# Solid Phase Microextraction High-Speed Gas Chromatography–Time-of-Flight Mass Spectrometry for Volatile Organic Compounds in Water

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Key Words: GC-TOFMS, Low Thermal Mass (LTM), Environmental

## 1. Introduction

Increasing demands for higher sample throughput are focusing more attention on the development of high-speed gas chromatograph (HSGC) systems. The use of Low Thermal Mass (LTM) columns mounted outside the GC oven has eliminated the traditional temperature ramping limitations associated with commercial GC ovens. LTM columns are capable of rapid heating (up to 1800°C/minute) as well as rapid cooling (~40 seconds to cool from 300°C to 50°C depending on the column length). LTM technology is particularly valuable for analysis of volatile organic compounds (VOCs), where run times can be less than 3 minutes. When relatively short capillary columns are rapidly temperature programmed, peaks are significantly narrower in width (often less than 1 second) than with traditional GC, and a fast recording detector is necessary. A time-of-flight mass spectrometer (TOFMS) is the ideal detector because it can record up to hundreds of spectra/second. For components with minimal chromatographic resolution, TOFMS provides the ability to perform spectral deconvolution because of its fast acquisition rates and spectral continuity.

The work here focuses on the analysis of VOCs in drinking water, similar to what would be done using EPA Method 524, a purge-and-trap GC-MS method. Depending on the waters, the work could be adapted for EPA Methods 624 (industrial and municipal wastewater) and 8260 (ground and surface waters).

## 2. Experimental Conditions

*Standards*

VOC standards were obtained from Restek Corporation. Dilutions were made in purge-and-trap grade methanol.

*SPME*

5 mL water samples in 10 mL headspace vials with crimp seals were incubated at 50°C for 1 minute, followed by headspace SPME extraction (still at 50°C) for 4 minutes while being agitated. The fiber was a 50/30 µm DVB/Carboxen/PDMS from Supelco.

The SPME fiber was desorbed for 1 minute into a 0.75 mm inlet liner under split conditions (20:1) at 270°C.

The SPME was fully automated using a Leap CombiPAL autosampler that was fully controlled through ChromaTOF®.

*Instrumentation*

GC:
Agilent 6890 gas chromatograph equipped with an RVM Scientific LTM setup with dual 5-inch column modules

Column 1:
10 m x 0.18 mm x 1.50 µm Rtx-TNT (Restek)

Column 2:
2 m x 0.18 mm x 0.20 µm Rtx-5 (Restek)

Connection:
The columns were connected in series. Column 2 ends in the MS.

Carrier:
Helium at 1.0 mL/minute, constant flow

Oven Program:
Column 1 was at 40°C for 1 minute during fiber desorption, then programmed at 560°C/minute to 320°C and held for 1.5 minutes. Column 2 started at 40°C for 1.5 minutes (the hold time for Column 1 plus the amount of time it took Column 1 to get to 320°C), and was then programmed at 120°C/minute to 220°C. Total GC run time was 3 minutes, with a cycle time of under 5.5 minutes (includes cooling time for both LTM columns).

| | |
|---|---|
| MS: | LECO Pegasus® TOFMS |
| Ionization: | Electron ionization at 70 eV |
| Source Temp: | 200°C |
| Stored Mass Range: | 45 to 350 u |
| Acquisition Rate: | 40 spectra/second |

Data Processing
LECO ChromaTOF software with Automated Peak Find and spectral deconvolution.

## 3. Results and Discussion

The low thermal mass (LTM) column assemblies essentially reverse the way columns are usually heated. Traditionally, the capillary column surface is usually as exposed as possible and placed in an air circulation GC oven. The low thermal mass of the capillary column allows it to adjust very rapidly to the temperature of the circulated air in the oven. The temperature programming speed then becomes limited by the speed that the air circulation oven can heat, while the cycle time mostly depends on how quickly the oven (which usually has a large thermal mass) can cool.

In the LTM design, a temperature sensing element is combined with the capillary column. Separately, an insulated heating wire element is paired with the capillary column temperature sensor combination. This resulting combination is packed together in a coil to minimize the exposed surface area of the capillary column. To prevent thermal gradients and cold spots at the edges of the torus-

shaped column assembly, a conducting foil wrap is used over its outer surface. A cross section of the LTM toroid is shown in Figure 1.

