Optimizing Standard Preparation

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Abstract:

Standard preparation can often be a time consuming, tedious process. The opportunity for human error or inconsistencies between individual preparation techniques can inhibit curve linearity and/or continuing calibration reproducibility. This application note will explore water matrix standard preparation techniques for USEPA Method 8260b.

Discussion:

There have been many advances in purge and trap analysis in the past ten years. These improvements vary from water management to limiting the amount of sample carryover. However, in creating a more efficient concentrator, the ability of the concentrator to tol rate large amounts of methanol has become an issue. Environmental laboratories are required to write and follow standard operating procedures in order to prove that sample handling and analysis is consistent. Chief among these standard operating procedures is standard preparation. Since new purge and trap concentrators a e no longer able to handle larger amounts methanol, the procedures for standard preparation may need to be altered to accommodate the concentrator's limitations. This application note will explore how methanol affects curve linearity and compound response.

Experimental:

The sampling system used for this study was the EST Analytical Centurion WS autosampler and Encon Evolution concentrator. The experiments were run in water mode with a 5mL purge volume. Coupled to the sampling system were an Agilent 7890A GC and 5975 inert XL MS. The GC was configured with a Restek Rtx-624 20m x 0.180mm x 1.0µm column. Experi ental parameters for both the purge and trap and GC/MS are listed in Tables 1 and 2 respectively.

Purge and Trap Concentrator	EST Encon Evolution
Trap Type	Vocarb 3000
Valve Oven Temp.	130ºC
Transfer Line Temp.	130ºC
Trap Temp.	35ºC
Moisture Reduction Trap (MoRT) Temp.	39ºC
Purge Time	11 min.
Purge Flow	40mL/min
Dry Purge Temp.	ambient
Dry Purge Flow	40mL/min
Dry Purge Time	1.0 min.
Desorb Pressure Control	On
Desorb Pressure	12psi
Desorb Time	1.0 min.
Desorb Temp.	260ºC
Moisture Reduction Trap (MoRT) Bake Temp.	230ºC
Bake Temp	260ºC
Sparge Vessel Bake Temp.	110ºC
Bake Time	8
Bake Flow	40mL/min
Purge and Trap Auto-Sampler	**EST Centurion WS**
Sample Size	5mL
Internal Standard Volume	5µL

Table 1: Purge and Trap Parameters

GC/MS	Agilent 7890A/5975 inert XL
Inlet	Split/Splitless
Inlet Temp.	200ºC
Inlet Head Pressure	20.198 psi
Mode	Split
Split Ratio	40:1
Column	Rtx-624 20m x 0.18mm I.D. 1µm film thickness
Oven Temp. Program	45ºC hold for 1 min., ramp 18ºC/min to 220ºC, hold for 0.3 min., 11.02 min. runtime
Column Flow Rate	0.8mL/min
Gas	Helium
Total Flow	35.8mL/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 35-265
Scans	3.12 scans/sec
Solvent Delay	0.7 min

Table 2: GC/MS Parameters

The USEPA Method 8260b standards were purchased from Restek. The compound concentration was 2000µg/ml for all of the analytes with the exception of tert-butyl alcohol which was at 10,000µg/ml and p&m-xylene which was at 4000µg/ml. The percent methanol in the standards was calculated using the 200ppb calibration standard as a reference due to the fact that the maximum amount of methanol was in this standard. These calculations are displayed in Table 3. Standards were prepared at two different concentrations in order to minimize the percent methanol differences seen when preparing a curve. Refer to Table 4 for standard concentrations.

