INNOVATIVE PRODUCTS, SUPERIOR SUPPORT

Determination of Volatile Organic Compounds in Air

Presenter: Anne Jurek, Senior Applications Chemist, EST Analytical

Abstract

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.

EPA METHODS

There two types of samples that will be discussed today:

- Dry
- Humid

Theoretical Canister Relative Humidity

- Density of water 0.998 g/cm^3 (i.e., 1.00 g/cm^3)
- X Volume injected into canister
- ÷ Volume of Gas in Canister
- ÷ Saturation Density at Temperature of Canister
- Example: 200µl in a 6L Canister at 22.5°C filled to 30psig

Theoretical Canister Relative Humidity

- 200µl ($0.2cm^3$) x 1.00 g/cm^3 = 0.2g of water in canister
- 6L ÷ 1000 L/m^3 x 3atm (30" HG to 30psig) = 0.018m^3 volume of gas in canister
- 0.2g ÷ 0.018m^3 = 11.09 g/m^3 vapor density in canister
- Saturation Vapor Density = 19.99g/m^3 at 22.5°C
- %Relative Humidity = Vapor Density ÷ Saturation Vapor Density x 100
- 11.09g/m^3 ÷ 19.99g/m^3 x 100 = 55.45 %RH

EPA METHOD TO-15

TO-15 method outlines sampling and analytical procedures for VOCs in air

- The air is sampled into a stainless steel canister
- A known volume of the sample is then directed from the canister to a pre-concentrator
- The pre-concentrator concentrates analytes and removes water from the samples
- The pre-concentrator then focuses the VOC analytes to the GC/MS for analysis

Initial Calibration Requirements for TO-15

- The GC/MS system must be calibrated at 5 concentrations that span the range of interest
- One of the calibration points from the ical must be the same as the daily calibration standard
- The calculated %RSD must be less than 30% for each compound in the calibration table with at most two exceptions at less than 40%

Initial Calibration Requirements for TO-15

- The area response must be within 40% of the mean area response of the ical for each internal standard
- These requirements must be met before any field samples can be run
- If these criteria are not met, inspect the system for problems and take the appropriate corrective actions and recalibrate

DAILY CALIBRATION FOR TO-15

- A BFB tune must pass the abundance criteria
- A check of the calibration curve must be performed once every 24 hours or after 20 field samples
- A mid level calibration standard needs to be analyzed and each target compound on the list must be ± 30% of the level in order to proceed with sample analysis

DAILY CALIBRATION FOR TO-15

- The IS response of the mid level calibration needs to be ± 40% of the ical IS responses
- To monitor for laboratory contamination, a laboratory method blank needs to be run once for every 24 hour sequence and be determined to be clean (This should be run after the calibration standard and before any samples)

TO-15 Air Sampling

Certified clean, leak free stainless steel pressure vessels of a desired volume (6L) are used for sample collection

Air samples are acquired in such a way that the sampling rate and duration can be controlled and collected in the sample vessel

Types of Air Tested

- Vapor Intrusion—chemicals in water or soil migrate and intrude into the indoor air
- Source emission testing—air pollution monitoring, for example stack emissions
- Indoor air quality—test indoor air for contamination, for example actively growing mold
- Remediation—tests for the removal of air pollution or ground pollution causing vapor intrusion

EXPERIMENTAL

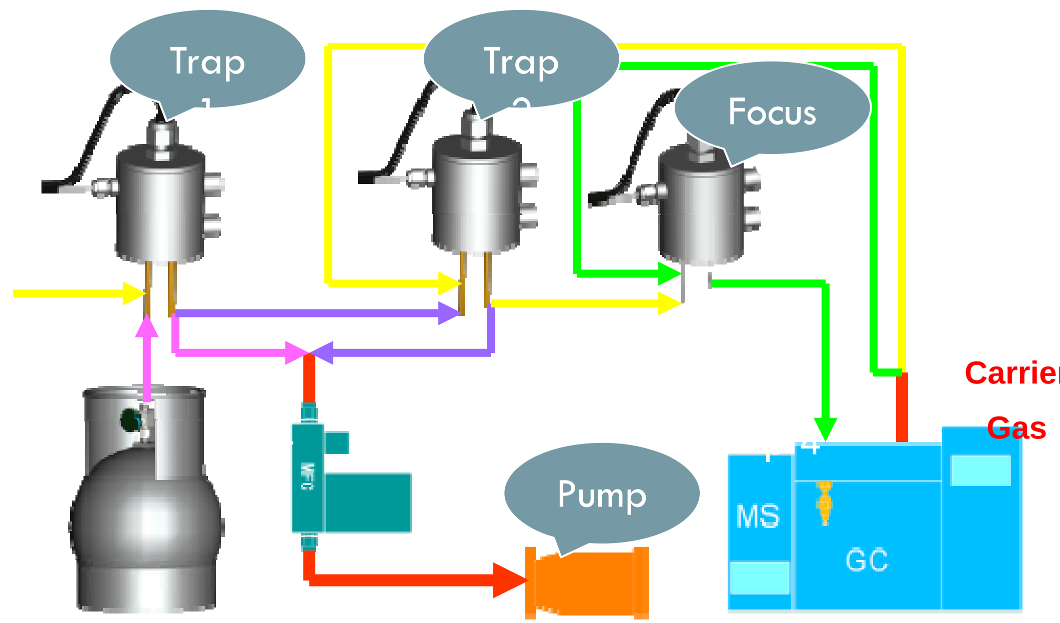
- The sampling system used for this study was the Nutech 8900DS pre-concentrator.
- The pre-concentrator was coupled to a GC/MS analysis system.
- The column used for this analysis was an Rxi-5, 60m x 0.32mm ID x 1.5µm film thickness

