

Solid Phase Microextraction of Cyanogen Chloride and Other Volatile Organic Compounds in Drinking Water with Fast Analysis by GC-TOFMS

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1. Introduction

Disinfection by-products are formed in drinking water due to a reaction of natural organic matter with chlorine, chloramines, and ozone; which are used to kill bacteria. In addition to trihalomethanes (e.g. chloroform, bromoform, etc.) and haloacetic acids, cyanogen chloride and bromide can be formed through disinfection. Cyanogen chloride (CNCl) is metabolized to cyanide in the body and the World Health Organization has issued a guideline of 70 ppb of total cyanogenic compounds in drinking water.

Methods of analysis for CNCl in drinking water include purge-and-trap (P&T) gas chromatography-mass spectrometry (GC-MS), static headspace GC-electron capture detector (ECD), and micro liquid-liquid extraction (LLE) GC-ECD. P&T GC-MS (EPA Method 524.2), has a quantification limit of 0.3 ppb for CNCl. The method is sensitive and reproducible because of the relatively large sample size (5 ml), and the exhaustive sampling approach of P&T. Static headspace is not as sensitive or precise as P&T, mainly because CNCl is so water-soluble. The micro LLE approach (EPA Method 551.1) uses methyl t-butyl ether and a "salting out" extraction to improve recovery for the hydrophilic CNCl, but the method is still not as sensitive as P&T.

An alternate approach to the methods above is solid phase microextraction (SPME). A syringe-type coated fiber is either immersed in an aqueous sample, or suspended in the headspace above the sample to collect volatile organic compounds (VOCs). Subsequently, the fiber is desorbed in a hot injector of a GC. This note describes preliminary method development work on SPME of CNCl in drinking water, with fast GC—Time-of-Flight Mass Spectrometry (TOFMS) to measure CNCl and VOCs in Las Vegas, Nevada drinking water.

2. Experimental Conditions

Drinking Water

Las Vegas uses Lake Mead, formed by the damming of the Colorado River, as its water source. Chlorination is the current form of disinfection.

Standards

CNCl was obtained from Protocol Analytical Supplies, Inc. Cyanogen bromide was purchased from Aldrich Chemical Company. All other VOCs were from Restek Corporation. A mixed standard containing all compounds used in this work was prepared in methanol, from the stock listed above. Working solutions of this standard were spiked into water to prepare aqueous samples for testing and calibration purposes.

SPME

2 ml of water was placed into a 4 ml vial. A micro stirring bar was placed into the vial and a holed cap with a PTFE-lined silicone septum was used to seal the vial. Stirring was started and a Carboxen/PDMS fiber from a manual SPME fiber holder (Supelco) was inserted into the headspace of the vial. After exactly 4 minutes, the fiber was retracted and removed from the vial.

VOCs were desorbed from the fiber via a splitless injector at 250°C. A 0.75 mm ID SPME injection sleeve (Supelco) was the liner for the injector. The injector was purged after 15 seconds.

GC Parameters:

Agilent 6890N

Column:

20 m x 0.25 mm x 0.71 μ m Rtx-TNT (Restek)

Carrier:

Helium at 5 ml/minute, constant flow

Injection:

SPME desorption

Oven Program:

-40°C (0.25 minute), 120°/minute to 80°,
80°/minute to 220°

Total Run Time:

3 minutes

Mass Spectrometer: LECO Pegasus III GC-TOFMS

Ionization: Electron ionization at 70eV

Source Temperature: 180°C

Stored Mass Range: 47 to 350 u

Acquisition Rate: 40 spectra/second

Data Processing

LECO ChromaTOF software with automatic Peak Find and Deconvolution.

3. Results

SPME sampling time was kept as short as possible while trying to maximize response for CNCl. Figure 1 shows that the maximum response for CNCl occurred at about 4 minutes, so this was set as the SPME sampling time.

