Monitor Volatile Organic Compounds in Water by Capillary GC – Without Cryogenic Refocusing

Ambient temperature purging and thermal refocusing allows effective extraction and collection of volatile organic compounds. The resulting efficient transfer of the compounds onto a capillary GC column provides excellent separation of the wide range of compounds specified by US EPA methods 502.2 and 524.2. Recovery and relative standard deviation were determined for water samples spiked with the six most volatile VOCs at 4µg/L, and for twelve representative volatiles spiked at 8µg/L in water. A water sample spiked with all 60 compounds was analyzed under the conditions used to analyze the six most volatile compounds. High recovery and low RSD values for most of the compounds demonstrate the usefulness of this technique for monitoring a wide range of compounds.

Key Words:
Carbotrap adsorbent tubes • drinking water • thermal desorption • volatile organic compounds

The purge and trap techniques specified in United States Environmental Protection Agency (US EPA) methods 502.2 (GC-conventional detectors) and 524.2 (GC-mass spectrometry) for monitoring volatile organic compounds (VOCs) in drinking water specify cryogenic refocusing to effectively transfer trapped analytes to the capillary GC column (1). However, ambient-temperature gas purging, followed by thermal refocusing of the sample, using Supelco's thermal extraction system, eliminates the need for cryogenic refocusing.

Six gaseous compounds are the most critical VOCs listed in methods 502.2 and 524.2. Their small molecular size and high volatility cause the lowest breakthrough volume on collection tubes and make them the most difficult compounds to refocus. Multi-bed Carbotrap™ collection and refocusing tubes, developed specifically for this application, allow these compounds (and less problematic VOCs as well) to be efficiently collected and subsequently transferred to the capillary column. These traps are part of a complete analysis system, the other components of which are a Supelco™ Dynamic Thermal Stripper, a Supelco Thermal Desorption Unit* (TDU), and a gas chromatograph equipped with a 60m x 0.32mm ID VOCOL™ capillary column (3.0µm phase film).

The collection tube, an 11.5cm x 4mm ID Carbotrap 302 tube, contains three beds of carbon-based adsorbent: Carbopack™ C, Carbopack B, and Carboxen™ 1001. The multi-bed design provides a wide range of surface areas to adsorb volatile organics according to molecular size. Furthermore, these carbon materials are hydrophobic, and thus adsorb analytes efficiently in the presence of water during the purging process. They also allow the removal of water while purging and during the dry cycle of the extraction process.

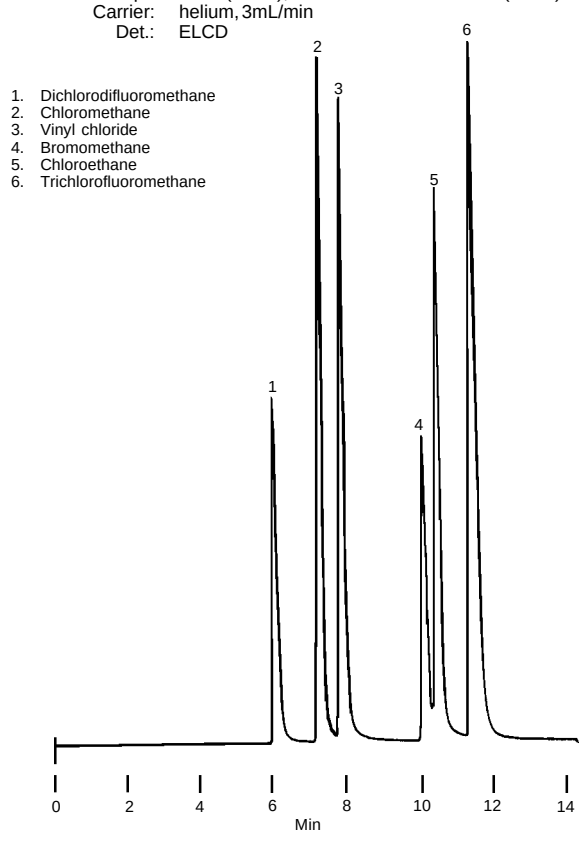
Figure A – Volatile Gases Purged/Thermally Desorbed from Water

