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ThP 129

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

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Introduction

The goal of this project is to show the applicability of EI GC/MS/MS measurement for the detection of EPA method 8270 analytes using a fast, highly selective and sensitive approach. EPA method 8270 is the primary semivolatile organic compound (SVOC) analysis for multiple types of matrices including soil and wastewater. Due to the high concentrations injected and number of target analytes monitored, 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 analyte extraction and large sample volumes that need to be shipped, which is costly for laboratories running this method routinely.

During the 2015 Pittsburgh Conference EPA announced that a tandem-quadrupole mass spectrometer could be used for EPA method 8270. This detection mode change will be included in revision E of the method. Due to the use of MS/MS detection technique, DFTPP spectrum analysis will not be necessary, but documentation of both mass analyzers' performance will be required. This document will be based on manufacturer's specifications using the internal calibration compound. The document will include mass resolution, mass assignment, and sensitivity results. Performance evaluations will be performed weekly, at minimum.

Materials and Method:

The analyte, internal standard, and surrogate standard solutions were 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} .

Three transitions for each analyte, surrogate and internal standard were selected and applied to this method from the Agilent Pesticide & Environmental Pollutant MRM Database. For compounds not currently in the Agilent MRM Database the transitions were obtained through the following steps. Individual SRM transitions were developed by acquiring a full scan data file with all the analytes to select the best candidates for precursor ions. Product ion analyses 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 transition.

The GC run time was 15 min. with a cool down/equilibration time of ~4 min, to give a total cycle time below 20 min.

Experimental

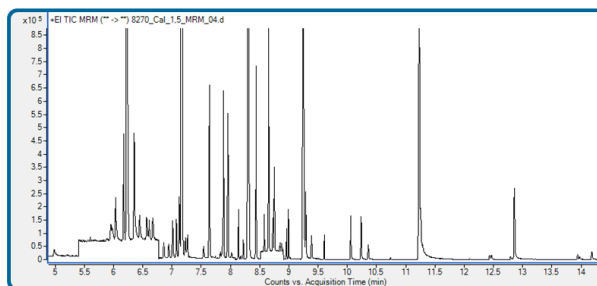


Figure 1. RTIC for the 1.5 pg μL^{-1} sample with analytes, ISTDs and surrogates. The five most intense peaks are the ISTDs, which were cut-off to show the analyte responses.

Instrument:

All of the data created for this study were acquired on an Agilent 7890A GC coupled to the Agilent 7010 Triple 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 the analyzer to allow more ions to be detected. The 7010 includes two gold-plated quartz 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 $^{\circ}\text{C}$
Oven temperature program	40 $^{\circ}\text{C}$ for 2.5 min 10 $^{\circ}\text{C}/\text{min}$ to 60 $^{\circ}\text{C}$, for 0 min 40 $^{\circ}\text{C}/\text{min}$ to 260 $^{\circ}\text{C}$, for 0 min 5 $^{\circ}\text{C}/\text{min}$ to 270 $^{\circ}\text{C}$, for 0 min 20 $^{\circ}\text{C}/\text{min}$ to 320 $^{\circ}\text{C}$, for 1 min
Carrier gas	Helium at 0.8 mL/min for 10 min then 1.5 mL/min
Transfer line temperature	300 $^{\circ}\text{C}$
Ionization mode	Electron Ionization
Source temperature	350 $^{\circ}\text{C}$
Quadrupole temperatures	150 $^{\circ}\text{C}$ 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

