Analysis of Volatile Organic Compounds Using US EPA Method 8260C by CDS 8500 Series Automated Purge and Trap Concentrator

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Application Note

Environmental

Abstract

The analytical performance of the CDS 8500 Series Purge and Trap is demonstrated for the EPA Method 8260C by GC/MS analysis.

Introduction

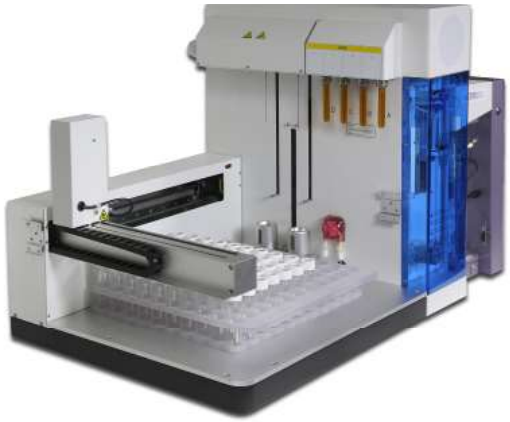
CDS Analytical's 8500 Series Purge and Trap System is a new, fully automated Purge and Trap concentrator for the trace measurement of purgeable volatile organic compounds (VOCs) in water. The standard for compliance for water testing is the official International Standard Organization method DIN-EN ISO 15009 and U.S. EPA method 500 and 8000 series for VOCs in water. In this application note, data is presented to demonstrate that the 8500 Series Purge and Trap System meets the water testing criteria set forth by US EPA method 8260D.

Experimental Setup

The 8500 Series Purge and Trap System 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 8260D.

Valve Oven Temperature	130°C
Transfer Line Temperature	130°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
Pyrge 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
Overflow Sensor	On
Desorb Preheat Temperature	245°C
Desorb Time	4 min
Desorb Drain Flow	250 mL/min
Desorb Temperature	250°C
Bake Parameters:	
Bake Time	4 min
Bake and Vessel Flow	200 mL/min
Trap Bake Temperature	260°C
Wet Trap Bake Temperature	260°C

Table 1. Purge and Trap Method Parameters.



A Shimadzu single quad GCMS-QP 2010 was used. GC/MS conditions are listed in Table 2. Carrier gas was supplied to the 8500 Series Purge and Trap and a heated transfer line from the 8500 Series Purge and Trap concentrator was plumbed into the carrier supply line of the split/spitless inlet.

Analytical Column	RTX-VMS (30 m × 25 mm × 140 μm)
Injector Temperature	240°C
Carrier Gas	He at 1.00 mL/min
Split Ratio	40:1
Oven Program	35°C Hold 4 min 90°C at 5°C/min 100°C at 12°C/min 220°C at 30°C/min Hold 2.67min
Mass Spectrometer:	
Interface Temperature	220°C
Ion Source Temperature	200°C
Scan Mode and Range	Full scan 35-260m/z
Scan Time	0.3 min
Scan Speed	833

Table 2. GCMS Conditions.

The following calibration mixes were purchased from Restek for performing method 8260D on the 8500 series: 8260B MegaMix®, VOA, 502.2, California Oxygenates, and 8260B acetates mixes. From those standards, a stock mixture of 200 μg/L was prepared. All other calibration standards were prepared from this stock solution. In total, six calibration standards were prepared between 2 and 200 μg/L, with the exception of those targets noted in Table 4. The internal standard was a 4 component 8260 internal standard mix, and the 8260 surogates was a 3 component mix. Both were diluted to a concentration of 25 μg/mL. 5 μL of this internal standard was added to each 5mL water sample by an onboard EPC on the 8500 autosampler (4 total reservoirs supported).

Results and Discussion

Figure 1 depicts the Total Ion Chromatogram (TIC) of a 20 μg/L calibration standard with internal standard and surrogates. All of the analytes are adequately resolved chromatographically. The chromatogram of the 6 gases is shown in Figure 2 peak separation and peak shape.

5 μL of the pre-mixed internal standard solution was precisely introduced to each water sample by the autosampler through an onboard EPC. The %RSD for all 4 internal standards was calculated from 6 replicate measurements and are shown in Table 3. The %RSDs are all 1% or less showing high reproducibility of the internal standard addition EPC of the 8500 autosampler. Figure 4 shows the overlay of the 6 extracted ion chromatograms for each of the internal standards.