Sample: 4µg/L VOC in water

Thermal Stripping
Purge40mL/min (10min), ambient, dried at 20mL/min, 44°C (4 min)
Collection Tube: Carbotrap 302
Cat. No.: **2-0356**

Thermal Desorption
Refocus Temp.: 300°C (5 min) at 2mL/min
Refocus Tube: Carbotrap 201
Desorption Temp.: 350°C (5 min)
Transfer Line/Valve
Compartment Temp.: 235°C
Column & Vent Flow: 3mL/min each

Chromatography
Column: **VOCOL, 60m x 0.32mm ID, 3.0µm film**
Cat. No.: **2-4157**
Col. Temp.: 35°C (8 min), then to 230°C at 4°C/min (4 min)
Carrier: helium, 3mL/min
Det.: ELCD



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The refocusing tube, an 11.5cm x 1mm/0.75mm ID Carbotrap 201 tube containing Carbopack B and Carboxen 1000, is used to collect the analytes desorbed from the larger-capacity Carbotrap 302 collection tube. The narrow ID tube (1mm tapered to 0.75mm) concentrates the sample into a narrow band for rapid, efficient transfer to the capillary column.

The gas purge/thermal refocusing procedure is easily performed. First, inert gas is passed through the sample in the Dynamic Thermal Stripper to purge the analytes, which are collected on the Carbotrap 302 tube. (Up to three 10-100mL samples can be purged simultaneously.) After analyte collection , the Carbotrap 302 tube is inserted in the desorption chamber in the thermal desorption unit and the analytes are thermally desorbed to the Carbotrap 201 refocusing tube in the TDU's secondary trapping port. The Carbotrap 201 tube, containing the refocused analytes, is then placed in the desorption chamber to thermally transfer the analytes to the capillary column. Rapid heating of the refocusing tube in the desorption chamber allows rapid transfer of the analytes onto the capillary column and results in superior separation of these critical compounds (Figure A).

In developing this application, we optimized system operating parameters for the six most volatile compounds. Recovery and relative standard deviation (RSD) data were determined for water samples spiked with our VOC Mix 6 at 4µg/L. High recovery and low RSD values for most of these compounds show the effectiveness of this technique for analysis of the gaseous compounds (Table 1).

We also determined recovery and RSD for twelve regulated volatiles spiked at 8µg/L in water. These compounds (VOC Mix 7) have elution times representative of the entire list of 60 compounds that must be screened. Again, high recovery and low RSD values for most of the compounds demonstrate the usefulness of this technique for monitoring a wide range of compounds (Table 1). A water sample spiked with all 60 compounds was analyzed under the conditions used to analyze the six most volatile compounds (Figure B), except that to detect the compounds we used electrolytic conductivity (ELCD) and photoionization (PID) detectors in series, as recommended by US EPA Method 502.2.

Ambient temperature purging and thermal refocusing, using Supelco's thermal extraction system, allows effective extraction and collection of volatile organic compounds. The resulting efficient transfer of the compounds onto a capillary column provides excellent separation of the wide range of compounds specified by US EPA methods 502.2 and 524.2. The technique is also useful for monitoring VOCs in samples other than drinking water, such as wastewater, groundwater, soils, and sludges. In addition to ambient-temperature extraction of volatiles, the thermal extraction system allows efficient thermal desorption and collection of high molecular weight compounds from difficult sample matrices, providing versatility for labs processing a wide variety of samples.