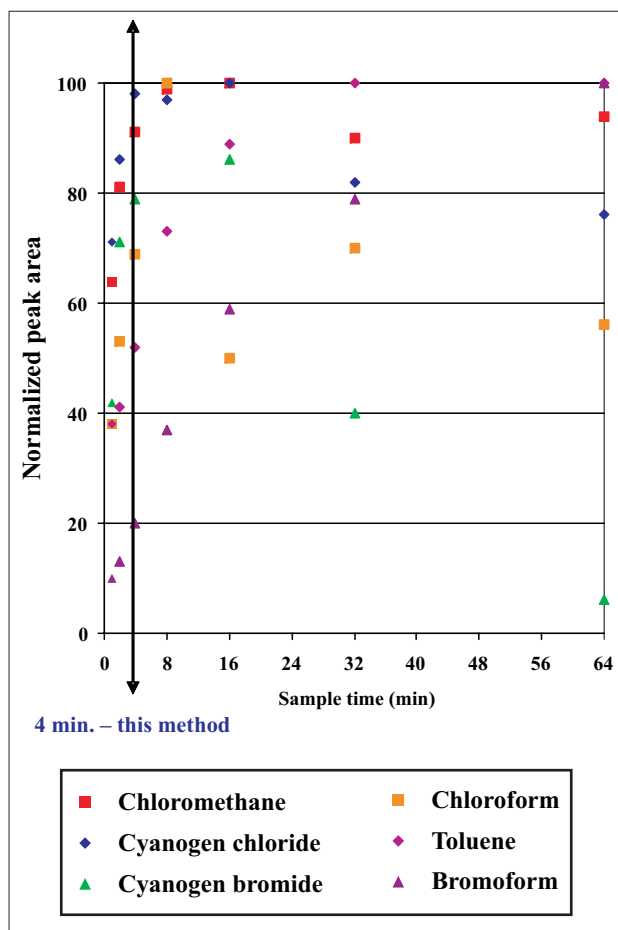


Figure 1. SPME headspace sampling efficiencies for a group of volatile organic compounds.

A high GC column flow rate of 5 ml/minute was used for two reasons. The first was to provide high flow through the inlet to speed desorption of the VOCs from the SPME fiber. The other reason was to chromatograph the VOCs as quickly as possible, knowing that the peak find and deconvolution algorithms available with TOFMS would provide the differentiation necessary for qualitative and quantitative measurements. Retention times and elution orders for the VOCs are illustrated in Table 1 and Figure 2. Note that many of the peak widths for the VOCs are less than one second wide. Narrow peak widths and spectral deconvolution explain the reason for acquiring MS data at a high 40 spectra/second rate.

Table 1. Retention times in seconds for a standard of VOCs sampled from water using SPME.

Peak#	Compound	RT (sec.)
1	Dichlorodifluoromethane	33.36
2	Chloromethane	38.65
3	Cyanogen chloride	44.98
4	Bromomethane	50.82
5	Chloroethane	53.55
6	Trichlorofluoromethane	60.25
7	Cyanogen bromide	63.90
8	1,1-Dichloroethene	65.05
9	Methylene chloride	66.90
10	trans-1,2-Dichloroethene	71.40
11	1,1-Dichloroethane	72.87
12	cis-1,2-Dichloroethene	76.82
13	Bromochloromethane	77.82
14	2,2-Dichloropropane	77.90
15	Chloroform	78.20
16	1,2-Dichloroethane	81.82
17	1,1,1-Trichloroethane	82.10
18	1,1-Dichloropropene	83.42
19	Benzene	84.17
20	Carbon tetrachloride	84.52
21	1,2-Dichloropropane	88.35
22	Dibromomethane	88.55
23	Trichloroethene	88.90
24	Bromodichloromethane	89.32
25	cis-1,3-Dichloropropene	93.42
26	trans-1,3-Dichloropropene	96.25
27	1,1,2-Trichloroethane	97.27
28	Toluene	97.77
29	1,3-Dichloropropane	98.90
30	Chlorodibromomethane	100.95
31	1,2-Dibromoethane	102.42
32	Tetrachloroethene	103.77
33	Chlorobenzene	108.25
34	1,1,1,2-Tetrachloroethane	108.30
35	Ethylbenzene	110.17
36	m-Xylene	111.22
37	p-Xylene	111.22
38	Bromoform	113.07
39	Styrene	113.90
40	o-Xylene	114.47
41	1,1,2,2-Tetrachloroethane	115.55
42	1,2,3-Trichloropropane	116.55
43	Isopropylbenzene	118.45
44	Bromobenzene	119.72
45	n-Propylbenzene	122.28
46	2-Chlorotoluene	122.36
47	4-Chlorotoluene	122.92
48	1,3,5-Trimethylbenzene	124.05
49	tert-Butylbenzene	127.45
50	1,2,4-Trimethylbenzene	127.55
51	1,3-Dichlorobenzene	129.35
52	sec-Butylbenzene	129.77
53	1,4-Dichlorobenzene	130.02
54	p-Isopropyltoluene	131.27
55	1,2-Dichlorobenzene	133.20
56	n-Butylbenzene	135.27
57	1,2-Dibromo-3-chloropropane	138.32
58	1,2,4-Trichlorobenzene	150.97
59	Naphthalene	152.25
60	1,2,3-Trichlorobenzene	155.35
61	Hexachlorobutadiene	155.65