The data summary is shown in Table 4 and lists the results for Retention Time (RT), Average Relative Response Factors (Avg RF), Percent Relative Standard Deviation (% RSD) of the initial calibration, Method Detection Limits (MDL), along with method accuracy as and % RSD. All analytes exceed the EPA 8260D method requirements. MDL were determined by analyzing replicate samples at a concentration of 2.0 μg/L.

Table 3. Internal standard components and their %RSDs (n=6).

Internal Standard Compound	%RSD
pentafluorobenzene	1.1
1,4-difluorobenzene	1.2
chlorobenzene-d5	0.8
1,4-dichlorobenzene-d4	1.0

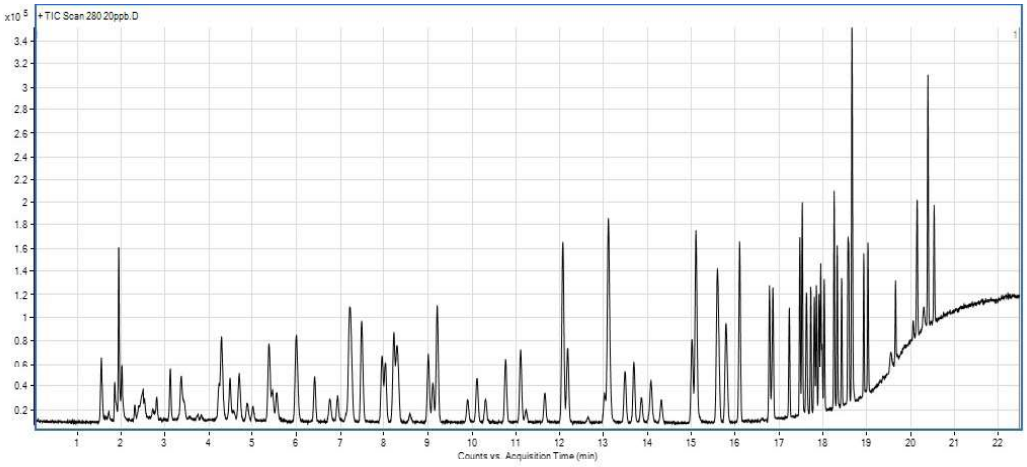


Figure 1. TIC of 8260D volatile organic standard mix at 20 μg/L with enlarged chromatogram of the 6 gasses.

Conclusion

The 8500 Series Purge and Trap System meets and exceeds the EPA Method 8260D over a concentration range from 2 to 200 µg/L. Although the 8500 series supports both water and soil sampling, only the capabilities for water analysis are demonstrated here. The new 8500 series utilitizes and onboard EPC to deliver internal standard to the sample at RSD <1%. This system helps support users in that all EPA regulatory requirements are meet to help save time and money.

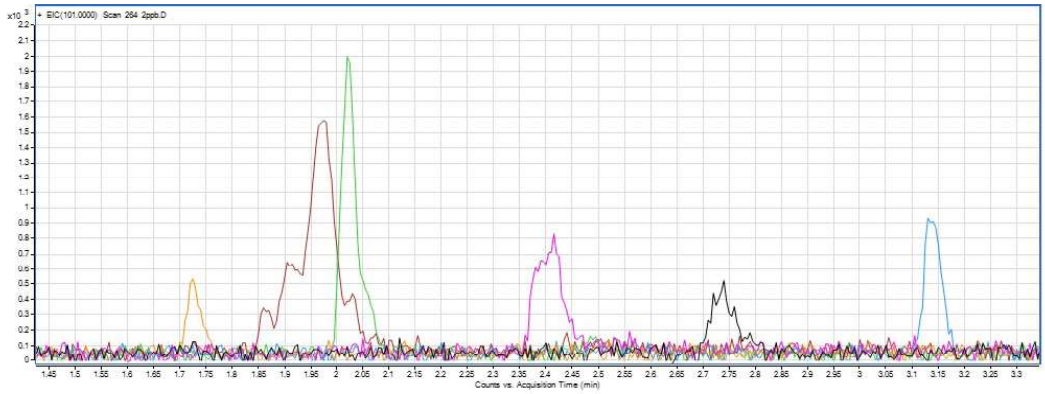


Figure 2. Extracted ion chromatograms of the first 6 gases in the chromatogram at 2 µg/L.