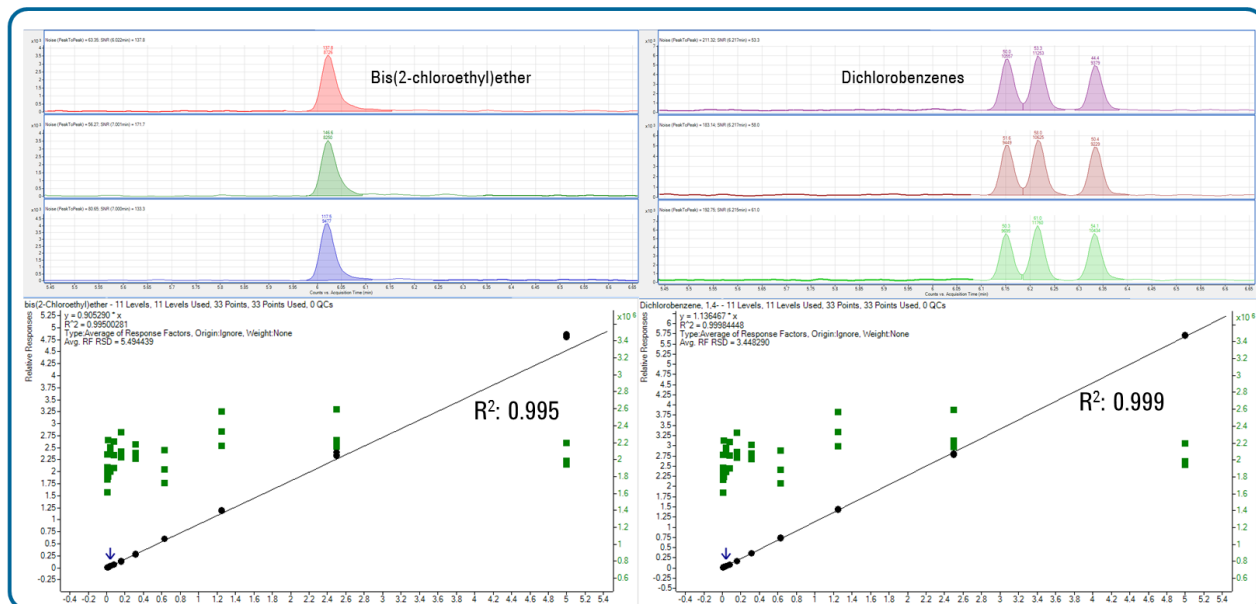


Figure 2. The left chromatogram is produced from 3 reps. of Bis(2-chloroethyl)ether at $0.1 \text{ pg } \mu\text{L}^{-1}$. The chromatogram on the right was produced from 3 reps. of the 3 dichlorobenzenes in the solution at $0.1 \text{ pg } \mu\text{L}^{-1}$. The chromatogram labels include the signal-to-noise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

