# Detection of VOCs by Agilent 8697 Headspace with 7010D GC/MS/MS Using Hydrogen Carrier Gas

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## Introduction

Volatile organic compounds (VOCs) are present in the environment and can alter the chemistry of the atmosphere. Current methods for analyzing these compounds use gas chromatography with a single quadrupole detector and the sample is introduced using a purge and trap[1]. With a triple quadrupole mass spectrometer (GC/TQ) as a detector, we can acquire in dynamic MRM (dMRM) mode which enables lower detection levels by minimizing interference from co-eluting compounds. Along with this TQ detector, we employed headspace as our sample introduction method and hydrogen carrier gas.

Table 1. List of volatile organic compounds (VOCs) analyzed.

| Compound Name | | |
|---|---|---|
| 1,1,1,2-Tetrachloroethane | 2-Propenenitrile (acrylonitrile) | Iodomethane |
| 1,1,1-Trichloroethane | 4-Chlorotoluene | Isopropylbenzene (cumene) |
| 1,1,2,2-Tetrachloroethane | Acetone | m+p-Xylene |
| 1,1,2-Trichloroethane | Benzene | Methacrylonitrile |
| 1,1-Dichloroethane | Bromobenzene | Methyl methacrylate |
| 1,1-Dichloroethene | Bromochloromethane | Methylene chloride |
| 1,1-Dichloropropene | Bromodichloromethane | MIBK |
| 1,2,3-Trichlorobenzene | Bromoform | MTBE |
| 1,2,3-Trichloropropane | Bromomethane | Naphthalene |
| 1,2,4-Trichlorobenzene | Carbon tetrachloride | n-Butylbenzene |
| 1,2,4-Trimethylbenzene | Chlorobenzene | n-Propylbenzene |
| 1,2-Dibromoethane (EDB) | Chloroethane | o-Xylene |
| 1,2-Dichlorobenzene | Chloroform | Pentachloroethane |
| 1,2-Dichloroethane | Chloromethane | p-Isopropyltoluene (cymene) |
| 1,2-Dichloropropane | cis 1,2-Dichloroethene | sec-Butylbenzene |
| 1,3,5-Trimethylbenzene | cis 1,3-Dichloropropene | Styrene |
| 1,3-Dichlorobenzene | DBCP | Tertbutylbenzene |
| 1,3-Dichloropropane | Dibromochloromethane | Tetrachloroethene |
| 1,4-Dichlorobenzene | Dibromomethane | Toluene |
| 1,4-Dioxane | Dichlorodifluoromethane | trans 1,2-Dichloroethene |
| 2,2-Dichloropropane | Diethyl ether | trans 1,3-Dichloropropene |
| 2-Butanone (MEK) | Ethyl methacrylate | Trichloroethene |
| 2-Chlorotoluene | Ethylbenzene | Trichloromonofluoromethane |
| 2-Hexanone | Hexachlorobutadiene | Vinyl chloride |

## Experimental

Standard mixtures containing VOCs were prepared at 0.05-200 ppb in water to a final volume of 10 mL with 5 g sodium sulfate present to decrease the partition coefficient and thus improve sensitivity. Internal standard was spiked into each vial at a final concentration of 10 ppb. Matrix spikes were prepared using an artificial wastewater mimic containing salt, flour, kaolin, beer, and Triton X-100. Standards and matrix spikes were injected from the headspace into a split/splitless inlet (SSL) in pulsed split mode with a 1 mm direct liner. A 20 m x 180 μm x 1 μm DB-624 column was used with a constant flow rate of 0.6 mL/min of hydrogen. Data was acquired in dMRM mode at 6 cycles per second with a gain of 5. The method contained 293 MRM transitions across 119 MRM groups. All 72 analytes elute in less than seven minutes, making this a fast method while maintaining good resolution.

Table 2. Agilent 8890 GC and 7010D TQ Parameters

| GC and MS Conditions: | |
|---|---|
| Inlet | MMI, pulsed split mode 200°C, split 30:1 10 psi pulse until 0.3 min |
| Column | DB-624 UI Column (20 m x 180 μm, 1 μm) |
| Carrier gas | 0.6 mL/min constant flow (hydrogen) |
| Oven (8.45 min run) | 35°C hold 0.25 min Ramp 25°C/min → 240°C, no hold |
| MSD Transfer Line | 250°C |
| Gain | 5 |
| Total MRMs | 293 |

Table 3. Agilent 8697 HS Parameters

| HS Conditions: | |
|---|---|
| Injection vol. | 1 mL |
| Temperatures | Oven 75°C Loop 75°C Transfer line 115°C |
| Times | 12 min vial equilibration 0.5min injection duration |
| Shaking | High, 250 shakes/min |

Figure 1. Agilent 8890 GC with 8697 headspace and 7010D TQ was used for this analysis.

