

## Increasing Sample Throughput for EPA Method 8270 by Employing a Split Injection

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### Background

- Splitless injections are typically employed for EPA Method 8270 because it provides a greater transfer of analytes onto the head of the column.
- The flow through the injection port is much slower with a splitless injection which can result in degradation of thermally labile compounds and adsorption of active analytes such as 2,4-dinitrophenol.
- Peak widths are typically broader with a splitless injection due to the comparatively slow transfer of analytes onto the head of the column.
- Here we will discuss the applicability of a **split** injection with EPA Method 8270 compounds.

### Experimental

- Increasing the initial oven temperature was the first goal of this work. By starting at a higher oven temperature analysis time and instrument cycle time are reduced.
- A split injection typically produces better repeatability from injection to injection. Repeatability studies were performed using both split and splitless optimized conditions.
- A 6 point calibration curve from 5 µg/mL to 160 µg/mL was evaluated for instrument sensitivity, linearity and peak shape
- Method ruggedness was evaluated by comparing both injection techniques with EPA Method 8270 generated extracts.

**Table I: Analysis conditions used for each experimental**

<b>Column:</b>	<b>Rxi®-5Sil MS, 30 m, 0.25 mm ID, 0.25 µm</b>
<b>Sample:</b>	8270 MegaMix®; Benzoic acid; 8270 Benzidines Mix; Acid Surrogate Mix (4/89 SOW); 1,4-dioxane; Revised B/N Surrogate Mix; SV Internal Standard Mix
<b>Diluent:</b>	Methylene chloride
<b>Conc.:</b>	40 µg/mL
<b>Carrier Gas:</b>	He, constant flow
<b>Flow Rate:</b>	1.2 mL/min.
<b>Transfer Line Temp.:</b>	280 °C
<b>Source Temp.:</b>	250 °C
<b>Quad Temp.:</b>	150 °C
<b>Tune Type:</b>	DFTPP
<b>Scan Range:</b>	35-550 amu
<b>Instrument:</b>	Agilent 7890A GC & 5975C MSD

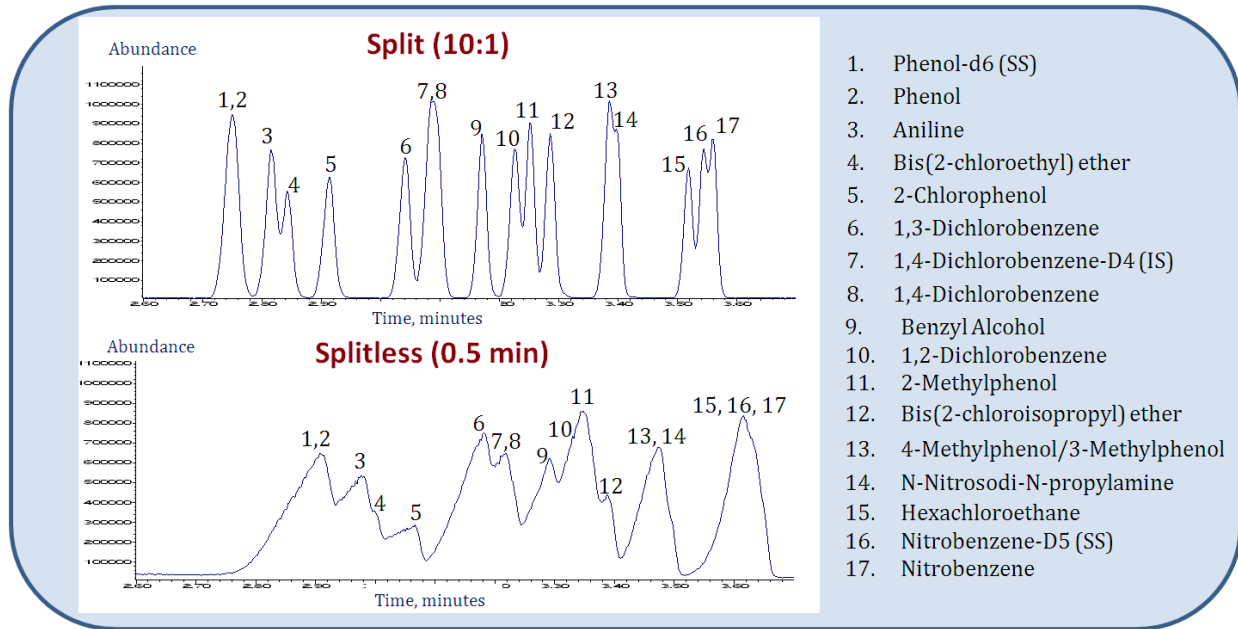
**Table II: Injector and oven conditions used for experimental**

