Large Volume Injection of Polycyclic Aromatic Hydrocarbons

Application Note

Environmental

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Abstract

Polycyclic Aromatic Hydrocarbons (PAHs) are formed from incomplete burning of carbon containing fuel. There are thousands of PAH compounds in the environment, and of those; there are several that have been established to be of concern for the environment. Extraction of PAH compounds involves a large amount of sample and solvent, and because of this, there is a lot of solvent waste. The use of Large Volume Injection (LVI) in conjunction with a Programmable Temperature Vaporizer (PTV) aids in eliminating some of this solvent waste, and reduces labor and shipping costs due to the ability to extract smaller volumes of sample without sacrificing sensitivity. This analysis will compare PAH compound response of a standard injection versus a large volume injection.

Introduction:

The most common practice for extraction of PAH compounds from a water matrix involves one liter of sample and more than 150mls of solvent. The sample goes through several liquid-liquid extraction and evaporation steps in order to achieve the final extract for sampling and analysis. USEPA Method 3511 proposes a micro-extraction technique that uses less than 5mls of sample and approximately 2mls of solvent. This technique is also much less time consuming. However, micro-extraction is not nearly as sensitive when analyzing for PAH compounds. In answer to this problem, laboratories can utilize Large Volume Injection in conjunction with a Programmable Temperature Vaporizer. When using this sampling technique, an analyst has the ability to inject several microliters of sample into the GC inlet, thus multiplying the amount of sample to be detected and analyzed by the MS. Consequently, sensitivity can be increased while extraction time and solvent use can be decreased.

Discussion:

As EPA detection limits get lower and lower, laboratories need to adapt to these expectations. Large Volume Injections enable laboratories to lower detection limits because the amount of sample introduced to the system is increased. Programmable Temperature Vaporization using solvent split mode is the usual technique for solvent elimination and pre-concentration of analytes. During vaporization, the analytes are transferred to the column for separation and analysis. When using LVI, the PTV inlet is set to solvent vent mode. The sample is introduced at a low temperature, and the solvent is eliminated using the purge flow to the split vent. The analytes are retained on the inlet liner while the solvent is vented. Next, the inlet is quickly heated in order transfer the analytes to the GC column in splitless mode. After the transfer, the inlet is set to purge any residual contaminants from the inlet.

Using LVI in conjunction with PTV enables laboratories to introduce more sample onto the GC column, therefore increasing sensitivity. This study will compare a 1μl injection of PAH compounds using a standard split/splitless injection to a 5μl injection of the same PAH compounds utilizing LVI and PTV.

Experimental:

The sampling system used for this analysis was the EST Analytical FLEX autosampler fitted with a 10µl liquid syringe. The Agilent 7890 GC and 5975 MS were used for separation and analysis. A Restek Rxi-5 Sil MS 30m x 250mm x 0.25μm column was mounted in the GC. The Agilent Split/Splitless inlet was used for the 1ul injections while the Titan PTV LVI was used for the 5ul injections. Refer to Tables 1 and 2 for the sampling and analysis parameters.

Autosampler	Flex (1μl)	Flex (5μl)
General		
Method Type	Liquid	Liquid
Rinse		
Rinse Volume	60% (6μl)	70% (7μl)
Rinse Fill Rate	50%	50%
Rinse Cycles	2	2
Rinse Dispense Rate	100%	100%
Waste Depth	50%	50%
Sample		
Sample Volume	10% (1μl)	50% (5μl)
Rinse Volume	50% (5μl)	60% (6μl)
Rinse Cycles	1	1
Pump Volume	50% (5μl)	60% (6μl)
Pump Cycles	3	3
Air Volume Gap		
Air Fill Volume	10% (1μl)	10% (1μl)
Single Injection Port		
Injection Rate	90%	90%
Injection Volume	20% (2µl)	60% (6µl)
Pre-Injection Delay	1 sec	1 sec
Post Injection Delay	1 sec	1 sec
Injection Start Output	End	End
Rinse		
Rinse Volume	60% (6μl)	70% (7μl)
Rinse Fill Rate	50%	50%
Rinse Cycles	2	2
Rinse Dispense Rate	100%	100%
Waste Depth	50%	50%

