EPA Method 8260C Using CDS Analytical 7000C Purge and Trap with a PAL System

Application Note
Environmental

Author:

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Abstract

CDS 7000C Purge and Trap Concentrator coupled to a PAL System is a powerful Purge and Trap automation solution. This application demonstrates EPA Method 8260C using the 7000C Purge and Trap with the PAL System. A CDS proprietary type X trap shows significant performance improvement against the type K trap.

Introduction

CDS Analytical's 7000C Purge and Trap concentrator designed for PAL System is the world's finest Purge and Trap automation solution. This instrumentation fully automates Purge and Trap for the trace measurement of purgeable volatile organic compounds (VOCs) in water, compliant with the official International Standard Organization method DIN-EN ISO 15009, U.S. EPA method 500 and 8000 series for VOCs in water. In this application note data is presented that the 7000C/PAL System exceeds the performance criteria set of EPA Method 8260C.

Experimental Conditions

A 7000C Purge and Trap concentrator connected to a PAL RTC Rail was used to collect the data. The Purge and Trap method parameters are shown in Table 1 which are standard for the analysis of VOCs defined in the EPA Method 8260C. The communications between the 7000C and RAL RTC were through TCP/IP protocol, and samples were transferred to the 7000C from RAL RTC Purge and Trap tool through a dilutor module. CDS's proprietary Type X trap was used.

Purge and Trap Model	**7000C-CTC PAL RTC**
Trap	Type X
Sample Size	5 mL
Purge Gas (He or N_2)	He
Purge Parameters:	
Valve Oven Temperature	130 °C
Transfer Line Temperature	130 °C
Hot Water Rinse Module Temperature	70 °C
Standby Flow	10 mL/min
Trap Ready Temperature	35 °C
Wet Trap Ready Temperature	45 °C
Sparge Vessel Heater	On
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:	
Water Rinse Volume	5 mL
Number of Water Rinses	3

Table 1: Purge and Trap Method 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	200 mL/min
Trap Bake Temperature	260 °C
Wet Trap Bake Temperature	260 °C

Table 1: Purge and Trap Method Parameters, continued.

A Shimadzu single quad GCMS-QP 2010 was used. GC/MS conditions are listed in Table 2. The RTC rail was mounted directly on top of the GC. Carrier gas was supplied to the 7000C and a heated transfer line from the 7000C Concentrator was plumbed into the carrier supply line of the split/spitless inlet.

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

Table 2: GC/MS Conditions

The internal and external calibration standards were diluted from stock solutions using high precision Hamilton syringes and Class-A volumetric flasks. The external calibration standard contained a 50 component 8260 calibration mix (Supelco #500607) and a 6 component 502.2 calibration gas mix (Supelco #47408). The external standards were diluted to concentrations of 200 µg/L and 5 µg/L with deionized water, then added to two separate 40 mL VOC vials until full. The internal standard was a 3 component 8260 internal standard mix (Supelco #CRM861183) mixed with 3 component VOA surrogate (Supelco #861135) diluted to a concentration of 25 µg/L. 5 mL of this internal standard was added to the 7000C internal standard module reservoir #1 (2 reservoirs supported). The calibration levels (Table 3) used in this study were achieved with the auto dilution function embedded in the PAL Sample Control (PSC) software.

Calibration Level	Concentration (µg/L)	Preparation Method
1	0.5	Auto Dilution
2	1.5	Auto Dilution
3	5	Manual
4	20	Auto Dilution
5	60	Auto Dilution
6	200	Manual

Table 3:Calibration Levels

Results and Discussion

Figure 1 is the Total Ion Chromatogram (TIC) of a 200 µg/L calibration standard with internal standard and surrogates. All of the analytes are adequately resolved chromatographically. The chromatogram of the 6 gases is enlarged in the insert in order to show the excellent separation and peak shapes.