GC/MS PARAMETERS

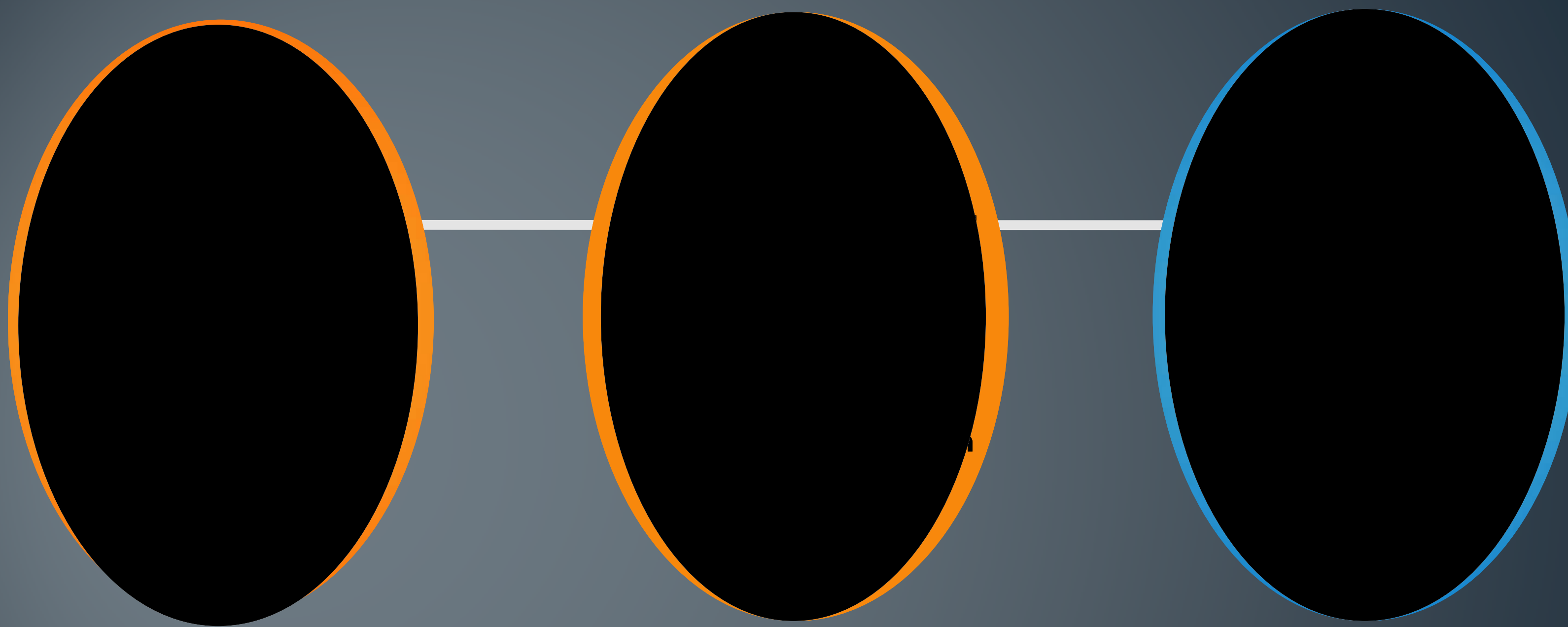
GC/MS	Agilent 7890A/5975C inert XL
Transfer Line Configuration	On Column Injection
Inlet Head Pressure	5.912 psi
Column	Rtx-5 60m x 0.32mm I.D. x 1.5µm film thickness
Oven Temp. Program	35ºC hold for 5 min., ramp 10ºC/min to 220ºC, hold for 4.5 min.
Column Flow Rate	1.2mL/min
Gas	Helium
Source Temp.	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

PRECONCENTRATOR

Three-Stage Concentration



8900 PRECONCENTRATOR



Very Narrow Band of Polar Compounds Are Sent to GC

Dry Standard Preparation

1. The TO-15 Gas Calibration Standard was acquired from Restek
2. The 6L Summa cans were cleaned
3. Using an auto-diluter the Calibration standards were prepared at 10ppb and 20ppb

Humidified Standard Preparation

1. Followed steps one and two established previously.
2. Boiled DI water and using a syringe, took 200ul of the boiling DI water and spiked the Summa cans with the DI water.
3. Using the auto-diluter the Calibration standards were prepared at 10ppb and 20ppb.