The LTM module is then mounted outside the GC oven connecting through the oven door (Figure 1). The GC oven is maintained at an isothermal temperature to allow the transfer lines from the injector and to the detector to remain heated.

Because of their low thermal mass, these assemblies can heat and cool very quickly. These assemblies are the most power-efficient approach known for the temperature programming of GC capillary columns because of their minimal surface area and low thermal mass.

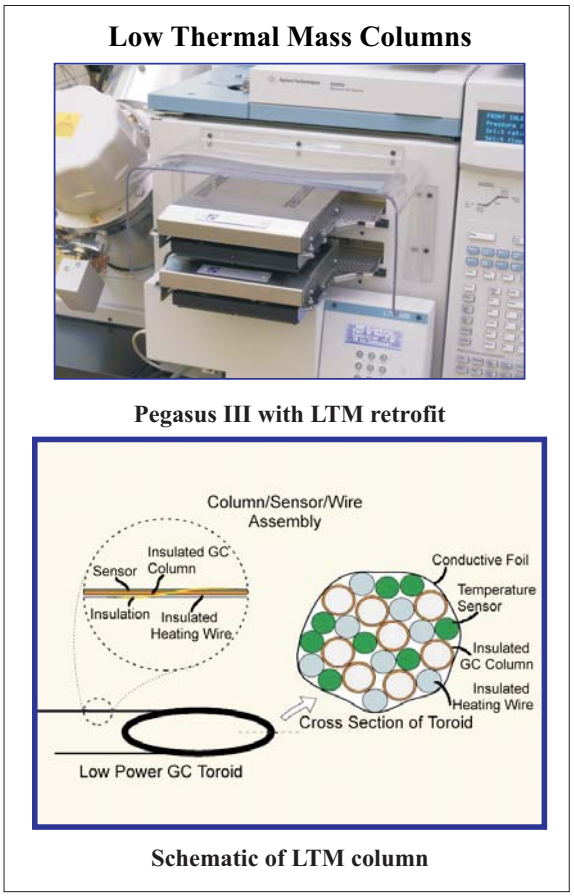


***Figure 1. Low thermal mass column setup for high-speed GC-TOFMS.***

The series combination of columns, with the very thick-film Rtx-TNT in front, was an attempt to refocus the most volatile compounds as they were being desorbed from the SPME fiber, without using any cryogenic cooling or split injection. In other words, the first column's purpose was to act as an open tubular trap, with the second column being the analytical column (the column charged with separating the volatiles). Experimental results showed that while there does not seem to be a breakthrough of compounds as volatile as 1,1-dichloroethene during splitless SPME, the second column does not have the necessary film thickness to refocus the analytes during their desorption from the first column. This necessitated the split injection. Fortunately, because of the ability of TOFMS to deliver a full mass spectrum even at low pg amounts for the volatiles analyzed in this work, a split injection does not seriously impact the overall sensitivity of the method. (Future work will employ a thicker film second column that is selective for VOCs. In addition, the volatiles gases, eg. vinyl choride, etc., will be studied.) Good (and fast) results were achieved for the volatiles determined in this study, with the last analyte (1,2,4-trichlorobenzene) eluting in just over 2 minutes.

Table 1. Calibration information for volatile organic compounds.