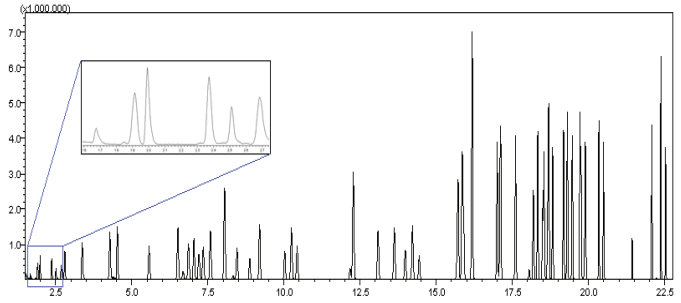

Figure 1. TIC of 8260C volatile organic standard mix at 200 µg/L with enlarged chromatogram of the 6 gasses.

Data summary Table 4 on the final pages lists the results for Retention Time (RT), Average Relative Response Factors (Avg RRF), Percent Relative Standard Deviation (% RSD) of the initial calibration, Method Detection Limits (MDL), along with method accuracy as Percent Recovery (% Rec) and as % RSD. All analytes exceed the EPA 8260C method requirements. MDL were determined by analyzing eleven replicate samples at a concentration of 1.0 µg/L. Precision and accuracy of recovery were measured by analyzing four replicates at a concentration of 5 µg/L.

The truncated TICs (18.5 min to 20 min) in Figure 2 illustrate the excellent repeatability at low concentration (1 µg/L). Figure 3 shows the six gases primary ion peaks at 0.5 µg/L concentration.

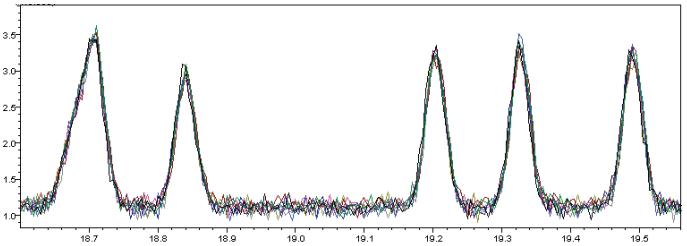

Figure 2. TICs overlaid from 18.5 min to 20 min.

The Internal Standard Module precisely delivered 1 µL of the pre-mixed internal standard solution to each sample. The reproducibility data from 8 runs is shown in Table 5. An excellent RDS < 2.4% is reported. Figure 4 is the time-shifted overlap of 8 1,4-Dichlorobenzene-d4 runs using the internal standard module.

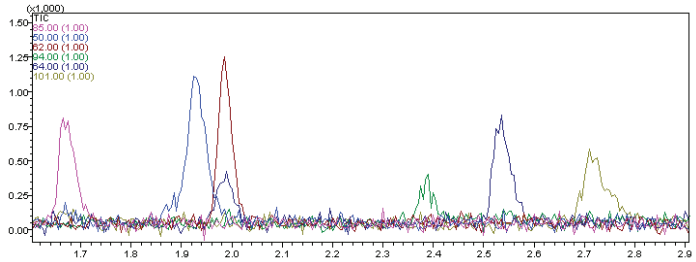

Figure 3. Six gases primary ion peaks at 0.5 µg/L concentration.

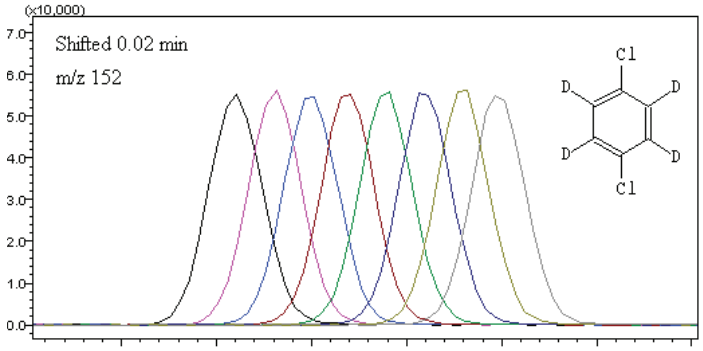

Figure 4. Overlap of eight 1,4-Dichlorobenzene-d4 runs from the internal standard module. The retention time of each peak has been shifted 1.2 seconds to show the consistency of the peak shape.

Although all the data above was collected in a 7000C with a CDS proprietary type X trap installed, a comparison test was performed against the regular type K (Vocarb 3000) trap.

Table 6 lists the Relative Response Factor (RRF) comparison between type X and type K trap, where an average of 30% increase in RRF from type X trap is observed. Figure 5 visualized the data in Table 6 for all the 8260C compounds.