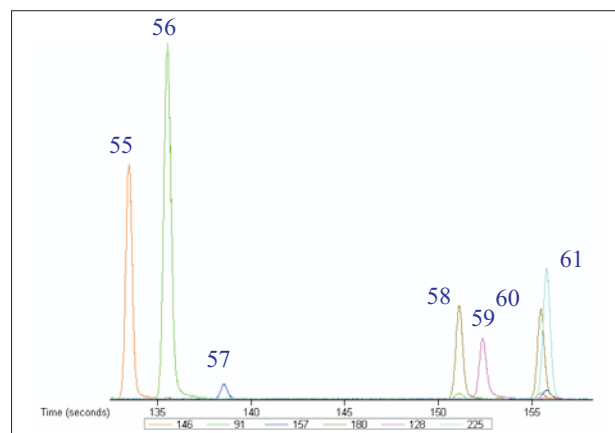
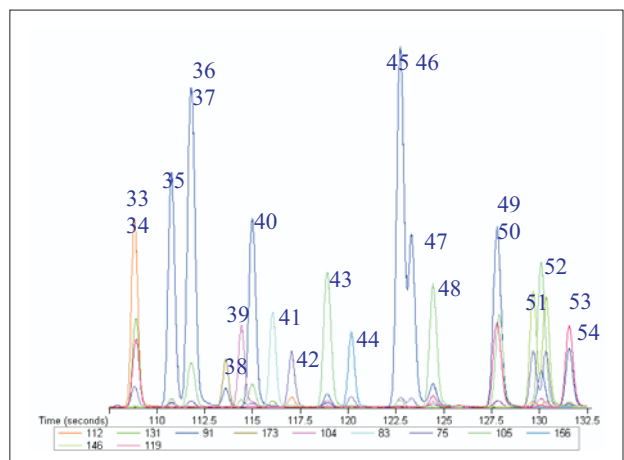
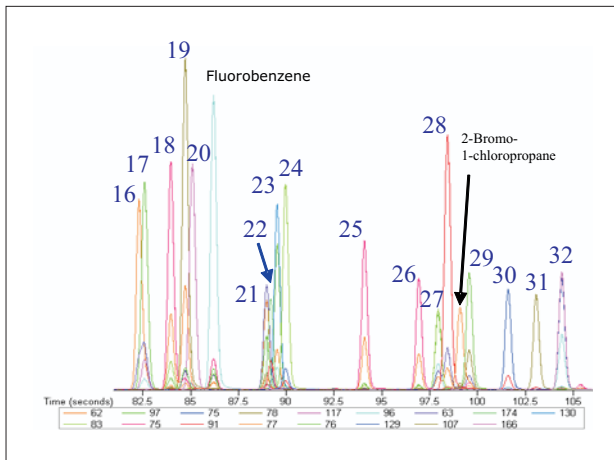
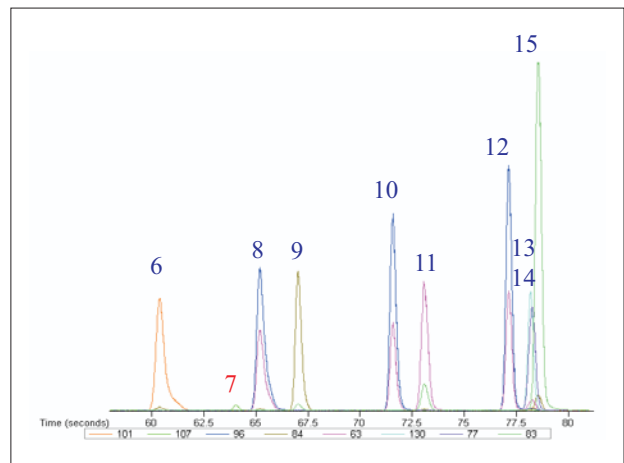
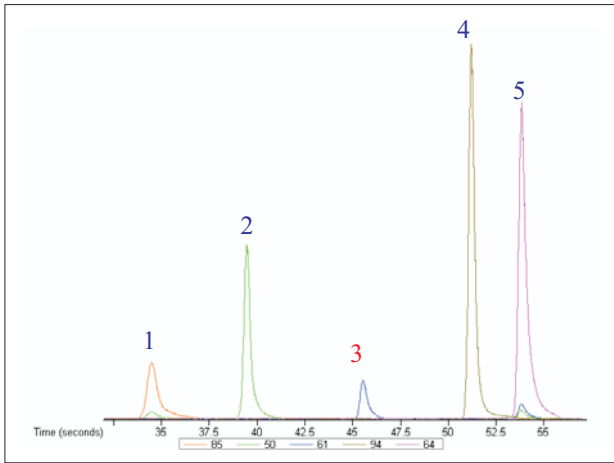