| Peak # | RT (sec) | Name | Masses | CC |
|---|---|---|---|---|
| 1 | 40.17 | Furan | 68 | 0.9992 |
| 2 | 41.21 | Diethyl ether | 74 | 0.9992 |
| 3 | 43.02 | Acrylonitrile | 53 | 0.9972 |
| 4 | 43.24 | 1,1-Dichloroethene | 96 | 0.9986 |
| 5 | 43.50 | Iodomethane | 142 | 0.9966 |
| 6 | 45.01 | 1,1,2-Trichlorotrifluoroethane | 151 | 0.9914 |
| 7 | 45.18 | Methylene chloride | 84 | 0.9977 |
| 8 | 47.20 | Carbon disulfide | 76 | 0.9961 |
| 9 | 52.22 | cis-1,2-Dichloroethene | 96 | 0.9968 |
| 10 | 54.72 | 1,1-Dichloroethane | 63 | 0.9985 |
| 11 | 59.63 | Chloroprene | 88 | 0.9986 |
| 12 | 60.49 | Methacrylonitrile | 67 | 0.9996 |
| 13 | 62.90 | Hexane | 57 | 0.9991 |
| 14 | 63.95 | trans-1,2-Dichloroethene | 96 | 0.9989 |
| 15 | 66.65 | Bromochloromethane | 130 | 0.9980 |
| 16 | 66.90 | 2,2-Dichloropropane | 77 | 0.9985 |
| 17 | 67.35 | Chloroform | 83 | 0.9986 |
| 18 | 71.39 | Tetrahydrofuran | 71 | |
| 19 | 72.39 | Pentafluorobenzene | 168 | ISTD |
| 20 | 73.76 | 1,2-Dichloroethane | 62 | 0.9988 |
| 21 | 73.96 | 1,1,1-Trichloroethane | 97 | 0.9993 |
| 22 | 75.66 | 1,1-Dichloropropene | 110 | 0.9991 |
| 23 | 76.61 | Benzene | 78 | 0.9993 |
| 24 | 77.01 | Carbon tetrachloride | 117 | 0.9988 |
| 25 | 79.03 | 1,4-Difluorobenzene | 114 | ISTD |
| 26 | 82.00 | 1,2-Dichloropropane | 63 | 0.9995 |
| 27 | 82.30 | Dibromomethane | 174 | 0.9988 |
| 28 | 82.55 | Trichloroethene | 130 | 0.9989 |
| 29 | 83.27 | Bromodichloromethane | 83 | 0.9991 |
| 30 | 83.75 | 2,5-Dimethylfuran | 96 | 0.9985 |
| 31 | 84.37 | Methyl methacrylate | 100 | 0.9995 |
| 32 | 88.26 | cis-1,3-Dichloropropene | 110 | 0.9993 |
| 33 | 91.73 | trans-1,3-Dichloropropene | 110 | 0.9987 |
| 34 | 92.28 | Toluene | 91 | 0.9988 |
| 35 | 92.53 | 1,1,2-Trichloroethane | 97 | 0.9996 |
| 36 | 94.18 | 1,3-Dichloropropane | 76 | 0.9995 |
| 37 | 94.48 | Ethyl methacrylate | 69 | 0.9995 |
| 38 | 95.55 | Dibromochloromethane | 129 | 0.9992 |
| 39 | 96.80 | 1,2-Dibromoethane | 107 | 0.9991 |
| 40 | 97.32 | Tetrachloroethene | 166 | 0.9985 |
| 41 | 100.67 | Chlorobenzene-d5 | 117 | ISTD |
| 42 | 100.87 | Chlorobenzene | 112 | 0.9993 |
| 43 | 101.17 | 1,1,1,2-Tetrachloroethane | 131 | 0.9989 |
| 44 | 102.19 | Ethylbenzene | 106 | 0.9985 |
| 45 | 102.84 | m- and p-Xylenes | 106 | 0.9984 |
| 46 | 104.21 | Bromoform | 173 | 0.9993 |
| 47 | 104.66 | Styrene | 104 | 0.9985 |
| 48 | 104.84 | o-Xylene | 106 | 0.9989 |
| 49 | 105.79 | cis-1,4-Dichloro-2-butene | 124 | 0.9985 |
| 50 | 106.41 | 1,1,2,2-Tetrachloroethane | 83 | 0.9991 |
| 51 | 106.98 | 1,2,3-Trichloropropane | 110 | 0.9992 |
| 52 | 107.33 | Isopropylbenzene | 120 | 0.9984 |
| 53 | 107.63 | trans-1,4-Dichloro-2-butene | 124 | 0.9974 |
| 54 | 107.88 | Bromobenzene | 156 | 0.9984 |
| 55 | 109.43 | 2-Chlorotoluene | 126 | 0.9983 |
| 56 | 109.58 | n-Propylbenzene | 120 | 0.9980 |
| 57 | 109.88 | 4-Chlorotoluene | 126 | 0.9972 |
| 58 | 110.73 | 1,3,5-Trimethylbenzene | 120 | 0.9967 |
| 59 | 111.35 | Pentachloroethane | 167 | 0.9976 |
| 60 | 112.70 | tert-Butylbenzene | 134 | 0.9887 |
| 61 | 112.76 | 1,2,4-Trimethylbenzene | 105 | 0.9978 |
| 62 | 113.70 | 1,3-Dichlorobenzene | 146 | 0.9972 |
| 63 | 114.10 | sec-Butylbenzene | 134 | 0.9978 |
| 64 | 114.10 | 1,4-Dichlorobenzene-d4 | 152 | ISTD |
| 65 | 114.27 | 1,4-Dichlorobenzene | 146 | 0.9993 |
| 66 | 115.10 | Isopropyltoluene | 134 | 0.9987 |
| 67 | 115.94 | 1,2-Dichlorobenzene | 146 | 0.9993 |
| 68 | 117.49 | n-Butylbenzene | 134 | 0.9982 |
| 69 | 118.84 | Hexachloroethane | 201 | 0.9992 |
| 70 | 119.64 | 1,2-Dibromo-3-chloropropane | 157 | 0.9994 |
| 71 | 119.96 | Nitrobenzene | 123 | 0.9993 |
| 72 | 126.50 | 1,2,4-Trichlorobenzene | 180 | 0.9986 |

