Ambient Headspace GC and GC-MSD Analysis of Non-Polar Volatiles in Water

Application

Gas Chromatography

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Abstract

Ambient headspace is an ideal method for prescreening samples prior to purge and trap (P&T) analysis. Instrumentation is protected from high level contaminants and rework is reduced. The nature of the technique also makes it attractive for high sample volume applications, such as monitoring of process water in food/beverage manufacturing.

Key Words

ambient headspace, drinking water, GC-FID, GC-micro ECD, GC-AED, GC-MSD, GC-MSD screener report, prescreening, purge and trap, retention time locking (RTL), nonpolar volatile organics

Introduction

Chlorination is a common practice for the disinfection of water supplies. The reaction of chlorine with dissolved organics in the water results in the formation of non-polar halogenated compounds. The principle compounds formed are the trihalomethanes. Usually, bromide salts are also present in water, and both brominated and chlorinated compounds are formed. Water sources also may be contaminated with industrial solvents, such as benzene, tetrachloroethene and methyl tertiary butyl ether (MTBE).

The analysis of these compounds is important to suppliers of drinking water, food and beverage processing companies, and industrial operations that discharge waste water.

Government regulations require that these compounds be measured in drinking water at part-per-billion (ppb) levels. Techniques like P&T are used routinely for this analysis. While P&T allows analysis at very low levels, problems arise with samples containing unexpectedly high levels of volatiles. Instrument contamination and subsequent carryover result in reduced productivity and higher cost. Prescreening using headspace analysis can prevent instrument contamination problems. Lab productivity is also increased with prescreening, because the approximate concentration range of analytes is known before P&T. Re-work of samples outside the P&T calibration range is eliminated.

Ambient headspace is a fast, low-cost technique for analyzing non-polar volatiles in water. It can be used instead of normal heated headspace for prescreening. For non-government regulated analyses, ambient headspace can also be used for routine work.

This application note describes a method evaluated on several different instrument systems and detectors. The choice of configuration is based on the specific measurement requirements.

Experimental

Sample Preparation

Sodium sulfate (Fisher Scientific, 10-60 mesh) and 2-mL autosampler vials (Agilent part number 5182-0543) were baked and stored at 100 °C to prevent contamination with volatiles. One-milliliter disposable serological pipettes (Corning) and aluminum crimp caps (Agilent part number 5181-1215) were used as received. Distilled water for preparation of standards and blanks was purified by constant purging with carbon-filtered helium.

Water samples are prepared for analysis as follows:

1. Sodium sulfate is added to each autosampler vial to form a layer of approximately 4 mm in height.
2. One milliliter of water sample is added to the vial with a disposable pipette.
3. The vial is immediately capped and crimped.
4. The sample is vortexed for about 3 seconds.

Standards are prepared as above, except 1 µL of spiking solution in methanol is added to 1 mL of purified water just before step 3. Only 1 µL is used to minimize the amount of methanol added to the water. The concentration of individual compounds in the spiking solution is 1,000 times higher than the desired final concentration in the vial.

A standards kit of volatiles in methanol was obtained from Supelco (part number 4-8804, Bellefonte, PA). The 58 compounds are divided into six different mixes. Spikes were prepared using one mix per vial.

Instrument Conditions

Table 1 lists the instrument conditions used.

Results and Discussion

Retention Time Locking

The method is designed for use on a variety of instrument configurations. Configurations used were GC-FID, GC-micro ECD, GC-AED, and GC-MSD. To simplify data analysis and comparison across the various instruments, retention time locking (RTL) is employed. RTL is a technique that matches the retention time (RT) from column-to-column and instrument-to-instrument to approximately 0.03 minutes[1]. Using RTL, compounds are identified by searching a table of retention times that have been collected under locked conditions.

This method is locked to a table of RTs of 65 volatile compounds from EPA method 8260. The table was created by running mixtures of standards on GC-MSD to confirm RTs based on mass spectra. The table is locked using tetrachloroethene at 4.247 minutes as the locking compound. To match the GC-MSD retention times to atmospheric pressure detectors, Agilent's method translation software[2] (MTL) is used in combination with RTL.

The mass spectra of the 65 compounds with retention times were collected into a user library. A screener database (SCD) was then constructed from this library reference. An SCD is used to screen for compounds based on RT and ion ratios. Combining precise RT with mass spectral information in the search reduces both false positives and false negatives in identifications.

Identifications for GC-FID and GC-micro-ECD used an RT table (Table 2) constructed with the GC RTL software. For each compound entry, the table contains the RT, molecular formula, and CAS number. Each detected peak in the chromatogram is searched against the table and a list of possible identities is generated. The more accurate and precise the RT control, the shorter the list of possible compounds for each peak.

The list of possible compounds is reduced further by searching with element information in addition to retention time. The presence or absence of a specific element can rule out compounds from the list. When used with GC-AED, this filtering can be extended further by using element ratios[3].

GC Column

The HP-5MS column chosen for this method is not necessarily the best or most common choice for volatiles. The desire is to use a column that is already in use in most laboratories. This column also allows ease of changing between ambient headspace and liquid injections, because the column is suitable for both. The flow characteristics of the column are compatible with the MSD and all other GC detectors.

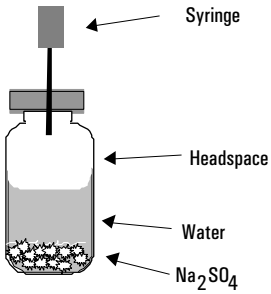
Inlet Liner

An injection port liner used with ambient headspace is small in volume compared to liners used for liquid injections. The sample is already a gas when injected, so there is no significant expansion. The small volume liner provides better peak shape for early eluting compounds that are not cold-trapped at the head of the column. A lower split ratio can be used, which results in better sensitivity. Liners of larger i.d. can be used sucessfully, but require higher split ratios to maintain peak shape.