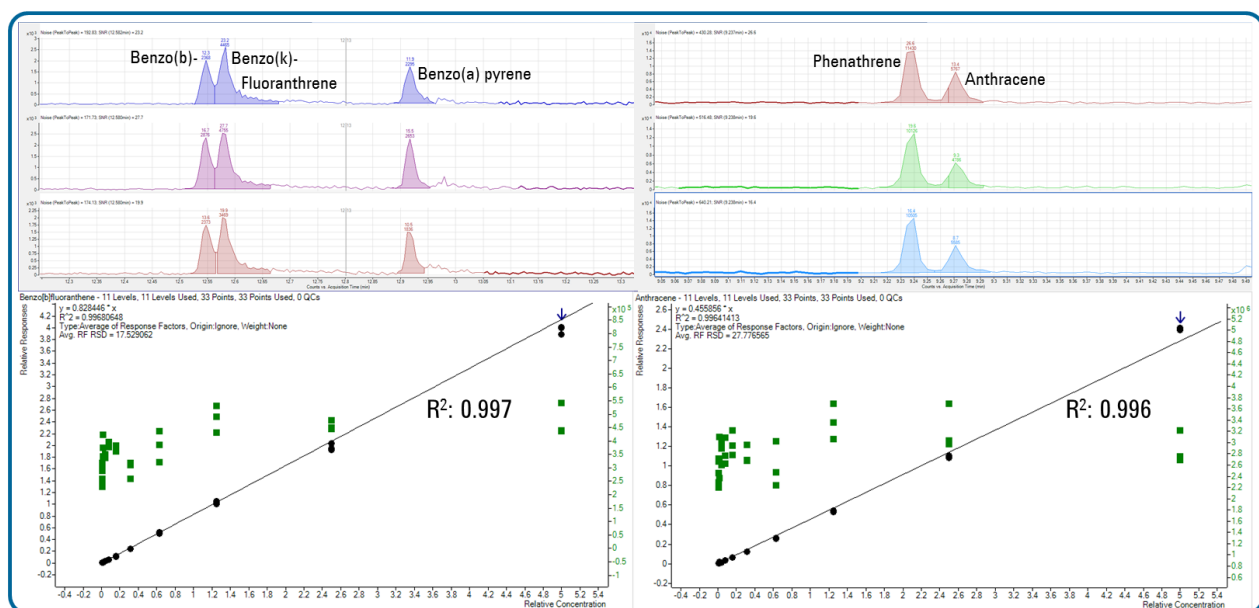


Figure 3. The left chromatogram is produced from 3 reps. of benzo(b) and benzo(k) fluoranthrene at $0.2 \text{ pg } \mu\text{L}^{-1}$. The chromatogram on the right was produced from 3 reps. of phenanthrene and anthracene at $0.1 \text{ pg } \mu\text{L}^{-1}$. The chromatogram labels include the signal-to-noise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

Results and Discussion

Table 1. This table was calculated with 7 replicates of 1µl, 10 pg µL⁻¹ injection of all analytes. The MDLs, LOQs, and LODs were calculate at the 95% confidence level. The quantifier transition was used to calculate the values below (all concentrations in pg µL⁻¹).