Retention times in seconds (RT secs), quantification masses (Masses), and correlation coefficients (CC) for calibration curves that range from 0.05 to 20 ppb are shown for the VOCs in Table 1. In some cases (mainly the more polar compounds), not all of the lower points were used for calibration. Tetrahydrofuran was a contaminant, not an analyte, but was listed in this column anyway for retention time information. Internal standards are listed as ISTD. The correlation coefficients, generally speaking, are excellent and indicate the linearity of the system, even down to levels as low as 50 ppt in water.

Figure 2 illustrates some important considerations for doing HSGC. The first is that the peaks generated when using short GC columns that are rapidly temperature programmed are very narrow, sometimes even less than one second wide. TOFMS, because of its fast acquisition rates (up to 500 spectra/second), is the ideal detector for HSGC. In addition, because the chromatography is compressed by fast GC column temperature programming, spectral deconvolution is necessary for accurate qualitative identification of compounds. TOFMS has two characteristics that make it the best MS for doing automated spectral deconvolution. The first, the acquisition speed, has already been mentioned (a rate of 40 spectra/second was used for this work). The other reason is spectral continuity, or the TOFMS ability to produce non-skewed spectra (spectra taken at any point across a pure chromatographic peak are essentially identical). In Figure 2, the difference in peak apexes for the two most closely eluting peaks is less than 250 ms, yet an excellent deconvolution led to high library similarities for closely eluting compounds.

Table 2 shows the results from using SPME HSGC-TOFMS for analyzing Las Vegas, Nevada drinking water. Las Vegas drinking water is sourced from Lake Mead. Trihalomethanes, in yellow, are common disinfection byproducts. The numbers for the trihalomethanes as determined with this method are similar to those determined by other methods, including traditional purge-and-trap GC-MS, only the analysis time (and cycle time) with SPME HSGC-TOFMS is substantially shorter.

**Table 2. SPME HSGC-TOFMS quantification results for volatile organic compounds in Las Vegas drinking water. The trihalomethanes are highlighted in yellow. Aqueous concentrations are listed in ppb (Conc ppb).**

| Name | Conc (ppb) |
|---|---|
| Chloroform | 29.3 |
| Benzene | 0.08 |
| Bromodichloromethane | 24.3 |
| Dibromochloromethane | 17.3 |
| Bromoform | 3.07 |
| Styrene | 0.17 |
| o-Xylene | 0.01 |
| 1,2,4-Trichlorobenzene | 0.02 |
| 1,2,3-Trichlorobenzene | 0.02 |