	<b>Split (Fast Cycle)</b>	<b>Split (Faster Cycle)</b>	<b>Splitless</b>
<b>Injection:</b>	1.0 $\mu$ L split (split ratio 10:1)	1.0 $\mu$ L split (split ratio 10:1)	1.0 $\mu$ L splitless (1.0 min)
<b>Liner:</b>	4mm Split Precision <sup>®</sup> Liner w/ Semivolatiles Wool	4mm Split Precision <sup>®</sup> Liner w/ Semivolatiles Wool	4mm Gooseneck Splitless w/Semivolatiles Wool
<b>Inj. Temp.:</b>	270 °C	270 °C	260 °C
<b>Split Vent Flow Rate:</b>	60 mL/min.	60 mL/min.	60 mL/min.
<b>Oven Temp:</b>	80 °C (hold 1 min.) to 280 °C at 25 °C/min. to 320 °C at 5 °C/min. (hold 1 min)	80 °C (hold 1 min.) to 320 °C at 25 °C/min. to 330 °C at 5 °C/min. (hold 2 min)	40 °C (hold 1 min.) to 280 °C at 25 °C/min. to 320 °C at 5 °C/min. (hold 1 min.)

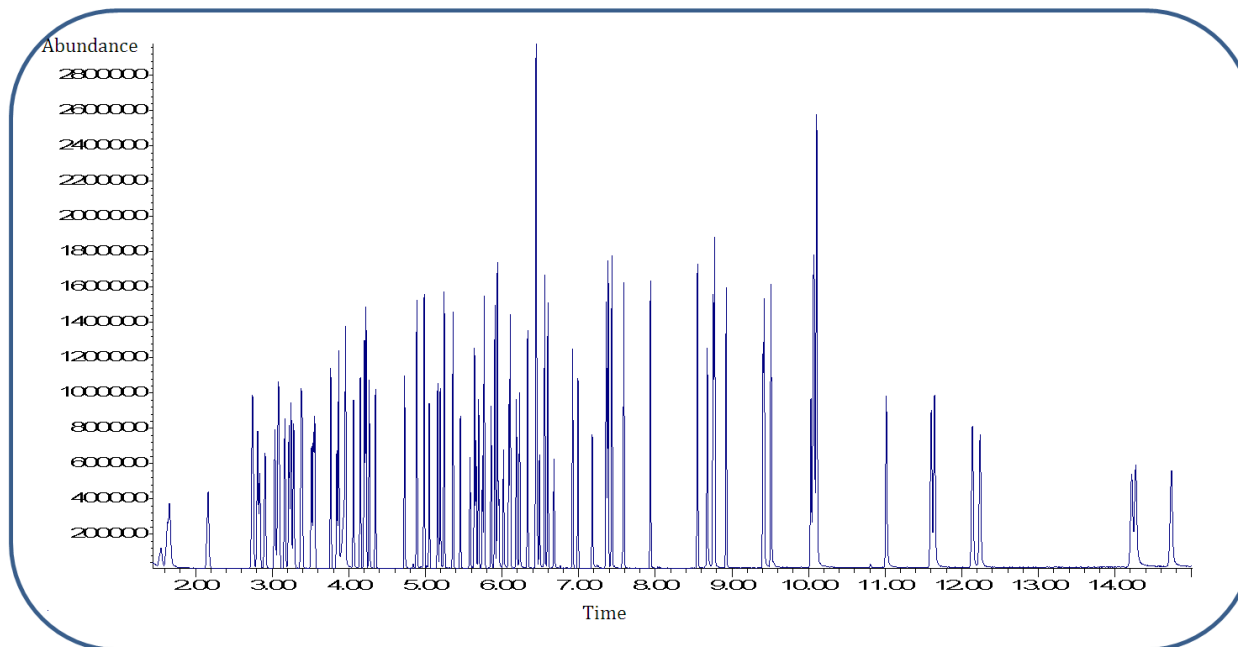
### Increased Sample Throughput

- Solvent focusing is required for splitless injection which means the initial oven temperature must be 20°C below the boiling point of the solvent. Methylene chloride has a boiling point of 40°C making solvent focusing difficult for splitless injections.
- Utilizing a split injection does not require solvent focusing, therefore allows a higher initial oven temperature because sharper initial injection bands are produced. Starting the oven temperature at 80°C was made possible by employing a 10:1 split injection; however this is not feasible with a splitless injection. **(Figure 1)**