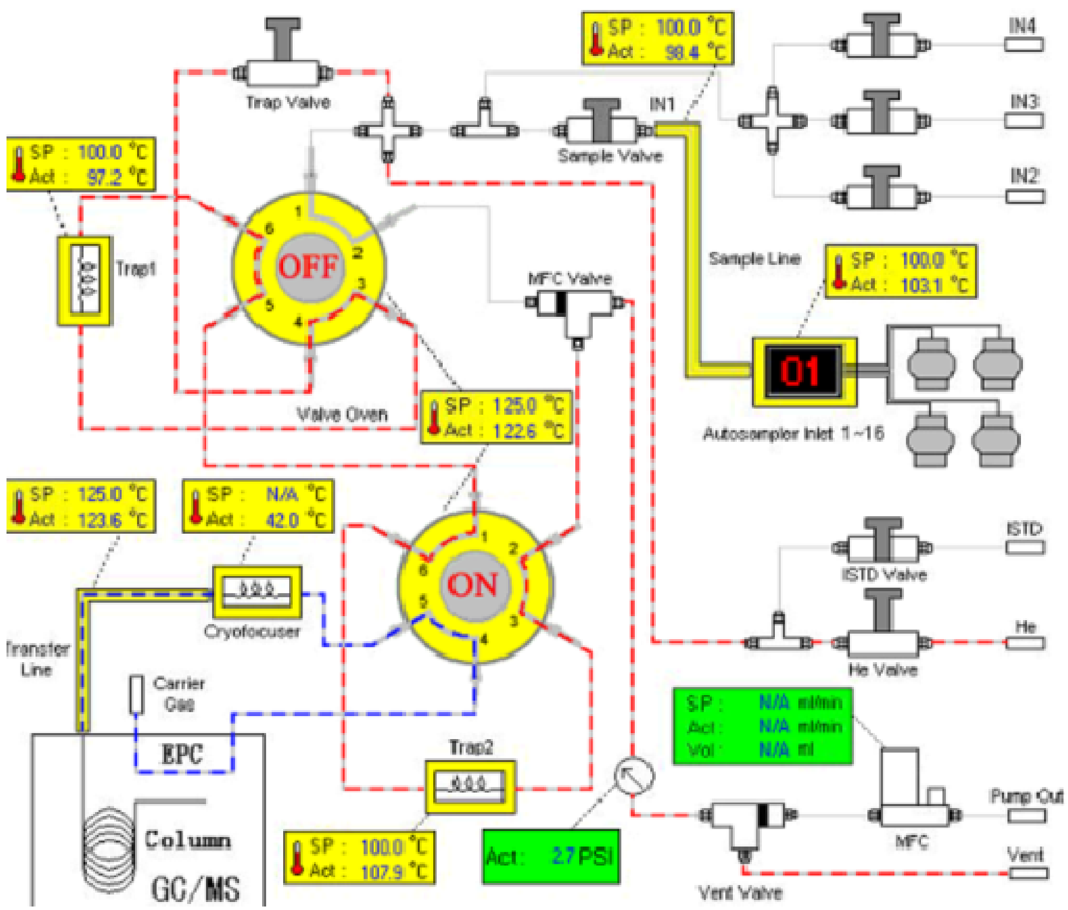
Calibration Curve

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

Nutech Pre-Concentrator Parameters

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

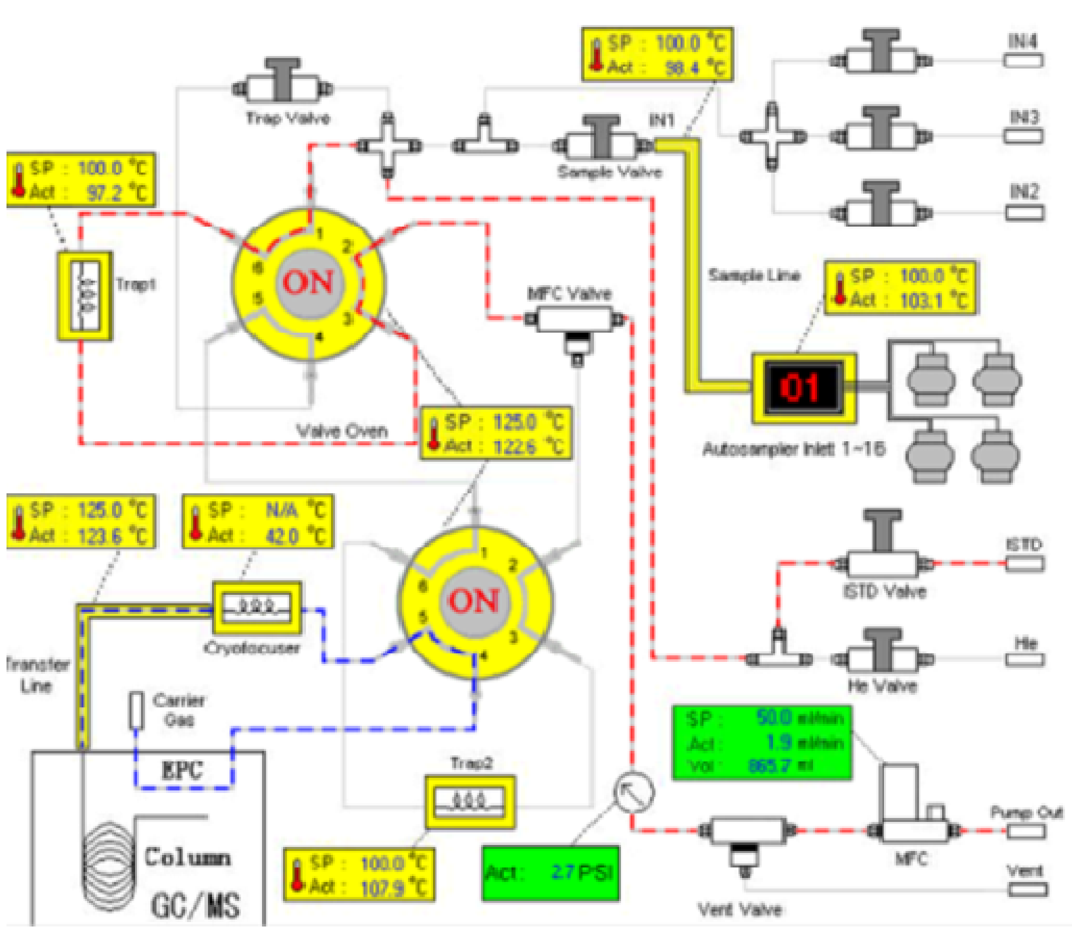
IDLE FLOW DIAGRAM



NUTECH PRE-CONCENTRATOR PARAMETERS