Name	RT	Avg Conc.	Std. Dev.	Conc. RSD %	MDL	LOQ	LOD	Avg Height	Area	Resp. RSD %
Phenol, 2-fluoro-	4.89	10.07	0.2021	2	0.64	2.02	0.61	126470	226121	5.9
Phenol-d5	5.916	11.38	0.2223	2	0.70	2.22	0.67	172953	170946	5.1
Phenol	5.926	10.28	0.2143	2.1	0.67	2.14	0.64	161576	162204	7.1
Aniline	5.93	12.16	0.5546	4.6	1.74	5.55	1.66	207179	268039	3.8
bis(2-Chloroethoxy)ether	6.006	10.80	0.0899	0.8	0.28	0.90	0.27	990182	829590	5.9
Chlorophenol, 2-	6.013	11.05	0.3094	2.8	0.97	3.09	0.93	109712	107208	6.8
Dichlorobenzene, 1,3-	6.14	10.72	0.0379	0.4	0.12	0.38	0.11	1349543	1028662	6.2
Dichlorobenzene, 1,4-	6.21	10.52	0.1109	1.1	0.36	1.11	0.33	1290261	1015165	6.7
Dichlorobenzene, 1,2-	6.32	10.73	0.0795	0.7	0.25	0.80	0.24	1287541	1050684	6
Benzyl alcohol	6.325	10.88	0.6008	5.5	1.89	6.01	1.80	113138	144658	10.5
Methylphenol, 2- (Cresol, o-)	6.423	11.05	0.5562	5	1.75	5.56	1.67	196269	204109	4.5
Methylphenol, 4- (Cresol, p-)	6.54	11.85	0.0729	5.7	2.11	6.73	2.02	201094	221416	6.8
Nitrosodip-n-propylamine	6.54	11.85	0.0729	5.7	2.11	6.73	2.02	201094	221416	6.8
Hexachloroethane	6.58	11.34	0.8666	7.6	2.72	8.67	2.60	318305	251612	11.1
Nitrobenzene-D5	6.64	11.12	0.5383	4.8	1.69	5.36	1.61	44545	42286	9.1
bis(2-Chloro-1-methylethyl)ether	6.65	10.49	0.1759	1.7	0.55	1.76	0.53	19456	27328	6.8
Nitrobenzene	6.65	11.51	0.3953	3.4	1.24	3.95	1.19	152908	143990	8.1
Isophenol	6.63	12.25	0.3901	2.9	1.13	3.60	1.08	299458	264122	6.5
Nitrophenol, 2-	6.88	14.80	0.5022	3.4	1.58	5.02	1.51	11193	13999	8.1
Dimethylphenol, 2,4- (2,4-xyleneol)	6.92	12.51	0.3979	3.2	1.25	3.98	1.19	156404	152150	6.6
bis(2-Chloroethoxy)methane	6.99	11.33	0.1516	1.3	0.48	1.52	0.45	2024479	1665540	5.9
Dichlorophenol, 2,4-	7.05	13.73	0.307	2.8	1.22	3.67	1.16	167776	123007	6.3
Trichlorobenzene, 1,2,4-	7.1	11.10	0.0324	0.3	0.10	0.32	0.10	670206	631498	5.7
Naphthalene	7.12	10.40	0.0741	0.7	0.23	0.74	0.22	122252	1153020	6.4
Chloroaniline, 4-	7.2	13.06	0.3156	2.4	0.99	3.16	0.95	388402	388904	5.2
Hexachlorobutadiene	7.24	10.87	0.0906	0.8	0.28	0.91	0.27	391407	348426	6.3
Phenyl, 4-chloro-3-methyl-	7.52	12.22	0.39	3.2	1.33	3.98	1.17	141173	125224	6.8
Methylnaphthalene, 2-	7.62	10.54	0.0461	0.4	0.14	0.46	0.14	219007	182173	6.1
Hexachlorocyclopentadiene	7.72	13.50	0.9219	6.8	2.90	8.22	2.77	24746	20883	10.6
Trichlorophenol, 2,4,6-	7.8	13.10	0.0706	7.4	3.05	9.71	2.91	82113	56410	12.5
Trichlorophenol, 2,4,5-	7.82	9.93	0.2322	3.3	1.02	3.23	0.97	84627	81922	5.3
1,1'-Bisphenol, 2-fluoro-	7.86	10.49	0.027	0.3	0.08	0.27	0.08	196261	129257	6
Chloronaphthalene, 2-	7.93	10.59	0.0825	0.8	0.26	0.82	0.25	2297069	1581753	6.2
Nitroaniline, 2-	8	12.90	0.4094	3.2	1.29	4.09	1.23	71516	45871	7.2
Dimethyl phthalate	8.11	8.95	0.1924	2.2	0.60	1.92	0.58	687978	386072	5.6
Dinitrotoluene, 2,6-	8.16	12.78	0.0741	3.7	1.49	4.74	1.42	46328	27818	6.2
Acenaphthylene	8.2	9.61	0.102	1.1	0.35	1.10	0.33	302293	208997	6.6
Nitroaniline, 4-	8.25	14.02	0.9273	6.6	2.91	9.27	2.78	17030	11358	9.7
Nitroaniline, 3-	8.26	15.23	1.0698	7	3.36	10.70	3.21	76655	49309	10.4
Acenaphthene	8.3	9.78	0.1109	1.1	0.35	1.11	0.33	387439	243854	5.7
Dinitrotoluene, 2,4-	8.4	14.04	0.7564	5.4	2.38	7.56	2.27	27008	17791	8.4