%Methanol Calculation						
Methanol in 200ppb Cal Standard	1µl/ml	2µl/ml	5µl/ml	10µl/ml	20µl/ml	0µl/ml
IS Methanol	1µl/ml	1µl/ml	1µl/ml	1µl/ml	1µl/ml	1µl/ml
Size Sample	5ml	5ml	5ml	5ml	5ml	5ml
Standard and IS Methanol	10µl/5ml	15µl/5ml	30µl/5ml	55µl/5ml	105µl/5ml	255µl/5ml
%Methanol in Purged Sample	0.2%	0.3%	0.6%	1.1%	2.1%	5.1%

Table 3: Percent Methanol Calculation

Standard Preparation						
Standard Concentrations	0.2% Methanol	0.3% Methanol	0.6% Methanol	1.1% Methanol	2.1% Methanol	5.1% Methanol
0.5ppb to 10ppb cal. standards	20ppm	10ppm	4ppm	2ppm	1ppm	400ppb
20ppb to 200ppb cal. standards	200ppm	100ppm	40ppm	20ppm	10ppm	4ppm

*%Methanol includes the added methanol from the internal standard

Table 4: Stock Standard Preparation for Calibration Curves

A nine point calibration curve was prepared and run for each percent methanol level. The calibration curve preparation is presented in Table 5. A range of 0.5 to 200ppb was used to establish the curve and Agilent Chemstation software was employed to ascertain the linear calibration of the analytes. The analytes were also examined to establish compound response versus percent methanol in the standards; these results are listed in Table 6. The 5.1% methanol results were excluded from the results table due to the fact that all of the compounds needed to be linear regressed and still the results were not linear to 200ppb.

Calibration Curve Preparation						
Calibration Standard Concentration	0.2% Methanol	0.3% Methanol	0.6% Methanol	1.1% Methanol	2.1% Methanol	5.1% Methanol
0.5ppb	2.5µl 20ppm std.	5µl 10ppm std.	12.5µl 4ppm std.	25µl 2ppm std.	50µl 1ppm std.	125µl 400ppb std.
1ppb	5µl 20ppm std.	10µl 10ppm std.	25µl 4ppm std.	50µl 2ppm std.	100µl 1ppm std.	250µl 400ppb std.
2ppb	10µl 20ppm std.	20µl 10ppm std.	50µl 4ppm std.	100µl 2ppm std.	200µl 1ppm std.	500µl 4ppb std.
5ppb	25µl 20ppm std.	50µl 10ppm std.	125µl 4ppm std.	250µl 2ppm std.	500µl 1ppm std.	1.25ml 4ppb std.
10ppb	50µl 20ppm std.	100µl 10ppm std.	250µl 4ppm std.	500µl 2ppm std.	1ml 1ppm std.	2.50ml 4ppb std.
20ppb	10µl 200ppm std.	20µl 100ppm std.	50µl 40ppm std.	100µl 20ppm std.	200µl 10ppm std.	500µl 4ppm std.
50ppb	25µl 200ppm std.	50µl 100ppm std.	125µl 40ppm std.	250µl 20ppm std.	500µl 10ppm std.	1.25ml 4ppm std.
100ppb	50µl 200ppm std.	100µl 100ppm std.	250µl 40ppm std.	500µl 20ppm std.	1ml 10ppm std.	2.50ml 4ppm std.
200ppb	100µl 200ppm std.	200µl 100ppm std.	500µl 40ppm std.	1ml 20ppm std.	2ml 10ppm std.	5.00ml 4ppm std.

* All standards diluted in De-ionized water into a 100ml volumetric flask.