## Results and Discussion

**Most compounds are detected at 0.05 ppb.**

Under our method conditions, 64 compounds are detected at 0.05 ppb with a signal to noise ratio greater than 3. Of the 72 compounds analyzed, and 51 compounds calibrate over the full 0.05-200 ppb range, with another 9 calibrating from 0.1-200 ppb, 4 calibrating 0.2-200 ppb, and the final 8 calibrating 0.5-200 ppb. Average RF curve fits were prioritized, and 45 compounds had an Avg RF RSD less than 20%. Linear and quadratic fits were used when applicable where $R^2$ was greater than 0.99 and accuracies were +/- 30%.

Table 4. Full calibration data for VOCs analyzed in this study, showing retention time (minutes), curve fit type, curve fit value (Avg RF RSD, linear $R^2$, or quadratic $R^2$), calibrated range (ppb), and what level the analyte was detected at (ppb) with S/N > 3.

| Compound Name | RT (min) | CF Type | Fit | Range | Detected at |
|---|---|---|---|---|---|
| Dichlorodifluoromethane | 0.83 | Quadratic | 0.998 | 0.5-200 | 0.05 |
| Chloromethane | 0.94 | Avg RF | 14.0 | 0.2-200 | 0.05 |
| Vinyl chloride | 1.01 | Linear | 0.991 | 0.2-200 | 0.2 |
| Bromomethane | 1.20 | Avg RF | 16.9 | 0.05-200 | 0.05 |
| Chloroethane | 1.25 | Avg RF | 15.5 | 0.05-200 | 0.05 |
| Trichloromonofluoromethane | 1.36 | Quadratic | 0.998 | 0.5-200 | 0.05 |
| Diethyl ether | 1.49 | Avg RF | 17.4 | 0.05-200 | 0.05 |
| 1,1-Dichloroethene | 1.58 | Linear | 0.991 | 0.05-200 | 0.05 |
| Acetone | 1.60 | Linear | 0.998 | 0.5-200 | 0.05 |
| Iodomethane | 1.65 | Avg RF | 18.6 | 0.05-200 | 0.05 |
| Methylene chloride | 1.77 | Quadratic | 0.999 | 0.5-200 | 0.05 |
| 2-Propenenitrile | 1.86 | Linear | 0.998 | 0.5-200 | 0.1 |
| trans 1,2-Dichloroethene | 1.88 | Avg RF | 15.3 | 0.05-200 | 0.05 |
| MTBE | 1.88 | Avg RF | 19.3 | 0.05-200 | 0.05 |
| 1,1-Dichloroethane | 2.04 | Avg RF | 19.1 | 0.05-200 | 0.05 |
| cis 1,2-Dichloroethene | 2.27 | Avg RF | 16.0 | 0.05-200 | 0.05 |
| Methacrylonitrile | 2.27 | Linear | 0.993 | 0.1-200 | 0.1 |
| 2,2-Dichloropropane | 2.27 | Linear | 0.998 | 0.05-200 | 0.05 |
| 2-Butanone (MEK) | 2.27 | Linear | 0.996 | 0.5-200 | 0.05 |
| Bromochloromethane | 2.36 | Avg RF | 19.7 | 0.05-200 | 0.05 |
| Chloroform | 2.38 | Linear | 0.997 | 0.05-200 | 0.05 |
| 1,1,1-Trichloroethane | 2.47 | Linear | 0.997 | 0.1-200 | 0.05 |
| 1,1-Dichloropropene | 2.53 | Linear | 0.995 | 0.2-200 | 0.05 |
| Carbon tetrachloride | 2.54 | Linear | 0.997 | 0.2-200 | 0.05 |
| Benzene | 2.62 | Avg RF | 17.1 | 0.05-200 | 0.05 |
| 1,2-Dichloroethane | 2.63 | Avg RF | 19.9 | 0.05-200 | 0.05 |
| Trichloroethene | 2.89 | Avg RF | 16.1 | 0.1-200 | 0.05 |
| 1,2-Dichloropropane | 2.99 | Avg RF | 13.9 | 0.1-200 | 0.1 |
| Methyl methacrylate | 3.02 | Linear | 0.996 | 0.5-200 | 0.1 |
| Dibromomethane | 3.04 | Linear | 0.999 | 0.1-200 | 0.05 |
| 1,4-Dioxane | 3.05 | Linear | 0.995 | 0.5-200 | 0.1 |
| Bromodichloromethane | 3.10 | Avg RF | 19.6 | 0.05-200 | 0.05 |
| cis 1,3-Dichloropropene | 3.30 | Quadratic | 0.999 | 0.1-200 | 0.05 |
| MIBK | 3.38 | Quadratic | 1.0 | 0.1-200 | 0.1 |
| Toluene | 3.47 | Quadratic | 0.999 | 0.05-200 | 0.05 |
| trans 1,3-Dichloropropene | 3.56 | Avg RF | 14.3 | 0.05-200 | 0.05 |

