

## Introduction

Air pollution is a growing problem due to the global economy and industrial development in many countries. As a result, the analysis of ambient air is a growing field. The Environmental Protection Agency developed Method TO-15 in order to analyze air pollution and this method will be presented in this application note.

## Discussion

The United States Environmental Protection Agency (USEPA) introduced Method TO-15 in order to determine the amount of Volatile Organic Compounds (VOCs) in air samples. The air samples are collected in prepared stainless steel canisters and analyzed by Gas Chromatography/Mass Spectrometry (GC/MS). This method is complicated by environmental factors such as high humidity in the air or the presence of CO<sub>2</sub> when the sample is collected.

The 8900 pre-concentrator uses a three stage trap system. The first stage uses a trap filled with glass beads. The trap is cooled to -150°C which traps the water and CO<sub>2</sub> within the beads. From here, the flow and temperature are controlled in order to release the VOCs from the glass beads while holding the water and CO<sub>2</sub> in within the trap. The second trap is composed of Tenax. This trap will retain the VOCs and release residual water and/or CO<sub>2</sub> that remains in the sample stream through the vent. Finally, the VOCs are sent through the cryofocuser which concentrates the VOCs for injection to the GC.

This application note will focus on EPA Method TO-15 and establish experimental parameters for the determination of VOCs in an air matrix.

## Experimental

The sampling system used for this study was the 8900 pre-concentrator. The pre-concentrator was coupled to an Agilent 7890A GC and 5975C inert XL MS analytical system. The transfer line of the pre-concentrator was configured directly to the Restek Rtx-5 60m x 0.32mm x 1.5µm column in the GC. The pre-concentrator and GC/MS parameters are listed in Tables 1 and 2 respectively.



8900 pre-concentrator Experimental Parameters			
<b>Trap 1</b>		<b>Internal Standard</b>	
Cooling Temp.	-150°C	Purge Flow	20ml/min
Preheat Temp.	10°C	Purge Time	30 sec.
Preheat Time	10 sec.	Volume	50ml
Desorb Temp.	20°C	ISTD Flow	100ml/min
Desorb Flow	10ml/min	<b>Sample</b>	
Desorb Time	240 sec.	Purge Flow	20ml/min
Bakeout Temp.	160°C	Purge Time	30 sec.
Flush Flow	100ml/min	Sample Flow	100ml/min
Flush Time	10sec	<b>GC</b>	
Sweep Flow	100ml/min	GC Remote Start	yes
Sweep Time	30sec	GC Run Time	28 min.
Timeout	15min.	Flush Sample Line	no
Temp. Target Range	10°C	GC Ready	yes
Stable Time	2 sec.	GC Ready Timeout	10 min.
Enable Cooling w/He	no	<b>Idle</b>	
<b>Trap 2</b>		Cryotrap 1	100°C
Cooling Temp.	-20°C	Transfer Line	125°C
Desorb Temp.	180°C	Valve Oven	125°C
Desorb Time	30 sec.	Cryotrap 2	100°C
Bakeout Temp.	190°C	Sample Line	100°C
Bakeout Time	360 sec.	Sample Oven	100°C
Timeout	15 min.	Auxiliary	60°C
Temp. Target Range	10°C		
Stable Time	2 sec.		
Enable Cooling w/He	no		
<b>Focuser</b>			
Cooling Temp.	-165°C		
Inject Time	30 sec.		
Timeout	15 min.		
Temp. Target Range	10°C		
Stable Time	30 sec.		

**Table 1: 8900 pre-concentrator Experimental Parameters**

<b>GC/MS</b>	<b>Agilent 7890A/5975C inert XL</b>
Transfer Line Configuration	On Column Injection
Inlet Head Pressure	5.912 psi
Column	Rtx-5 60m x 0.32mm I.D. x 1.5µm film thickness
Oven Temp. Program	35°C hold for 5 min., ramp 10°C/min to 220°C, hold for 4.5 min.
Column Flow Rate	1.2mL/min
Gas	Helium
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	180°C
Scan Range	m/z 35-265
Scans	3.12 scans/sec
Solvent Delay	3.5 min

