Analysis of Volatile Organic Compounds in Soil Sample by EPA Method 8260 using CDS 7000C Dynamic Headspace Module

Application Note
Environmental

Author:

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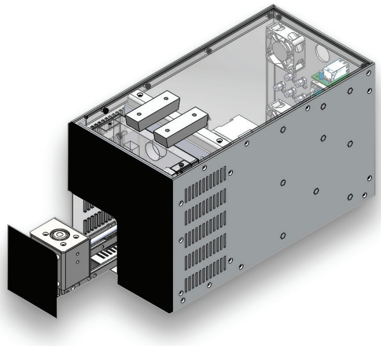
Abstract
The CDS 7000C is the industry's first Purge and Trap concentrator seamlessly integrated with the PAL system. This application note demonstrated the analytical performance of the Dynamic Headspace Module as an option in the CDS 7000C purge and trap system, by following the soil sample testing scheme defined in the EPA Method 8260.

Introduction
Purge and Trap technique was first brought up in the 60s by Zlatkis et al in response to the Clean Water Act. This technique still remains today as the most sensitive method in extracting and concentrating volatile organic compounds (VOC) from liquids and solids to Gas Chromatograph (GC). The modern Purge and Trap process involves purging the sample with an inert gas in a sealed environment (sparge vessel) at the appropriate temperature. The gas going through the sample will establish thermal equilibrium with VOCs in the sample, therefore transferring the VOCs from an aqueous state to a vapor. After eliminating the moisture through the wet trap, the gas is then swept to an analytical trap that absorbs and retains the VOCs, where they are transferred to the GC/MS for separation and quantification.

United States Environmental Protection Agency (USEPA) developed a series of methods (500 family and 600 family), which focus on using the Purge and Trap technique in VOC testing. These methods evolved and were integrated into a general method 8260 to cover both water and soil samples. To accommodate the EPA methods and automate the process, CDS Analytical launched the industry's first microprocessor-controlled Purge and Trap concentrator in 1980. The most recent breakthrough is the highly efficient CDS 7000C concentrator that is integrated to the PAL System. The previous application note demonstrated the 7000C's analytical performance in the water sample, where the CDS proprietary X type trap improved the Relative Response Factor (RRF) by an average of 30%.

In this application note, we continue to demonstrate the analytical performance of this setup in soil sample through the Dynamic Headspace Module, which is also seamlessly integrated to the PAL system. Dynamic Headspace sampling was first described by Teranishi et al, which has close tie to the Purge and Trap technique. These two techniques are similar to each other, and work on the same physics principle as direct thermal volatilization of analytes. The difference is where the thermal equilibrium was established.



7000C Dynamic Headspace Module

Experimental Setup

Instrument

The 7000C Dynamic Headspace Module has a maximum temperature of 300 °C with user settable needle height. A sample stirring mechanism could be activated at user-selectable speed in compliance with 8260 soil method. The soil sample is stored in a 20 mL headspace vial with a pre-loaded magnetic bar and then

Purge and Trap Model	**7000C-Headspace-CTC PAL RTC**
Trap	Type X
Purge Gas (He or N_2)	He
Headspace Parameters:	
Valve Oven Temperature	180 °C
Transfer Line Temperature	180 °C
Vial Station Temperature	40 °C
Stirrer Power Output	40%
Purge Parameters:	
Valve Oven Temperature	130 °C
Transfer Line Temperature	130 °C
Pre-purge warmup	1 min
Standby Flow	10 mL/min
Trap Ready Temperature	35 °C
Wet Trap Ready Temperature	45 °C
Purge Time	11 min
Purge Flow	40 mL/min
Purge Temperature	40 °C
Dry Purge Time	2 min
Dry Purge Flow	200 mL/min
Dry purge Temperature	35 °C
Foam Sensor	On
Desorb Parameters:	
Over Flow Sensor	On
Desorb Preheat Temperature	245 °C
GC Start Signal	Desorb
Desorb Time	6 min
Desorb Drain Flow	250 mL/min
Desorb Temperature	250 °C
Bake Parameters:	
Bake Time	4 min
Bake and Vessel Flow @MFC	300 mL/min
Trap Bake Temperature	260 °C
Wet Trap Bake Temperature	260 °C

Table 1. Purge and Trap Method Parameters (Soil Mode).