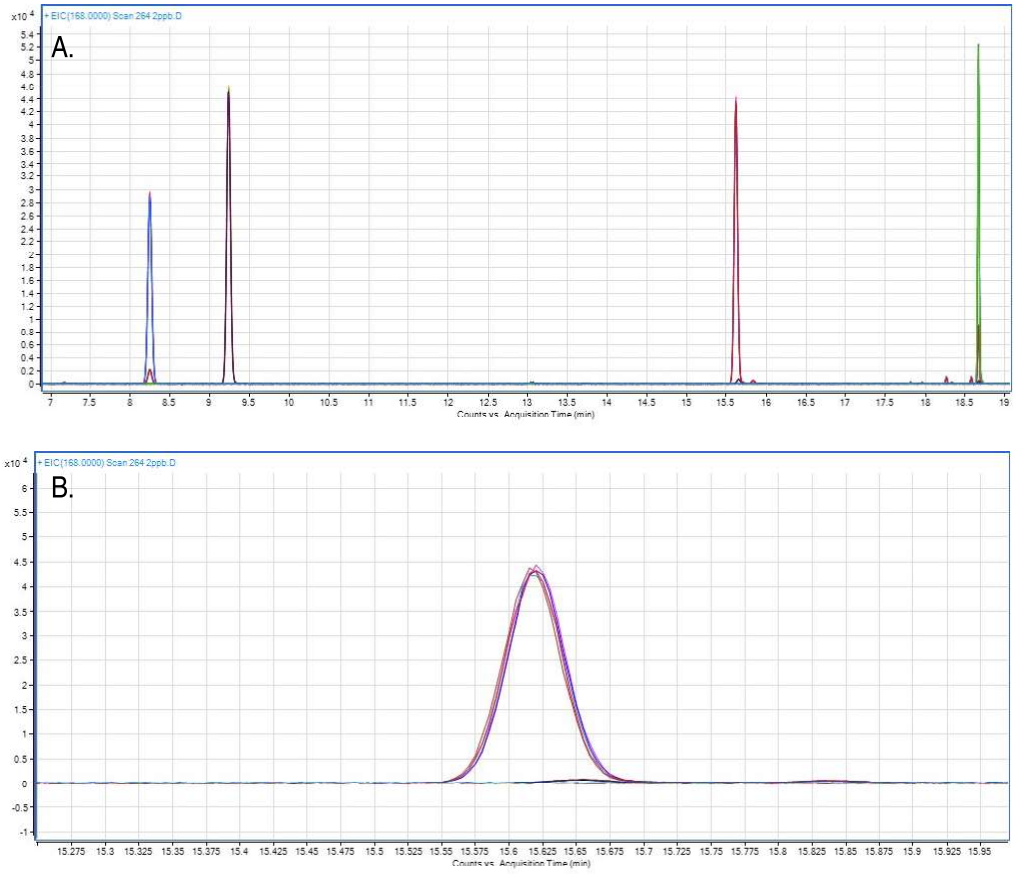


Figure 3. A) Overlay of 6 replicates of the internal standard mixture containing (from left to right) pentafluorobenzene, 1,4-difluorobenzene, chlorobenzene-d5, and 1,4-dichlorobenzene-d4. (B) Magnified chromatogram of chlorobenzene-d5

Table 3. Summary of the correlation coefficient and average response factor (RF) for each compound. The method detection limit (MDL) was determined from replicate measurements at 2 µg/L unless specified otherwise. At 2 µg/L, the accuracy and %RSD were also determined. For all compounds, n=6.