- Starting the oven at 80°C provides over a 4.5 min time savings for overall analysis time for a fast temperature program that does not compromise resolution of PAHs. **(Figure 2)**
- An even faster cycle time is made possible by adjusting the oven temperature program. **(Table II)** However, this time program results in a decrease in resolution of some PAHs. **(Figure 3)**
- Overall, by starting the oven at 80°C decreases analysis time and provides time savings on the oven cool down time allowing for increased sample throughput **(Table III)**

**Figure 1: Comparison of peak shapes for early eluting compounds using a Split (10:1) and Splitless (0.5 min hold) injection at 80°C initial oven temperature**



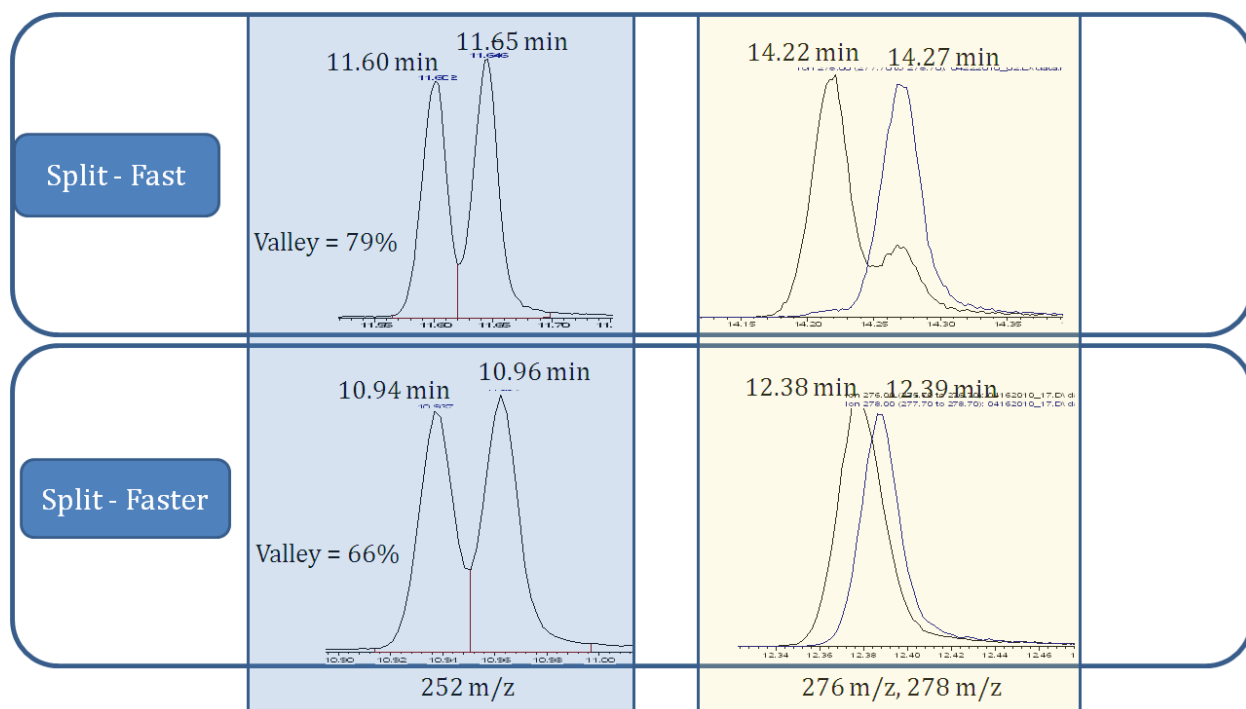
**Figure 2: Fast Analysis of EPA Method 8270 with a 10:1 Split Injection**



**Table III: Comparison of Analysis conditions and Instrument cycle time**

	Split - Fast	Split - Faster	Splitless
Total run time (min.):	21	18.5	25.5
Sample analysis (min.):	18	15	20
Oven cooling (min.):	3	3.5	5.5
<b>Number of samples analyzed:</b>	<b>30</b>	<b>34</b>	<b>24</b>
(Data based on a 10.5 hour sample analysis period, following quality assurance and method performance samples, in a 12 hour shift.)			