Table 5: Calibration Curve Preparation

Compound	0.2% Methanol		0.3% Methanol		0.6% Methanol		1.1% Methanol		2.1% Methanol	
	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF
Dichlorodifluoromethane	6.10	0.597	6.76	0.440	4.77	0.368	11.00	0.197	11.54	0.255
Chloromethane	9.88	0.626	4.89	0.456	4.10	0.426	11.74	0.245	9.76	0.289
Vinyl Chloride	7.23	0.578	3.08	0.428	3.26	0.408	7.99	0.239	7.55	0.266
Bromomethane	8.64	0.313	4.26	0.233	12.02	0.247	11.75	0.145	0.995*	0.143
Chloroethane	8.20	0.353	5.83	0.267	3.66	0.265	7.74	0.160	8.13	0.166
Trichlorofluoromethane	2.88	0.837	4.18	0.636	4.57	0.625	5.36	0.378	6.62	0.389
diethyl ether	3.68	0.416	3.81	0.323	5.24	0.331	5.42	0.194	2.84	0.202
1,1,2-trichlorofluoroethane	5.71	0.495	4.09	0.379	5.05	0.383	8.96	0.225	6.74	0.227
1,1-Dichloroethene	5.42	0.449	3.52	0.347	3.48	0.350	4.61	0.204	6.84	0.215
Acetone	11.10	0.192	7.07	0.127	14.52	0.165	11.53	0.092	0.995*	0.402
Iodomethane	13.31	0.427	9.38	0.370	10.79	0.365	7.56	0.211	15.04	0.202
Carbon Disulfide	10.55	1.248	5.69	0.934	8.69	0.919	6.70	0.512	12.70	0.556
Carbon Disulfide	4.56	0.774	8.22	0.577	6.58	0.597	4.71	0.348	7.39	0.361
Methylene Chloride	8.72	0.500	7.83	0.386	6.04	0.387	9.75	0.237	12.90	0.246
acetonitrile	8.65	0.062	9.02	0.035	13.64	0.041	7.54	0.026	9.08	0.031
Tert Butyl Alcohol	9.01	0.066	14.90	0.030	12.82	0.045	13.76	0.022	0.998*	0.038
MTBE	3.75	1.623	1.72	1.218	2.81	1.266	3.56	0.745	2.99	0.764
cis-1,2-Dichloroethene	5.43	0.499	4.86	0.388	3.19	0.384	9.17	0.236	10.65	0.246
acrylonitrile	12.01	0.224	10.17	0.176	9.56	0.197	9.54	0.110	6.28	0.116
Isopropylether	7.23	1.774	4.14	1.293	4.49	1.344	4.86	0.791	4.89	0.797
Vinyl acetate	8.71	1.283	4.24	1.000	2.81	1.060	9.25	0.616	7.18	0.576
1,1-Dichloroethane	5.05	1.012	3.18	0.738	2.73	0.764	4.85	0.447	5.70	0.460
Ethyl Tert Butyl Ether (ETBE)	2.60	1.813	2.28	1.310	3.49	1.340	2.68	0.805	2.45	0.818
trans-1,2-Dichloroethene	7.80	0.594	3.21	0.440	2.82	0.442	7.60	0.275	7.15	0.284
