Analysis of Volatile Organic Compounds Using US EPA Method TO-17 by Automated Cryogen-free Thermal Desorption

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Application Note

Environmental

Summary

This Application Note demonstrates the sensitivity of the CDS 7550S coupled to a GC/MS for the analysis of TO-17 volatile organic compounds (VOCs) ranging in volatility from propene to naphthalene. The data shows that CDS 7550S meets and exceeds the criteria set forth in US EPA Method TO-17. Detailed instrument method parameters are presented along with clean blank chromatogram, precision, linearity, and calibration curves for several groups of compounds.

Thermal Desorption adsorbent tubes are used to capture the VOCs listed in US EPA Method TO-17. To quantitatively analyze the captured compounds, the CDS 7550S has been designed with 350°C ultra high temperature inert valve oven, integrated zero-degassing tube heater, pressure controlled Internal Standard Module, proprietary Pre-heat and Pre-desorb focusing, as well as a Peltier module to capture gas phase VOCs with boiling points far below ambient temperature. To accommodate the demand of high throughput jobs, the system adopts a high precision 72-position robotic system with software-calibration capability on the tube length. This Application Note will demonstrate the performance of this system and the analysis of volatile organic compounds ranging in polarity and volatility.

Experiment Setup

The main instruments used in this application were a CDS 7550S as the GC front-end device, and an Agilent 6890 GC with a 5975B MS as the separation and detection devices. Detailed instrument parameters are listed in Table 1. The 7550S was configured with a capillary focusing trap packed with Tenax TA adsorbent. The primary sampling tube was a three-bed ¼" OD x 3.5" length CAMSCO tube (part number SU644-4), packed with Carbograph 2/Carbograph 1/Carboxen 1000. The calibration standard was prepared by a gas standard cylinder purchased from Restek with 65 TO-17 compounds calibrated at 1 ppm concentration. When making the calibration standard, a CAMSCO thermal desorption tube was attached to a CDS gas addition device with a selectable sample loop from 1-mL, 2-mL and 5-mL volume, which was pre-filled with internal standard at room atmosphere pressure, then the sample loop was fully purged with He gas into the thermal desorption tube. In the purging step, a Restek flow meter (ProFLOW) was used to adjust the flow meter to 60 ml/min. The purging time was calculated so that a total volume of 1L gas, including the volume of the gas standard, was purged through the thermal desorption tube. Then the thermal desorption tube was detached from the gas addition device and moved to the CDS 7550S for analysis. The 7550S was also equipped with an Internal Standard (IS) Module that is able to deliver 5-mL of gas-phase IS. The internal pressure of the sample loop module is precisely modulated at 1 psi. All of the sample pathways in the IS modules are inert-coated to minimize active site for carryover.

Thermal desorption conditions
Tube Heater rest: 38°C
Tube desorb: 300°C
Dry: 38°C, 0.5 min
IS loop: 5.0 mL
IS fill: 1 min
IS transfer: 1 min
Trap type: Tenax TA
Trap rest: -20 °C with Peltier
Trap pre-heat: 15 s
Trap desorb: 300°C
Oven: 275°C
Transfer line: 250°C

GC/MS conditions
Agilent 6890 GC
OVEN
Initial temp: 35 °C (On) Maximum temp: 260 °C
Initial time: 4.00 min Equilibration time: 0.50 min
Ramps:

#	Rate	Final temp	Final time
1	5.00	90	0.00
2	12.00	150	0.00
3	30.00	250	1.67

Run time: 25.00 min

Front Inlet (Split/Splitless)
Mode: Split
Initial temp: 220 °C (On)
Pressure: 7.03 psi (On)
Split ratio: 5:1
Gas type: Helium

Column:
Restek Rtx-VMS 30.0 m x 250.00 um x 1.40 um
flow: 1.0 mL/min

Agilent 5975B MS
Acquisition Mode: Scan
Solvent Delay: 1.53 min
Low Mass: 35.0
High Mass: 260.0
MS Quad: 150 °C
MS Source: 230 °C

Table 1. Instrument Parameters.

Results and Discussion

All of the sample flow pathway in 7550S is inert-coated to minimize carryover and avoid target compounds degradation at high temperatures. The O-ring seal at the thermal desorption tube is made of Kalrez, which has the most inertness at high temperatures among various elastomers. The system presents a clean blank GC/MS chromatogram, as shown in Figure 1.