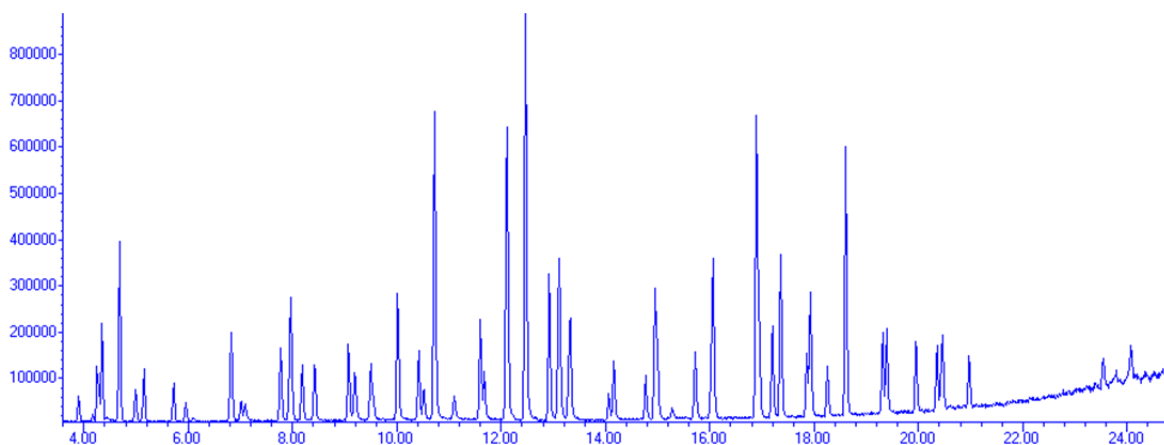
**Table 2: GC/MS Experimental Parameters**

Standards and certified summa cans were acquired from Restek. The summa cans were cleaned using the 2100B Canister Cleaning System while the 2201A Dynamic Diluter was used to prepare the Internal Standard (IS) and TO-15 standard. The IS was diluted to 20ppb and a 50ml aliquot of this standard was used in order to hold the IS and surrogate levels to a constant 5ppb. The TO-15 standard was also diluted to 20ppb and a series of standard volumes of this dilution were used for the calibration curve. Refer to Table 3. The study was done with both dry and humidified air standards in order to determine the effect of humidity on the results.

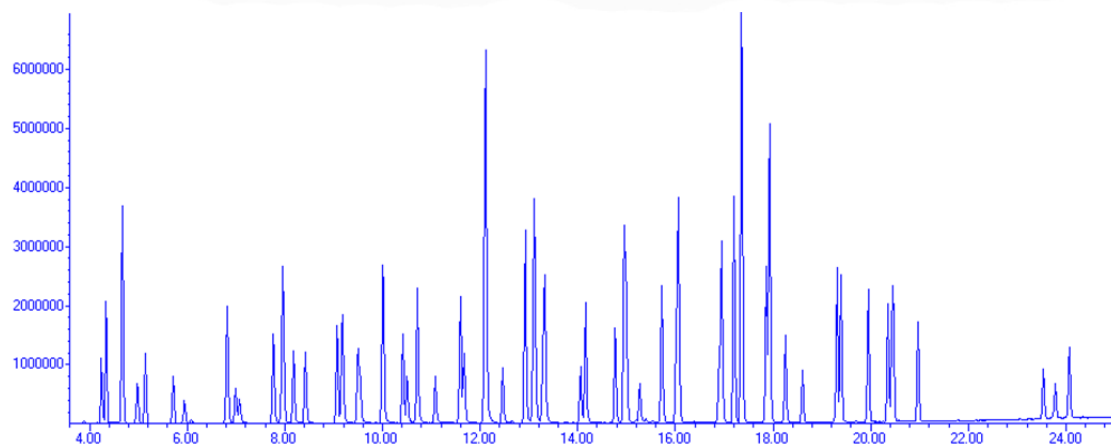
Calibration Curve		
Standard	Volume	Calibration Level
10ppb	40ml	2ppb
20ppb	50ml	5ppb
20ppb	100ml	10ppb
20ppb	150ml	15ppb
20ppb	200ml	20ppb
20ppb	250ml	25ppb
20ppb	400ml	40ppb