Among all the 8260C compounds, 2,2-dichloropropane, which is commonly considered as a testing compounds to trace the active site in the flow path, shows a significant improvement in RRF. Figure 6 shows the chromatogram comparison at 20 µg/L concentration for such compound. This set of data is showing the advantage of the type X trap surface treatment technology in terms of eliminating active site.

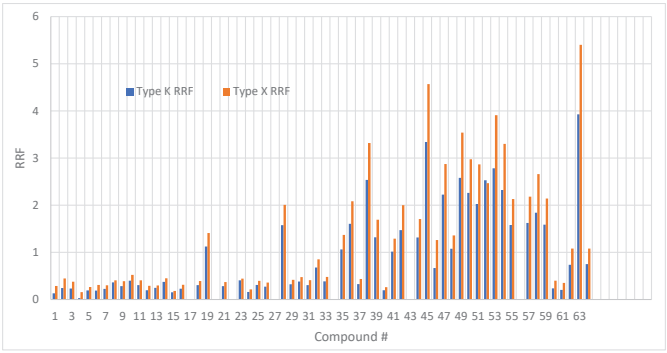

Figure 5. RRF comparison for 8260C compounds between type X trap and type K trap.

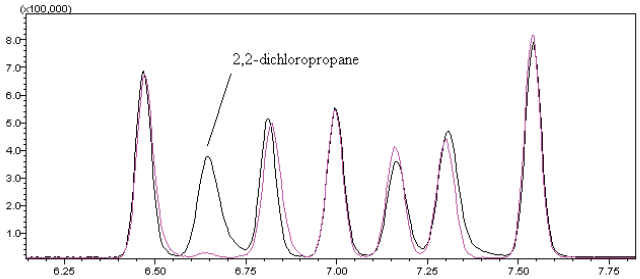

Figure 6. Chromatogram zoom-in overlap between runs using type K trap (black line) and type X trap (red line) at 20 µg/L

Conclusion

The 7000C Purge and Trap solution for PAL System easily meets and exceeds the EPA Method 8260C over a concentration range from 0.5 µg/L to 200 µg/L with excellent MDLs. Many of the technical advantages in the system, including the Auto Dilution function and the Internal Standard Module, are proven to be working to save precious time for end users in the instrument calibration and sample measurement. The proprietary type X trap plays a key factor in improving the system performance.

No.	Compound	RT (min)	Avg RRF	RRF %RSD	MDL (µg/L)	Replicates (RSD%)	Recovery (%)
1	Dichlorodifluoromethane	1.639	0.287	2.43	0.06	2.3	99.6
2	Methane, chloro-	1.875	0.449	3.87	0.07	2.7	99.2
3	Vinyl chloride	1.952	0.376	3.67	0.06	2.3	99.3
4	Methane, bromo-	2.326	0.155	18.03	0.06	3.9	83.1
5	Ethyl Chloride	2.511	0.265	6.08	0.13	4.5	107.0
6	Trichloromonofluoromethane	2.653	0.310	2.79	0.09	4.1	96.0
7	Ethene, 1,1-dichloro-	3.317	0.301	3.88	0.09	3.7	96.6
8	Methylene Chloride	4.228	0.408	8.17	0.09	3.9	98.1
9	Ethene, 1,2-dichloro-, (trans)-	4.471	0.390	7.13	0.09	3.8	100.8
10	Ethane, 1,1-dichloro-	5.506	0.522	5.47	0.10	4.3	97.0
11	Ethene, 1,2-dichloro-, (cis)-	6.461	0.409	3.18	0.05	2.0	97.9
12	Propane, 2,2-dichloro-	6.6	0.291	5.74	0.06	4.6	90.9
13	Methane, bromochloro-	6.809	0.300	4.80	0.12	4.5	96.1
14	Trichloromethane	6.991	0.450	6.07	0.15	6.1	93.6
15	Carbon Tetrachloride	7.145	0.183	4.09	0.15	5.8	98.5
16	Ethane, 1,1,1-trichloro-	7.296	0.312	6.38	0.09	3.9	94.6
17	Dibromofluoromethane	7.369	Surrogate				
18	1-Propene, 1,1-dichloro-	7.531	0.392	6.26	0.07	3.1	95.5
19	Benzene	7.996	1.409	2.84	0.06	2.2	99.8
20	1,2-Dichloroethane-d4	8.327	Surrogate				
21	Ethane, 1,2-dichloro-	8.416	0.370	2.62	0.10	3.7	100.3
22	Benzene, fluoro-	8.83		Internal Standard			
23	Trichloroethylene	9.15	0.444	3.32	0.10	3.8	100.9
24	Methane, dibromo-	9.983	0.213	4.05	0.10	4.0	98.0
25	Propane, 1,2-dichloro-	10.205	0.396	2.73	0.11	4.5	99.8
26	Methane, bromodichloro-	10.393	0.359	6.65	0.06	2.6	91.2
27	Toluene-D8	12.168	Surrogate				
28	Toluene	12.236	2.008	5.73	0.09	3.1	109.3
29	Tetrachloroethylene	13.051	0.419	6.27	0.12	4.9	104.5
30	Ethane, 1,1,2-trichloro-	13.586	0.476	3.11	0.15	5.4	103.2
31	Methane, dibromochloro-	13.949	0.409	8.88	0.12	5.8	86.8
32	Propane, 1,3-dichloro-	14.181	0.852	4.14	0.09	3.4	101.6
33	Ethane, 1,2-dibromo-	14.41	0.480	3.79	0.12	4.9	95.6
34	Chlorobenzene-d5	15.649		Internal Standard			
35	Benzene, chloro-	15.685	1.370	3.34	0.06	2.1	103.4
36	Ethylbenzene	15.82	2.086	3.27	0.10	3.8	106.0
37	1,1,1,2-Tetrachloroethane	15.866	0.437	4.57	0.12	5.2	99.2
38	m,p-Xylene	16.148	3.317	4.98	0.08	2.8	108.3