ethyl acetate	10.66	0.104	9.96	0.077	11.82	0.090	8.21	0.050	11.27	0.053
2-Butanone	10.01	1.039	10.48	0.790	8.71	0.907	13.64	0.535	0.998*	1.053
2,2-Dichloropropane	3.83	0.859	2.54	0.635	2.84	0.629	9.12	0.354	5.36	0.324
Bromochloromethane	5.99	0.355	5.10	0.257	2.09	0.262	5.30	0.161	9.51	0.172
propionitrile	12.27	0.096	14.39	0.067	11.56	0.075	11.03	0.040	6.37	0.042
methacrylonitrile	12.14	0.567	13.52	0.439	12.52	0.484	10.01	0.280	8.07	0.284
THF	7.66	0.227	11.59	0.171	6.94	0.195	8.92	0.110	13.30	0.116
Chloroform	7.61	1.055	13.75	0.831	7.37	0.812	9.59	0.497	9.83	0.504
methyl acrylate	8.24	0.628	5.41	0.480	5.15	0.518	4.49	0.294	5.29	0.313
Dibromofluoromethane SUR	5.67	0.537	13.58	0.434	7.47	0.418	14.23	0.272	14.00	0.277
1,1,1-Trichloroethane	2.66	0.926	2.48	0.704	3.27	0.704	3.47	0.430	5.34	0.433
2-Chloroethylvinylether	4.87	0.409	3.74	0.319	4.08	0.330	7.86	0.195	4.36	0.208
Carbon Tetrachloride	8.34	0.707	13.76	0.521	13.79	0.526	10.18	0.320	10.58	0.328
1,1-Dichloropropene	2.47	0.818	2.43	0.617	2.22	0.618	4.69	0.382	6.95	0.392
methyl acetate	4.59	1.892	2.75	1.424	2.49	1.515	2.73	0.911	3.35	0.915
isobutyl alcohol	10.38	0.031	0.998*	0.014	0.998*	0.021	8.15	0.009	14.64	0.010
Tert Amyl Methyl Ether	2.89	1.771	2.74	1.291	3.54	1.334	3.57	0.817	3.85	0.825
Benzene	3.84	2.330	2.52	1.716	2.33	1.751	1.99	1.066	4.92	1.109
1,2-Dichloroethane	3.23	0.826	2.28	0.620	1.89	0.636	4.85	0.394	9.43	0.414
propyl acetate	9.17	0.630	4.39	0.451	3.82	0.513	5.97	0.316	4.19	0.309
Trichloroethene	6.06	0.378	2.40	0.265	2.82	0.282	3.04	0.178	6.65	0.181
1,2-Dichloropropane	3.01	0.354	4.57	0.247	3.08	0.261	2.97	0.164	3.8	0.161
methyl methacrylate	5.77	0.302	3.50	0.223	3.34	0.243	6.18	0.150	6.42	0.153
Dibromomethane	6.12	0.213	2.70	0.157	3.96	0.168	3.82	0.105	5.31	0.108
Bromodichloromethane	4.28	0.281	1.98	0.200	4.62	0.217	4.05	0.135	3.93	0.130
2-chloroethanol	7.67	0.154	7.48	0.113	7.09	0.118	13.25	0.078	8.51	0.074
2-nitropropane	6.00	0.144	11.49	0.104	10.58	0.117	7.52	0.064	11.15	0.062