Compound	RT (min)	R^2	Avg. RF	MDL (µg/L)	Concentration (µg/L)	Accuracy (%)	RSD (%)
dichlorodifluoromethane	1.725	0.968	0.10	0.8	1.82	91.0	14.7
chloromethane	1.970	0.993	0.56	0.2	1.95	97.7	3.1
vinyl chloride	2.020	0.994	0.44	0.3	1.75	87.5	4.7
bromomethane	2.415	0.996	0.19	0.2	2.00	99.4	8.0
trichlorofluoromethane	2.740	0.992	0.17	0.7	2.27	113.3	9.3
diethyl ether	3.145	0.997	0.25	0.2	1.96	98.2	3.3
carbon disulfide	3.410	0.995	0.51	0.3	2.58	128.8	3.7
1,1-dichloroethene	3.385	0.990	0.23	0.3	1.84	92.1	4.5
1,1,2-trichlorotrifluoroethane	3.455	0.995	0.07	1.7	2.85	142.3	19.2
methylene chloride	4.255	0.998	0.35	0.4	2.10	105.2	6.2
trans-1,2-dicloroethene	4.505	0.994	0.26	0.3	2.07	103.3	5.3
methyl acetate	4.610	1.000	0.07	0.5	2.44	122.2	6.9
methyl-tert-butyl ether	4.720	0.996	0.81	0.1	1.62	81.1	2.7
acetone[1]	4.320	1.000	0.53	1.4	1.39	68.5	12.9
tert-butanol*	4.910	0.998	0.10	1.8	12.28	122.8	4.6
acetonitrile	5.030	0.999	0.29	0.3	2.30	114.8	4.2
diisopropyl ether	5.400	0.994	1.21	0.1	2.08	103.8	2.0
chloroprene	5.475	0.993	0.26	0.5	1.85	92.4	8.0
acryonitrile	5.475	1.000	0.44	0.6	1.66	83.1	12.1
vinyl acetate	6.025	0.999	0.63	0.2	2.65	132.4	2.1
ethyl-tert-butyl ether	6.025	0.999	0.46	0.1	1.98	98.9	1.8
cis-1,2-dichloroethene	6.440	0.999	0.34	0.3	2.25	112.6	3.7
bromochloromethane	6.785	0.996	0.14	0.2	1.94	96.8	2.9
cholorform	6.965	0.983	0.35	0.4	2.53	126.3	4.9
carbon tetrachloride	7.175	0.999	0.09	0.4	1.70	85.2	8.1
methyl acrylate	7.240	1.000	0.78	0.2	2.08	103.9	3.0
tetrahydrofuran	7.250	1.000	0.21	0.2	2.16	107.9	3.3
ethyl acetate**	7.250	1.000	0.05	0.7	4.53	90.6	4.9
1,1,1-trichloroethane	7.295	1.000	0.16	0.5	2.07	103.7	7.5
dibromofluoromethane (SURR)	7.280						
2-butanone[1]	7.520	1.000	0.23	0.2	5.93	118.57	2.6
1,1-dichloropropene	7.530	0.991	0.22	0.9	1.81	90.5	15.8
benzene	7.980	0.996	0.84	0.3	2.11	105.3	4.0
propionitrile	8.025	1.000	0.18	0.4	1.86	92.8	6.0
methacrylonitrile	8.060	0.999	0.39	0.1	1.85	92.7	2.2
pentafluorobenzene (IS)	8.125						
tert-amyl-methyl ether	8.330	0.999	0.27	0.2	2.12	106.1	3.6

