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

Application Note
Environmental

Author:

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Abstract

This Application Note demonstrates the analytical performance of a CDS 7550S thermal desorber coupled to a GCMS for the analysis of TO-17 volatile organic compounds (VOCs) ranging in volatility from Dichlorodifluoromethane to Naphthalene. The data shows that the performance of 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 various 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 with a wide range of boiling points, 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 retain the lightest VOCs with boiling point far below ambient temperature. To accommodate the demand of high throughput work, 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 different polarity and volatility.

Experiment

The main instruments used in this application were the CDS 7550S as the GC front-end device, and the Agilent 6890 GC with 5975B MS as the separation and detection device. The detailed instrument parameters were listed in Table 1. The 7550S is configured with a capillary focusing trap with Tenax TA adsorbent packed in. ¼" OD x 3.5" length CAMSCO Carbograph 2/Carbograph 1/Carboxene 1000 packed thermal desorption tubes (part number SU644-4) were used as the primary sampling tubes. 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 is pre-filled with internal standard at room atmosphere pressure, then the sample loop is 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 is calculated so that a total volume of 1L gas, including the volume of the gas standard, is 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 20 psi. All the sample path in the IS modules are inert-coated to minimize active site for carry over.

CDS 7550S Thermal Desorber 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:	Capillary Tenax TA
Trap Rest:	-20 °C
Trap Pre-heat:	15 s
Trap Desorb:	300°C
Valve Oven:	275°C
Transfer Line:	250°C

Agilent 6890 GC Conditions

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 Conditions

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: Instruments conditions

Results and Discussions

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

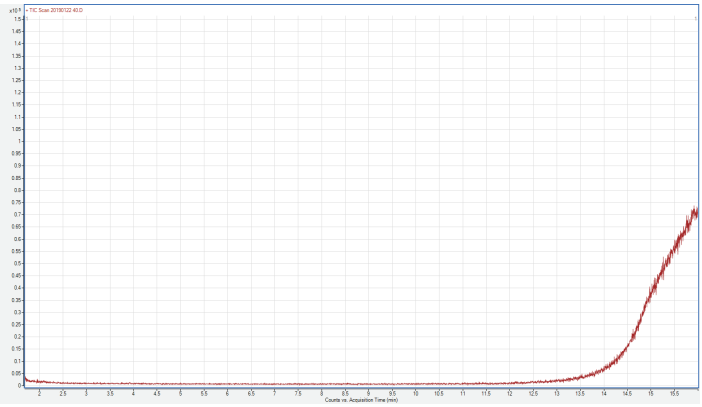

Figure 1: CDS 7550S system blank chromatogram with Tenax TA trap in the Peltier module

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 feed into the internal standard module of 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.

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 concentration. As seen in Figure 3, the trap desorption and GC separation resulted in narrow peaks with great resolution for all the TO-17 compounds.

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

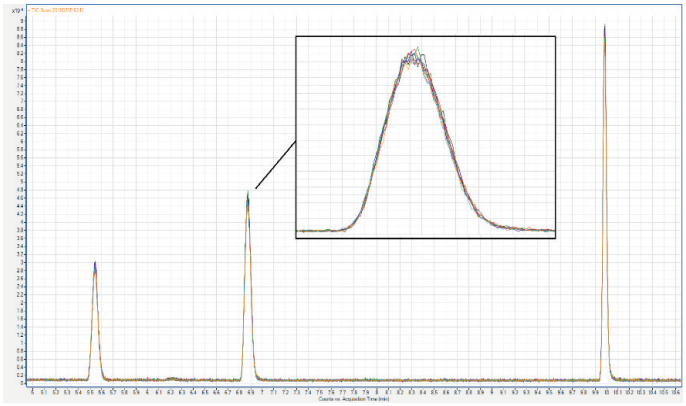

Figure 2: Overlapped internal standard chromatograms (n=9). The peaks are, from left to right, of Bromochloromethane, 1,4-Diflourobenzene, and Chlorobenzene-d5.