**Figure 3: Resolution of Benzo[b]fluorathene; Benzo[k]fluoranthene and Dibenz[a,h]anthracene; Indeno[1,2,3-cd]pyrene with different cycle times**



### Repeatability

- A split injection with the Precision® Liner packed with Semivolatiles Wool provided lower relative standard deviations (%RSD) compared to a splitless injection. **(Table IV)**
- Starting with a lower variance between injections allows more injections before system maintenance is required.

**Table IV: Average (n=5) relative response factors (RF) at 0.5 ng on-column**

COMPOUND	SPLIT (10:1)		SPLITLESS	
	RF	%RSD	RF	%RSD
Pyridine	1.534	2.14	1.038	9.00
Phenol	1.861	0.65	1.857	5.01
N-Nitroso-di-n-propylamine	1.053	2.40	1.266	2.68
2,4-Dichlorophenol	0.317	2.44	0.325	3.14
Naphthalene	1.249	0.51	1.238	2.46
Hexachlorocyclopentadiene	0.407	1.00	0.414	4.62
2-Nitroaniline	0.395	3.12	0.514	3.02
Acenaphthylene	2.188	0.90	2.139	1.03
2,4-Dinitrophenol	0.113	8.16	0.127	12.92
N-Nitrosodiphenylamine	0.712	1.49	0.694	1.08
Pentachlorophenol	0.115	2.91	0.098	5.48
Phenanthrene	1.252	0.69	1.259	1.81
AVG %RSD		2.80		6.13

### Calibration

- A calibration curve was run at 160, 120, 80, 40, 20, and 5 µg/mL to evaluate the linearity of the split injection and instrument sensitivity. **(Table V)**
- When analyzing below the typical calibration range at 1 µg/mL (0.1 ng on-column) 2, 4-dinitrophenol had a response factor of 0.044, which is still well above the method minimum response factor of 0.01.
- By employing a 10:1 split injection the concentrated samples are less overloaded providing narrower, symmetric peak shapes, compared to a splitless injection.

**Table V: Split Injection (10:1) Calibration Average Response Factors at 160 - 5 µg/mL**

Compound	Average RF	Average %RSD
Pyridine	1.533	0.891
Phenol	1.787	2.357
N-Nitroso-di-n-propylamine	0.991	1.578
2,4-Dichlorophenol	0.272	2.563
Naphthalene	0.998	4.575
Hexachlorocyclopentadiene	0.383	5.557
2-Nitroaniline	0.414	5.757
Acenaphthylene	1.824	3.240
2,4-Dinitrophenol	0.157	26.239
N-Nitrosodiphenylamine	0.608	3.355
Pentachlorophenol	0.127	15.971
Phenanthrene	1.082	4.715

### **Ruggedness**

- A soil extract from a UST removal site was provided by Fairway Laboratories for the ruggedness evaluation between split and splitless injections.
- A 10:1 split injection decreases the overall amount of material that is deposited onto the column, therefore increasing the amount of samples that can be analyzed before system maintenance is necessary. **(Figure 4)**
- A DFTPP tune criteria and a continuing calibration check standard was evaluated and passed prior to sample extract analysis.
- Although the 2,4-Dinitrophenol response factor was initially higher for a splitless injection, it declined much quicker than the split injection method. **(Figure 5)**
- The same amount of sample was deposited on the wool inside the liner (picture below), however with a split injection 34 more sample extracts were analyzed before maintenance was required

Figure 4: A split injection reduces the amount of sample deposited on-column therefore increasing column lifetime