**Table 3: Calibration Curve**

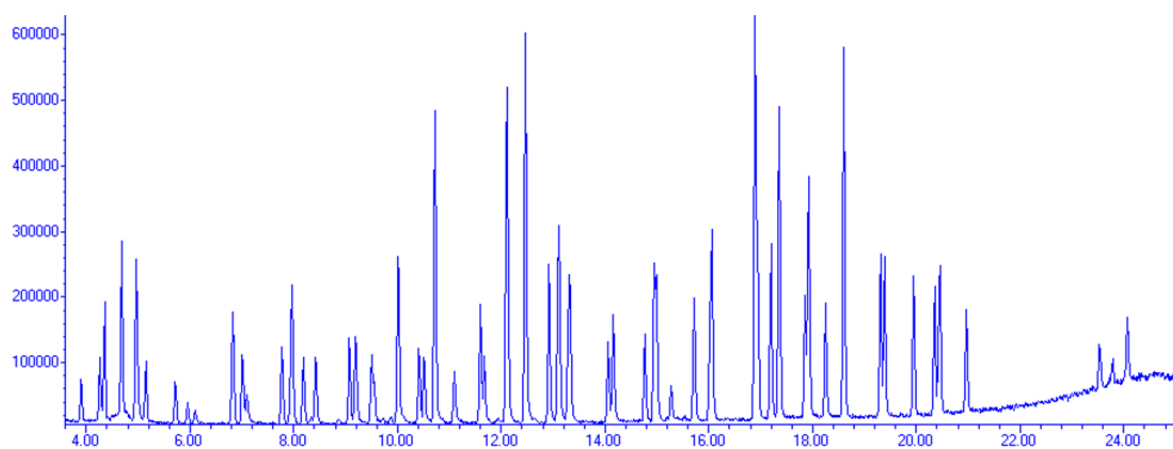
After the calibration curve was established, a series of seven replicate 2ppb standards were run in order to establish the minimum detection limit (MDL) of the system. Finally, a series of seven replicate 20ppb standards were run so as to determine the precision and accuracy of the system. The curve, MDL and precision and accuracy results of both the dry and the humidified standards are listed in Table 4, while both the 2ppb and 20ppb chromatograms of the TO-15 dry and humidified standards are displayed in Figures 1 through 4.



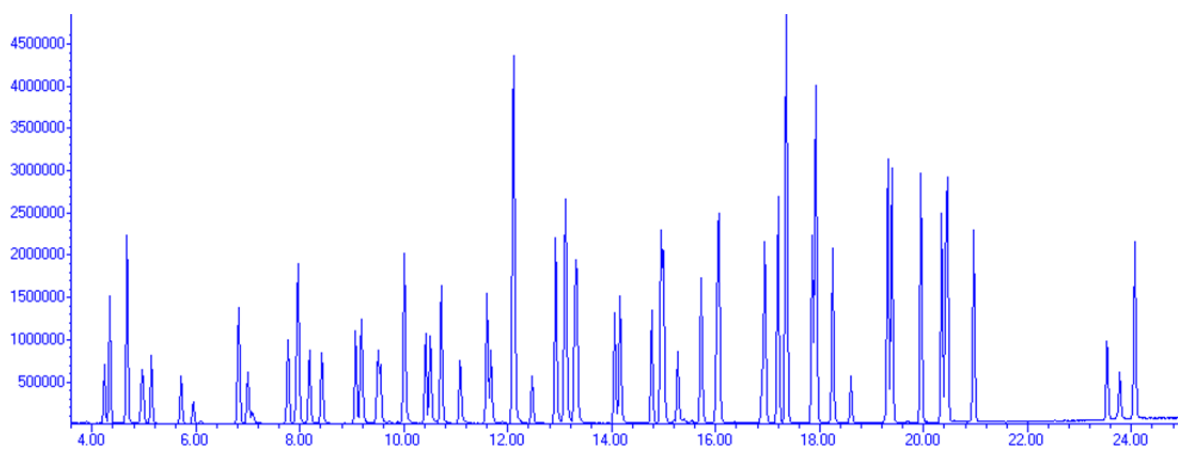
**Figure 1: 2ppb Dry Standard Chromatogram**