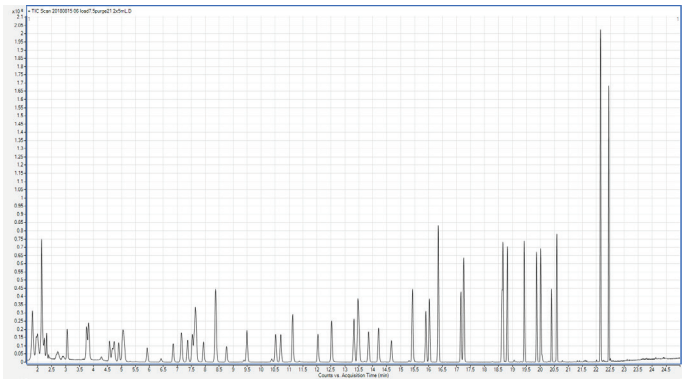

Figure 3: TO-17 GC/MS chromatogram at 10 ppbv sample concentration

The calibration curves and the linearities (R2) 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.

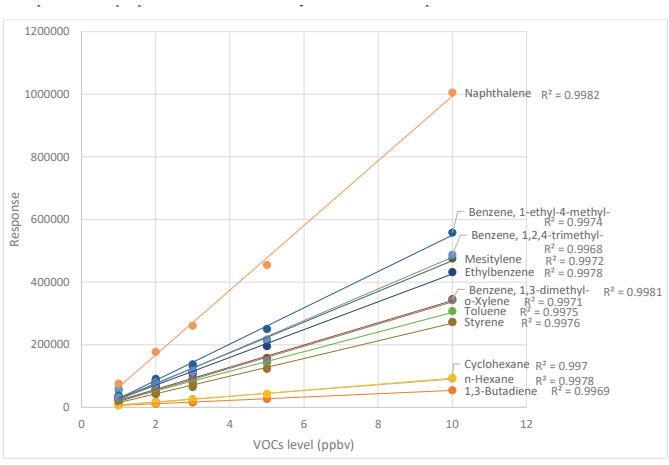

Figure 4: Calibration for Hydrocarbons

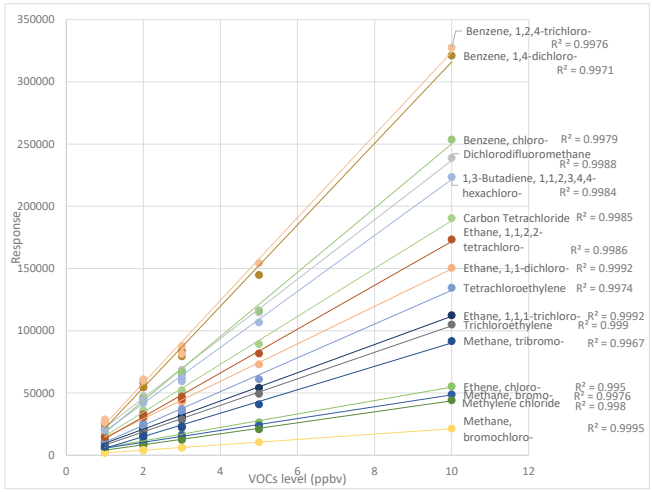

Figure 5: Calibration for Halogenated Hydrocarbons

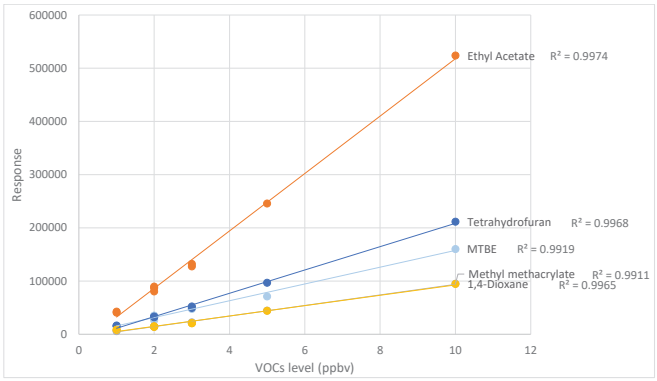

Figure 6: Calibration for Esters

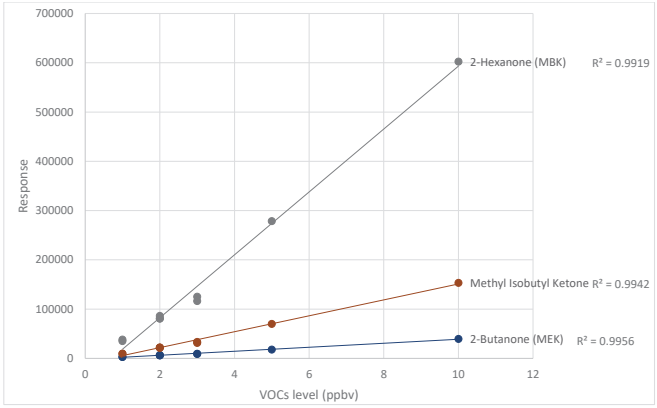

Figure 7: Calibration for Ketones

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 0.3% from Naphthalene.

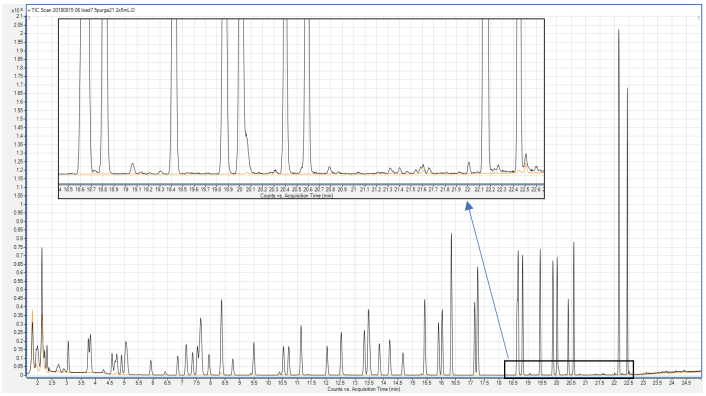

Figure 8: Carryover after 10 ppbv TO-17 sample test

Conclusion

The results demonstrate that the quantitative performance of the CDS 7550S system meets and exceeds the method criteria for US EPA Method TO-17. Limited carryover among TO-17 compounds shows excellent sample recovery. The linearity, RSD and resolution makes it clear that the CDS 7550S system is well suitable for analyzing a wide range of VOCs.

Type of Compounds	Compound Name	R^2