Dibenzofuran	8.42	10.15	0.107	1.1	0.34	1.09	0.32	416265	323232	5.9
Chlorophenyl phenyl ether, 4-	8.63	10.41	0.1059	1	0.33	1.06	0.32	1444002	805225	5.9
Fluorene	8.63	10.15	0.114	1.1	0.36	1.14	0.34	3427305	2252308	6.1
Nitrosodiphenylamine, N-	8.71	8.82	0.2707	3.1	0.85	2.71	0.81	268767	179403	5.9
Azobenzene	8.73	8.03	0.1678	2.1	0.53	1.68	0.50	154738	95404	6.5
Trichlorophenol, 2,4,6-	8.78	10.24	0.4598	4.5	1.45	4.60	1.38	14126	10854	10.4
4-bromophenyl phenyl ether	8.94	8.89	0.2464	2.8	0.77	2.46	0.74	384182	255786	6.4
Hexachlorobenzene	8.97	8.90	0.331	3.7	1.04	3.31	0.99	684285	430711	6.1
Pentachlorophenol	9.09	8.59	0.5017	5.8	1.58	5.02	1.51	4614	7250	15.1
Phenanthrene	9.24	8.88	0.058	0.7	0.18	0.58	0.17	118313	797742	7.4
Anthracene	9.27	7.25	0.1487	2	0.46	1.47	0.44	596959	659963	7.7
Carbazole	9.37	8.69	0.3451	4	1.08	3.45	1.04	396024	282913	10
Di-n-butyl phthalate	9.58	6.78	0.2012	3	0.63	2.01	0.60	308569	194243	6.5
Fluoranthene	10.03	8.41	0.2526	3	0.79	2.53	0.76	616955	562227	9.5
Pyrene	10.21	6.07	0.2794	3.5	0.88	2.79	0.84	749624	651542	10
p-Terphenyl-d14	10.35	8.57	0.4851	5.7	1.52	4.65	1.46	205455	201195	12.1
Butyl benzyl phthalate	10.74	7.49	0.406	5.4	1.28	4.06	1.22	28335	19784	12.2
3,3'-Dichlorobenzidine	11.25	7.86	0.4474	5.7	1.41	4.47	1.34	11924	10104	15.5
Benzo[a]anthracene	11.26	7.56	0.0884	0.9	0.21	0.68	0.21	264189	240364	16.4
Chrysene	11.3	6.96	0.0496	0.7	0.16	0.50	0.15	226969	259895	12
Bis(2-ethylhexyl) phthalate	11.35	4.94	0.5529	11.2	1.74	5.53	1.66	33791	29137	13.5
Di-n-octyl phthalate	12.2	5.03	0.3034	6	0.95	3.03	0.91	26887	26800	15.6
Benzo[b]fluoranthene	12.55	8.61	0.2251	2.6	0.71	2.25	0.68	110854	116780	16.5
Benzo[k]fluoranthene	12.58	7.27	0.3518	4.8	1.11	3.52	1.06	106993	129483	16.4
Benzo[g]jovene	12.92	6.50	0.1678	2.6	0.59	1.69	0.50	88952	87175	13.7
Indeno[1,2,3-cd]jovene	14.09	5.89	0.3755	6.4	1.18	3.76	1.13	146328	150588	11.3
Dibenzo[a,h]anthracene	14.13	6.28	0.4556	7.3	1.43	4.56	1.37	48381	52387	10.6
Benzo[g,h,i]perylene	14.35	6.01	0.3535	5.9	1.11	3.53	1.06	182644	217684	11

Conclusions

With the adoption of the triple quadrupole mass spectrometers in EPA method 8270E, the goal of this study was to show that the Agilent 7010 Triple Quadrupole GC/MS system fulfills the method requirements. The data generated demonstrate significantly improved limits of detection and limits of quantitation with the addition of MS/MS for this analysis. Many of the analytes were easily observed at the 0.1 pg µL⁻¹ level. With these new detection levels laboratories will be able to inject a smaller amount into the GC/MS reducing maintenance time and consumables. It will be also possible to start with smaller sample volumes, to decrease the amount of solvent used for extraction, and eliminate the “blow-down”/concentration step in the sample preparation.

During the method evaluation the calculated limits of quantitation for some of the phthalates were much higher than expected due to contamination from plastics during a sample preparation procedure. Glass beakers and glass/metal syringes were used for this study, but the solvents and other components that came in contact with the sample had enough residue of plastics to produce a non-zero blank sample.