<table>
<tr><td>Gas Chromatograph:</td><td>Shimadzu GC 2010</td></tr>
<tr><td>Analytical Column:</td><td>Rtx-VMS (30 m x 0.25 mm x 1.40 µm)</td></tr>
<tr><td>Injector Temperature:</td><td>135 °C</td></tr>
<tr><td>Carrier Gas:</td><td>Helium @ 1.0 mL/min</td></tr>
<tr><td>Split Ratio:</td><td>40:1</td></tr>
<tr><td>Oven Program:</td><td><table>
<tr><td>Rate</td><td>Temperature</td><td>Hold Time</td></tr>
<tr><td></td><td>35 °C</td><td>4 min</td></tr>
<tr><td>5 °C/min</td><td>90 °C</td><td>0</td></tr>
<tr><td>12 °C/min</td><td>150 °C</td><td>0</td></tr>
<tr><td>30 °C/min</td><td>220 °C</td><td>2.67 min</td></tr>
</table></td></tr>
<tr><td>Mass Spectrometer:</td><td>Shimadzu GCMS-QP 2010</td></tr>
<tr><td>GC Transfer Line Temperature:</td><td>220 °C</td></tr>
<tr><td>Ion Source Temperature:</td><td>200 °C</td></tr>
<tr><td>Function Type:</td><td>Full Scan</td></tr>
<tr><td>Solvent Delay:</td><td>1.0 min</td></tr>
<tr><td>Scan Range:</td><td>m/z 35-260</td></tr>
<tr><td>Scan Time:</td><td>0.3 sec</td></tr>
<tr><td>Scan Speed:</td><td>833</td></tr>
</table>

Table 2. GC/MS Conditions.

Calibration Level	Concentration (µg/L)	Preparation Method
1	1.0	Auto dilution from 20 µg/L stock standard
2	3.0	Auto dilution from 20 µg/L stock standard
3	10.0	Auto dilution from 20 µg/L stock standard
4	20.0	Auto dilution from 400 µg/L stock standard
5	60.0	Auto dilution from 400 µg/L stock standard
6	200.0	Auto dilution from 400 µg/L stock standard

Table 3. Automated External Calibration Standard Preparation.

transferred to the Dynamic Headspace Module by the PAL's magnetic dilutor tool. The sample is then filled with fixed amount (10 mL) of distilled water and heated to setting temperature. After the thermal equilibrium is reached, the purging step begins to bring VOC from the sample matric to the 7000C concentrator as shown in Figure 1. The 7000C parameters for this application are shown in Table 1, For the separation and detection stage, a Shimadzu 2010/ QP 2010 GCMS was used. The GCMS parameters are shown in Table 2.

Internal Standard

The internal standard was prepared from a 3 component 8260 internal standard stock mix (Supelco #CRM861183), and further diluted to 125 mg/L concentration. Around 5 mL of such diluted internal standard was added to the Internal Standard Module of 7000C. In the soil mode, each sample vial has 5 mL of deionized water to simulate the sample. The internal standard was first loaded with a fixed volume of 2 μL to a high precision valve groove. Then 5 mL of deionized water flushed the groove to bring all the 2 μL internal standard into the sample vial. This procedure is compliant with EPA Method 5035. The final concentration of the internal standard in the sample is 25 μg/L and the final volume of the sample reached 10 mL.

Automated Calibration

The 7000C system featured automated calibration with external calibration standard diluted by a preset method, where two stock solutions at different concentration were diluted into 6 external calibration standards, ranging from 1 to 200 μg/L as shown in Table 3.

The external calibration standard was prepared from a 50 component 8260 calibration mix (Supelco #500607) and a 6 component 502.2 calibration gas mix (Supelco #47408). Two stock external standards were diluted to 400 μg/L and 20 μg/L respectively and added to two separate 20 mL headspace vials.

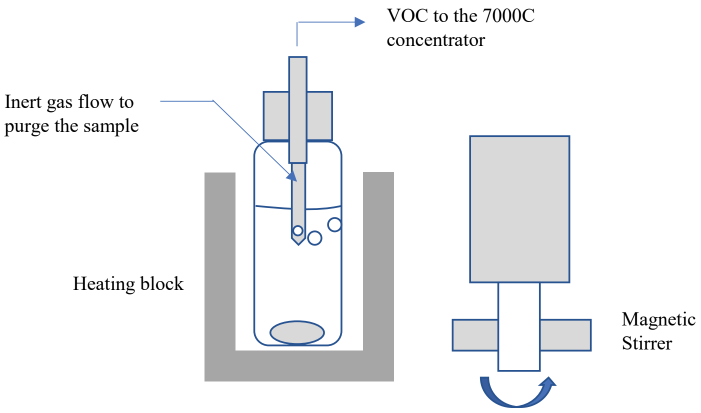


Figure 1. Sample purged in vial station of the 7000C Dynamic Headspace Module.