**Figure 2: 20ppb Dry Standard Chromatogram**



**Figure 3: 2ppb Humid Standard Chromatogram**



**Figure 4: 20ppb Humid Standard Chromatogram**

Compound	Dry Air Standards					Humid Air Standards				
	Compound RF	Curve %RSD	MDL (2ppb)	Precision (20ppb)	Accuracy (20ppb)	Compound RF	Curve %RSD	MDL (2ppb)	Precision (20ppb)	Accuracy (20ppb)
propene	0.847	9.96	0.17	1.46	90.91	0.834	7.59	0.36	2.79	98.39
Dichlorodifluoromethane	2.595	10.15	0.12	1.71	90.60	2.628	6.58	0.33	1.98	103.19
Chloromethane	1.190	10.11	0.15	1.73	90.80	0.961	7.09	0.39	2.10	104.05
Vinyl Chloride	1.034	8.84	0.10	2.04	91.24	1.010	5.97	0.30	2.10	104.44
1,3-Butadiene	0.896	8.59	0.15	2.12	91.10	0.864	6.26	0.33	2.95	100.61
Bromomethane	0.874	9.52	0.10	2.15	90.49	0.840	6.30	0.37	2.30	103.21
Chloroethane	0.563	9.57	0.13	2.25	90.81	0.538	6.44	0.32	2.82	101.07
Ethanol	0.123	9.01	0.22	2.72	90.36	0.082	26.10	3.36	7.84	97.35
Trichlorofluoromethane	0.563	10.69	0.24	2.24	90.59	0.426	4.56	0.30	2.85	106.62
1,2-Dichlorotetrafluoroethane	2.605	10.72	0.14	1.98	91.09	2.005	5.05	0.31	2.59	106.74
1,1,2-trichlorofluoroethane	2.652	9.52	0.13	2.09	90.21	2.580	5.93	0.31	2.43	102.54
Acrolein	0.228	6.82	0.27	1.69	94.44	0.251	7.75	0.52	4.76	95.38
1,1-Dichloroethene	0.973	7.78	0.17	1.94	91.44	0.918	6.22	0.47	2.62	100.38
Acetone	1.154	10.13	0.51	0.90	92.14	1.592	10.80	0.46	3.09	115.56
2-propanol	0.848	4.67	0.13	2.53	91.61	0.606	23.79	0.48	6.39	70.68
Carbon Disulfide	2.943	9.25	0.10	1.93	89.92	2.773	5.25	0.26	2.11	102.77
Methylene Chloride	0.888	9.15	0.08	1.60	90.37	0.854	5.88	0.39	2.29	102.61
MTBE	2.786	9.21	0.08	1.64	100.74	2.907	5.31	0.39	2.82	100.97
cis-1,2-Dichloroethene	1.059	8.83	0.18	1.91	90.77	1.001	5.57	0.35	2.73	99.99
Vinyl acetate	1.662	14.60	0.05	1.53	97.64	2.154	3.22	0.39	2.67	100.25
1,1-Dichloroethane	1.920	9.25	0.11	1.78	90.46	1.859	5.62	0.33	2.46	101.91
trans-1,2-Dichloroethene	1.085	9.82	0.14	1.90	90.03	1.013	5.29	0.38	2.50	101.99
ethyl acetate	0.214	6.72	0.21	2.13	88.22	0.391	4.62	0.52	3.62	103.57
2-Butanone	2.384	6.00	0.09	1.87	90.84	3.131	5.76	0.39	2.84	102.31
THF	0.823	13.47	0.15	1.31	94.63	1.184	5.44	0.51	3.26	99.31
Chloroform	2.157	8.44	0.12	2.06	90.91	2.127	5.02	0.28	2.24	103.78
1,1,1-Trichloroethane	2.262	9.05	0.11	1.76	90.68	2.215	4.75	0.30	2.33	103.34
Carbon Tetrachloride	2.224	8.62	0.11	1.93	90.48	2.105	5.32	0.31	2.16	103.84
Cyclohexane	1.821	8.49	0.10	1.97	91.29	1.700	5.06	0.36	2.72	100.02
Benzene	3.411	9.57	0.09	1.89	90.16	3.237	5.93	0.30	2.18	102.28
1,2-Dichloroethane	1.449	6.48	0.30	2.15	92.23	1.480	5.52	0.43	2.41	103.61
Heptane	0.519	8.95	0.10	1.32	90.79	0.503	4.33	0.24	2.26	105.84