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

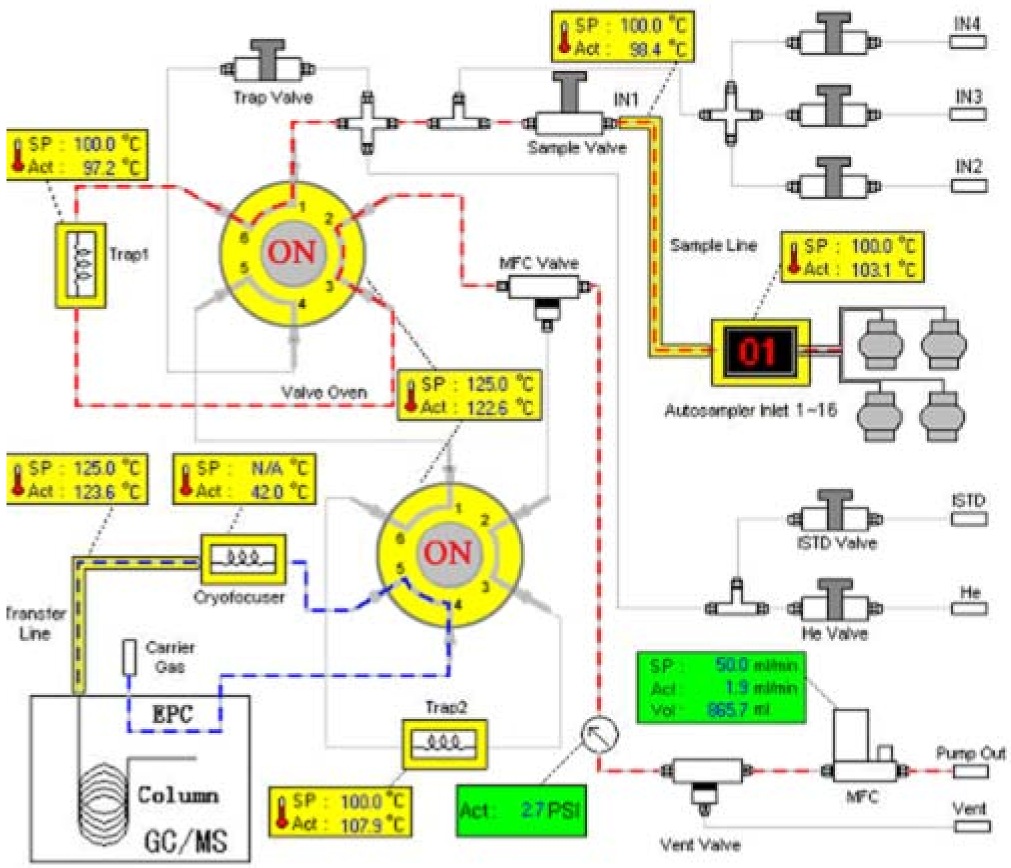
Loading Internal Standard



Nutech Pre-Concentrator 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

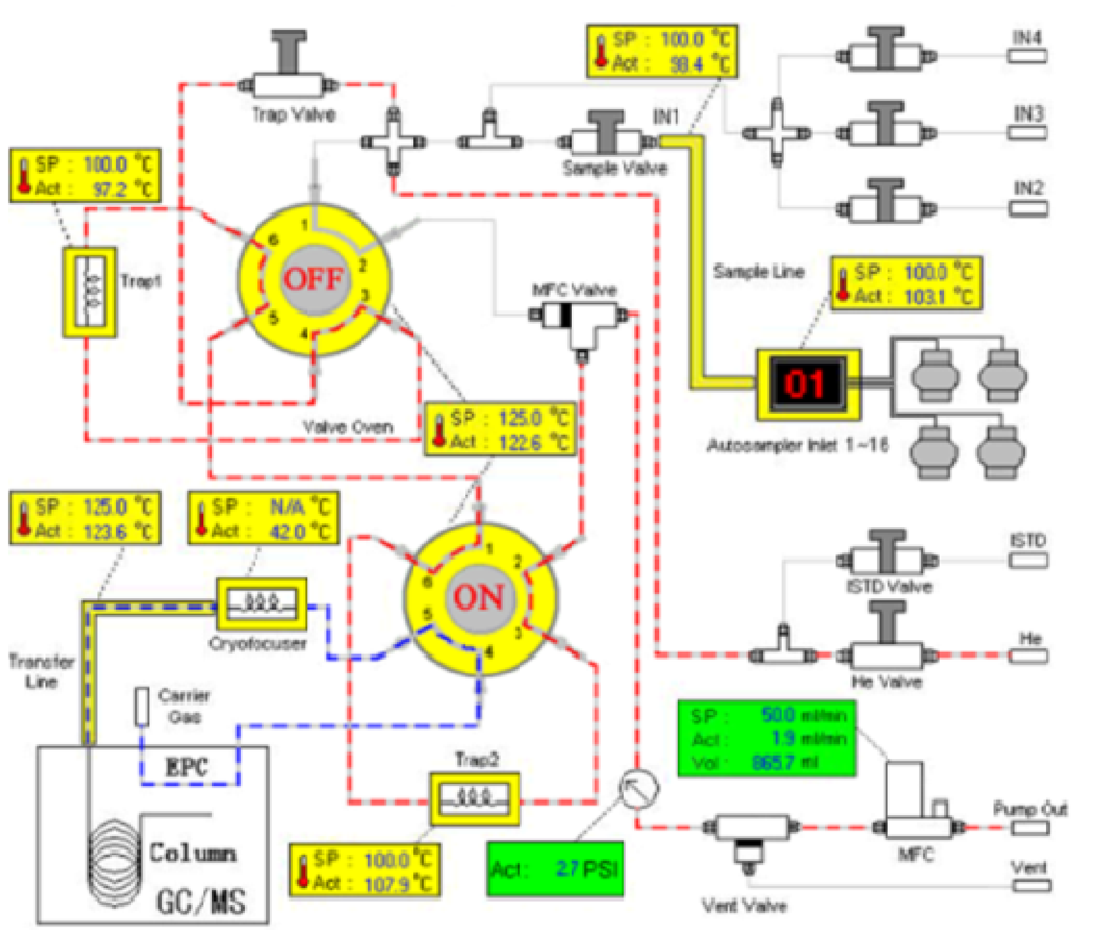
Loading Trap 1 Flow Diagram