Autoinjector

Ambient headspace is done using a gastight syringe. The largest volume syringe that can be used with the autoinjector is a 100-µL syringe (only half the volume can be injected). Note, the sampling depth of 20 mm is a critical parameter. This depth corresponds to drawing sample from the headspace and not from the water (Figure 1). Failure to set this parameter correctly will result in injecting 50 µL of salt solution into the inlet, causing instrument failure.

To minimize carryover between samples, the syringe is washed first with methanol and then water. Trace amounts of methanol in the syringe will give a peak on some detectors. The three water washes are required to minimize the residual methanol while allowing the maximum number of runs between solvent replenishment. If only trace level samples are being analyzed, the methanol wash can be eliminated, and the water washes can be reduced to one.



Software controlled variable sampling depth allows precise positioning of the syringe needle tip in the vial

Figure 1. Headspace sampling from a 2 mL autosampler vial.

Table 1. Instrument Conditions

Gas Chromatograph	**Agilent 6890 or 6850**
Injection Port	**Split/splitless**
Temperature	200 °C
Liner	Deactivated 1-mm i.d. (Restek 20973)
Carrier gas	Helium
Inlet pressure	20 psi (adjusted to lock), constant pressure
Split ratio	1:1
Column	HP-5MS, 30 m x 0.25 mm x 0.25 µm, part numbers 19091S-433 (for 6890) or 19091S-433E (for 6850)
Initial temperature	35 °C
Initial time	2 min
Temperature ramp	18 °C/min
Final temperature	70 °C
Final time	0 min
Ramp A	45 °C/min
Final temperature A	250 °C
Final time A	0 min
Autoinjector	**Agilent 7683**
Syringe	100-µL gastight injector, 5183-2042
Injection volume	50 µL
Solvent A	Methanol, 1 wash
Solvent B	Water, 3 washes
Sample rinses	None
Sample pumps	3
Injection speed	Fast plunger
Viscosity delay	5
Sampling depth	20 mm
FID Conditions	
Temperature	250 °C
Hydrogen	40 mL/min
Air	450 mL/min
Helium makeup	45 mL/min
AED Conditions	
Makeup gas	15 mL/min
Reagent gases	
Hydrogen	15 psi
Oxygen	10 psi
Temperatures	
Transfer line	250 °C
Cavity	250 °C
Solvent vent	None
5973 MSD Conditions	
GC inlet pressure	6.6 psi (adjusted to lock), constant pressure
Temperatures	
Source	230 °C
Quad	150 °C
Transfer line	260 °C
Mass range	35-300 amu
Scans	5.27/sec
Samples	2
Threshold	50
EM voltage	BFB.u tune voltage
Solvent delay	None
Micro-ECD Conditions	
Temperature	250 °C
Makeup gas	Nitrogen
Constant column + makeup flow	60 mL/min

Software for RTL Ambient Headspace on GC

Commercial software

GC ChemStation software *revision A.05.04 or higher*
GC RTL software *revision A.05.02*

User contributed software

GC RTL volatiles database
GC RTL autolocker
GC RTL autosearcher

Software for RTL Ambient Headspace on GC/MSD

Commercial software

MS ChemStation software *revision B.01.00 or higher*

User-contributed software

MS RTL volatiles screener database
MS RTL volatiles library

Table 2. Volatiles Ambient (HS)