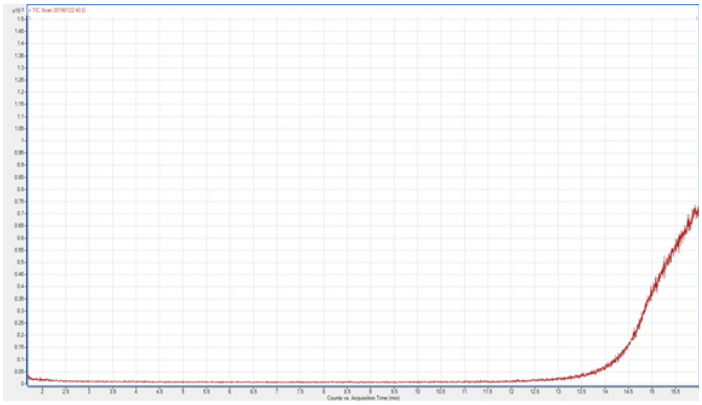

Figure 1 CDS 7550S system blank chromatogram with Tenax TA trap in Peltier module.

A gas standard cylinder that contains three internal compounds (Bromochloromethane, 1,4-Diflourobenzene, and Chlorobenzene-d5) were pressure-regulated down to 28 psi and then fed into the internal standard module of the 7550S. A conditioned blank thermal desorption sample tube was loaded to the system to introduce internal standard and then desorbed to the trap. A consecutive nine samples were run, and the results was depicted in Figure 2 as overlapped chromatograms and Table 2 with calculated RSDs. The enlarged part in Figure 2 displays good consistency of the peak area and high precision in retention time, which is a performance indicator of the quantitative desorption process.

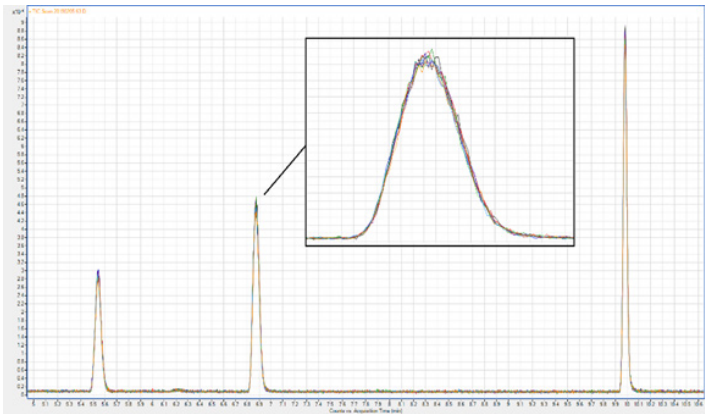

Figure 2. Overlapped internal standard chromatograms (n=9). The peaks are, from left to right, of Bromochloromethane, 1,4-Diflourobenzene, and Chlorobenzene-d5.

US EPA Method TO-17 gas samples were loaded with a CDS gas addition equipment with user selectable 1, 2, and 5-mL loops to add TO-17 gas mix onto the sample tube at desired sample concentrations. As seen in Figure 3, the trap desorption and GC separation resulted in narrow peaks with great resolution for all the TO-17 compounds.

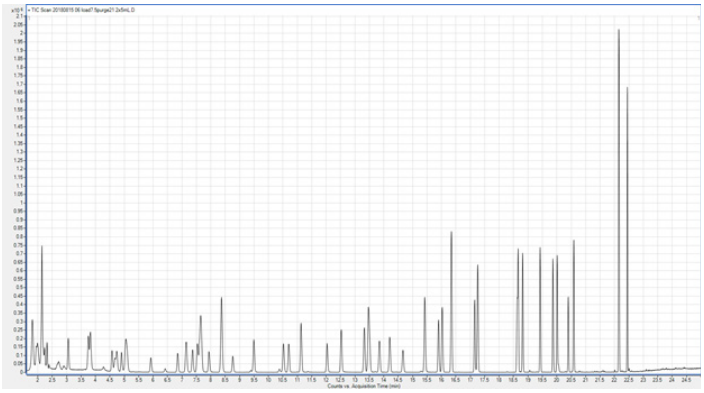

Figure 3. TO-17 GC/MS chromatogram at 10 ppbv.

A detachable Peltier module with the minimum cooling temperature of -25 °C was used in this application. The trap cooling element is semiconductor based and does not require cryogen. The trap heating element is equiped with a proprietary Pre-Desorb mechanism, which makes the effective trap heating rate over 150 °C/s. This fast rising temperature improves focusing, especially for early eluting compounds. This Peltier module only consumes 10 mL/min of Nitrogen.

The calibration curves and the linearities (R^2) for hydrocarbons, halogenated hydrocarbons, esters, and ketones are shown in Figure 4, 5, 6, 7, respectively. Table 3 lists the original data. The thermal desorption technique provides excellent linearity for all TO-17 compounds.