*Calibration range is bewteen 10 and 1000 µg/L

**MDL was determined from the 5 µg/L calibration level

[1]Calibration range is bewteen 5 and 500 µg/L

Compound	RT (min)	R^2	Avg. RF	MDL (µg/L)	Concentration (µg/L)	Accuracy (%)	RSD (%)
1,2-dichloroethane	8.365	0.996	0.24	0.2	1.90	95.2	3.0
isopropyl acetate	9.040	1.000	0.30	0.2	1.99	99.4	3.0
trichloroethene	9.145	0.995	0.19	0.5	1.84	91.8	8.4
1,4-difluorobenzene (IS)	9.205						
dibromomethane	9.930	0.995	0.13	0.4	2.40	120.0	4.8
1,2-dichloropropane	10.155	0.999	0.30	0.1	2.01	100.7	1.3
bromodichloromethane	10.345	1.000	0.22	0.3	1.90	95.1	4.4
methyl methacrylate	10.805	0.999	0.36	0.1	1.73	86.6	2.6
propyl acetate	11.145	1.000	0.41	0.2	1.93	96.6	3.3
cis-1,3-dichloropropene	11.690	1.000	0.23	0.2	1.52	76.2	3.7
toluene-d8 (SURR)	12.105						
toluene	12.215	0.999	0.56	0.4	2.22	110.8	5.0
tetrachloroethene	13.055	0.991	0.11	1.1	1.49	74.5	24.4
4-methyl-2-pentanone[1]	13.145	1.000	0.16	0.1	1.95	97.3	2.3
trans-1,3-dichloropropene	13.190	0.999	0.18	0.3	2.18	109.2	4.4
1,1,2-trichloroethane	13.525	0.998	0.20	0.3	1.85	92.4	5.3
ethyl methacrylate	13.720	0.997	0.50	0.1	1.76	87.9	2.3
dibromochloromethane	13.900	0.997	0.21	0.1	1.61	80.6	1.9
1,3-dichloropropane	14.110	0.997	0.37	0.2	1.99	99.4	2.5
1,2-dibromoethane	14.350	0.999	0.23	0.3	2.32	115.8	4.1
butyl acetate	15.060	1.000	0.18	0.1	1.89	94.7	1.5
2-hexanone[1]	15.045	1.000	0.60	0.2	4.53	90.7	1.6
chlorobenzene-d5 (IS)	15.595						
chlorobenzene	15.660	0.999	0.54	0.1	2.24	112.2	1.7
ethylbenzene	15.815	0.994	0.79	0.4	1.56	78.1	8.7
1,1,1,2-tetrachloroethane	15.840	1.000	0.19	0.1	1.94	96.8	1.7
m-xylene	16.130	0.999	0.68	0.4	1.83	91.3	7.6
o-xylene	16.800	0.999	0.37	0.4	2.20	110.2	5.5
p-xylene	16.800	0.999	0.37	0.4	2.20	110.2	5.5
bromoform	16.855	0.998	0.26	0.1	1.51	75.4	2.6
styrene	16.875	0.999	1.17	0.3	2.15	107.7	3.8
amyl acetate	17.490	0.999	0.64	0.4	1.99	99.7	6.6
1-bromo-4-fluorobenzene (SURR)	17.545						
bromobenzene	17.640	0.997	0.42	0.2	1.62	80.8	3.1
cis-1,4-dichloro-2-butene	17.645	1.000	0.20	0.3	1.72	86.1	5.4
isopropylbenzene	17.965	0.991	1.11	0.4	1.73	86.8	7.4
n-propylbenzene	17.740	0.985	1.46	0.8	1.45	72.4	16.9
1,1,2,2-tetrachloroethane	17.820	1.000	0.83	0.1	2.37	118.5	1.6
2-chlorotoluene	17.870	0.992	1.04	0.7	1.41	70.3	14.8

[1]Calibration range is bewteen 5 and 500 µg/L

Compound	RT (min)	R^2	Avg. RF	MDL (µg/L)	Concentration (µg/L)	Accuracy (%)	RSD (%)
1,3,5-trimethylbenzene	17.965	0.991	1.11	0.4	1.74	86.8	7.1
trans-1,4-dichloro-2-butene	17.990	0.998	0.18	0.4	1.79	89.6	6.4
4-chlorotoluene	18.045	0.992	1.09	0.3	1.40	70.2	7.5
tert-butylbenzene	18.270	0.988	1.05	0.4	1.60	80.0	7.9
pentachloroethane	18.270	1.000	0.22	0.3	2.02	100.8	4.8
1,2,4-trimethylbenzene	18.340	0.992	1.19	0.3	1.73	86.6	4.8
sec-butylbenzene	18.440	0.981	1.26	0.3	1.55	77.6	5.8
p-isopropyltoluene	18.580	0.978	1.07	0.4	1.40	70.0	9.1
1,3-dichlorobenzene	18.605	0.994	0.81	0.7	1.50	74.8	14.1
1,4-dichlorobenzene-d4 (IS)	18.655						
1,4-dichlorobenzene	18.685	0.994	0.83	1.1	1.44	72.1	12.6
n-butylbenzene	18.945	0.980	1.01	0.5	1.88	94.2	8.8
1,2-dichlorobenzene	19.040	0.995	0.84	0.6	1.91	95.3	9.2
1,2-dibromo-3-chloropropane	19.665	1.000	0.31	0.2	1.89	94.6	3.0
nitrobenzene	20.045	0.999	0.09	2.3	4.57	91.4	15.7
1,2,4-trichlorobenzene	20.160	0.997	0.48	0.9	1.63	81.7	17.6
naphthlane	20.405	0.997	2.72	0.2	1.64	81.9	4.4
1,2,3-trichlorobenzene	20.550	0.993	0.53	0.7	1.62	81.1	14.3