Figure 2. Chromatogram of VOCs using fast TOFMS (40 spectra/second) after sampling of spiked water with SPME. Total analysis time is less than 3 minutes. Diagnostic extracted ions are plotted for each VOC. Refer to Peak# in Table 1 for compound identifications.

Internal standard calibration curves (using either fluorobenzene or bromochloropropane) were developed for most of the VOCs, ranging from 0.2 to 40 ppb. The calibration curve for CNCl is shown in Figure 3.

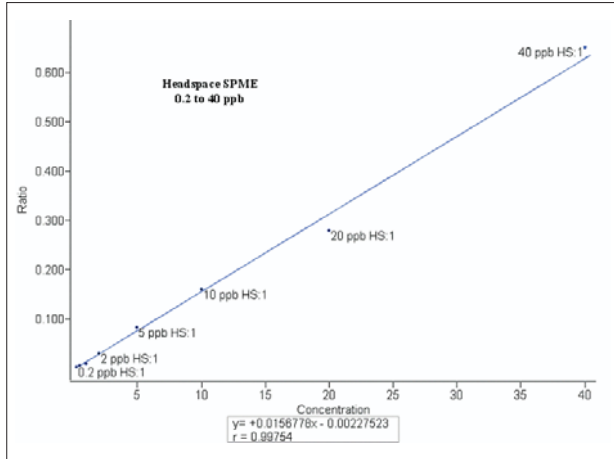


Figure 3. TOFMS calibration curve from 0.2 to 40 ppb for cyanogen chloride.

Because the TOFMS detector voltage was set relatively high for poorly detected cyano compounds, the detector saturated on some VOC base peak ions at higher concentrations (e.g. chloroform, bromodichloromethane). Since these same ions are typically used for quantification, the calibration curves for these compounds had a limited range. Fortunately, ChromaTOF provides an elegant solution to this problem through the use of Extended Range Calibration.

In Extended Range Calibration, a less intense mass is used for quantification in the higher range. Figure 4 indicates how the entries are made in the Calibration Table. The resulting calibration curves for chloroform are plotted in Figure 5. The beauty of Extended Range Calibration is that range selection is automatic for unknown analysis. No operator intervention is necessary.

Calibration Table - "THMs Calib"						
Analyte	Absolute R.T. (sec)	Name	Min Valid Conc	Max Valid Conc	Range Conc	Masses
1*	78.555	Chloroform	0.10000	10.000	1	83
2	89.955	Bromodichloromethane	0.10000	10.000	1	83
3	99.08	2-Bromo-1-chloropropane	2.5000	7.5000	1	77
4	101.605	Dibromochloromethane	0.10000	60.000	1	129
5	113.605	Bromoform	0.10000	60.000	1	173

Range 1 - Base Peak Quant Masses

Range 2 - Less Intense Quant Masses

Calibration Table - "THMs Calib"						
Analyte	Absolute R.T. (sec)	Name	Min Valid Conc	Max Valid Conc	Range Conc	Masses
1*	78.555	Chloroform	10.000	60.000	2	87
2	89.955	Bromodichloromethane	10.000	60.000	2	129
3	99.08	2-Bromo-1-chloropropane	2.5000	7.5000	1	77
4	101.605	Dibromochloromethane	0.10000	60.000	1	129
5	113.605	Bromoform	0.10000	60.000	1	173

Figure 4. Extended range calibration for chloroform and bromodichloromethane. In the top table, the most intense ions (83) are used for the lower level curve (up to 10 ppb). The bottom table shows the switch to less intense ions (87 and 129) for levels from 10 to 40 ppb because the detector saturates when the most intense ion is used in this range.