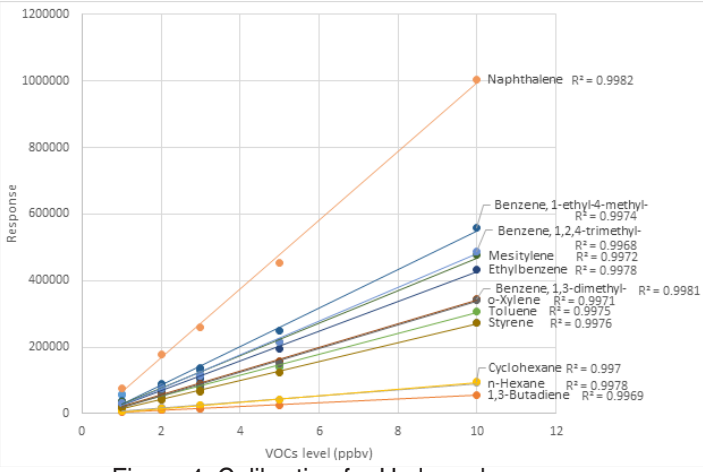

Figure 4. Calibration for Hydrocarbons.

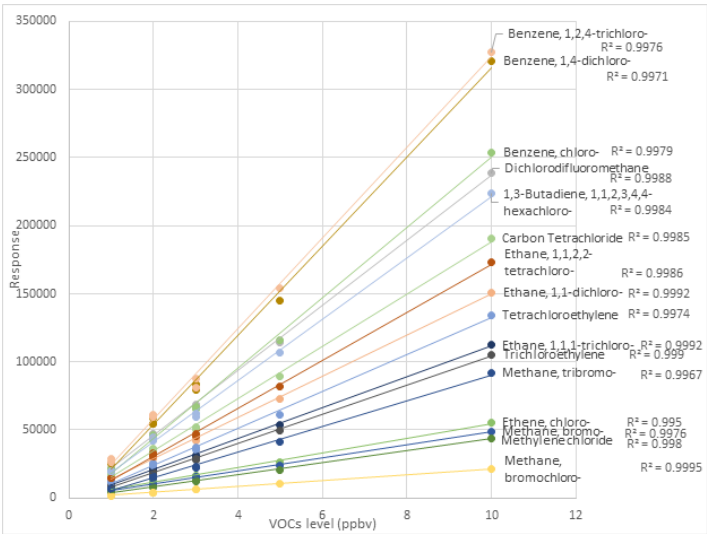

Figure 5. Calibration for Halogenated Hydrocarbons.

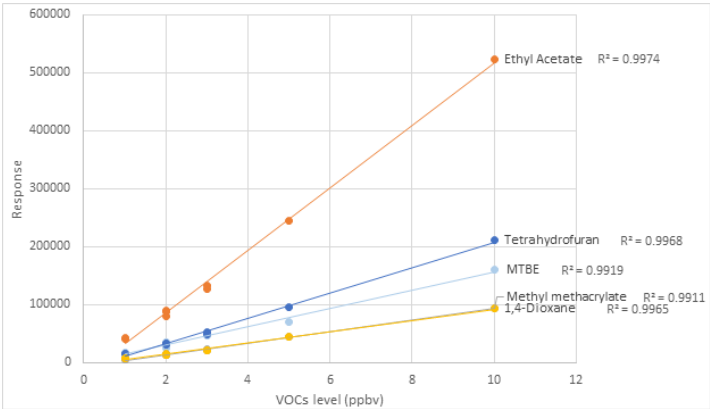

Figure 6. Calibration for Esters.

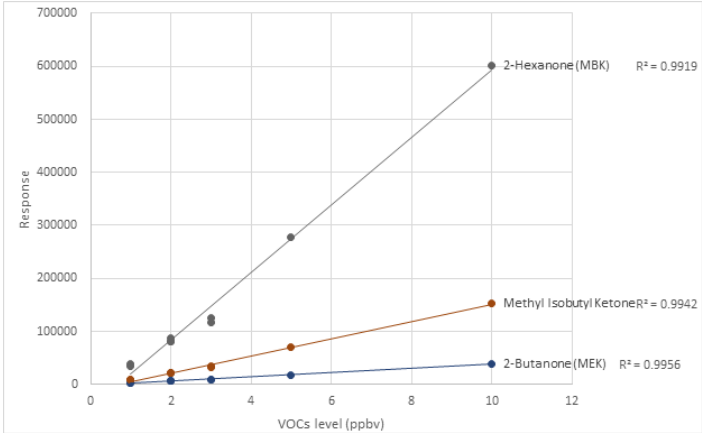

Figure 7. Calibration for Ketones.

After desorbing a sample, a blank run was executed to measure the system carryover. In Figure 8, the chromatogram in black color is from a 10 ppbv sample and the yellow one is from the tube blank immediately following that sample. The enlarged part in Figure 8 shows that most of the TO-17 compounds are not detected with the exception for a few high boilers. The biggest carryover is less than 0.03 ppbv (Naphthalene).

