Utilizing High Efficiency Electron Ionization and MS/MS to Reduce Injection Volumes and Sample Extract Volumes for EPA 8270

Matthew Curtis[1]; Fred Feyerherm[3]; Dale Walker[3]; Ron Honnold[2]

ASMS 2015
Poster #Th

Introduction

The goal of this project is to show the applicability of EI GC/MS/MS measurement for the detection of EPA 8270 analytes using a fast low maintenance interval method. EPA method 8270 is the primary semivolatile organic carbon (SVOC) analysis for multiple types of matrices including soil and water. Due to the high concentrations injected and number of target analytes in this mixture; column degradation, inlet contamination, and ion source contamination may occur causing significant instrument down time. In addition, the sample preparation requires large amounts of solvent for sample extraction and large sample volumes that need to be shipped, which is costly for large labs running this method routinely.

During the 2015 Pittsburg Conference the EPA announced that a tandem-quadrupole mass spectrometer could be used for EPA method 8270 which will be revision E. Due to the use of MS/MS transitions for analysis, DFTPP spectrum analysis will not be necessary, but a document of performance from both MSs will be required. This is based on the specification by the manufacture using the internal calibration compound. This document will include mass resolution, mass assignment, and sensitivity; and performed weekly at minimal.

Materials and Method:

The analyte solution, internal standard solution and surrogate solution were all purchased from AccuStandard, Inc (New Haven, CT). The surrogate solution was spiked into the analyte solution prior to serial dilution with dichloromethane. 1:2 serial dilutions were performed from 100 pg µL^{-1} down to 0.1 pg µL^{-1}.

The analytes, surrogates and internal standard compounds were sent to the Agilent MRM Transition Database and three transitions were selected and applied to this method. For compounds not currently in the Agilent MRM Transitions Database the transitions were developed following these set of steps. Individual SRM transitions were developed by acquiring a full scan data file will all of the analytes to select the best candidates for precursor ions. Product ion anlyses were performed at two different collision energies, to select the optimal product ions. After the transitions were identified the collision energy was optimized for each individual transition per compound.

The GC run time is 15 min. with a cool down/equilibration time of ~4 min. to give a total

Experimental

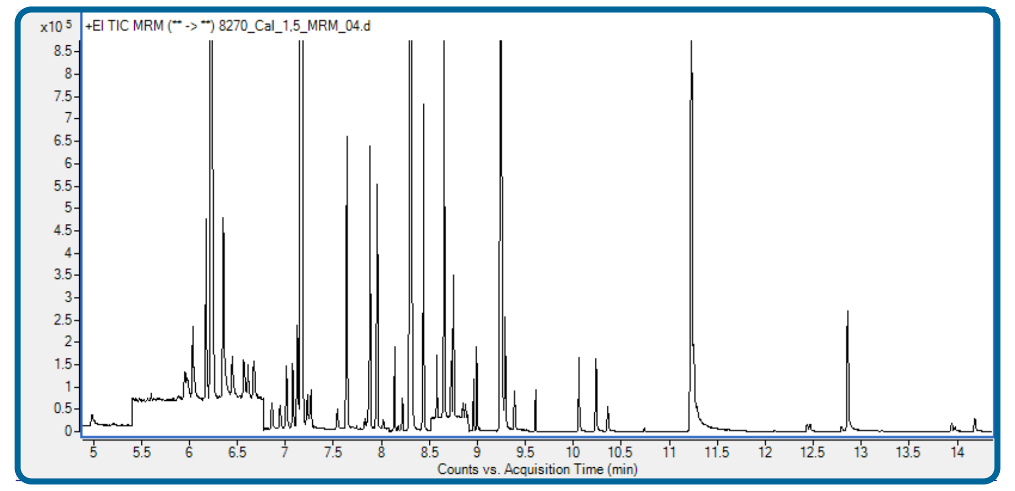

Figure 1. RTIC for the 1.5 pg µL^{-1} sample with analytes, ISTDs and surrogates. The five most intense peaks are the ISTDs, which were cut-off to show the analyte responses.

Instrument:

All of the data created for this study was acquired on and Agilent 7890A GC coupled to the Agilent 7010 tandem-quadrupole mass spectrometer. The Agilent 7010 has the high efficiency ion source that increases the ion current exiting the source to provide more ions into analyzer to allow more ions to be detected. The 7010 includes two gold-plated quatrz quadrupoles and a hexapole collision-cell.