Table 1. Recovery of Gaseous Volatile Compounds from Water, Using Ambient Temperature Purge/Trap — Thermal Desorption Technique

Compound	Recovery (%)	RSD (%)
VOC Mix 6, 4µg/L each compound		
Dichlorodifluoromethane	84.6	2.9
Chloromethane	57.2	5.3
Vinyl chloride	72.1	5.3
Bromomethane	27.2	7.1
Chloroethane	59.2	6.2
Trichlorofluoromethane	86.2	4.3
VOC Mix 7, 8µg/L each compound		
Vinyl chloride	69.2	5.8
1,1-Dichloroethylene	57.7	2.7
Chloroform	71.6	2.1
1,1,1-Trichloroethane	96.4	4.2
Carbon tetrachloride	73.3	7.2
Benzene	78.9	0.5
1,2-Dichloroethane	70.9	3.2
Trichloroethane	74.1	3.3
Bromodichloromethane	65.5	4.6
Dibromochloromethane	53.4	7.8
Bromoform	38.1	12.7
1,4-Dichlorobenzene	76.8	3.8

Reference

1. Federal Register *52*, No. 130, July 8 1987, pp. 25690-25717.

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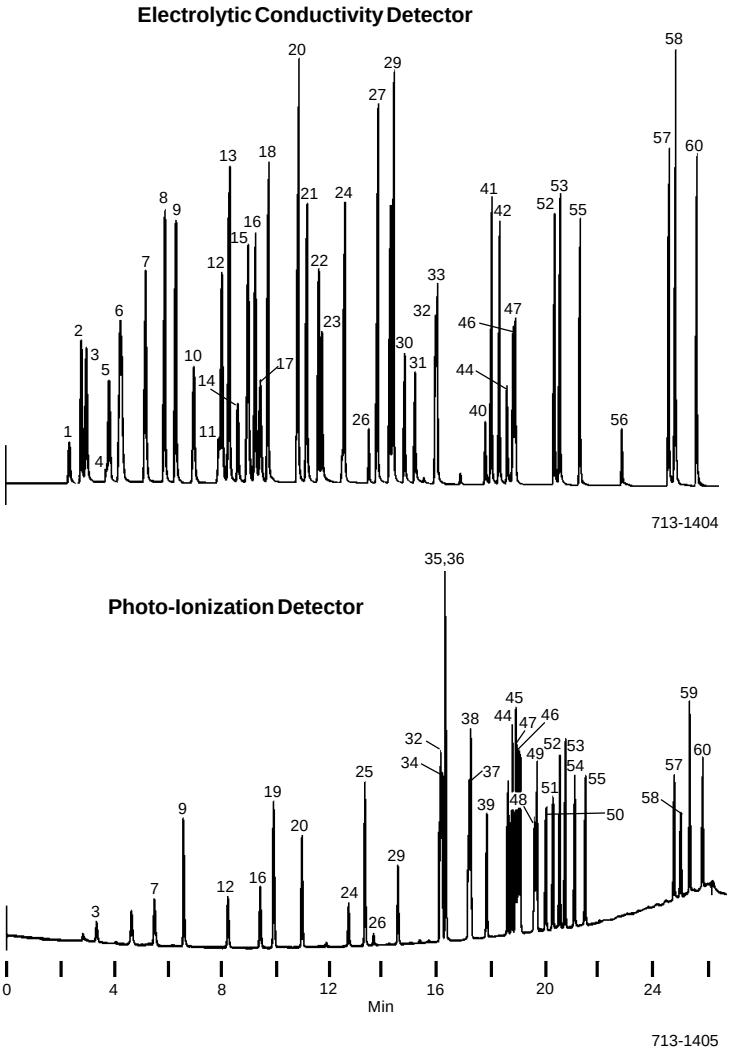
Figure B — Volatile Organic Compounds Purged/Thermally Desorbed from Water