Nutech Pre-Concentrator Parameters

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

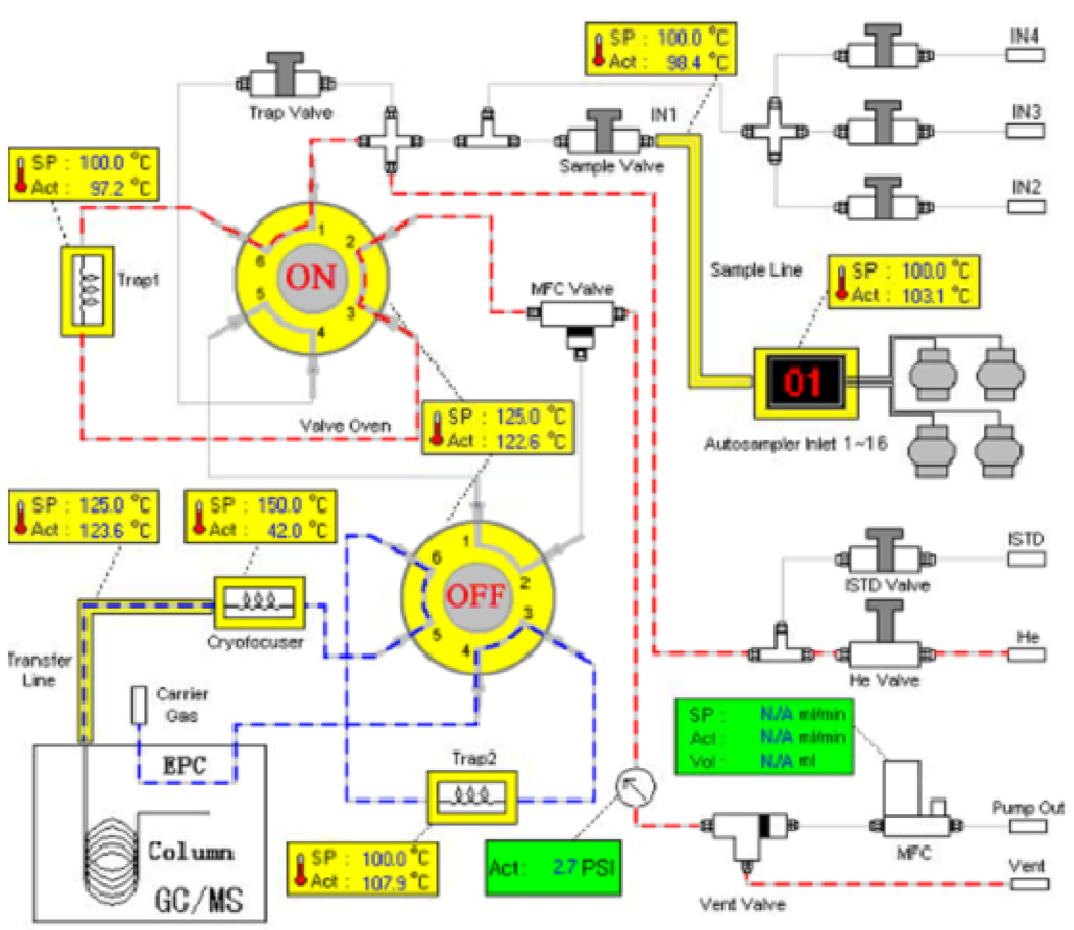
Transferring Trap 1 to Trap 2



Nutech Pre-Concentrator Parameters

Focuser	
Cooling Temp.	-165°C
Inject Time	30 sec.
Timeout	15 min.
Temp. Target Range	10°C
Stable Time	30 sec.