GC and MS Parameters:		
Column	DB-5MS UI, 20m, 0.18 mm ID, 0.18 µm film	
Injection volume	1.0 µL	4mm single taper, UI liner
Pulsed-Splitless mode	40 psi	For 0.5 min
	Purge flow to split vent	100 mL/min at 0.5 min
S/SL inlet temperature	250 °C	
Oven temperature program	40 °C for 2.5 min	
	10 °C/min to 60 °C, for 0 min	
	40 °C/min to 260 °C, for 0 min	
	5 °C/min to 270 °C, for 0 min	
	20 °C/min to 320 °C, for 1 min	
Carrier gas	Helium at 0.8 mL/min for 10 min	
	then 1.5 mL/min	
Transfer line temperature	300 °C	
Ionization mode	Electron Ionization	
Source temperature	350°C	
Quadrupole temperatures	150°C for both	
Acquisition type	MRM	
Collision Gas	Nitrogen at 1.5 mL min^{-1}	
	Helium at 4 ml min^{-1}	
Electron Energy	-70 eV	
Ionization parameters used in the method		
High Sensitivity Ion Source		

Results and Discussion

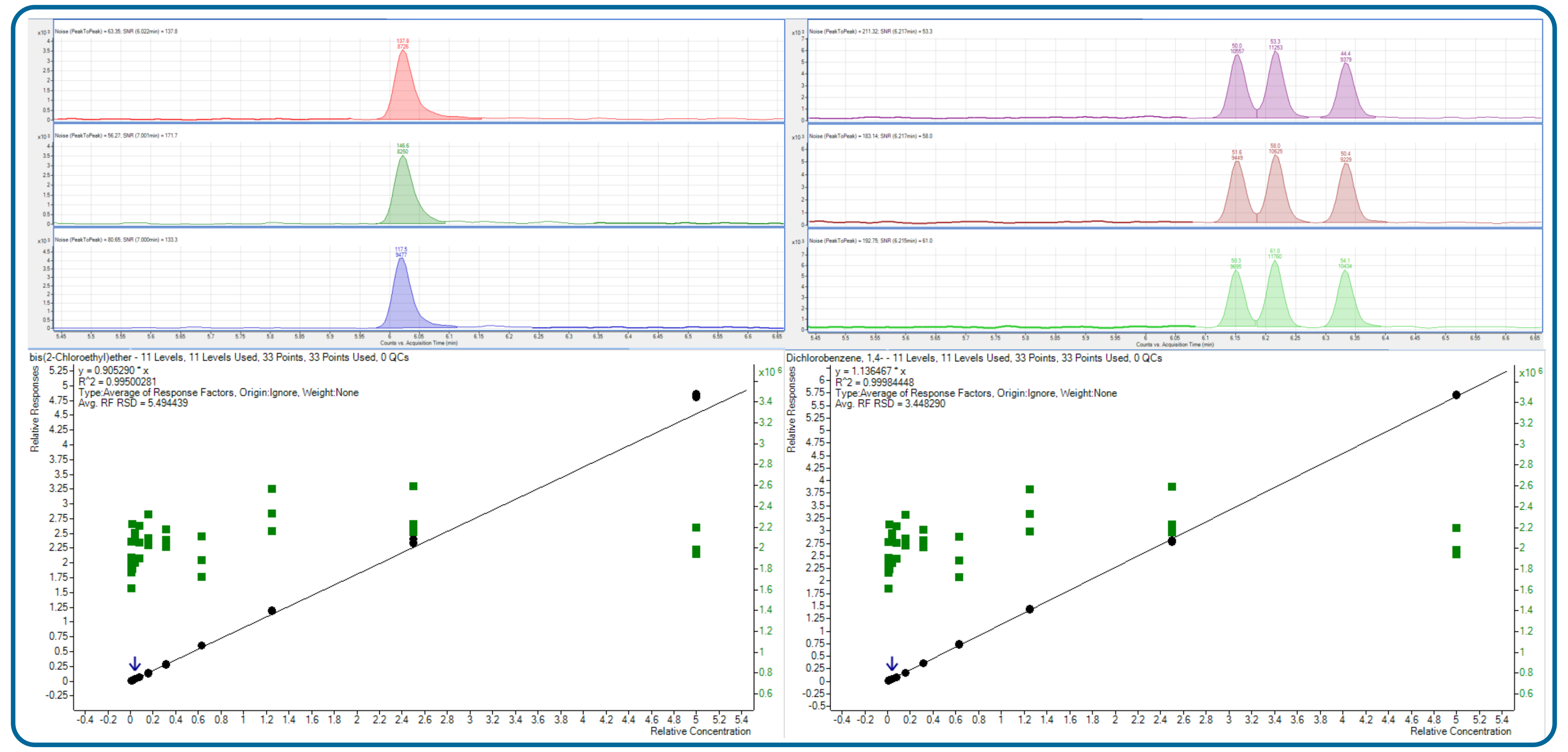

Figure 2. The left chromatogram is produced from 3 reps. of Bis(2-chloroethyl)ether at 0.1 pg µL^{-1}. The chromatogram on the right was produced from 3 reps. of the 3 dichlorobenzenes in the solution at 0.1 pg µL^{-1}. The chromatogram labels include the signal-to-noise on-top and the area below. Each calibration is from 0.1 pg µL^{-1} to 100 pg µL^{-1}, and include the ISTD responses (green squares). The curve is calculated with "Average of Response Factors."