FID RT	Compound Name	CAS No.	Molecular Formula	Weight	MSD RT	MSD Target & Qualifier Ions			
1.196	air, nitrogen	7727-37-9	N:2,	28.0	1.191	14	16	30	14
1.196	air, argon	7440-37-1	Ar:1,	40.0	1.191	40	42	40	40
1.217	dichlorodifluoromethane	75-71-8	C:1,Cl:2,F:2,	120.9	1.220	85	87	101	50
1.240	chloromethane	74-87-3	C:1,H:3,Cl:1,	50.5	1.244	50	52	49	47
1.240	water	7732-18-5	H:2,O:1,	18.0	1.242	17	19	16	16
1.261	vinyl chloride	75-01-4	C:2,H:3,Cl:1,	62.5	1.266	62	64	61	60
1.267	methanol	67-56-1	C:1,H:4,O:1,	32.0	1.267	31	29	15	30
1.313	bromomethane	74-83-9	C:1,H:3,Br:1,	93.9	1.317	94	96	93	95
1.331	chloroethane	75-00-3	C:2,H:5,Cl:1,	64.5	1.333	64	66	49	51
1.403	trichlorofluoromethane	75-69-4	C:1,Cl:3,F:1,	135.9	1.407	101	103	66	105
1.496	1,1 - dichloroethylene	75-35-4	C:2,H:2,Cl:2,	96.9	1.499	61	96	98	63
1.547	methylene chloride	75-09-2	C:1,H:2,Cl:2,	84.9	1.551	49	84	86	51
1.670	trans - 1,2 - dichloroethene	156-60-5	C:2,H:2,Cl:2,	96.9	1.673	61	96	98	63
1.725	MTBE methyl-t-butyl ether	1634-04-4	C:5,H:12,O:1,	88.1	1.702	73	57	41	43
1.744	1,1-dichloroethane	75-34-3	C:2,H:4,Cl:2,	99.0	1.745	63	65	83	85
1.931	cis - 1,2 - dichloroethene	156-59-4	C:2,H:2,Cl:2,	96.9	1.933	61	96	98	63
1.982	2,2-dichloropropane	590-20-7	C:3,H:6,Cl:2,	113.0	1.983	49	130	128	
2.001	bromochloromethane	74-97-5	C:1,H:2,Cl:1,Br:1,	129.4	2.002	77	79	97	61
2.008	chloroform	67-66-3	C:1,H:1,Cl:3,	119.4	2.009	83	85	47	48
2.247	1,1,1-trichloroethane	71-55-6	C:2,H:3,Cl:3,	133.4	2.246	97	99	61	63
2.283	1,2 - dichloroethane	107-06-2	C:2,H:4,Cl:2,	99.0	2.284	62	64	49	63
2.343	1,1 - dichloropropene	563-58-6	C:3,H:4,Cl:2,	111.0	2.345	75	39	110	77
2.402	benzene	71-43-2	C:6,H:6,	78.1	2.402	78	77	51	52
2.403	carbon tetrachloride	56-23-5	C:1,Cl:4,	153.8	2.406	117	119	121	82
2.805	1,2, - dichloropropane	78-87-5	C:3,H:6,Cl:2,	113.0	2.814	95	130	132	97
2.805	trichloroethene	79-01-6	C:2,H:1,Cl:3,	131.4	2.801	63	62	39	76
2.846	dibromomethane	74-95-3	C:1,H:2,Br:2,	173.9	2.840	93	174	95	172
2.902	bromodichloromethane	75-27-4	C:1,H:1,Cl:2,Br:1,	163.8	2.902	83	85	47	48
3.339	cis - 1,3 - dichloropropene	10061-01-5	C:3,H:4,Cl:2,	111.0	3.334	75	39	77	110
3.688	trans - 1,3 - dichloropropene	10061-02-6	C:3,H:4,Cl:2,	111.0	3.677	75	39	77	110
3.700	toluene	108-88-3	C:7,H:8,	92.1	3.689	91	92	65	63
3.761	1,1,2 - trichloroethane	79-00-5	C:2,H:3,Cl:3,	133.4	3.754	97	83	99	61
3.900	chloropicrin	76-06-2	C:1.Cl:3,N:1,O:2,	162.9	3.888	76	41	78	49
3.944	1,3 - dichloropropane	142-28-9	C:3,H:6,Cl:2,	113.0	3.937	117	119	82	47
4.077	chlorodibromomethane	124-48-1	C:1,H:1,Cl:1,Br:2,	208.3	4.066	129	127	131	48
4.214	1,2, - dibromoethane	106-93-4	C:2,H:4,Br:2,	173.9	4.203	107	109	79	81
4.247	tetrachloroethene	127-18-4	C:2,Cl:4,	165.9	4.245	166	164	129	131
4.671	chlorobenzene	108-90-7	C:6,H:5,Cl:1,	112.6	4.663	112	77	114	51
4.707	1,1,1,2 - tetrachloroethane	630-20-6	C:2,H:2,Cl:4,	167.9	4.701	131	133	117	119
4.836	ethylbenzene	100-41-4	C:8,H:10,	106.2	4.821	91	106	51	65
4.913	p - xylene	106-42-3	C:8,H:10,	106.2	4.904	91	106	105	77
4.914	m-xylene	108-38-3	C:8,H:10,	106.2	4.902	91	106	105	77
5.072	bromoform	75-25-2	C:1,H:1,Br:3,	252.8	5.060	173	175	171	93
5.137	o - xylene	95-47-6	C:8,H:10,	106.2	5.129	104	103	78	51
5.143	styrene	100-42-5	C:8,H:8,	104.2	5.110	91	106	105	77
5.317	1,1,2,2 - tetrachloroethane	79-34-5	C:2,H:2,Cl:4,	167.9	5.304	83	85	95	61
5.378	1,2,3 - trichloropropane	96-18-4	C:3,H:5,Cl:3,	147.4	5.365	75	110	77	61
5.413	isopropylbenzene	98-82-8	C:9,H:12,	120.2	5.404	105	120	77	79
5.505	bromobenzene	108-86-1	C:6,H:5,Br:1,	157.0	5.463	77	156	158	51
5.646	2 - chlorotoluene	95-49-8	C:7,H:7,Cl:1,	126.6	5.626	91	120	92	65
5.646	n - propylbenzene	103-65-1	C:9,H:12,	120.2	5.639	91	126	89	63
5.680	4 - chlorotoluene	106-43-4	C:7,H:7,Cl:1,	126.6	5.671	91	126	125	63
5.760	1,3,5 - trimethylbenzene	108-67-8	C:9,H:12,	120.2	5.746	105	120	77	119
5.933	tert - butylbenzene	98-06-6	C:10,H:14,	134.2	5.924	119	91	134	77
5.944	1,2,4 - trimethylbenzene	95-63-6	C:9,H:12,	120.2	5.928	105	120	77	119
6.032	1,3 - dichlorobenzene	541-73-1	C:6,H:4,Cl:2,	147.0	6.021	146	148	111	75
6.054	sec - butylbenzene	135-98-8	C:10,H:14,	134.2	6.043	105	134	91	77
6.076	1,4 - dichlorobenzene	106-46-7	C:6,H:4,Cl:2,	147.0	6.066	146	148	111	75
6.142	p - isopropyltoluene	99-87-6	C:10,H:14,	134.2	6.127	119	134	91	117
6.227	1,2 - dichlorobenzene	95-50-1	C:6,H:4,Cl:2,	147.0	6.213	146	148	111	75
6.341	n - butylbenzene	104-51-8	C:10,H:14,	134.2	6.320	91	92	134	65
6.514	1,2, - dibromo - 3 - chloropropane	96-12-8	C:3,H:5,Cl:1,Br:2,	236.4	6.494	157	75	155	39
7.011	1,2,4 - trichlorobenzene	120-82-1	C:6,H:3,Cl:3,	181.5	6.981	180	182	184	145
7.057	naphthalene	91-20-3	C:10,H:8,	128.2	7.026	128	127	129	51
7.163	hexachlorobutadiene	87-68-3	C:4,Cl:6,	260.8	7.146	225	227	223	190
7.181	1,2,3 - trichlorobenzene	87-61-6	C:6,H:3,Cl:3,	181.5	7.151	180	182	184	145