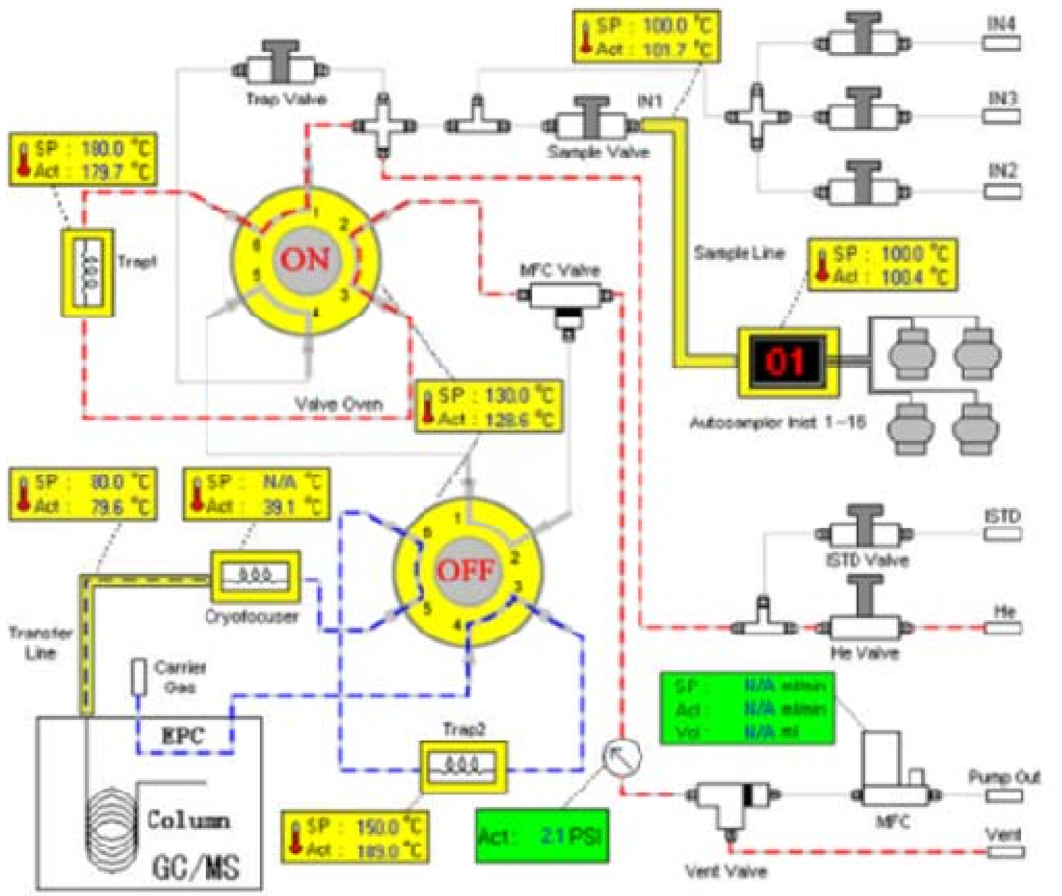
TRANSFERRING TRAP 2 TO CRYOFOCUSER



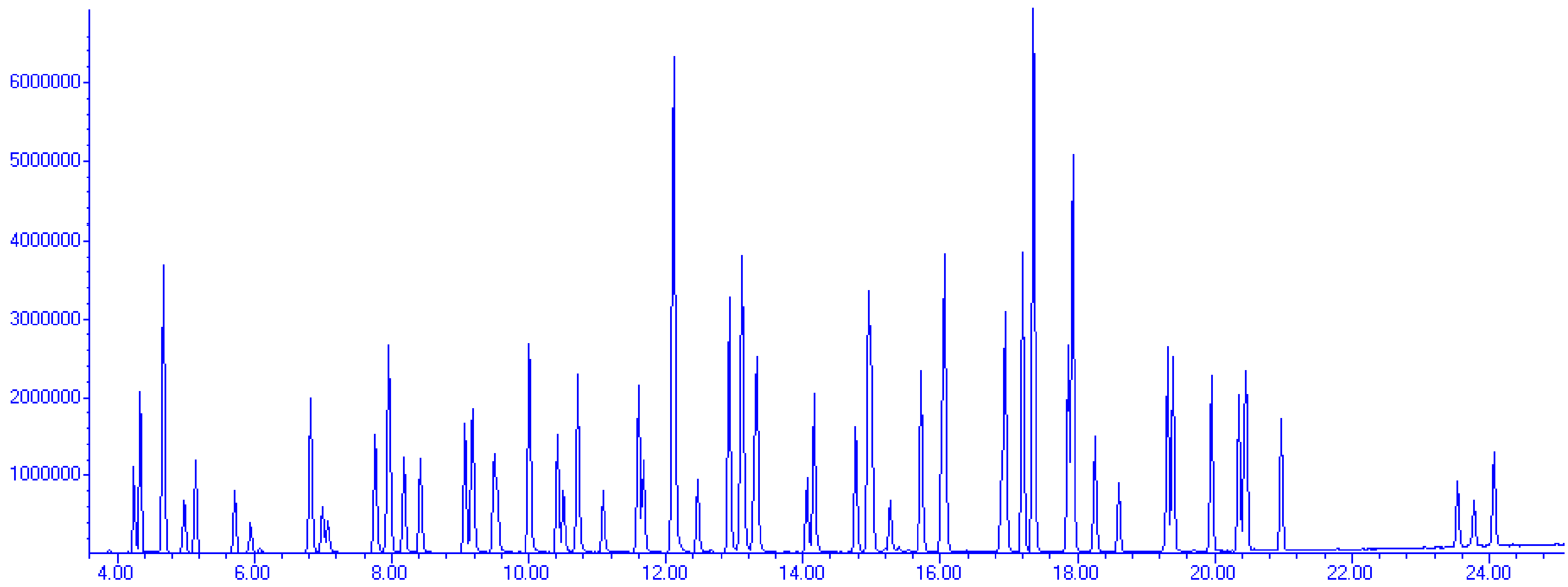
Nutech Pre-Concentrator Parameters

GC	
GC Remote Start	yes
GC Run Time	28 min.
Flush Sample Line	no
GC Ready	yes
GC Ready Timeout	10 min.