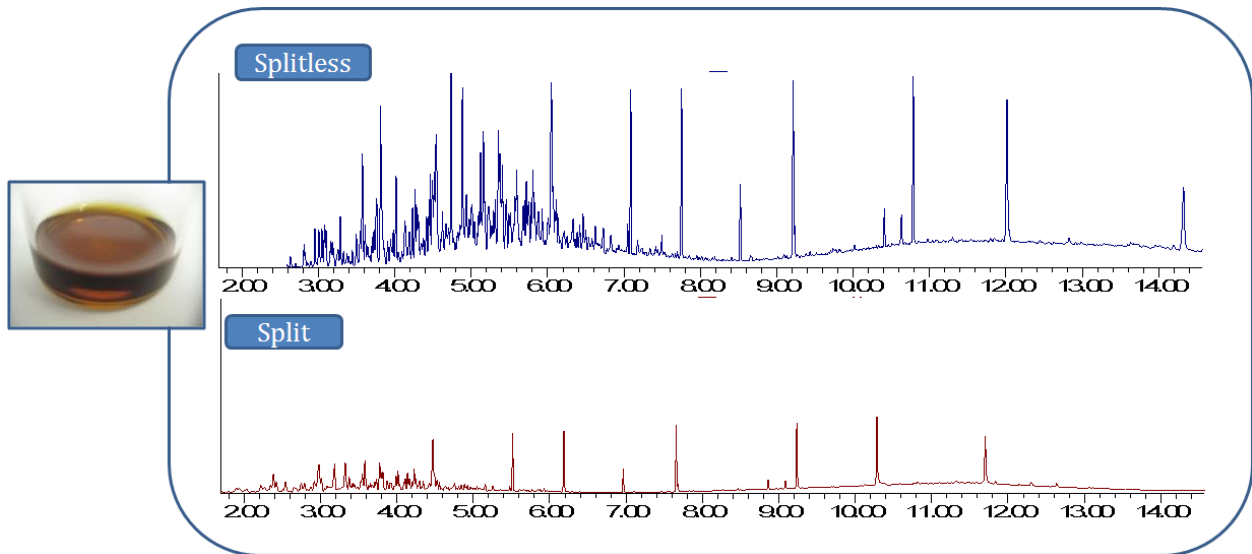
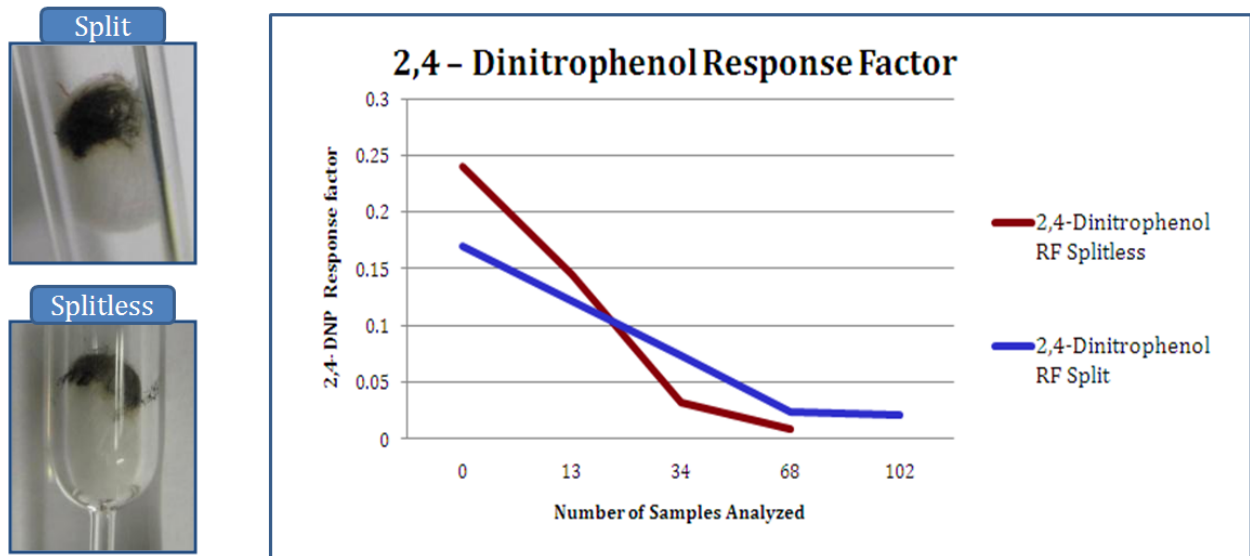


Figure 5: More sample extracts analyzed by split injection before maintenance was necessary because of a slower decline of 2,4-DNP response



## Conclusion

- Increased sample throughput was achieved by increasing the initial oven temp to 80°C.
- Injection-to-injection repeatability increased by employing a 10:1 split injection for semivolatiles analysis compared to a splitless injection.
- A linear calibration curve ranging from 160 – 5 µg/mL (16 – 0.5 ng on-column) is possible with a 10:1 split injection
- By splitting off a portion of the sample, and with increased flow through the liner, more sample injections can be made before a continuing calibration check does not pass.