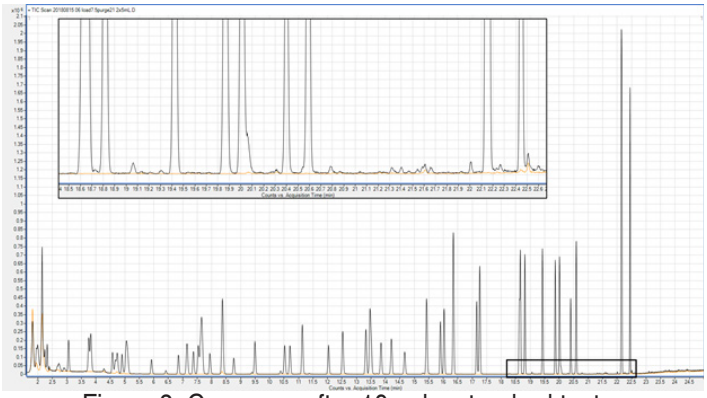

Figure 8. Carryover after 10 ppbv standard test.

ISTD	Bromochloromethane	1,4-Diflourobenzene	Chlorobenzene-d5
Retention time	0.06%	0.04%	0.03%
Peak Area	2.07%	1.83%	1.86%

Table 2. Internal Standard RSD.

#	Compound Name	R^2
1	Propene	0.9747
2	Dichlorodifluoromethane (Freon 12)	0.9988
3	Ethane, 1,2-dichloro-1,1,2,2-tetrafluoro- (Freon 114)	0.9981
4	Chloromethane	0.8068
5	Ethene, chloro-	0.9950
6	1,3-Butadiene	0.9969
7	Methane, bromo-	0.9976
8	Trichloromonofluoromethane (Freon 11)	0.9992
9	Ethyl Chloride	0.9714
10	Ethene, 1,1-dichloro-	0.9985
11	Carbon disulfide	0.9987
12	Ethanol	0.9762
13	Ethane, 1,1,2-trichloro-1,2,2-trifluoro- (Freon 113)	0.9983
14	2-Propenal (Acrolein)	0.8520
15	Methylene chloride	0.9980
16	Isopropyl Alcohol	0.9944
17	Acetone	0.9701
18	Ethylene, 1,2-dichloro-, (E)-	0.9980
19	n-Hexane	0.9978
20	Propane, 2-methoxy-2-methyl- (MTBE)	0.9919
21	Ethane, 1,1-dichloro-	0.9992
22	Acetic acid ethenyl ester (Vinyl Acetate)	0.8945
23	Ethylene, 1,2-dichloro-, (Z)-	0.9986
24	Cyclohexane	0.9970
25	Methane, bromochloro-	ISTD
26	Trichloromethane	0.9984
27	Carbon Tetrachloride	0.9985
28	Tetrahydrofuran	0.9968
29	Ethyl Acetate	0.9974
30	Ethane, 1,1,1-trichloro-	0.9992
31	2-Butanone (MEK)	0.9956
32	Propane, 2-chloro-2-nitro-	0.9930
33	Benzene	0.9915
34	Ethane, 1,2-dichloro-	0.9994
35	Trichloroethylene	0.9990
36	Benzene, 1,4-difluoro-	ISTD
37	Propane, 1,2-dichloro-	0.9992
38	Methane, bromodichloro-	0.9987
39	Methyl methacrylate	0.9965
40	1,4-Dioxane	0.9911
41	1-Propene, 1,3-dichloro-, (Z)-	0.9964
42	Toluene	0.9975
43	Tetrachloroethylene	0.9974
44	Methyl Isobutyl Ketone	0.9942
45	1-Propene, 1,3-dichloro-, (E)-	0.9984
46	Ethane, 1,1,2-trichloro-	0.9992
47	Methane, dibromochloro-	0.9985
48	Ethane, 1,2-dibromo-	0.9980
49	2-Hexanone (MBK)	0.9919
50	Chlorobenzene-d5	ISTD
51	Benzene, chloro-	0.9979
52	Ethylbenzene	0.9978
53,54	m,p-Xylene	0.9981
55	o-Xylene	0.9971
56	Methane, tribromo-	0.9967
57	Styrene	0.9976
58	Ethane, 1,1,2,2-tetrachloro-	0.9986
59	Benzene, 1-ethyl-4-methyl-	0.9974
60	Mesitylene	0.9972
61	Benzene, 1,2,4-trimethyl-	0.9968
62	Benzene, 1,3-dichloro-	0.9976
63	Benzene, 1,4-dichloro-	0.9971
64	Benzyl chloride	0.9822
65	Benzene, 1,2-dichloro-	0.9975
66	1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	0.9984
67	Benzene, 1,2,4-trichloro-	0.9976
68	Naphthalene	0.9957

Table 3. Linear coefficients of several types of compounds.