**Table 4: Experimental Results**

Compound	Dry Air Standards					Humid Air Standards				
	Compound RF	Curve %RSD	MDL (2ppb)	Precision (20ppb)	Accuracy (20ppb)	Compound RF	Curve %RSD	MDL (2ppb)	Precision (20ppb)	Accuracy (20ppb)
Trichloroethene	0.340	8.28	0.12	1.44	90.99	0.328	5.42	0.35	2.23	105.64
1,2-Dichloropropane	0.285	8.12	0.09	1.69	91.43	0.291	5.19	0.29	2.60	108.79
methyl methacrylate	0.136	8.74	0.24	2.83	93.27	0.266	7.50	0.23	2.54	110.11
1,4-Dioxane	0.069	7.62	0.17	3.19	96.91	0.067	14.39	0.32	4.27	77.84
Bromodichloromethane	0.545	7.41	0.12	1.36	91.69	0.569	5.21	0.21	2.55	110.17
cis-1,3-Dichloropropene	0.409	5.24	0.07	1.40	95.58	0.443	4.40	0.22	2.38	108.79
4-methyl-2-pentanone	0.263	8.07	0.17	2.01	94.46	0.542	11.81	0.26	3.13	110.02
Toluene	0.555	7.24	0.13	1.42	91.89	0.537	4.52	0.27	2.15	106.56
trans-1,3-Dichloropropene	0.294	10.00	0.05	1.80	99.23	0.380	4.44	0.28	2.54	107.59
1,1,2-Trichloroethane	0.274	7.29	0.08	1.44	97.69	0.301	5.23	0.24	2.85	109.97
Tetrachloroethene	0.322	7.43	0.12	1.49	91.01	0.291	5.18	0.24	2.92	106.54
Dibromochloromethane	0.462	6.89	0.10	1.44	96.47	0.489	5.77	0.21	2.71	110.32
2-Hexanone	0.183	13.60	0.18	2.17	99.90	0.358	15.23	0.27	4.32	108.86
1,2-Dibromoethane	0.371	8.71	0.10	1.30	99.02	0.422	5.24	0.20	2.64	109.05
Chlorobenzene	0.869	6.48	0.16	1.24	87.07	0.810	4.14	0.20	1.34	106.59
Ethylbenzene	1.443	5.03	0.16	1.24	91.48	1.426	4.49	0.26	1.22	107.04
Xylene (m+p)	1.085	6.57	0.17	1.46	93.79	1.119	3.99	0.61	1.37	108.87
Styrene	0.630	10.74	0.21	1.94	93.19	0.749	5.47	0.32	2.34	111.40
Xylene (o)	1.153	5.78	0.10	1.66	93.54	1.239	4.79	0.31	2.45	112.71
Bromoform	0.433	7.58	0.12	1.92	92.97	0.508	7.96	0.26	2.91	115.01
BFB SUR	0.520	10.01	N/A	1.25	104.71	0.635	2.27	0.30	2.08	97.80
1,1,2,2-Tetrachloroethane	0.421	7.67	0.21	1.77	83.95	0.695	10.67	0.21	2.78	121.21
1,3,5-Trimethylbenzene	0.945	8.69	0.18	2.12	85.59	1.392	8.77	0.24	1.98	113.27
1,2,4-Trimethylbenzene	0.703	7.48	0.16	1.81	85.99	1.110	12.22	0.22	2.06	115.26
4-Ethyl Benzene	0.779	8.11	0.22	1.78	84.29	1.179	9.75	0.29	2.13	113.19
Benzyl Chloride	0.486	7.18	0.09	1.59	88.61	0.942	7.59	0.12	2.22	112.01
1,3-Dichlorobenzene	0.432	5.93	0.19	1.30	86.01	0.648	9.74	0.21	2.32	114.01
1,4-Dichlorobenzene	0.431	6.70	0.10	2.38	86.22	0.643	10.89	0.19	2.24	115.21
1,2-Dichlorobenzene	0.368	7.15	0.14	1.62	87.49	0.578	14.40	0.22	2.31	118.05
1,2,4-Trichlorobenzene	0.121	14.71	0.45	2.38	95.88	0.179	14.93	0.33	7.28	108.46
Naphthalene	0.209	19.16	0.20	3.95	96.04	0.310	18.10	0.67	6.19	93.99
Hexachlorobutadiene	0.114	11.27	0.16	2.27	90.86	0.205	21.87	0.19	6.04	127.91
Average	0.975	8.79	0.15	1.86	91.96	1.037	7.75	0.37	2.88	105.48

**Table 4: Experimental Results**

## Conclusions

TO-15 method requirements were met or exceeded using the 8900 pre-concentrator. The average precision of the system was less than 2%RSD for the dry standards and less than 3%RSD for the humidified standards while the average %accuracy was about 92% for the dry standard and 105% for the humid standard. The 8900 pre-concentrator has the advantage of using multiple ports on the back of the system for sample addition or the option of the 16 port auto-sampler for a larger sample load. Other options include a can cleaner and an auto-diluter; both of these options were also used for this study. Overall, the system performance for this analysis was excellent.

## References

*Determination of Volatile Organic Compounds (VOCs) in Air Collected In Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), Compendium Method TO-15, United States Environmental Protection Agency, January, 1999.*