Compound	0.2% Methanol		0.3% Methanol		0.6% Methanol		1.1% Methanol		2.1% Methanol	
	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF	Curve %RSD	Ave. Curve RF
cis-1,3-Dichloropropene	3.13	0.581	2.53	0.406	4.66	0.419	5.07	0.262	6.75	0.253
4-methyl-2-pentanone	6.49	0.432	5.00	0.300	5.24	0.353	4.83	0.213	7.31	0.213
Toluene-d8 SUR	3.41	1.292	3.33	0.895	4.63	0.942	2.47	0.623	5.23	0.611
Toluene	3.80	0.899	2.70	0.639	2.54	0.679	2.97	0.435	4.96	0.426
ethyl methacrylate	4.01	0.542	5.75	0.384	4.36	0.421	5.69	0.261	5.99	0.251
trans-1,3-Dichloropropene	4.61	0.565	6.16	0.383	5.76	0.404	6.96	0.249	8.28	0.244
1,1,2-Trichloroethane	3.29	0.322	2.88	0.232	2.40	0.246	3.74	0.158	5.36	0.154
Tetrachloroethene	6.73	0.357	6.97	0.231	8.96	0.243	9.42	0.160	4.67	0.143
1,3-Dichloropropane	2.93	0.569	2.09	0.408	2.91	0.430	1.98	0.278	3.97	0.274
isopropyl acetate	6.50	0.097	1.69	0.071	10.40	0.077	8.93	0.049	6.58	0.046
butyl acetate	4.48	0.279	4.18	0.198	2.92	0.221	6.21	0.137	4.98	0.130
Dibromochloromethane	6.27	0.358	8.32	0.249	9.40	0.265	11.76	0.163	13.39	0.157
2-Hexanone	5.04	0.307	8.80	0.220	7.11	0.263	5.05	0.153	10.98	0.156
1,2-Dibromoethane	5.30	0.331	2.72	0.240	2.49	0.258	2.92	0.163	4.73	0.161
Chlorobenzene	5.66	1.118	1.78	0.738	3.79	0.744	6.39	0.555	8.40	0.539
1,1,1,2-Tetrachloroethane	3.89	0.376	6.68	0.250	6.69	0.248	7.26	0.178	9.29	0.169
Ethylbenzene	3.75	1.964	2.54	1.322	2.38	1.323	2.55	0.963	4.32	0.931
Xylene (m+p)	4.02	3.096	3.23	1.027	2.56	1.027	3.02	0.756	4.88	0.734
Styrene	5.03	1.242	3.59	0.829	4.48	0.818	4.47	0.592	5.25	0.579
Xylene (o)	4.32	1.566	3.38	1.035	2.02	1.036	2.96	0.757	3.52	0.722
n-amyl acetate	3.70	0.850	2.24	0.567	3.75	0.588	6.81	0.408	7.01	0.367
Bromoform	8.78	0.273	11.04	0.186	13.72	0.184	14.76	0.129	14.61	0.117
Isopropylbenzene	5.01	1.945	3.8	1.292	4.19	1.279	3.16	0.933	4.22	0.899
cis-1,4-dichloro-2-butene	8.18	0.189	12.37	0.126	12.50	0.127	0.999*	0.081	0.997*	0.076
BFB SUR	10.69	1.051	4.73	0.667	7.01	0.631	10.72	0.528	14.71	0.509
Bromobenzene	5.97	1.379	3.43	0.880	5.06	0.846	4.64	0.664	9.88	0.657
1,2,3-Trichloropropane	3.57	1.183	4.66	0.785	4.03	0.779	6.86	0.581	4.59	0.556
1,1,2,2-Tetrachloroethane	6.44	0.909	3.72	0.617	3.38	0.603	4.5	0.462	3.39	0.446
n-Propylbenzene	3.05	4.183	2.02	2.707	2.54	2.551	2.99	2.033	4.21	1.940
trans-1,4-dichloro-2-butene	6.87	0.327	5.76	0.221	6.54	0.225	6.55	0.158	5.10	0.143
2-Chlorotoluene	4.22	0.788	2.12	0.514	3.51	0.487	2.57	0.386	5.77	0.374
4-Chlorotoluene	4.54	0.824	1.79	0.535	2.77	0.509	3.38	0.406	10.01	0.402
1,3,5-Trimethylbenzene	2.70	2.832	2.95	1.805	3.07	1.717	3.34	1.352	3.99	1.305
tert-Butylbenzene	2.80	2.430	2.63	1.558	2.96	1.475	3.02	1.176	4.67	1.130
pentachloroethane	9.48	0.360	8.07	0.285	6.74	0.272	0.997*	0.199	9.08	0.216
sec-Butylbenzene	3.27	0.732	3.76	0.469	2.42	0.449	2.98	0.352	7.23	0.339
1,2,4-Trimethylbenzene	4.20	2.917	2.97	1.865	2.76	1.778	2.92	1.395	4.56	1.349
nitrobenzene	8.91	0.077	11.32	0.029	14.98	0.031	0.997*	0.016	14.74	0.015
1,3-Dichlorobenzene	5.52	1.558	2.32	1.018	2.89	0.947	5.94	0.764	13.10	0.771
1,4-Dichlorobenzene	8.12	1.620	5.59	1.072	9.00	1.019	11.54	0.818	7.56	0.768
Isopropyltoluene	3.75	3.001	4.36	1.915	4.46	1.818	3.89	1.437	5.63	1.375
1,2,-Dichlorobenzene	4.87	1.510	1.845	0.992	3.38	0.930	4.16	0.739	7.02	0.719
n-Butylbenzene	4.31	2.643	3.83	1.722	4.10	1.618	6.08	1.257	7.05	1.225
1,2-Dibromo-3-chloropropane	8.86	0.204	7.93	0.135	7.02	0.135	10.46	0.096	7.87	0.091
1,2,4-Trichlorobenzene	4.50	0.945	3.02	0.633	8.22	0.608	4.12	0.458	12.11	0.465
Naphthalene	8.98	3.167	4.73	2.097	2.22	2.056	5.48	1.528	5.75	1.499
Hexachlorobutadiene	5.07	0.334	11.38	0.237	5.40	0.211	7.45	0.161	14.66	0.170
1,2,3-Trichlorobenzene	7.84	0.903	2.55	0.600	4.15	0.570	4.21	0.428	8.93	0.437
Average	6.15	0.907	5.40	0.619	5.60	0.619	6.50	0.422	7.52	0.427