| Compound Name | RT (min) | CF Type | Fit | Range | Detected at |
|---|---|---|---|---|---|
| Ethyl methacrylate | 3.60 | Quadratic | 0.999 | 0.1-200 | 0.1 |
| 1,1,2-Trichloroethane | 3.66 | Avg RF | 19.0 | 0.05-200 | 0.05 |
| Tetrachloroethene | 3.74 | Avg RF | 18.4 | 0.05-200 | 0.05 |
| 1,3-Dichloropropane | 3.74 | Avg RF | 14.9 | 0.05-200 | 0.05 |
| 2-Hexanone | 3.78 | Quadratic | 0.999 | 0.1-200 | 0.05 |
| Dibromochloromethane | 3.86 | Avg RF | 14.1 | 0.05-200 | 0.05 |
| 1,2-Dibromoethane (EDB) | 3.93 | Linear | 0.998 | 0.05-200 | 0.05 |
| Chlorobenzene | 4.18 | Avg RF | 13.9 | 0.05-200 | 0.05 |
| 1,1,1,2-Tetrachloroethane | 4.21 | Avg RF | 17.5 | 0.05-200 | 0.05 |
| Ethylbenzene | 4.23 | Avg RF | 17.9 | 0.05-200 | 0.05 |
| m+p-Xylene | 4.29 | Avg RF | 17.3 | 0.05-200 | 0.05 |
| o-Xylene | 4.51 | Avg RF | 13.5 | 0.05-200 | 0.05 |
| Styrene | 4.51 | Avg RF | 11.9 | 0.05-200 | 0.05 |
| Bromoform | 4.62 | Avg RF | 16.3 | 0.05-200 | 0.05 |
| Isopropylbenzene (cumene) | 4.70 | Avg RF | 18.2 | 0.05-200 | 0.05 |
| 1,1,2,2-Tetrachloroethane | 4.86 | Avg RF | 20.0 | 0.05-200 | 0.05 |
| 1,2,3-Trichloropropane | 4.86 | Linear | 0.998 | 0.05-200 | 0.05 |
| Bromobenzene | 4.88 | Avg RF | 11.4 | 0.05-200 | 0.05 |
| n-Propylbenzene | 4.93 | Avg RF | 18.2 | 0.05-200 | 0.05 |
| 2-Chlorotoluene | 4.99 | Avg RF | 16.8 | 0.05-200 | 0.05 |
| 1,3,5-Trimethylbenzene | 5.03 | Avg RF | 18.2 | 0.05-200 | 0.05 |
| 4-Chlorotoluene | 5.05 | Avg RF | 15.9 | 0.05-200 | 0.05 |
| Tertbutylbenzene | 5.22 | Avg RF | 18.1 | 0.05-200 | 0.05 |
| Pentachloroethane | 5.23 | Avg RF | 9.3 | 0.05-200 | 0.05 |
| 1,2,4-Trimethylbenzene | 5.25 | Avg RF | 16.3 | 0.05-200 | 0.05 |
| sec-Butylbenzene | 5.35 | Quadratic | 0.996 | 0.05-200 | 0.05 |
| 1,3-Dichlorobenzene | 5.42 | Avg RF | 14.7 | 0.05-200 | 0.05 |
| p-Isopropyltoluene (cymene) | 5.43 | Avg RF | 15.9 | 0.05-200 | 0.05 |
| 1,4-Dichlorobenzene | 5.47 | Avg RF | 13.7 | 0.05-200 | 0.05 |
| n-Butylbenzene | 5.67 | Quadratic | 0.995 | 0.05-200 | 0.05 |
| 1,2-Dichlorobenzene | 5.69 | Avg RF | 14.0 | 0.05-200 | 0.05 |
| DBCP | 6.15 | Avg RF | 17.6 | 0.05-200 | 0.05 |
| 1,2,4-Trichlorobenzene | 6.64 | Avg RF | 9.8 | 0.05-200 | 0.05 |
| Hexachlorobutadiene | 6.74 | Quadratic | 0.992 | 0.05-200 | 0.05 |
| Naphthalene | 6.79 | Avg RF | 12.5 | 0.05-200 | 0.05 |
| 1,2,3-Trichlorobenzene | 6.94 | Avg RF | 11.0 | 0.05-200 | 0.05 |
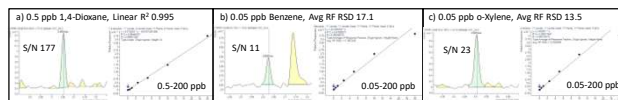
Figure 2. Chromatograms and calibration curves for several VOC compounds.