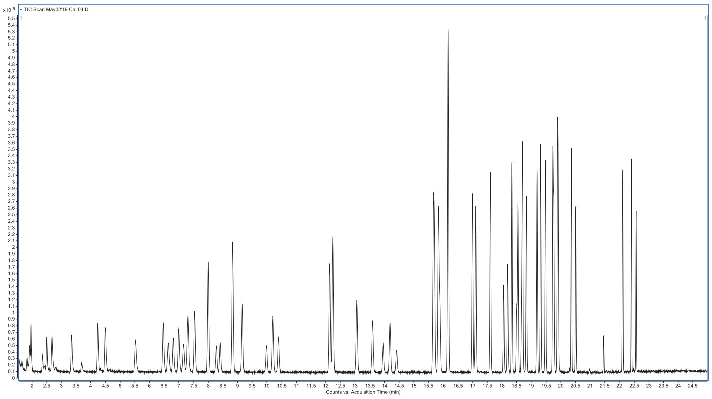


Figure 2. TIC of the external calibration standard (20 μg/L) mixed with surrogates and internal standards.

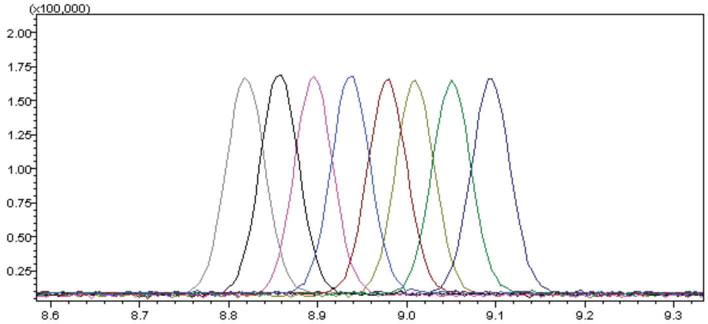


Figure 3. Overlap of eight 1,4-Dichlorobenzene-d4 runs from the internal standard module. The retention time of each peak has been shifted 1.2 seconds to show the consistency of the peak shape.

Internal Standard	Benzene, fluoro-	Chlorobenzene-d5	1 ,4-Dichlorobenzene-d4
RSD (%)	1.889	2.868	3.027

Table 4. Internal Standard Module Reproducibility (n=8).

Results and Discussion

The Total Ion Chromatogram (TIC) of a 20 μg/L external calibration standard mixed with internal standard and surrogates is shown in Figure 2. From the chromatogram, all the analytes are adequately resolved.

The Internal Standard Module delivered 2 μL of the pre-mixed internal standard solution to each soil sample along with 5 mL of deionized water. The reproducibility data are summarized in Table 4. The RSD ≤ 3.0% in soil mode is observed. Figure 3 is the time-shifted overlap of 8 1,4-Dichlorobenzene-d4 runs using the internal standard module.

Table 5 shows the results for Method Detection Limits (MDL), Percent Relative Standard Deviation (% RSD) of the initial calibration, Average Relative Response Factors (Avg RRF), along with RRF % RSD and Carryover. All analytes exceed the EPA 8260C method requirements. MDL were determined by analyzing eleven replicate samples at a concentration of 1.0 μg/L. Most target compounds had carryover <0.4%

Conclusion

The analytical performance of the 7000C Dynamic Headspace Module easily meets and exceeds the EPA Method 8260C in soil sample over a concentration range from 1 μg/L to 200 μg/L with excellent MDLs. The high sample capacity and fully automated calibration method provides a valuable tool for high throughput studies. The CDS proprietary Type X trap proves to be the optimal choice to achieve excellent analytical performance.