*Linear Regression Value

Table 6: Data Summary

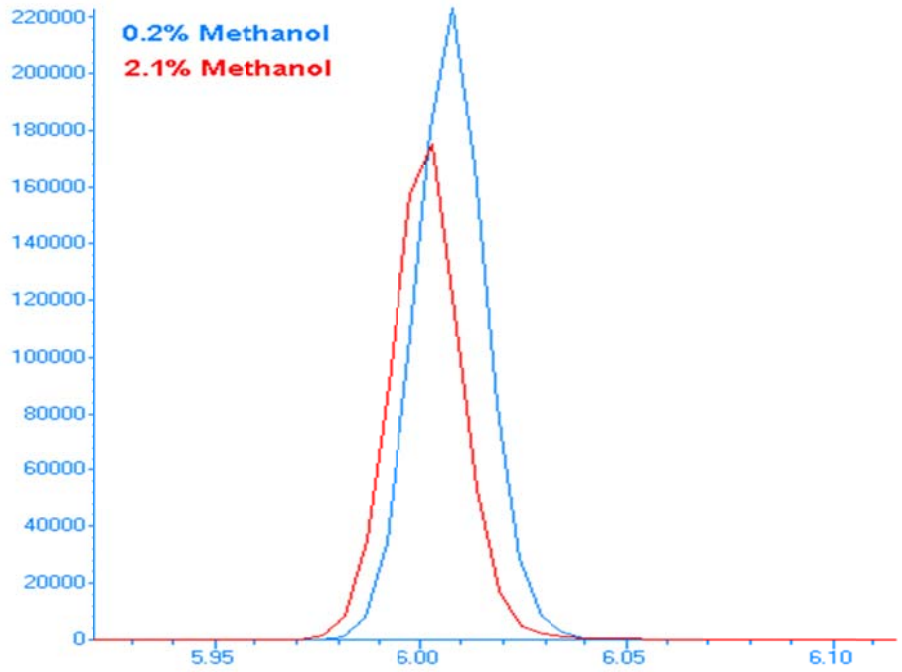

Figure 1: Overlay of Bromoform Response Ion 173 (Blue plot 0.2% Methanol, Red plot 2.1% Methanol)