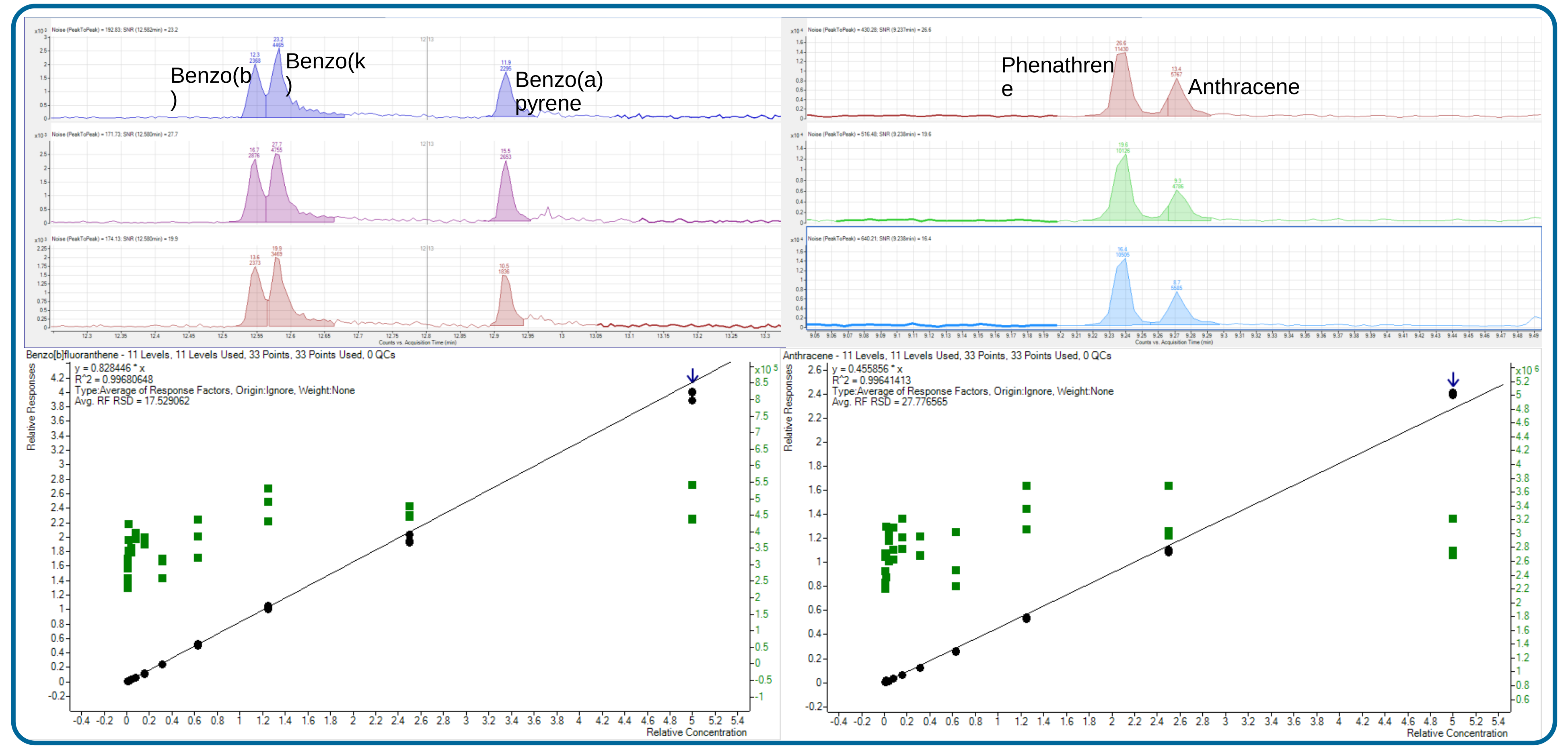

Figure 3. The left chromatogram is produced from 3 reps. of benzo(b) and benzo(k) fluoranthrene at 0.2 pg µL^{-1}. The chromatogram on the right was produced from 3 reps. of phenanthrene and anthracene at 0.1 pg µL^{-1}. The chromatogram labels include the signal-to-noise on-top and the area below. Each calibration is from 0.1 pg µL^{-1} to 100 pg µL^{-1}, and include the ISTD responses (green squares). The curve is calculated with "Average of Response Factors."

Results and Discussion

Table 1. This table was created with 10 replicates of 10 pg µL^{-1} for all analytes. The MDLs, LOQs, and LODs were calculate at the 95% confidence level. The quantifier transition was used to calculate the values below.

