference		11.1	25.2	3.39	20.5
E-6	THM 1000	26.3	19.2	8.9	0.7*
	GC/MS	28.3	20.7	9.67	1.01
% Difference		7.33	7.52	8.29	36.3
E-12	THM 1000	22.6	18.4	9.3	0.8*
	GC/MS	23.5	18.4	9.78	1.17
% Difference		3.90	0	5.03	37.6
E-23	THM 1000	20.9	16.6	8.7	0.7*
	GC/MS	25.7	18.4	9.20	1.10
% Difference		20.6	10.3	5.59	44.4
E-26	THM 1000	27.1	20.7	9.6	0.7*
	GC/MS	28.7	19.8	8.63	0.96
% Difference		5.73	4.44	10.6	31.3
E-39	THM 1000	29.4	22.3	10.5	0.8*
	GC/MS	27.8	20.3	9.30	0.91
% Difference		5.59	9.39	12.1	12.9
E-40	THM 1000	29.7	20.8	9.3	0.6*
	GC/MS	34.6	22.9	10.1	1.02
% Difference		15.2	9.61	8.25	51.8
E-43	THM 1000	25.4	18.2	8.6	0.7*
	GC/MS	31.6	21.4	9.92	0.95
% Difference		21.8	16.2	14.2	30.3
E-49	THM 1000	16.0	11.5	5.5	0.4*
	GC/MS	19.9	14.1	6.71	0.68
% Difference		21.7	20.3	19.8	51.8
E-60	THM 1000	30.4	21.2	9.4	0.6*
	GC/MS	33.6	23.6	10.6	1.05
% Difference		10.0	10.7	12.0	54.5
E-61	THM 1000	28.3	20.6	9.5	0.7*
	GC/MS	35.2	23.8	10.2	0.97
% Difference		21.7	14.4	7.11	32.3
E-67	THM 1000	26.1	18.0	8.0	0.5*
	GC/MS	32.9	22.0	9.61	0.93
% Difference		23.0	20.0	18.3	60.1
E-72	THM 1000	27.5	19.5	8.7	0.7*
	GC/MS	30.9	22.2	10.2	1.06
% Difference		11.6	13.0	15.9	40.9
W-3	THM 1000	33.7	21.7	8.2	0.3*
	GC/MS	35.8	22.5	8.93	0.62
% Difference		6.04	3.62	8.52	69.9
W-11	THM 1000	31.1	20.4	8.5	0.3*
	GC/MS	38.3	26.1	10.5	0.71
% Difference		9.43	24.5	21.0	81.2
W-44	THM 1000	31.7	21.4	9.1	0.4*
	GC/MS	32.8	23.0	9.56	0.69
% Difference		3.41	7.21	4.93	53.2

Sample		Chloroform ppb	Dichlorobromomethane ppb	Dibromochlormethane ppb	Bromoform ppb
W-51	THM 1000	22.3	14.0	6.5	0.3*
	GC/MS	26.9	15.6	7.19	0.57
% Difference		18.7	10.8	10.1	62.1
W-61	THM 1000	34.9	22.9	9.5	0.5*
	GC/MS	35.9	24.6	10.4	0.55
% Difference		2.82	7.16	9.04	9.52
W-67	THM 1000	38.7	25.7	10.5	0.4*
	GC/MS	38.4	25.7	10.8	0.77
% Difference		0.78	0	2.82	63.2
W-75	THM 1000	33.3	21.0	9.5	0.5*
	GC/MS	37.9	21.3	9.69	0.65
% Difference		12.9	1.42	1.98	26.1
W-79	THM 1000	27.3	15.7	5.4	0.6*
	GC/MS	28.6	16.6	5.80	0.89
% Difference		4.65	5.57	7.14	38.9

Reporting level for THM 1000 is 5 ppb.

Reporting level for GC/MS is 0.5 ppb

* Value is between the MDL and reporting level.