Sample Preparation

In the analysis of trace volatile compounds, it is critical to maintain low blank levels. The sample vials, reagent water, sodium sulfate, and laboratory environment must be free of contamination by volatiles. Store the vials and sodium sulfate in a laboratory glassware oven at 100 °C. Prepare the reagent water by purging distilled water with carbon-filtered helium in a gas-washing bottle at room temperature. Purge the water continuously to keep it ready for immediate use. Contamination via laboratory air typically is due to use of solvents in the lab or by cross-contamination from garments of lab personnel. Be careful choosing the sample preparation area.

Experiments were carried out to determine the relative effects of temperature and "salting out" on the headspace extraction efficiency. Raising the temperature of the autosampler tray to 60 °C increased the recovery of most compounds. However, the addition of sodium sulfate provides similar efficiency at room temperature. In practice, the sodium sulfate and vials are allowed to cool to room temperature. Sodium sulfate is added to each vial to a height of approximately 4 mm.

Blanks and samples are treated similarly. A 1-mL aliquot is pipetted into a vial containing sodium sulfate and crimped immediately. Spikes are prepared the same way, but 1 µL of spiking solution is added with a 5-µL GC syringe just before crimping. Note, when the tip of the syringe is placed into the water, agitation is minimized.

The caps are crimped tightly enough that they cannot be rotated by hand. Baking the caps at 100 °C caused improper sealing and resulted in leaks. Therefore, the crimp caps are used unbaked.

Vortexing for 3 seconds is sufficient to transfer the volatiles to the headspace. If a vortex mixer is not available, vigorous manual shaking for 15 seconds will suffice.

GC-FID

Figure 2 shows the FID chromatogram of a 20-ppb standard spike of volatiles mix 4. The FID response to the volatiles varies significantly with halogen content. Bromochloromethane and 2,2-dichloropropane are not resolved. Peak 7, tetrachloroethene at 4.247 minutes, is the locking peak used for RTL.

In this method, the split ratio is initially set to 1. A spike containing the mixture from Figure 2 is run and the peak shape of peaks 2 and 4 are inspected for tailing. If they tail, the split ratio is increased until the tailing is just minimized. In this specific setup, the split ratio was set to 2.

The chromatogram shows that the FID can provide a broad-based screen for nonpolar volatiles in the low ppb range.

Figure 3 shows the FID chromatogram and the MSD total ion chromatogram (TIC) of a 20-ppb standard spike of methyl-t-butylether (MTBE) in blank water. MTBE is often found in groundwater due to oxygenated gasoline leaking from underground storage tanks. MTBE can be detected at low ppb levels using either detector.

In both Figures 2 and 3, a large methanol solvent peak is present. This is due to the 1-µL methanol-based spiking solution.

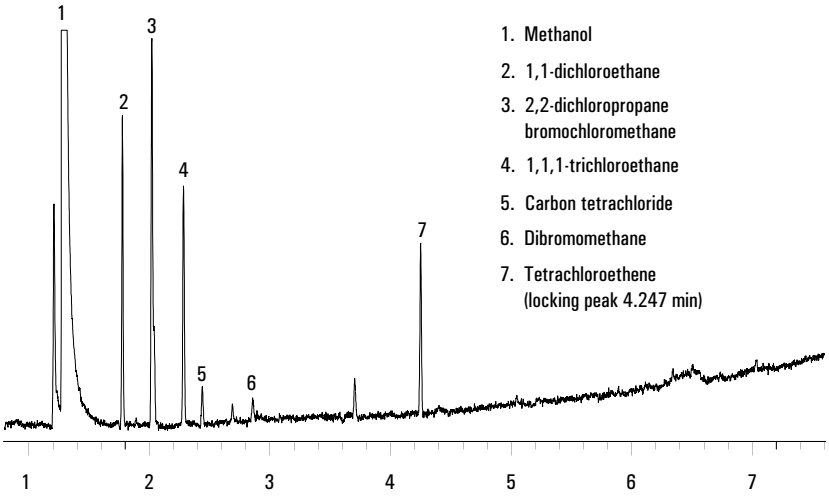


Figure 2. 20 ppb spiked standard (mix 4) in blank water by FID.