Name	RT	Avg Conc.	Std. Dev.	Avg Conc./Std. Dev.	Conc. RSD	MDL	LOQ	LOD	Avg Height	Avg. Resp	Resp. RSD
Phenol, 2-fluoro-	4.89	10.0703	0.2021	49.83	2	0.6352	2.0211	0.6063	128470	226121	5.9
Phenol-d5	5.916	11.3828	0.2223	51.2	2	0.6986	2.2231	0.6669	172853	170946	5.1
Phenol	5.926	10.2847	0.2143	48	2.1	0.6733	2.1426	0.6428	161570	192204	7.1
Aniline	5.93	12.1613	0.5546	21.93	4.6	1.7429	5.5459	1.6638	207179	268039	3.8
bis(2-Chloroethyl)ether	6.006	10.7991	0.0899	120.09	0.8	0.2826	0.8993	0.2698	993182	829590	5.9
Chlorophenol, 2-	6.013	11.0545	0.3094	35.73	2.8	0.9722	3.0936	0.9281	109712	107208	6.8
Dichlorobenzene, 1,3-	6.14	10.719	0.0379	282.8	0.4	0.1191	0.379	0.1137	1349543	1026662	6.2
Dichlorobenzene, 1,4-	6.21	10.5228	0.1109	94.92	1.1	0.3484	1.1085	0.3326	1296281	1015185	6.7
Dichlorobenzene, 1,2-	6.32	10.7349	0.0795	134.97	0.7	0.2499	0.7953	0.2386	1287541	1050684	6
Benzyl alcohol	6.335	10.8768	0.6008	18.1	5.5	1.888	6.0078	1.8023	113138	144658	10.5
Methylphenol, 2- (Cresol, o-)	6.423	11.0513	0.5562	19.87	5	1.7479	5.5617	1.6685	196269	204109	4.5
Methylphenol, 4- (Cresol, p-)	6.54	11.8485	0.6728	17.61	5.7	2.1144	6.7281	2.0184	201094	221416	6.8
Nitrosodi-n-propylamine, N-	6.54	10.5232	0.609	17.28	5.8	1.9138	6.0896	1.8269	10599	9735	7.2
Hexachloroethane	6.58	11.3446	0.8666	13.09	7.6	2.7236	8.6665	2.5999	318305	251612	11.1
Nitrobenzene-D5	6.64	11.1243	0.5363	20.74	4.8	1.6854	5.3631	1.6089	44545	42286	9.1
bis(2-Chloro-1-methylethyl)ether	6.65	10.489	0.1759	59.62	1.7	0.5529	1.7593	0.5278	19456	27328	6.8
Nitrobenzene	6.65	11.5138	0.3953	29.13	3.4	1.2423	3.9531	1.1859	152606	143690	8.1
Isophorone	6.83	12.247	0.3601	34.01	2.9	1.1317	3.601	1.0803	299458	264122	6.5
Nitrophenol, 2-	6.88	14.7971	0.5022	29.46	3.4	1.5782	5.022	1.5066	11193	13999	8.1
Dimethylphenol, 2,4- (2,4-xylenol)	6.92	12.5107	0.3979	31.44	3.2	1.2505	3.9792	1.1938	156404	152150	6.6
bis(2-Chloroethoxy)methane	6.99	11.3289	0.1516	74.72	1.3	0.4765	1.5162	0.4549	2024479	1660540	5.9
Dichlorophenol, 2,4-	7.05	13.7321	0.387	35.48	2.8	1.2162	3.87	1.161	105776	122607	8.3
Benzoic acid	7.06	0.1573	0.0176	8.93	11.2	0.0554	0.1762	0.0529	60412	52372	6.5
Trichlorobenzene, 1,2,4-	7.1	11.0956	0.0324	342.64	0.3	0.1018	0.3238	0.0971	670206	631499	5.7
Naphthalene	7.12	10.3965	0.0741	140.33	0.7	0.2328	0.7408	0.2223	1222532	1153020	6.4
Chloroaniline, 4-	7.2	13.0561	0.3156	41.37	2.4	0.9918	3.156	0.9468	389402	368904	5.2
Hexachlorobutadiene	7.24	10.8693	0.0906	120.03	0.8	0.2846	0.9055	0.2717	391407	348426	6.3