Table 4. Initial Calibration Results for VOCs Listed at 0.5 – 200 µg/L

39	o-Xylene	16.975	1.693	3.88	0.08	3.0	105.0
40	Bromoform	17.065	0.261	12.24	0.09	5.6	83.8
41	Styrene	17.087	1.291	7.85	0.05	2.3	96.1
42	Cumene	17.584	1.999	5.87	0.07	2.7	105.8
43	Benzene, 1-bromo-4-fluoro-	18.034	Surrogate				
44	Benzene, bromo-	18.168	1.706	3.58	0.09	3.3	99.2
45	Benzene, propyl-	18.308	4.567	5.67	0.07	2.6	107.9
46	Ethane, 1,1,2,2-tetrachloro-	18.472	1.262	3.65	0.10	4.2	96.4
47	2-Chlorotoluene	18.516	2.873	3.85	0.07	2.4	107.4
48	1,2,3-Trichloropropane	18.639	1.358	3.25	0.08	3.0	104.3
49	Benzene, 1,3,5-trimethyl-	18.669	3.540	4.77	0.09	3.5	107.8
50	4-Chlorotoluene	18.801	2.973	4.70	0.07	2.8	106.7
51	Benzene, tert-butyl-	19.162	2.866	6.24	0.10	3.9	106.8
52	Benzene, 1,2,4-trimethyl-	19.284	2.469	5.09	0.11	3.2	106.8
53	Sec-Butylbenzene	19.447	3.908	8.00	0.07	3.0	108.3
54	p-Isopropyltoluene	19.697	3.300	7.32	0.07	2.9	106.6
55	Benzene, 1,3-dichloro-	19.729	2.129	4.36	0.09	3.5	102.1
56	1,4-Dichlorobenzene-d4	19.855	Internal Standard				
57	Benzene, 1,4-dichloro-	19.875	2.182	5.25	0.08	2.9	103.4
58	Benzene, butyl-	20.326	2.658	8.75	0.06	2.7	106.7
59	Benzene, 1,2-dichloro-	20.475	2.141	4.25	0.06	2.0	104.6
60	Propane, 1,2-dibromo-3-chloro-	21.424	0.399	6.40	0.21	10.6	85.7
61	Hexachlorobutadiene	22.057	0.353	17.88	0.13	5.8	107.5
62	Benzene, 1,2,4-trichloro-	22.075	1.080	7.18	0.09	3.8	98.6
63	Naphthalene	22.364	5.402	7.40	0.07	2.5	107.7
64	Benzene, 1,2,3-trichloro-	22.522	1.082	7.04	0.08	3.1	99.7

Table 4. Initial Calibration Results for VOCs Listed at 0.5 – 200 µg/L, continued.