Table 1: FLEX Autosampler Experimental Parameters

GC/MS	Agilent 7890/5975 (1µl)	Agilent 7890/5975 (5µl)
Inlet	Split/Splitless	PTV Solvent Vent
Inlet Temp.	280ºC	45ºC for 0.2 min, 200ºC/min to 125ºC for 0 min, 700ºC/min to 280ºC for 33.5min
Inlet Head Pressure	11.809 psi	11.809 psi
Split	20:1	NA
Purge Flow to Split Vent	NA	50ml/min at 1.5 min
Vent Flow	NA	100ml/min
Vent pressure	NA	0psi until 0.1min
Cryo	NA	On at 50ºC
Liner	Restek SKY liner, Splitless, Single Taper with Glass Wool, 4mm x 6.5 x 78.5	TITAN XL SB Deactivated Liner with Glass Wool
Column	Rxi-5Sil MS 30m x 0.25mm I.D. x 0.25μm film thickness	Rxi-5Sil MS 30m x 0.25mm I.D. x 0.25μm film thickness
Oven Temp. Program	45ºC hold for 4.0 min, ramp 10ºC/min to 320ºC hold for 2.0 min, 33.5 min run time	45ºC hold for 4.0 min, ramp 10ºC/min to 320ºC hold for 2.0 min, 33.5 min run time
Column Flow Rate	1.0ml/min.	1.0ml/min.
Gas	Helium	Helium
Total Flow	24ml/min	54.4ml/min.
Source Temp.	230ºC	230ºC
Quad Temp.	150ºC	150ºC
MS Transfer Line Temp.	280ºC	280ºC
Solvent Delay	5.0 min	5.0 min
Acquisition Mode	Scan	Scan
Scan Range	m/z 35-500	m/z 35-500
Sampling Rate	3.12 scans/sec	3.12 scans/sec

Table 2: GC/MS Experimental Parameters

The PAH standards were acquired from Restek. Two different curves were run for the experiment. The 1μl injection curve standard range was from 0.5 ppm to 200ppm or 0.50 to 200ng on column. For the large volume, 5μl, injection the standard range was from 0.05ppm to 50ppm or 0.25 to 250ng on column. Next seven replicates of the low standard were run in order to determine MDLs. Finally, in order to ascertain the precision and accuracy of the injection techniques, seven replicates of the mid-point of each curve were run. Experimental results are listed in Table 3 and 4, while the chromatograms of the two injections are displayed in Figures 1 and 2.

1µl Injection, Standard Injection					
Compound	Curve %RSD	Ave. Curve RF	MDL	%RSD 50ng	%Recovery 50ng
Naphthalene	4.46	1.083	0.04	0.58	102.35
Acenaphthalene	9.99	1.761	0.11	0.64	112.36
Acenaphthene	4.62	1.175	0.06	0.56	102.47
Fluorene	5.72	1.303	0.11	0.64	108.24
Phenanthrene	6.58	1.234	0.09	0.46	99.58
Anthracene	5.31	1.102	0.09	0.70	106.33
Fluoranthene	4.25	1.097	0.08	1.14	108.21
Pyrene	5.24	1.139	0.07	1.46	106.19
Benz(a)anthracene	12.62	1.044	0.06	0.50	102.75
Chrysene	10.13	1.105	0.11	0.84	97.26
Benzo(b)fluoranthene	12.03	1.386	0.16	1.41	103.19
Benzo(k)fluoranthene	10.43	1.623	0.16	1.57	103.88
Benzo(a)pyrene	11.07	1.296	0.14	1.63	106.55
Indeno(1,2,3-cd)pyrene	12.01	0.940	0.12	1.49	111.47
Dibenz(a,h)anthracene	11.09	1.069	0.17	1.21	111.71
Benzo(g,h,i)perylene	10.70	1.166	0.06	2.17	109.59
Ave.	8.52	1.220	0.10	1.06	105.76

Table 3: Experimental Results Summary 1µl Injection

5µl Injection, Large Volume Injection					
Compound	Curve %RSD	Ave. Curve RF	MDL	%RSD 50ng	%Recovery 50ng
Naphthalene	6.81	0.990	0.01	0.31	105.50
Acenaphthalene	13.53	1.631	0.02	0.87	114.32
Acenaphthene	5.24	1.013	0.02	0.62	105.38
Fluorene	6.11	1.019	0.04	1.02	107.50
Phenanthrene	7.01	1.064	0.04	0.42	102.94
Anthracene	8.56	0.951	0.03	0.52	106.19
Fluoranthene	4.49	0.907	0.03	1.56	102.66
Pyrene	4.60	0.916	0.01	1.41	101.58
Benz(a)anthracene	13.26	0.994	0.03	0.78	103.41
Chrysene	9.85	0.953	0.02	0.75	101.24
Benzo(b)fluoranthene	7.82	1.131	0.06	0.82	110.10
Benzo(k)fluoranthene	4.02	1.204	0.03	1.42	107.61
Benzo(a)pyrene	11.85	1.002	0.03	0.95	115.29
Indeno(1,2,3-cd)pyrene	12.49	0.867	0.08	2.23	116.32
Dibenz(a,h)anthracene	7.45	1.003	0.09	1.24	110.34
Benzo(g,h,i)perylene	5.68	0.990	0.05	1.19	106.42
Ave.	8.05	1.040	0.04	1.01	107.30