Phenol, 4-chloro-3-methyl-	7.52	12.2249	0.39	31.34	3.2	1.2258	3.9005	1.1701	141172	125224	8.3
Methylnaphthalene, 2-	7.62	10.5352	0.0461	228.45	0.4	0.1449	0.4612	0.1383	2198007	1821273	6.1
Hexachlorocyclopentadiene	7.72	13.4986	0.9219	14.64	6.8	2.8971	9.2186	2.7656	24746	20083	10.5
Trichlorophenol, 2,4,6-	7.8	13.0978	0.9706	13.49	7.4	3.0502	9.7058	2.9117	82113	56410	12.6
Trichlorophenol, 2,4,5-	7.82	9.9282	0.3232	30.72	3.3	1.0158	3.2322	0.9697	84827	81932	5.3
1,1'-Biphenyl, 2-fluoro-	7.86	10.4863	0.027	388.7	0.3	0.0848	0.2698	0.0809	1862901	1292537	6
Chloronaphthalene, 2-	7.93	10.5929	0.0825	128.41	0.8	0.2592	0.8249	0.2475	2287069	1581753	6.2
Nitroaniline, 2-	8	12.8968	0.4094	31.5	3.2	1.2867	4.0942	1.2283	71516	45871	7.2
Dimethyl phthalate	8.11	8.9452	0.1924	46.49	2.2	0.6047	1.924	0.5772	687978	386072	5.6
Dinitrotoluene, 2,6-	8.16	12.7618	0.4741	26.92	3.7	1.4898	4.7405	1.4222	46828	27918	6.2
Acenaphthylene	8.2	9.6082	0.1102	87.19	1.1	0.3463	1.102	0.3306	302293	208097	6.6
Nitroaniline, 4-	8.25	14.0242	0.9273	15.12	6.6	2.9141	9.2727	2.7818	17030	11358	9.7
Nitroaniline, 3-	8.26	15.2317	1.0698	14.24	7	3.3619	10.6977	3.2093	76655	49339	10.4
Acenaphthene	8.3	9.7843	0.1108	88.3	1.1	0.3482	1.108	0.3324	387438	243854	5.7
Dinitrotoluene, 2,4-	8.4	14.043	0.7564	18.57	5.4	2.377	7.5636	2.2691	27008	17731	8.4
Dibenzofuran	8.42	10.1509	0.1087	93.34	1.1	0.3418	1.0875	0.3262	4163056	2523322	5.9
Chlorophenyl phenyl ether, 4-	8.63	10.4055	0.1059	98.24	1	0.3329	1.0592	0.3177	1444002	805825	5.9
Fluorene	8.63	10.1535	0.114	89.04	1.1	0.3584	1.1403	0.3421	3427305	2252308	6.1
Nitrosodiphenylamine, N-	8.71	8.8186	0.2707	32.58	3.1	0.8507	2.7069	0.8121	268767	179403	5.9
Azobenzene	8.73	8.0273	0.1678	47.85	2.1	0.5272	1.6777	0.5033	1554738	959484	6.5
Tribromophenol, 2,4,6-	8.78	10.2379	0.4598	22.26	4.5	1.4451	4.5983	1.3795	14135	10834	10.4
4-bromophenyl phenyl ether	8.94	8.8861	0.2464	36.07	2.8	0.7743	2.4638	0.7391	384182	255788	6.4
Hexachlorobenzene	8.97	8.9022	0.331	26.9	3.7	1.0402	3.3099	0.993	694285	430711	6.1
Pentachlorophenol	9.09	8.5879	0.5017	17.12	5.8	1.5767	5.017	1.5051	4614	7250	15.1
Phenanthrene	9.24	8.8777	0.058	153.04	0.7	0.1823	0.5801	0.174	1193313	797742	7.4
Anthracene	9.27	7.2495	0.1467	49.43	2	0.4609	1.4667	0.44	596059	456893	7.7
Carbazole	9.37	8.6905	0.3451	25.18	4	1.0845	3.451	1.0353	369024	282913	10
Di-n-butyl phthalate	9.58	6.7796	0.2012	33.7	3	0.6323	2.012	0.6036	308569	194243	6.5