a) 0.5 ppb 1,4-Dioxane, Linear $R^2$ 0.995 — S/N 177 — 0.5-200 ppb
b) 0.05 ppb Benzene, Avg RF RSD 17.1 — S/N 11 — 0.05-200 ppb
c) 0.05 ppb o-Xylene, Avg RF RSD 13.5 — S/N 23 — 0.05-200 ppb

## Results and Discussion

**All VOC gases calibrated more than 2 orders of magnitude.**

Early eluting VOC gases co-elute with water, resulting in distorted peak shapes. By running in dMRM mode, some of this distortion can be reduced, but not fully eliminated. We observed that at low ppb concentrations, vinyl chloride and bromomethane exhibit better peak shape with hydrogen carrier gas than with helium, but chloromethane peak shape is slightly better with helium carrier. Even though some of the gases exhibit distorted peak shapes at low levels, all six gases still calibrated over a range spanning at least 2.5 orders of magnitude.
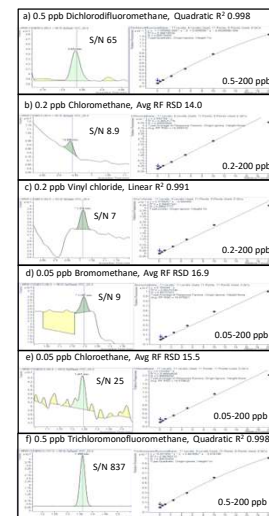
a) 0.5 ppb Dichlorodifluoromethane, Quadratic $R^2$ 0.998 — S/N 65 — 0.5-200 ppb
b) 0.2 ppb Chloromethane, Avg RF RSD 14.0 — S/N 8.9 — 0.2-200 ppb
c) 0.2 ppb Vinyl chloride, Linear $R^2$ 0.991 — S/N 7 — 0.2-200 ppb
d) 0.05 ppb Bromomethane, Avg RF RSD 16.9 — S/N 9 — 0.05-200 ppb
e) 0.05 ppb Chloroethane, Avg RF RSD 15.5 — S/N 25 — 0.05-200 ppb
f) 0.5 ppb Trichloromonofluoromethane, Quadratic $R^2$ 0.998 — S/N 837 — 0.5-200 ppb

Figure 3. Chromatograms and calibration curves of the six VOC gases.

**Wastewater matrix spikes maintained sensitivity and reproducibility.**

Eight replicate matrix spikes were prepared in artificial wastewater for each of the following levels: 0.05 ppb, 0.5 ppb, and 50 ppb. For compounds that calibrated down to 0.05 ppb, the average response RSD value at 0.05 ppb was 19.8 and the average concentration RSD was 15.9. The average concentration RSD for the 50 ppb replicates was 12.2 and the average response RSD was 14.9. The addition of matrix did not appear to negatively impact peak shape, sensitivity, or reproducibility.
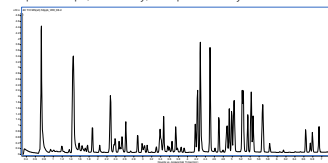
Figure 4. Total ion chromatogram of a 50 ppb wastewater matrix spike.

## Conclusions

**All 72 compounds successfully calibrated over multiple orders of magnitude using a combination of new techniques for VOC analysis.**

- Hydrogen carrier gas does not drastically diminish sensitivity.
- The 7010D TQ in dMRM mode enables sensitivity to detect low ppb levels.
- Static headspace is a reproducible sample introduction technique for VOCs.
- Further method development may be necessary to improve peak shape of the gases.

## References

[1]Quimby, B., et al. "Volatile organic compounds analysis in drinking water with headspace GC/MSD using hydrogen carrier gas and hydroinert source." *Agilent Technologies application note*, publication number 5994-4963EN, 2022

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