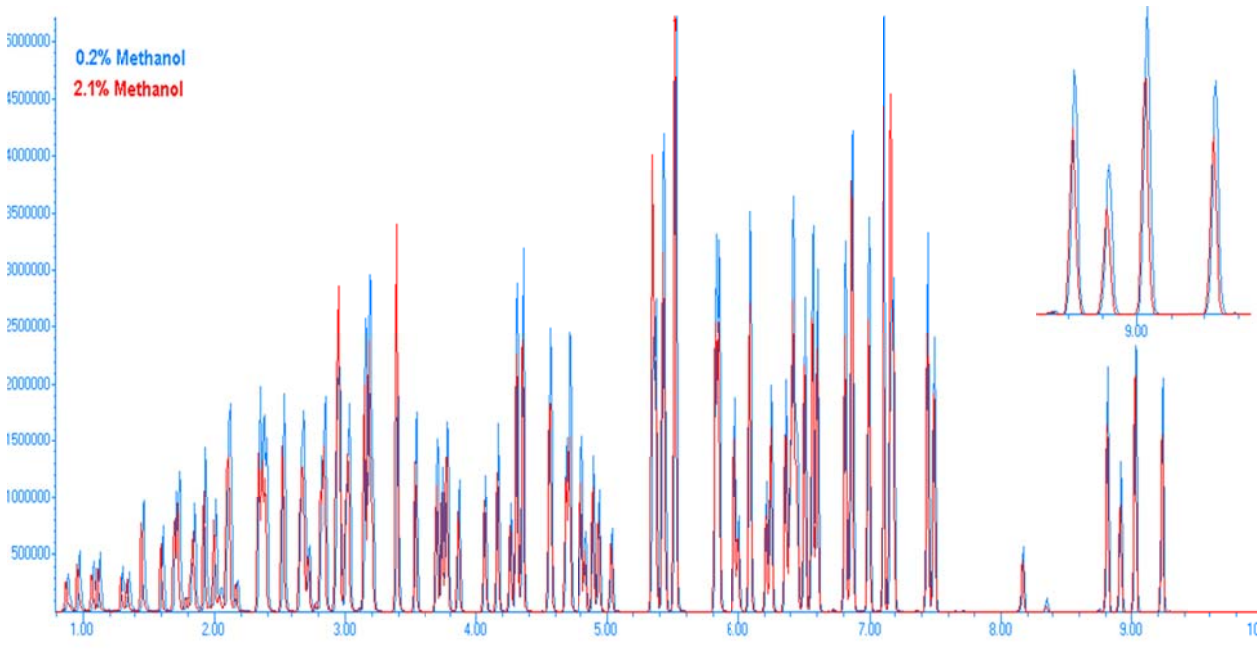

Figure 2: Overlay of 50ppb Standard Chromatograms with 0.2% (Blue) and 2.1% (Red) Methanol

Conclusion:

The Encon Evolution proved to be an excellent system for handling large amounts of methanol. Compound responses passed for all of the SPCC compounds up to 2.1% methanol, but the Bromoform response decreased dramatically with the increased percent of methanol in the standards. Curve linearity was consistent through the study up to 2.1% methanol; however at 5.1% methanol linearity could not be achieved. Overall, 5.1% methanol in the standards was too much for the system to handle and the recommendation would be to introduce less than 2% methanol for better results. It should be noted that the lower the methanol volume in the calibration standards produced the optimum compound responses. (For a standard preparation illustration with 0.2% methanol refer to Appendix A.)

Appendix A

Standard and Curve Preparation Illustration for 0.2% Methanol

To Make an 8260 Standard at 200ppm Diluted in P&T Methanol				
Amount	**Restek Part #**	**Standard**	**Concentration**	**Final Vol.**
200µl	30265	2-Cleve	2.0mg/ml	2.0ml
200µl	30633	Cal Mix #1	2.0mg/ml	2.0ml
200µl	30042	502.2 Cal Mix #1	2.0mg/ml	2.0ml
200µl	30489	Acetates	2.0mg/ml	2.0ml
200µl	30465	Cal Oxy	2.0-10.0mg/ml	2.0ml
200µl	30287	1,4-Dioxane	2.0mg/ml	2.0ml
160µl	30073	Surr. Mix	2.5mg/ml	2.0ml
80µl	30006	VOA Cal Mix #1	5.0mg/ml	2.0ml

Use 2ml volumetric flask and dilute standards to 2.0ml in purge and trap methanol

To Make a 10x Dilution of the 8260 Standard (From 200ppm to 20ppm) Diluted in P&T Methanol

200µl of 200ppm standard diluted to 2.0ml in purge and trap methanol

To Make an 8260 Internal Standard at 50ppm Diluted in P&T Methanol				
Amount	**Restek Part #**	**Standard**	**Concentration**	**Final Vol.**
125µl	30074	8260IS	2.0mg/ml	5.0ml

Use 5ml volumetric flask and dilute standards to 5.0ml in purge and trap methanol

Note: Restek Standards used for this Standard Preparation example. Standard choices and concentrations are dependent on Customer needs.

To Prepare an 8260 Curve Diluted in De-ionized/UV Treated Water			
Concentration	**Standard**	**Standard Amount**	**Final Vol.**
0.5ppb	20ppm	2.5µl	100ml
1ppb	20ppm	5µl	100ml
2ppb	20ppm	10µl	100ml
5ppb	20ppm	25µl	100ml
10ppb	20ppm	50µl	100ml
20ppb	200ppm	10µl	100ml
50ppb	200ppm	25µl	100ml
100ppb	200ppm	50µl	100ml
200ppb	200ppm	100µl	100ml

Water Standards

Fill 40ml Vial with final standard leaving no headspace in the vial.

Soil Standards

Add 5ml of final standard to a 40ml vial.

With courtesy of

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