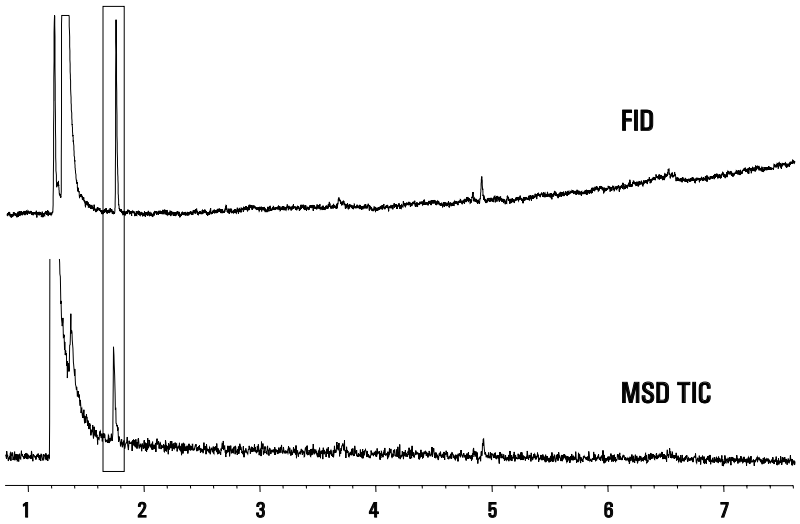


Figure 3. 20 ppb MTBE spike in blank water.

GC-MSD

The TICs of the six standard mixes spiked into blank water are shown in Figure 4. Using the MSD data, the following steps are taken:

1. Determine identity and retention time for each compound.
2. Create a spectral library of the 58 compounds.
3. Create a screener database by combining the results of steps 1 and 2.

There are nine pairs of compounds that overlap chromatographically. However, use of extracted ions differentiates all of the overlapped peaks. Peak identification with the screener software is accomplished using precise retention time, extracted ions, and spectral cross-correlation. The process used by the screener software is as follows:

1. Takes the retention time of the first compound in the database and extracts the target and qualifier ion chromatograms.
2. Integrates the ion chromatograms over a user specified time search window.
3. Compares the ratio of each qualifier ion to the target ion.
4. If the ratios fall within user specified criteria, the compound is marked as a "hit".
5. The results from steps 2 through 4 determine how the compound is reported.
6. Perform a cross-correlation between the sample spectrum and the library spectrum to aid in confirmation.
7. Repeat this process for each compound in the Screener Database.
8. Combine the results into a user definable report format and print the report.

Figure 5 shows the GC-MSD screener report for a tap water sample. Of the 65 compounds in the screener database, four were reported. A "?" in the status column indicates that the target ion was found, but that one or more of the qualifier ratios did not meet criteria. The out-of-range qualifiers are listed in the report. An "X" in the status column means that the target ion was found and that all of the qualifier ratios met criteria. The number in the "XCR" column indicates the quality of the match of the sample spectrum to the library spectrum, with 1.0 being a perfect cross-correlation.

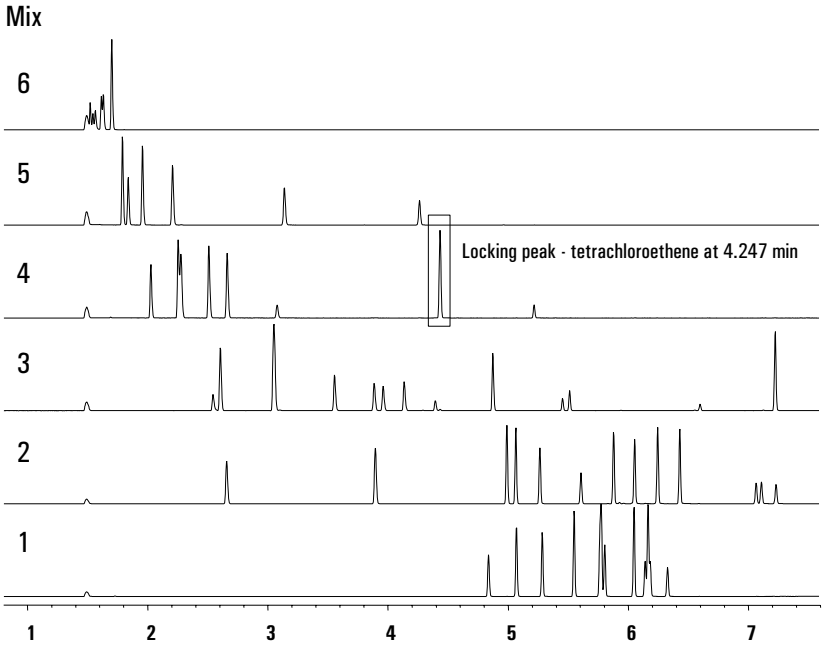


Figure 4. Six VOA calibration standard mixes by MSD.

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 Screen Report    (Not Reviewed)

  Data File : D:\DATA\AHS_MSD2\Sample1.D                  Vial: 6
  Acq On    : 10 Aug 1999  17:20                      Operator: Mikeski
  Sample    : Sample1 unfiltered  #2                    Inst    : GC/MS Ins
  Misc      :                                         Multiplr: 1.00
                                                   Sample Amount: 0.00
  MS Integration Params: RTEINT.P

 Screen File: AMHSMOD1.RES              Extraction Window: +/- 0.150 min
 Screen Database: AMHSMOD1.SCD          Qualifier Mode   : Absolute
                                        Qualifier %      : 20
                                        Zero qualifiers  : Included
                                        Subtraction Mode : Relative Areas


                                                    Target      Qualifiers
    Compound               Status ExpRT  Delta m/z   Resp. Out of Range  XCR
-------------------------------------------------------------------------------
 17 bromochloromethane        ?   2.002 +0.008  49      476 130,128     0.07
 18 chloroform                x   2.009 -0.003  83     4817             1.00
 27 bromodichloromethane      x   2.902 -0.000  83     3091             0.98
 33 chlorodibromomethane      x   4.066 +0.007 129      801             0.94


Screen Report Mon Aug 16 12:12:48 1999
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Figure 5. GC-MSD Screener report.