Compound	**Fluorobenzene**	**Chlorobenzene-d5**	**1,4-Dichlorobenzene-d4**
RSD% (n=8)	1.449	1.478	2.338

Table 5: Reproducibility of Internal Standard Addition.

ID#	Compound Name	Type K RRF	Type X RRF
1	Dichlorodifluoromethane	0.131	0.287
2	Methane, chloro-	0.242	0.448
3	Vinyl chloride	0.233	0.376
4	Methane, bromo-	0.03	0.155
5	Ethyl Chloride	0.192	0.265
6	Trichloromonofluoromethane	0.191	0.31
7	Ethene, 1,1-dichloro-	0.226	0.301
8	Methylene Chloride	0.362	0.408
9	Ethene, 1,2-dichloro-, (trans)-	0.282	0.39
10	Ethane, 1,1-dichloro-	0.401	0.521
11	Ethene, 1,2-dichloro-, (cis)-	0.307	0.408
12	Propane, 2,2-dichloro-	0.196	0.291
13	Methane, bromochloro-	0.248	0.299
14	Trichloromethane	0.373	0.45
15	Carbon Tetrachloride	0.154	0.183
16	Ethane, 1,1,1-trichloro-	0.228	0.312
17	Dibromofluoromethane		
18	1-Propene, 1,1-dichloro-	0.305	0.391
19	Benzene	1.122	1.409
20	1,2-Dichloroethane-d4		
21	Ethane, 1,2-dichloro-	0.285	0.369
22	Benzene, fluoro-		
23	Trichloroethylene	0.405	0.444
24	Methane, dibromo-	0.16	0.213
25	Propane, 1,2-dichloro-	0.31	0.396
26	Methane, bromodichloro-	0.271	0.359
27	Toluene-D8		
28	Toluene	1.576	2.008
29	Tetrachloroethylene	0.325	0.419
30	Ethane, 1,1,2-trichloro-	0.382	0.476
31	Methane, dibromochloro-	0.307	0.409
32	Propane, 1,3-dichloro-	0.678	0.852
33	Ethane, 1,2-dibromo-	0.384	0.48
34	Chlorobenzene-d5		
35	Benzene, chloro-	1.062	1.37
36	Ethylbenzene	1.606	2.085
37	1,1,1,2-Tetrachloroethane	0.326	0.437
38	m,p-Xylene	2.536	3.317
39	o-Xylene	1.318	1.693
40	Bromoform	0.196	0.261

41	Styrene	1.014	1.291
42	Cumene	1.473	1.999
43	Benzene, 1-bromo-4-fluoro-		
44	Benzene, bromo-	1.315	1.706
45	Benzene, propyl-	3.341	4.567
46	Ethane, 1,1,2,2-tetrachloro-	0.668	1.262
47	2-Chlorotoluene	2.226	2.873
48	1,2,3-Trichloropropane	1.077	1.358
49	Benzene, 1,3,5-trimethyl-	2.58	3.54
50	4-Chlorotoluene	2.261	2.973
51	Benzene, tert-butyl-	2.025	2.866
52	Benzene, 1,2,4-trimethyl-	2.53	2.469
53	Sec-Butylbenzene	2.783	3.908
54	p-Isopropyltoluene	2.323	3.3
55	Benzene, 1,3-dichloro-	1.581	2.129
56	1,4-Dichlorobenzene-d4		
57	Benzene, 1,4-dichloro-	1.625	2.182
58	Benzene, butyl-	1.84	2.658
59	Benzene, 1,2-dichloro-	1.588	2.141
60	Propane, 1,2-dibromo-3-chloro-	0.236	0.399
61	Hexachlorobutadiene	0.204	0.353
62	Benzene, 1,2,4-trichloro-	0.735	1.08
63	Naphthalene	3.927	5.402
64	Benzene, 1,2,3-trichloro-	0.749	1.082

Table 6: Relative Respond Factor (RRF) comparison between type X and type K trap