Table 4: Experimental Results Summary 5µl Injection

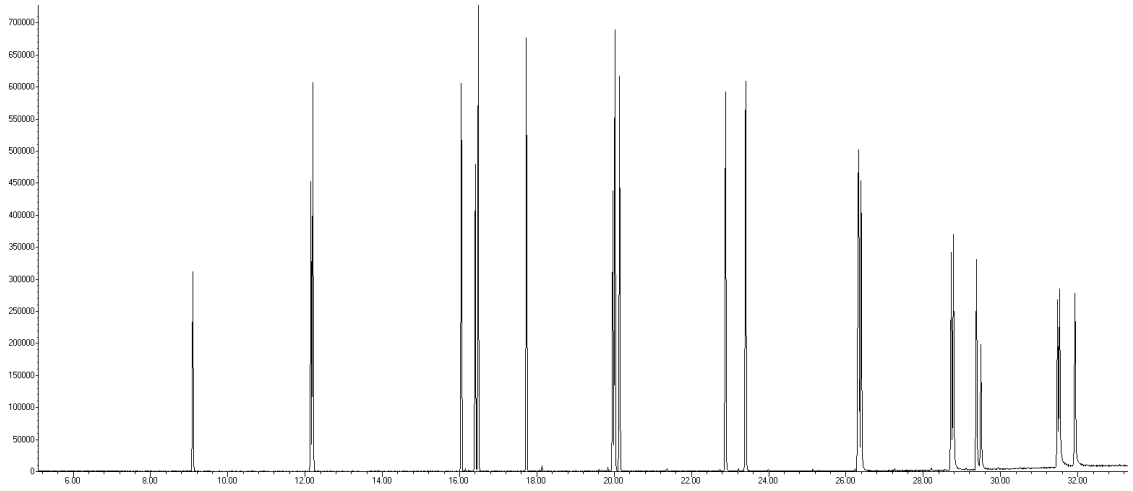

Figure 1: 50ng on column, 1ul Injection

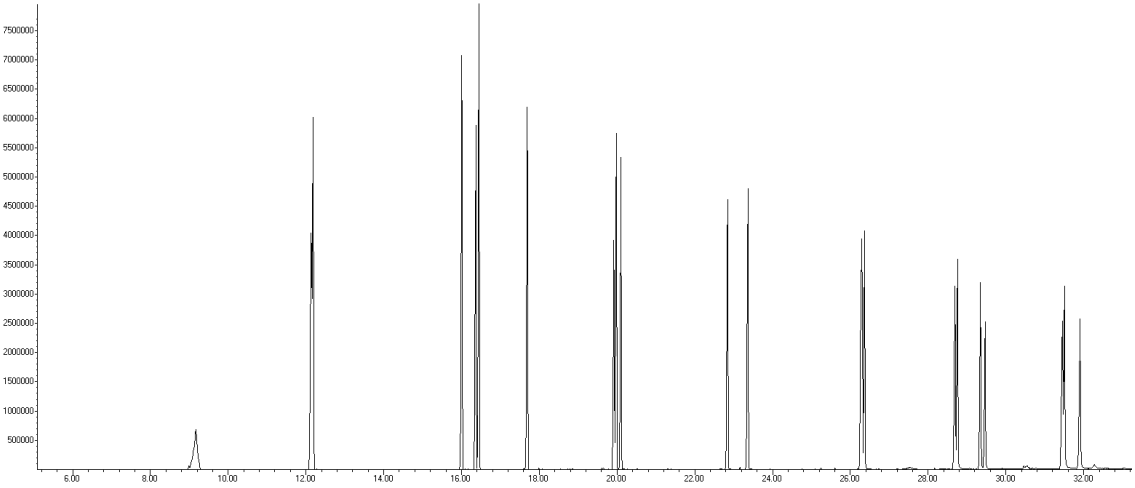

Figure 1: 50ng on column, 5ul Injection

Conclusions:

The LVI technique, in conjunction with PTV, enabled the curve range to go down to 0.25ng on column without sacrificing compound response. The ability to inject more than one microliter of sample onto the GC column enhances the sensitivity of the system. When comparing the results of a standard injection to an LVI, the linearity, compound response, detection limits, and precision and accuracy were all comparable. Consequently, the use of LVI in conjunction with the FLEX Autosampling system is a viable option for PAH analysis. Furthermore, as detection limits become more and more stringent, the volume of the injection can increase in order to accommodate the new requirements.

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