As an example, the extracted ion chromatograms for chlorodibromomethane found in a tap water sample are shown in Figure 6. In this case, the search window was 0.1 minutes. The ratios of ions 127, 131, and 48 to the target ion 129, met criteria. In Figure 7, the sample spectrum matches the chlorodibromomethane library spectrum, resulting in a high XCR.

The combination of precise RT, qualifier ion ratios, and cross-correlation gives high confidence in chlorodibromomethane being present in the sample.

GC-AED

Figure 8 shows the chromatograms resulting from ambient headspace analysis on four different GC systems. Note how closely the RTs match system to system as a result of RTL.

The AED is useful in this type of analysis for the following reasons:

1. The carbon 193 nm chromatogram is very sensitive (about five times better than the FID).
2. The AED carbon channel responds to all compounds that contain carbon, even those that exhibit little or no response in the FID (examples: CO_2, CS_2, CCl_4).
3. The response factors for each element are independent of compound structure, allowing quantitation without having to run standards for all compounds.
4. With proper calibration, the element mole ratios (empirical formulae) can be calculated for unknown compounds.
5. The specificity of the AED differentiates the individual halogens in unknowns.

The chromatograms in Figure 8 show that the C 193 channel provides low-level general-purpose screening for volatiles. The chlorine and bromine channels clearly indicate which compounds contain each halogen.

Combining GC-AED with GC-MSD provides the broadest possible screening capability. The AED will show the presence of any volatile, its element content, and the concentration of the compound based on element response factors. GC-MSD identifies the volatile based on spectral information. This approach maximizes the speed and efficiency with which unknown compounds can be identified and quantitated.

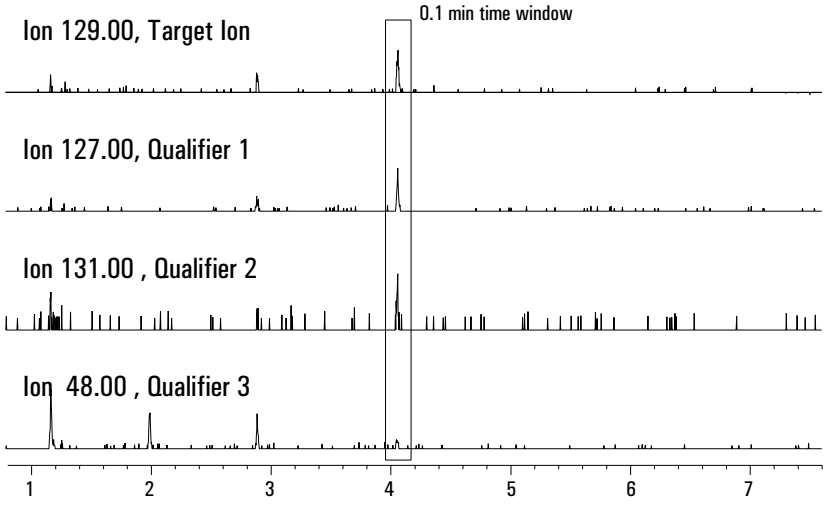

Figure 6. Extracted ions used by Screener to look for chlorodibromomethane.

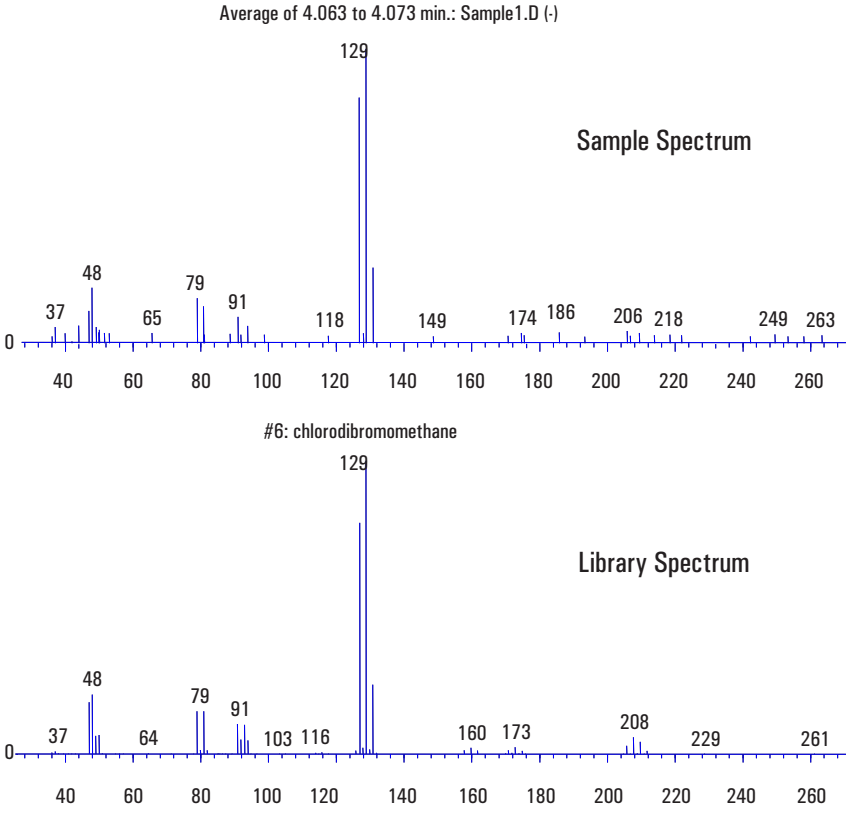

Figure 7. Sample and library spectra used by Screener for cross correlation.