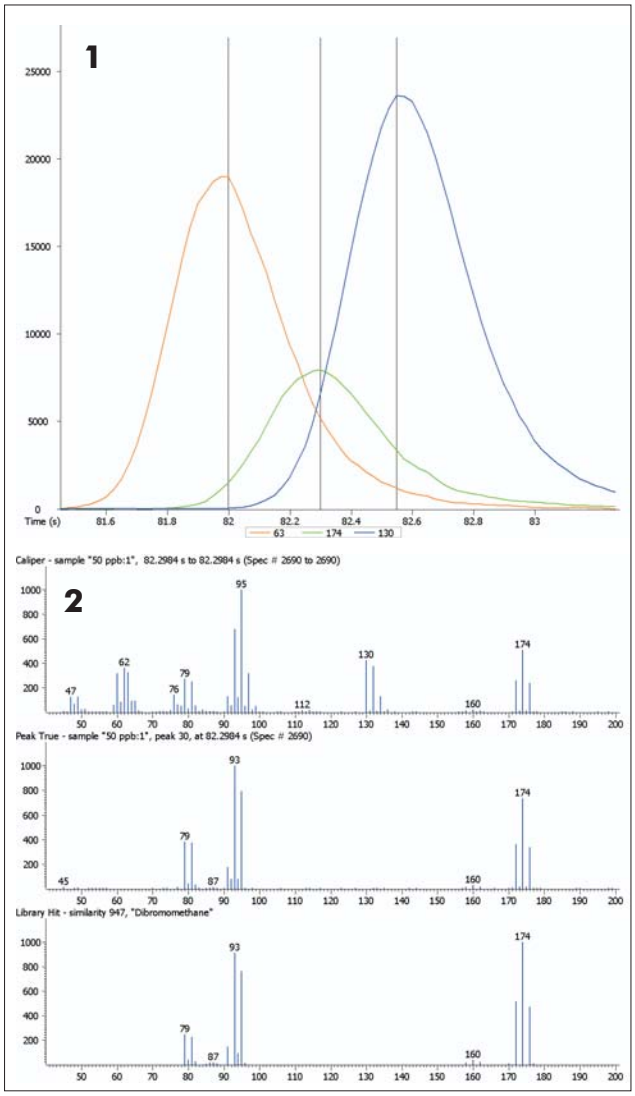


*Figure 2. (1) Automated peak find of three closely eluting peaks (1,2-dichloropropane; dibromomethane; trichloroethene). Each vertical line is a peak marker. The peak apexes of dibromomethane and trichloroethene are less than 250 ms apart. (2) Spectral deconvolution of dibromomethane from coeluting trichloroethene. Note in the caliper mass spectrum the 130 and other ions from trichloroethene. These ions are missing from the Peak True, or deconvoluted spectrum, and the library similarity is very high (947 out of 1000).*

Because TOFMS is always acquiring a full mass spectrum, and as stated before, working in the low pg range, it is possible to do non-target compound analysis simultaneously with the target compounds. This is not possible with other MS systems, like quadrupoles, where selected ion recording is used for the best sensitivity, which limits them to target analyses. Figure 3 illustrates this concept by showing dichloroacetonitrile (a disinfection byproduct) in drinking water that was located automatically by a peak find algorithm that is integral to ChromaTOF software. Note that this peak was buried underneath a very large coeluting peak (bromo-dichloromethane).

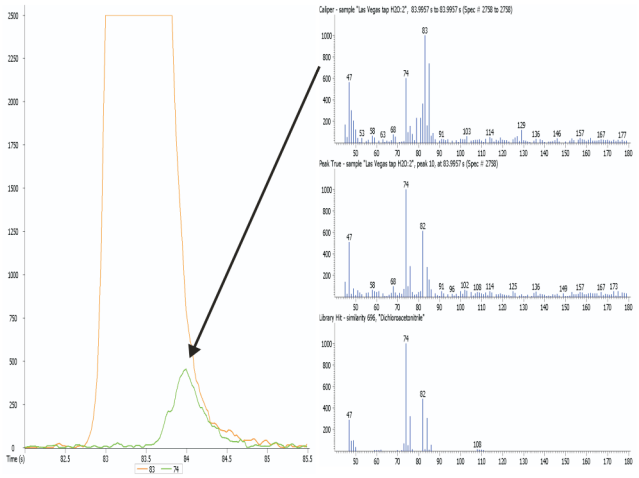

***Figure 3. Dichloroacetonitrile located automatically underneath the much larger bromodichloromethane peak. The caliper mass spectrum contains ions from the larger peak, but the Peak True, or deconvoluted spectrum (middle), gives a relatively good library similarity for dichloroacetonitrile.***

## 4. Conclusions

SPME HSGC-TOFMS was used to quantitatively analyze VOCs in Las Vegas drinking water. Calibration curves down to 50 ppt were achieved for most of the VOCs. The total chromatographic time was about 3 minutes, and the cycle time was approximately 5.5 minutes, a substantial improvement over traditional purge-and-trap GC-MS methods. Automated peak find and spectral deconvolution improved the accuracy of the qualitative analysis, including the ability to determine non-target compounds.

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