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#126

Determination of Volatile Organic Compounds in Air

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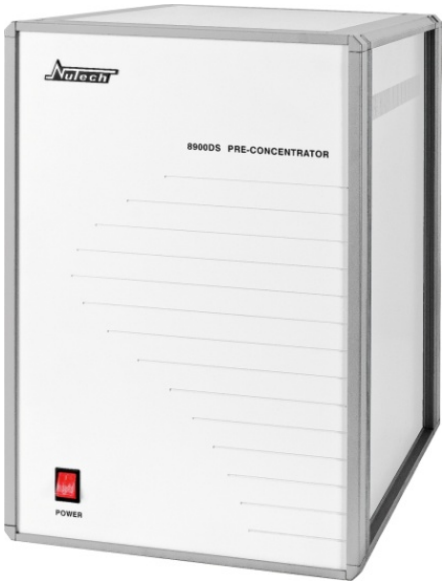
Introduction

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. However, the presence of water in the air samples can sometimes complicate the analysis of the volatile polar compounds. This poster will examine optimum experimental conditions for the detection of volatile organic compounds in an air sample. Furthermore, a comparison will be drawn between how the analytes react when the samples are dry versus when there is water present.

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 CO2 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 CO2 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 CO2 in within the trap. The second trap is composed of Tenax. This trap will retain the VOCs and release residual water and/or CO2 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 1.5um column in the GC. The pre-concentrator and GC/MS parameters are listed in Tables 1 and 2 respectively.

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

Table 1: 8900 pre-concentrator Experimental Parameters

GC/MS	Agilent 7890A/5975C inert XL
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	35ºC hold for 5 min., ramp 10ºC/min to 220ºC, hold for 4.5 min.
Column Flow Rate	1.2mL/min
Gas	Helium
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
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.