GC-micro ECD

Also shown in Figure 8 is the analysis performed with GC-micro ECD. The signal-to-noise ratio is very high for those compounds that are responsive on ECD. The Agilent micro-ECD is uniquely suited for the detection of ultra low-level polyhalogenated compounds. It has a high response factor for polyhalogenated compounds and a low response factor for other compounds, minimizing interferences.

The micro-ECD peaks in Figure 8 were searched against the GC RTL volatiles database. A portion of the search report is shown in Figure 9. For each peak, the possible identities and information useful for GC-MSD analysis are given.

The sensitivity of the micro-ECD is demonstrated in Figure 10, where the polyhalogenates in mix four are easily detected at 20 parts per trillion. The detection limit observed with the

micro-ECD is comparable to that seen in routine P&T methods.

To further demonstrate the detection capability of the micro-ECD, Figure 11 shows the chromatogram from Figure 8 with an expanded Y axis. This tap water sample has >75 discernable peaks. One interesting compound detected was chloropicrin (trichloronitromethane). Chloropicrin was used as a chemical warfare agent in World War 1. However, its presence at ppt levels in drinking water is not surprising, as it is a known disinfection byproduct[4]. The identification of the compound was confirmed by GC-MSD with single-ion monitoring on multiple masses.

Figure 11 shows the same tap water after passage through a commercial spigot filter. The filter lowers the level of detected compounds by a factor of 100 to 300 fold.

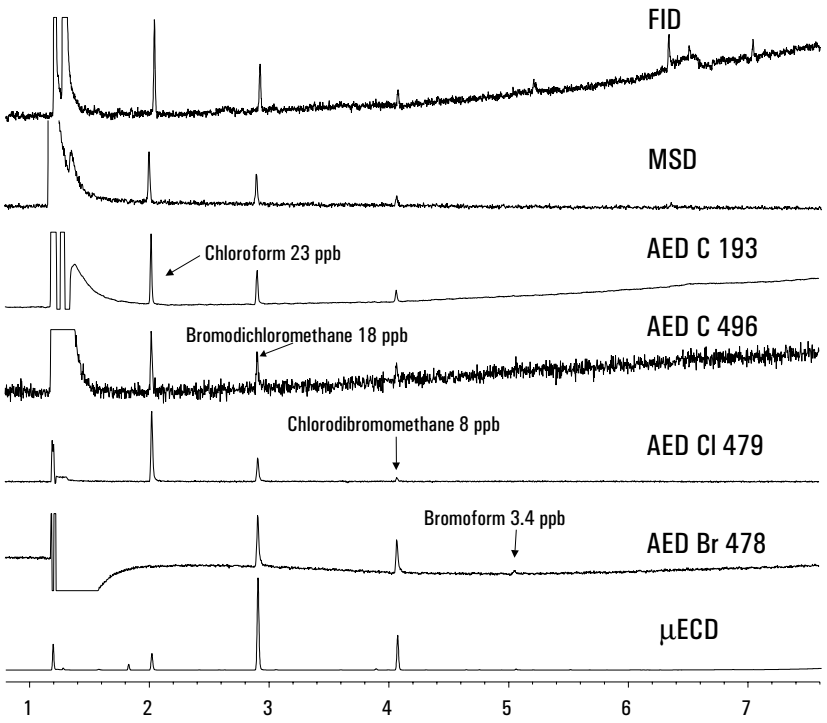

Figure 8. Local tap water sample RT locked on four instrument systems.

Precision

The precision of the technique is illustrated in Figure 12. The raw area repeatability for 10 consecutive vials of a tap water sample is 6.1% RSD. Note that this is measured with a peak present in the ppt concentration range. The retention time precision is also very good, a result of the Agilent 6890 oven and pneumatics performance.

The precision over an extended period of time also was tested. A series of 15 samples spiked with 200 ppb benzene was prepared in blank water and run in groups of five. The first group was run immediately as a control. The second group was left at room temperature and run 4 hours later. The last group, also held at room temperature, was run 24 hours later. The raw area repeatability for all 15 vials was 10% RSD. This includes the uncertainty introduced with the 1-µL spiking process. The maximum deviation of the retention time of benzene was 0.002 minutes.

```
Data File:    D:\HPCHEM\1\DATA\AHS_ECD2\NIXONU_2.D
Sample Name:  Nixon U #2
Instrument 1 9/30/99 8:44:34 AM

==================================================================
          Results of Table Auto-Search for Signal 1
==================================================================

Search results for 2.019 +/- 0.015 minutes
                                                        Weight
 2.008   chloroform                                     119.38
   CAS No.       67-66-3
   Mol_Formula   C:1,H:1,Cl:3,
   MSD RT        2.009
   MSD Target & Qualifier Ions   83    85    47    48

Search results for 2.905 +/- 0.015 minutes
   RT   Compound Name                                   Weight
 2.902   bromodichloromethane                          163.83
   CAS No.       75-27-4
   Mol_Formula   C:1,H:1,Cl:2,Br:1,
   MSD RT        2.902
   MSD Target & Qualifier Ions   83    85    47    48
```

Figure 9. GC RTL autosearch report.