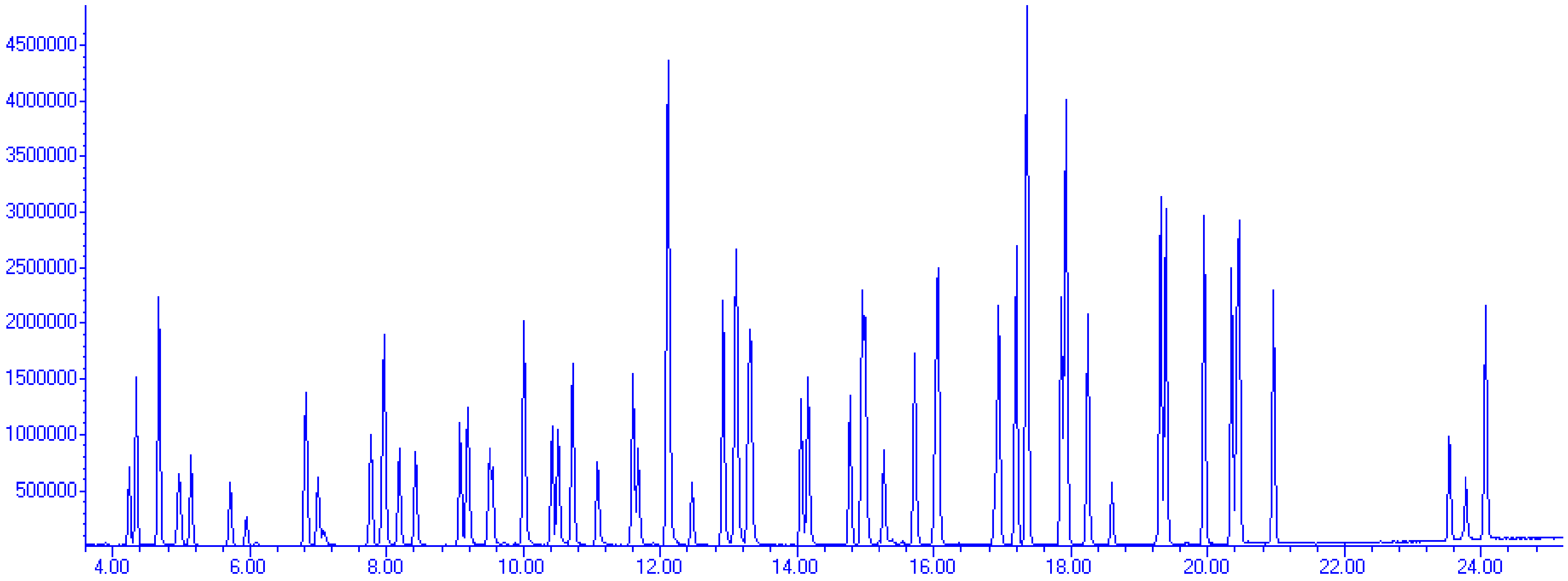
Injecting the Sample to the GC



20ppb TO-15 Dry Standard



20PPB TO-15 HUMID STANDARD



RESULTS

Compound	Dry Air Standards			Humid Air Standards		
	RF	Curve %RSD	MDL (2ppb)	RF	Curve %RSD	MDL (2ppb)
Propene	0.847	9.96	0.17	0.834	7.59	0.36
Dichlorodifluoromethane	2.595	10.15	0.12	2.628	6.58	0.33
Chloromethane	1.190	10.11	0.15	0.961	7.09	0.39
Vinyl Chloride	1.034	8.84	0.10	1.010	5.97	0.30
1,3-Butadiene	0.896	8.59	0.15	0.864	6.26	0.33
Bromomethane	0.874	9.52	0.10	0.840	6.30	0.37
Chloroethane	0.563	9.57	0.13	0.538	6.44	0.32
Ethanol	0.123	9.01	0.22	0.082	26.10	3.36
Trichlorofluoromethane	0.563	10.69	0.24	0.426	4.56	0.30
1,2-Dichlorotetrafluoroethane	2.605	10.72	0.14	2.005	5.05	0.31
1,1,2-trichlorofluoroethane	2.652	9.52	0.13	2.580	5.93	0.31
Acrolein	0.228	6.82	0.27	0.251	7.75	0.52
1,1-Dichloroethene	0.973	7.78	0.17	0.918	6.22	0.47
Acetone	1.154	10.13	0.51	1.592	10.80	0.46
2-propanol	0.848	4.67	0.13	0.606	23.79	0.48
Carbon Disulfide	2.943	9.25	0.10	2.773	5.25	0.26

RESULTS

Compound	Dry Air Standards			Humid Air Standards		
	RF	Curve %RSD	MDL (2ppb)	RF	Curve %RSD	MDL (2ppb)
Methylene Chloride	0.888	9.15	0.08	0.854	5.88	0.39
MTBE	2.786	9.21	0.08	2.907	5.31	0.39
cis-1,2-Dichloroethene	1.059	8.83	0.18	1.001	5.57	0.35
Vinyl Acetate	1.662	14.60	0.05	2.154	3.22	0.39
1,1-Dichloroethane	1.920	9.25	0.11	1.859	5.62	0.33
trans-1,2-Dichloroethene	1.085	9.82	0.14	1.013	5.29	0.38
Ethyl Acetate	0.214	6.72	0.21	0.391	4.62	0.52
2-Butanone	2.384	6.00	0.09	3.131	5.76	0.39
THF	0.823	13.47	0.15	1.184	5.44	0.51
Chloroform	2.157	8.44	0.12	2.127	5.02	0.28
1,1,1-Trichloroethane	2.262	9.05	0.11	2.215	4.75	0.30
Carbon Tetrachloride	2.224	8.62	0.11	2.105	5.32	0.31
Cyclohexane	1.821	8.49	0.10	1.700	5.06	0.36
Benzene	3.411	9.57	0.09	3.237	5.93	0.30
1,2-Dichloroethane	1.449	6.48	0.30	1.480	5.52	0.43
Heptane	0.519	8.95	0.10	0.503	4.33	0.24

Results

Compound	Dry Air Standards			Humid Air Standards		
	RF	Curve %RSD	MDL (2ppb)	RF	Curve %RSD	MDL (2ppb)
Trichloroethene	0.340	8.28	0.12	0.328	5.42	0.35
1,2-Dichloropropane	0.285	8.12	0.09	0.291	5.19	0.29
Methyl Methacrylate	0.136	8.74	0.24	0.266	7.50	0.23
1,4-Dioxane	0.069	7.62	0.17	0.067	14.39	0.32
Bromodichloromethane	0.545	7.41	0.12	0.569	5.21	0.21
cis-1,3-Dichloropropene	0.409	5.24	0.07	0.443	4.40	0.22
4-methyl-2-pentanone	0.263	8.07	0.17	0.542	11.81	0.26
Toluene	0.555	7.24	0.13	0.537	4.52	0.27
trans-1,3-Dichloropropene	0.294	10.00	0.05	0.380	4.44	0.28
1,1,2-Trichloroethane	0.274	7.29	0.08	0.301	5.23	0.24
Tetrachloroethene	0.322	7.43	0.12	0.291	5.18	0.24
Dibromochloromethane	0.462	6.89	0.10	0.489	5.77	0.21
2-Hexanone	0.183	13.60	0.18	0.358	15.23	0.27
1,2-Dibromoethane	0.371	8.71	0.10	0.422	5.24	0.20
Chlorobenzene	0.869	6.48	0.16	0.810	4.14	0.20
Ethylbenzene	1.443	5.03	0.16	1.426	4.49	0.26
Xylene (m+p)	1.085	6.57	0.17	1.119	3.99	0.61

RESULTS

Compound	Dry Air Standards			Humid Air Standards		
	RF	Curve %RSD	MDL (2ppb)	RF	Curve %RSD	MDL (2ppb)
Styrene	0.630	10.74	0.21	0.749	5.47	0.32
Xylene (o)	1.153	5.78	0.10	1.239	4.79	0.31
Bromoform	0.433	7.58	0.12	0.508	7.96	0.26
BFB SUR	0.520	10.01	N/A	0.635	2.27	N/A
1,1,2,2-Tetrachloroethane	0.421	7.67	0.21	0.695	10.67	0.21
1,3,5-Trimethylbenzene	0.945	8.69	0.18	1.392	8.77	0.24
1,2,4-Trimethylbenzene	0.703	7.48	0.16	1.110	12.22	0.22
4-Ethyl Benzene	0.779	8.11	0.22	1.179	9.75	0.29
Benzyl Chloride	0.486	7.18	0.09	0.942	7.59	0.12
1,3-Dichlorobenzene	0.432	5.93	0.19	0.648	9.74	0.21
1,4-Dichlorobenzene	0.431	6.70	0.10	0.643	10.89	0.19
1,2,-Dichlorobenzene	0.368	7.15	0.14	0.578	14.40	0.22
1,2,4-Trichlorobenzene	0.121	14.71	0.45	0.179	14.93	0.33
Naphthalene	0.209	19.16	0.20	0.310	18.10	0.67
Hexachlorobutadiene	0.114	11.27	0.16	0.205	21.87	0.19
Average	0.975	8.79	0.15	1.037	7.75	0.37