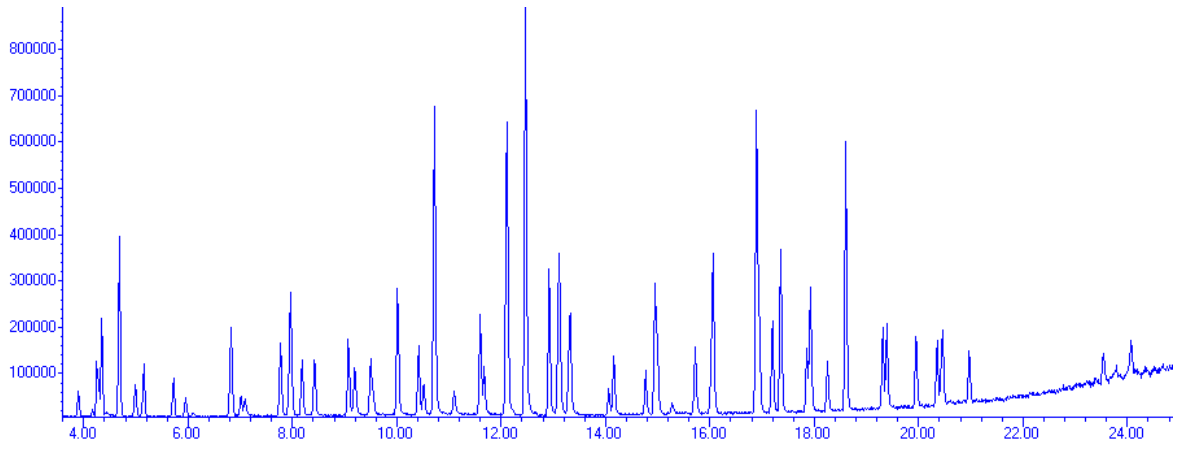


Figure 1: 2ppb Dry Standard Chromatogram

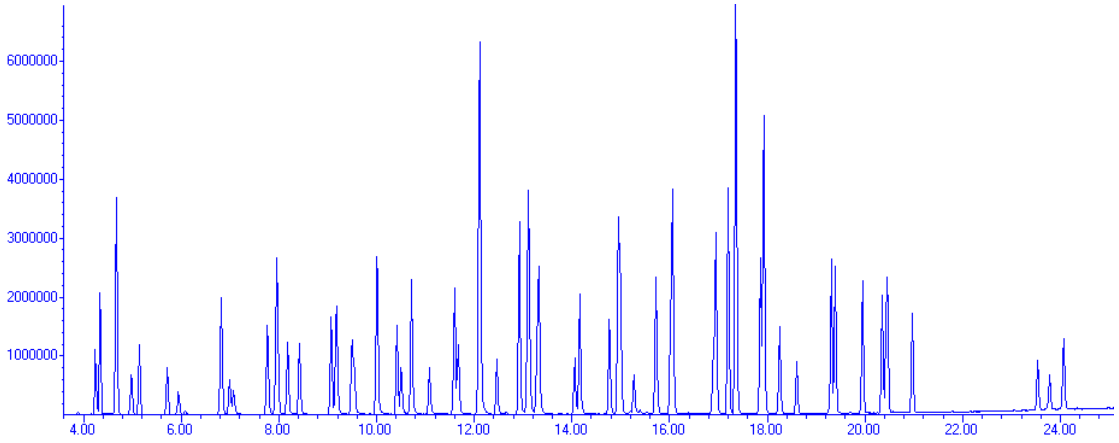


Figure 2: 20ppb Dry Standard Chromatogram

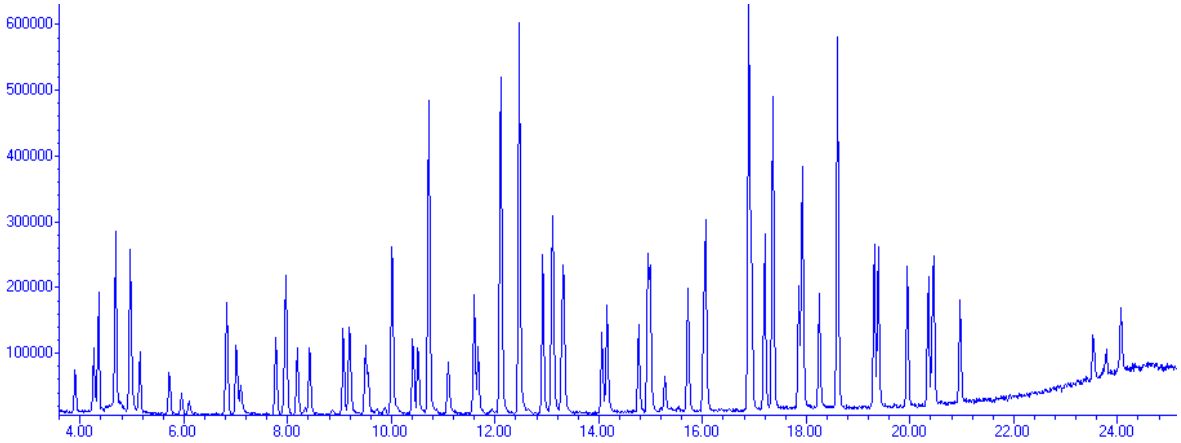


Figure 3: 2ppb Humid Standard Chromatogram

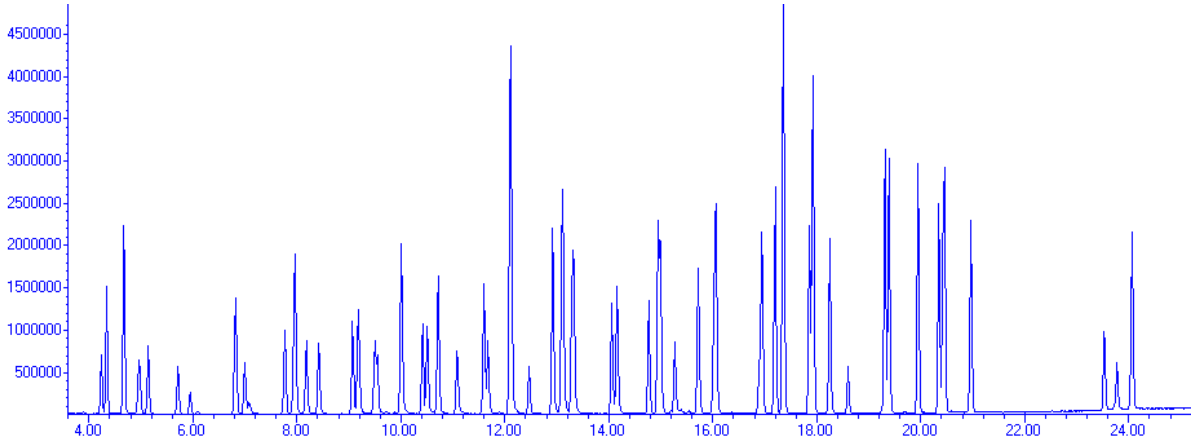


Figure 4: 20ppb Humid Standard Chromatogram

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.	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	0.2	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	0.3	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.

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