Fluoranthene	10.03	8.4077	0.2526	33.29	3	0.7938	2.5258	0.7577	616055	562227	9.5
Pyrene	10.21	8.0653	0.2794	28.87	3.5	0.878	2.7937	0.8381	749624	661642	10
p-Terphenyl-d14	10.35	8.5718	0.4851	17.67	5.7	1.5246	4.8514	1.4554	205455	201195	12.1
Butyl benzyl phthalate	10.74	7.4914	0.406	18.45	5.4	1.2758	4.0596	1.2179	28635	19784	12.2
3,3'-Dichlorobenzidine	11.25	7.8642	0.4474	17.58	5.7	1.406	4.4739	1.3422	11924	10104	15.5
Benz[a]anthracene	11.26	7.555	0.0684	110.5	0.9	0.2149	0.6837	0.2051	264169	240364	16.4
Chrysene	11.3	6.9638	0.0496	140.52	0.7	0.1557	0.4956	0.1487	220569	259985	17
Bis(2-ethylhexyl) phthalate	11.35	4.937	0.5528	8.93	11.2	1.7373	5.5281	1.6584	33791	28137	13.5
Di-n-octyl phthalate	12.2	5.0343	0.3034	16.6	6	0.9534	3.0336	0.9101	26867	26900	15.6
Benzo[b]fluoranthene	12.55	8.6085	0.2251	38.25	2.6	0.7073	2.2508	0.6752	110854	116793	16.5
Benzo[k]fluoranthene	12.58	7.2654	0.3518	20.65	4.8	1.1054	3.5175	1.0553	106593	129453	16.4
Benzo[a]pyrene	12.92	6.5011	0.1678	38.73	2.6	0.5275	1.6785	0.5035	68952	81715	13.7
Indeno[1,2,3-cd]pyrene	14.09	5.8901	0.3755	15.68	6.4	1.1802	3.7554	1.1266	146328	150858	11.3
Dibenz[a,h]anthracene	14.13	6.2799	0.4556	13.78	7.3	1.4317	4.5557	1.3667	48381	52387	10.6
Benzo[g,h,i]perylene	14.35	6.0143	0.3535	17.02	5.9	1.1108	3.5347	1.0604	182644	217684	11

Conclusions

With the adoption of the tandem-quadrupole mass spectrometer into the EPA method 8270E, it was necessary to show the possible performance with these analytes. The data provided in this poster shows the increased limit of detection and limit of quantitation possible with the addition of MS/MS for this experiment. Many of the analytes were easily observed at the 0.1 pg µL^{-1} level. With these new detection levels labs would be able to inject a smaller amount into the GC/MS reducing maintenance time and consumables. It would be also possible to start with a smaller sample volume to decrease the amount of solvent used for extraction, and eliminate the "blow-down"/concentration step in the sample preparation. One issue observed is the limit of quantitation for some of the phthalates were much higher than expected due to the normal contamination from plastics during a sample preparation procedure. Glass beakers and glass/metal syringes were used for this study, but the solvents an other components that came in contact with the sample had enough residue of plastics to produce a non-zero blank sample.