Figure 1. 50 ppb THM from THM 1000

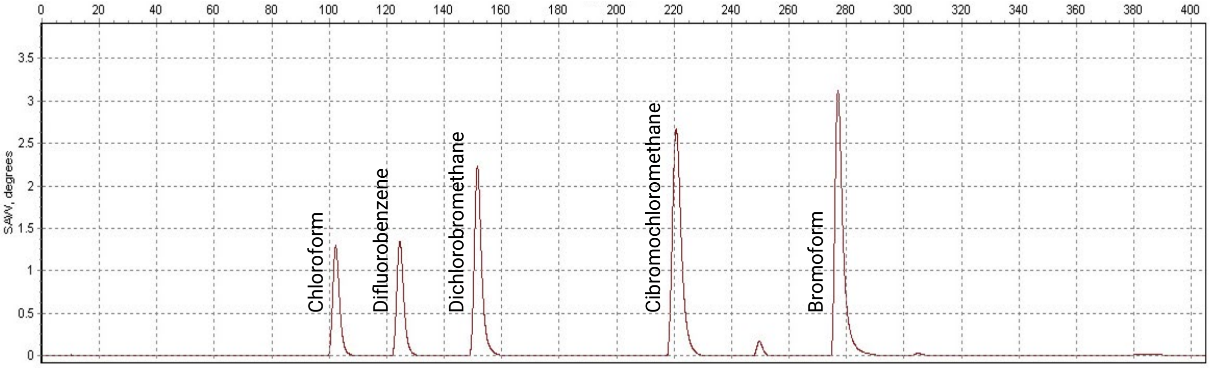


Figure 2. Blank from THM 1000

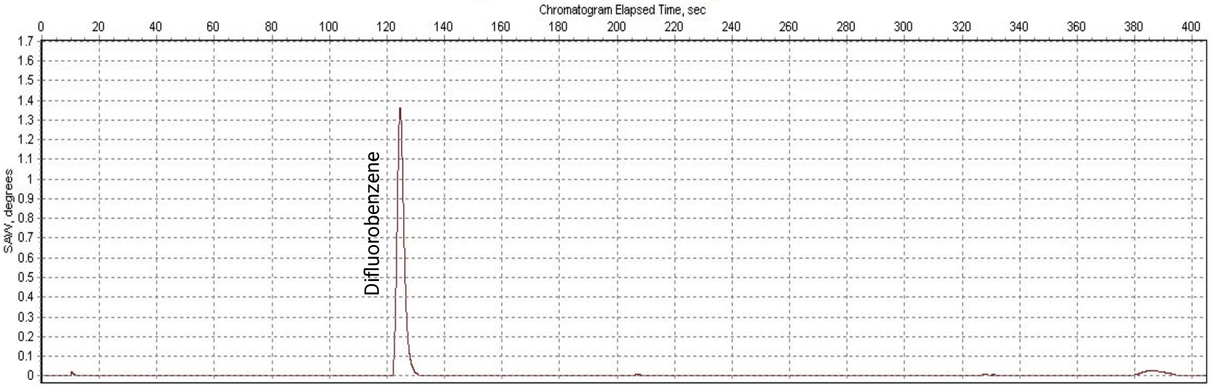


Figure 3. 10 ppb Method 524.3 Standard by GC/MS

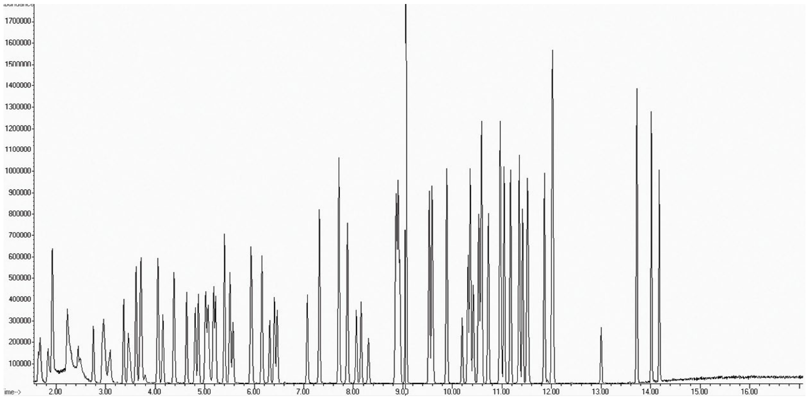
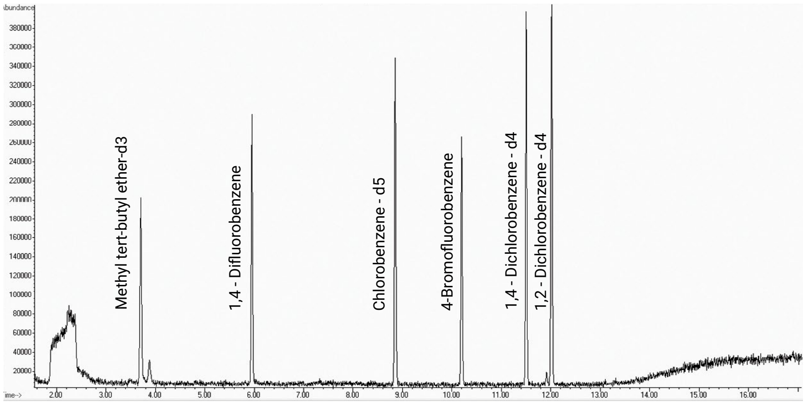


Figure 4. Blank by GC/MS



Conclusions

Reliable and timely THM data is essential for water treatment process optimization. The analysis using the THM 1000 offers a fast, accurate alternative to GC/MS for in-house monitoring of THMs in drinking water plants. The instrument can save facilities time and money as well as offer flexibility in monitoring the treatment process.

Acknowledgement

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References

EPA Method 501.3. Measurement of Trihalomethanes in Drinking Water with Gas Chromatography/Mass Spectrometry and Selected Ion Monitoring. U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water: Cincinnati, Ohio, 1996.

EPA Method 524.3. Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0, EPA-815-09-009; U.S. Environmental Protection Agency, Office of Ground Water and Drinking Water: Cincinnati, Ohio, June 2009.

YSI Incorporated
1725 Brannum Lane
Yellow Springs, OH 45387

Tel +1 937.767.7241
xylem-lab@xyleminc.com

YSI.com/Lab-Solutions