RESULTS

Compound	Dry Air Standards		Humid Air Standards	
	Precision (20ppb)	Accuracy (20ppb)	Precision (20ppb)	Accuracy (20ppb)
Propene	1.46	90.91	2.79	98.39
Dichlorodifluoromethane	1.71	90.60	1.98	103.19
Chloromethane	1.73	90.80	2.10	104.05
Vinyl Chloride	2.04	91.24	2.10	104.44
1,3-Butadiene	2.12	91.10	2.95	100.61
Bromomethane	2.15	90.49	2.30	103.21
Chloroethane	2.25	90.81	2.82	101.07
Ethanol	2.72	90.36	7.84	97.35
Trichlorofluoromethane	2.24	90.59	2.85	106.62
1,2-Dichlorotetrafluoroethane	1.98	91.09	2.59	106.74
1,1,2-trichlorofluoroethane	2.09	90.21	2.43	102.54
Acrolein	1.69	94.44	4.76	95.38
1,1-Dichloroethene	1.94	91.44	2.62	100.38
Acetone	0.90	92.14	3.09	115.56
2-propanol	2.53	91.61	6.39	70.68
Carbon Disulfide	1.93	89.92	2.11	102.77

RESULTS

Compound	Dry Air Standards		Humid Air Standards	
	Precision (20ppb)	Accuracy (20ppb)	Precision (20ppb)	Accuracy (20ppb)
Methylene Chloride	1.60	90.37	2.29	102.61
MTBE	1.64	100.74	2.82	100.97
cis-1,2-Dichloroethene	1.91	90.77	2.73	99.99
Vinyl Acetate	1.53	97.64	2.67	100.25
1,1-Dichloroethane	1.78	90.46	2.46	101.91
trans-1,2-Dichloroethene	1.90	90.03	2.50	101.99
Ethyl Acetate	2.13	88.22	3.62	103.57
2-Butanone	1.87	90.84	2.84	102.31
THF	1.31	94.63	3.26	99.31
Chloroform	2.06	90.91	2.24	103.78
1,1,1-Trichloroethane	1.76	90.68	2.33	103.34
Carbon Tetrachloride	1.93	90.48	2.16	103.84
Cyclohexane	1.97	91.29	2.72	100.02
Benzene	1.89	90.16	2.18	102.28
1,2-Dichloroethane	2.15	92.23	2.41	103.61
Heptane	1.32	90.79	2.26	105.84

RESULTS

Compound	Dry Air Standards		Humid Air Standards	
	Precision (20ppb)	Accuracy (20ppb)	Precision (20ppb)	Accuracy (20ppb)
Trichloroethene	1.44	90.99	2.23	105.64
1,2-Dichloropropane	1.69	91.43	2.60	108.79
Methyl Methacrylate	2.83	93.27	2.54	110.11
1,4-Dioxane	3.19	96.91	4.27	77.84
Bromodichloromethane	1.36	91.69	2.55	110.17
cis-1,3-Dichloropropene	1.40	95.58	2.38	108.79
4-methyl-2-pentanone	2.01	94.46	3.13	110.02
Toluene	1.42	91.89	2.15	106.56
trans-1,3-Dichloropropene	1.80	99.23	2.54	107.59
1,1,2-Trichloroethane	1.44	97.69	2.85	109.97
Tetrachloroethene	1.49	91.01	2.92	106.54
Dibromochloromethane	1.44	96.47	2.71	110.32
2-Hexanone	2.17	99.90	4.32	108.86
1,2-Dibromoethane	1.30	99.02	2.64	109.05
Chlorobenzene	1.24	87.07	1.34	106.59
Ethylbenzene	1.24	91.48	1.22	107.04
Xylene (m+p)	1.46	93.79	1.37	108.87

RESULTS

Compound	Dry Air Standards		Humid Air Standards	
	Precision (20ppb)	Accuracy (20ppb)	Precision (20ppb)	Accuracy (20ppb)
Styrene	1.94	93.19	2.34	111.40
Xylene (o)	1.66	93.54	2.45	112.71
Bromoform	1.92	92.97	2.91	115.01
BFB SUR	1.25	104.71	2.08	97.80
1,1,2,2-Tetrachloroethane	1.77	83.95	2.78	121.21
1,3,5-Trimethylbenzene	2.12	85.59	1.98	113.27
1,2,4-Trimethylbenzene	1.81	85.99	2.06	115.26
4-Ethyl Benzene	1.78	84.29	2.13	113.19
Benzyl Chloride	1.59	88.61	2.22	112.01
1,3-Dichlorobenzene	1.30	86.01	2.32	114.01
1,4-Dichlorobenzene	2.38	86.22	2.24	115.21
1,2,-Dichlorobenzene	1.62	87.49	2.31	118.05
1,2,4-Trichlorobenzene	2.38	95.88	7.28	108.46
Naphthalene	3.95	96.04	6.19	93.99
Hexachlorobutadiene	2.27	90.86	6.04	127.91
Average	1.86	91.96	2.88	105.48

CONCLUSIONS

- Both the dry and the humidified samples met or exceeded all the TO-15 method requirements
- The dry standard produced much lower MDL's than the humid standard
- The humid curve displayed much higher %RSDs over the curve range for the polar compounds due to the water reacting with the polar compounds

CONCLUSIONS

- The humid curve also had higher %RSDs for the heavier compounds due to the water inhibiting the heavier compounds from trapping/desorbing efficiently
- The average precision of the system at 20ppb was less than 5%RSD for both dry and humid standards

CONCLUSIONS

- The accuracy of the system at 20ppb resulted in 80 to 100% recoveries for all of the target compounds for the dry samples and between 70% and 130% for the humidified standards
- The humid calibration better represents real world samples and should be used in order to attain a more accuracy in sample results

Thank You . . . Questions

EST Analytical

Phone: 513-642-0100

Email: ajurek@estanalytical.com

Web: www.estanalytical.com