1. Dichlorodifluoromethane
2. Chloromethane
3. Vinyl chloride
4. Bromomethane
5. Chloroethane
6. Trichlorofluoromethane
7. 1,1-Dichloroethylene
8. Methylene chloride
9. trans-1,2-Dichloroethylene
10. 1,1-Dichloroethane
11. 2,2-Dichloropropane
12. cis-1,2-Dichloroethylene
13. Chloroform
14. Bromochloromethane
15. 1,1,1-Trichloroethane
16. 1,1-Dichloropropylene
17. Carbon tetrachloride
18. 1,2-Dichloroethane
19. Benzene
20. Trichloroethylene
21. 1,2-Dichloropropane
22. Bromodichloromethane
23. Dibromomethane
24. cis-1,3-Dichloropropylene
25. Toluene
26. trans-1,3-Dichloropropylene
27. 1,1,2-Trichloroethane
28. 1,3-Dichloropropane
29. Tetrachloroethylene
30. Dibromochloromethane
31. 1,2-Dibromomethane
32. Chlorobenzene
33. 1,1,1,2-Tetrachloroethane
34. Ethylbenzene
35. m-Xylene
36. p-Xylene
37. o-Xylene
38. Styrene
39. Isopropylbenzene
40. Bromoform
41. 1,1,2,2-Tetrachloroethane
42. 1,2,3-Trichloropropane
43. n-Propylbenzene
44. Bromobenzene
45. 1,3,5-Trimethylbenzene
46. 2-Chlorotoluene
47. 4-Chlorotoluene
48. tert-Butylbenzene
49. 1,2,4-Trimethylbenzylene
50. sec-Butylbenzene
51. p-Isopropyltoluene
52. 1,3-Dichlorobenzene
53. 1,4-Dichlorobenzene
54. n-Butylbenzene
55. 1,2-Dichlorobenzene
56. 1,2-Dibromo-3-chloropropane
57. 1,2,4-Trichlorobenzene
58. Hexachlorobutadiene
59. Naphthalene
60. 1,2,3-Trichlorobenzene

Conditions as for Figure A, except: Sample, VOC Mixes 1-6 in water, 8µg/L each component.

Thermal Desorption Unit — See back page

Dynamic Thermal Stripper — See back page

VOCOL Capillary Column
60m x 0.32mm ID x 3.0µm film — **2-4157**

Carbotrap 302 Tube
11.5cm x 6mm OD x 4mm ID — **2-0356**

Carbotrap 201 Tube
11.5cm x 6mm OD x 1mm/0.75mm ID — **2-0361**

*Manufactured by Dynatherm, Inc.

VOC Mixes
2000µg/mL each component in 1mL methanol.

VOC Mix 1	**4-8775**	**VOC Mix 5**	**4-8797**
VOC Mix 2	**4-8777**	**VOC Mix 6**	**4-8799**
VOC Mix 3	**4-8779**	**VOC Mix 7**	**4-8802**
VOC Mix 4	**4-8786**	**VOC Mix 8**	**4-8803**

For composition, and for other environmental standards, refer to the Supelco catalog.

Supelco Thermal Desorption Equipment

Thermal Desorption Unit*

Use our thermal desorption unit to deliver organic compounds onto a GC column *without dilution.* The undiluted samples ensure much greater sensitivity. You also save the time and costs involved in sample desorption. And, because a thermal desorption tube can be reused many times, you save on adsorption tube purchases.

Supelco Thermal Desorption Unit

110VAC	**2-2819**
220VAC	**2-2829**

Purge and Trap Unit*

Collect volatile and some semivolatile organic compounds from solid or liquid matrices — *at ambient temperatures.* This single tube unit offers off-line purge and trap capabilities which are convenient for analyzing smaller numbers of water samples. The unit also heat conditions adsorbent tubes. A very useful accessory for quantitative and qualitative analyses of environmental, food, flavor, and fragrance samples.

Supelco Purge and Trap Unit

110VAC	**2-2840**

Dynamic Thermal Stripper*

Use our dynamic thermal stripper to purge organic compounds from samples and trap them on a thermal desorption tube. Transfer the tube to a Supelco Thermal Desorption Unit for delivery to a GC column. Purging, trapping, and thermal desorption are highly efficient for PCBs, polynuclear aromatic hydrocarbons, and other water pollutants. You can also use this unit to analyze dry samples (plastics, etc.) by dynamic headspace analysis. The unit will accommodate up to three samples of 10-100ml volume, single samples of larger size.

Supelco Dynamic Thermal Stripper

110VAC	**2-2822**
220VAC	**2-2827**

*Manufactured by Dynatherm, Inc.

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