Linearity

The linear dynamic range (LDR) of the technique was measured and is shown in Table 3. Five concentrations of nonpolar halogenated volatiles covering the range of 0.02 to 200 ppb were analyzed using the micro-ECD. The correlation coefficients for six compounds are all 0.99 or better, demonstrating that the technique is linear. The upper end of the LDR in this case is limited by saturation of the micro-ECD. This data, taken with that of other detectors, indicates the linear range of the sampling technique extends at least from 0.02 ppb to 2000 ppb. In practice, the LDR is determined by the detector used.

Table 3. µECD Linearity, 0.02-200 ppb includes error in spiking 1 µL

Compound	Corr. Coef.
Chloroform	0.994
1,1,1-trichloroethane	0.999
Carbon tetrachloride	0.999
Dibromomethane	0.990
Tetrachloroethene	0.998
Bromoform	0.996

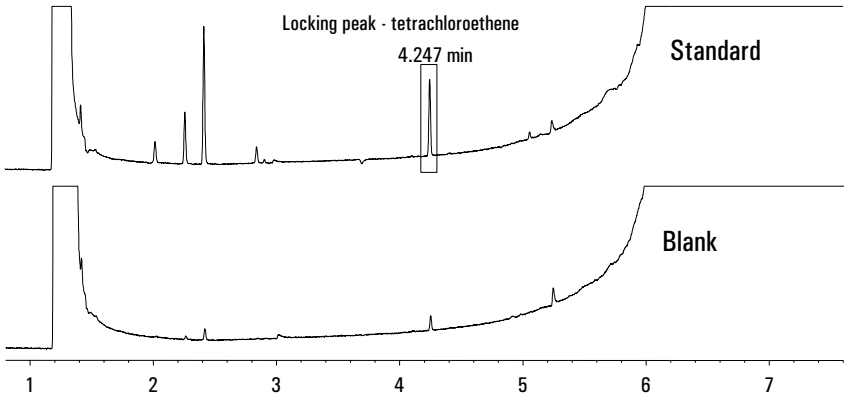

Figure 10. 20 ppt mix 4 in blank water by µECD.

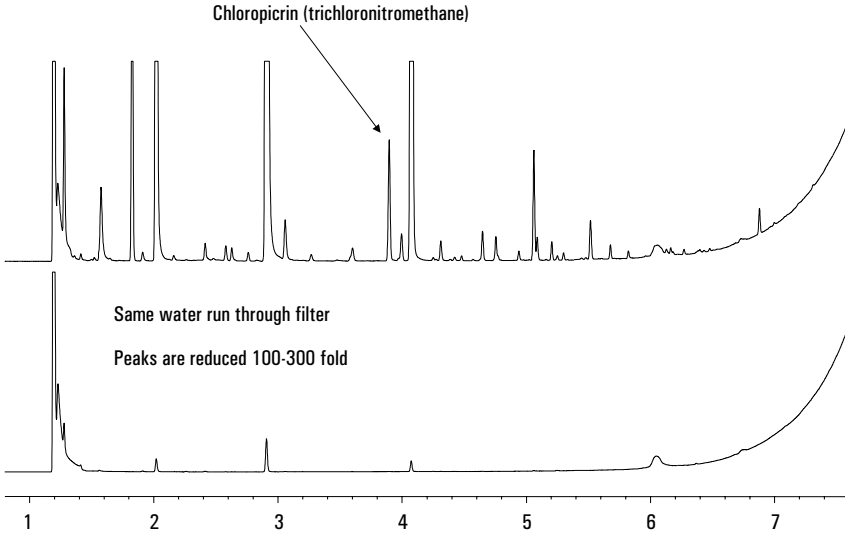

Figure 11. Local tap water sample by µECD.

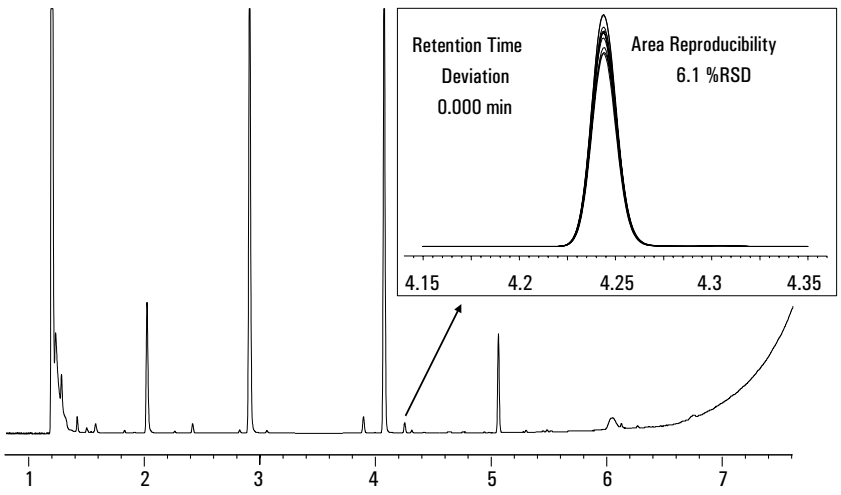

Figure 12. Chromatograms from 10 analyses of tap water, overlaid all in the same scale.

Conclusions

Ambient headspace is a fast, low cost, simple, and robust technique for the analysis of nonpolar volatile organics in water. The technique is easily implemented on an Agilent 6890 or 6850 GC. Given the broad range of detectors available for these GCs, the sensitivity, selectivity, and linear dynamic range can be matched to analyst's needs.

Ambient headspace is an ideal method for prescreening samples prior to P&T analysis. Instrumentation is protected from high level contaminants and rework is reduced. The nature of the technique also makes it attractive for high sample volume applications, such as monitoring of process water in food/beverage manufacturing.

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