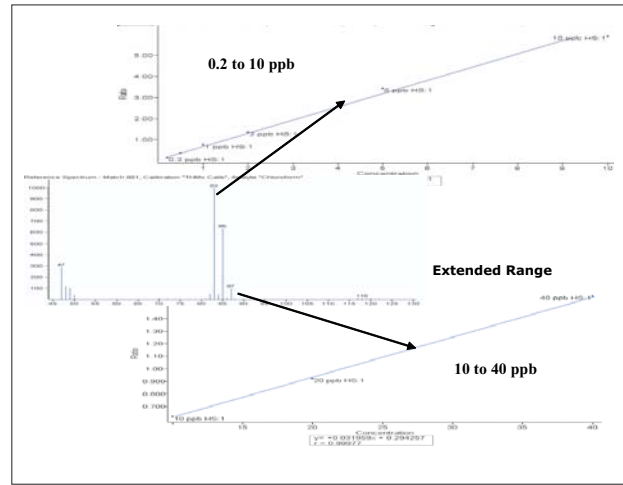


Figure 5. Lower and extended range calibration curves for chloroform. The top curve from 0.2 to 10 ppb is built using the 83 ion, while the bottom curve (10 to 40 ppb) uses the less intense ion 87 due to detector saturation for 83 in this range.

A summary of Las Vegas drinking water quantification results is shown in Table 2. Fourteen replicate water samples were drawn during a constant flushing of the tap. Cyanogen chloride was detected in all of the samples. Total trihalomethanes (THMs) averaged around 45 ppb. The EPA limit for THMs is 100 ppb.

Table 2. Quantification of VOCs in Las Vegas drinking water by SPME GC-TOFMS.

Compound	ppb	RSD %
Cyanogen chloride	2.8	26
Cyanogen bromide	ND	ND
Chloroform	16	17
Bromodichloromethane	16	8
Dibromochloromethane	12	10
Bromoform	1.1	11

RSD% is the relative standard deviation for fourteen analyses. ND is not detected.

Estimated detection limits (EDLs) in drinking water for select compounds measured using the SPME GC-TOFMS method are shown in Table 3. These were calculated by extrapolation of the 0.2 ppb standard, based on the quantification mass and a signal-to-noise of 3 as the detection limit. Obviously the method is very sensitive, capable of measuring many VOCs in the ppt range. CNCl has an excellent detection limit also.

Table 3. Estimated detection limits for select VOCs in drinking water using SPME GC-TOFMS.

Compound	Mass	EDL (ppb)
Cyanogen chloride	61	0.03
Cyanogen bromide	105	0.1
Chloroform	83	0.0003
Bromodichloromethane	83	0.0005
Dibromochloromethane	129	0.001
Bromoform	173	0.002

Method Development Observations

Direct aqueous sampling of tap water using SPME resulted in degradation of the fiber, and even though rinsing in a methanol/water solution could restore fiber performance, headspace sampling is preferred for VOCs.

Some carryover occurs with the Carboxen/PDMS fiber when it is desorbed at 250°C for 15 seconds. To decrease carryover, higher desorption temperatures are preferred (320°C maximum) versus increased desorption time.

Although it was not done in this work, since all sampling and analysis was performed almost simultaneously, free chlorine should be quenched to halt production of disinfection byproducts during sample storage and SPME.

Cryogenic oven cooling during SPME desorption is time-consuming, but necessary to refocus low boiling volatiles on the GC column. A thicker film GC column might permit a higher oven start temperature.

4. Conclusions

SPME is a simple, inexpensive, and sensitive method for sampling cyanogen chloride and other volatiles in drinking water.

61 VOCs were chromatographed in less than 3 minutes using a fast GC method. The high acquisition rate of TOFMS defines peaks less than 1 second wide, and enables spectral deconvolution of coeluting peaks. Extended Range Calibration enabled hands-off measurement for compounds whose typical quantification ions saturated the MS detector.

5. References

World Health Organization, Water and Sanitation, Guidelines for drinking water quality.

http://www.who.int/water_sanitation_health/GDWQ/Chemicals/cyanogenchloridefull.htm#General

B. Cancho, F. Ventura, M.T. Galceran, Simultaneous determination of cyanogen chloride and cyanogen bromide in treated water at sub- $\mu\text{g/L}$ levels by a new GC-ECD method, *J. Chromatogr. A* 897 (2000) 307-315.