Hydrocarbons	1,3-Butadiene	0.9969
	n-Hexane	0.9978
	Cyclohexane	0.9970
	Toluene	0.9975
	Ethylbenzene	0.9978
	Benzene, 1,3-dimethyl-	0.9981
	o-Xylene	0.9971
	Styrene	0.9976
	Benzene, 1-ethyl-4-methyl-	0.9974
	Mesitylene	0.9972
	Benzene, 1,2,4-trimethyl-	0.9968
	Naphthalene	0.9982
Halogenated Hydrocarbons	Dichlorodifluoromethane (Freon 12)	0.9988
	Ethene, chloro-	0.9950
	Methane, bromo-	0.9976
	Methylene chloride	0.9980
	Ethane, 1,1-dichloro-	0.9992
	Methane, bromochloro-	0.9995
	Carbon Tetrachloride	0.9985
	Ethane, 1,1,1-trichloro-	0.9992
	Trichloroethylene	0.9990
	Tetrachloroethylene	0.9974
	Benzene, chloro-	0.9979
	Methane, tribromo-	0.9967
	Ethane, 1,1,2,2-tetrachloro-	0.9986
	Benzene, 1,4-dichloro-	0.9971
	1,3-Butadiene, 1,1,2,3,4,4-hexachloro-	0.9984
	Benzene, 1,2,4-trichloro-	0.9976
Esters	Propane, 2-methoxy-2-methyl- (MTBE)	0.9919
	Tetrahydrofuran	0.9968
	Ethyl Acetate	0.9974
	Methyl methacrylate	0.9965
	1,4-Dioxane	0.9911
Ketones	2-Butanone (MEK)	0.9956
	Methyl Isobutyl Ketone	0.9942
	2-Hexanone (MBK)	0.9919

Table 3: Linear coefficients of various types of compounds