Compound	MDL (µg/L)	Replicate RSD (%)	Average RRF (1-200 µg/L)	RRF RSD (%)	Carryover (%)
Dichlorodifluoromethane	0.273	5.85	0.172	7.39	0.16
Methane, chloro-	0.153	3.17	0.357	7.22	0.08
Vinyl chloride	0.149	3.44	0.336	7.08	0.08
Methane, bromo-	0.114	5.40	0.096	13.16	0.00
Ethyl Chloride	0.286	6.24	0.240	6.23	0.00
Trichloromonofluoromethane	0.185	3.98	0.296	10.73	0.00
Ethene, 1,1-dichloro-	0.180	6.42	0.186	13.56	0.00
Methylene Chloride	0.159	4.51	0.253	5.69	0.00
Ethene, 1,2-dichloro-, (trans)-	0.176	6.33	0.237	13.95	0.00
Ethane, 1,1-dichloro-	0.130	4.65	0.311	16.65	0.00
Ethene, 1,2-dichloro-, (cis)-	0.084	2.77	0.253	15.95	0.00
Propane, 2,2-dichloro-	0.093	4.01	0.187	16.39	0.00
Methane, bromochloro-	0.191	5.54	0.172	4.18	0.00
Trichloromethane	0.180	5.71	0.322	7.45	0.03

Table 5. MDL, initial calibration, and carryover results (continued on the following page).

Compound	MDL (µg/L)	Replicate RSD (%)	Average RRF (1-200 µg/L)	RRF RSD (%)	Carryover (%)
Carbon Tetrachloride	0.153	4.84	0.155	12.54	0.00
Ethane, 1,1,1-trichloro-	0.224	7.73	0.228	13.55	0.00
Dibromofluoromethane (Surr)	0.263	7.93	0.150	5.97	-
1-Propene, 1,1-dichloro-	0.139	4.37	0.252	12.39	0.00
Benzene	0.151	4.38	0.904	7.33	0.00
1,2-Dichloroethane-d4 (Surr)	0.246	6.85	0.147	3.11	-
Ethane, 1,2-dichloro-	0.112	3.41	0.210	5.09	0.00
Benzene, fluoro- (IS)	-	-	-	-	-
Trichloroethylene	0.196	6.06	0.239	9.10	0.00
Methane, dibromo-	0.127	3.92	0.110	4.40	0.34
Propane, 1,2-dichloro-	0.177	5.90	0.222	5.81	0.00
Methane, bromodichloro-	0.237	8.14	0.227	6.58	0.00
Toluene-D8 (Surr)	0.212	6.18	1.032	9.20	-
Toluene	0.106	3.00	1.430	8.90	0.00
Tetrachloroethylene	0.179	5.21	0.318	11.33	0.00
Ethane, 1,1,2-trichloro-	0.213	6.48	0.277	4.85	0.00
Methane, dibromochloro-	0.179	6.30	0.251	6.67	0.00
Propane, 1,3-dichloro-	0.096	2.90	0.488	5.02	0.00
Ethane, 1,2-dibromo-	0.125	4.05	0.256	5.71	0.00
Chlorobenzene-d5 (IS)	-	-	-	-	-
Benzene, chloro-	0.175	5.43	0.974	7.60	0.06
Ethylbenzene	0.148	4.30	1.516	10.34	0.02
1,1,1,2-Tetrachloroethane	0.209	7.27	0.295	7.11	0.00
2-Chlorotoluene	0.164	4.72	2.316	7.07	0.11
1,2,3-Trichloropropane	0.116	3.37	0.661	5.80	0.00
Benzene, 1,3,5-trimethyl-	0.173	5.17	2.855	9.64	0.11
4-Chlorotoluene	0.181	5.36	2.379	7.80	0.12
Benzene, tert-butyl-	0.187	5.89	2.309	9.32	0.06
Benzene, 1,2,4-trimethyl-	0.124	3.70	2.839	9.41	0.11
Sec-Butylbenzene	0.189	5.79	3.407	9.86	0.10
p-Isopropyltoluene	0.168	5.30	2.707	10.08	0.15
Benzene, 1,3-dichloro-	0.214	6.37	1.601	7.71	0.11
1,4-Dichlorobenzene-d4 (IS)	-	-	-	-	-
Benzene, 1,4-dichloro-	0.201	5.56	1.644	8.21	0.12
Benzene, butyl-	0.173	5.46	2.375	8.97	0.28
Benzene, 1,2-dichloro-	0.158	4.62	1.484	6.45	0.09
Propane, 1,2-dibromo-3-chloro-	0.221	6.68	0.190	7.17	0.36
Hexachlorobutadiene	0.149	5.53	0.386	12.29	0.68
Benzene, 1,2,4-trichloro-	0.146	5.18	0.888	10.29	0.32
Naphthalene	0.053	1.83	2.721	6.93	0.24
Benzene, 1,2,3-trichloro-	0.152	5.40	0.827	9.53	0.26

Table 5. MDL, initial calibration, and carryover results, cont'd.