

Using the PSD for Backflushing on the Agilent 8890 GC System

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Abstract

An Agilent 8890 series GC equipped with an Agilent capillary flow technology Deans switch coupled to flame ionization detection and flame photometric detection was used to analyze a heavy hydrocarbon distillate: residual fuel oil. Residual fuel oils typically contain hydrocarbons in the range from C₁₀ to C₇₀ with a significant amount of sulfur-containing compounds. To prevent carryover without requiring excessive column bake-out periods, the use of backflushing is necessary. An electronic pneumatic control (EPC) module called the pneumatic switching device (PSD) was used to accomplish both Deans switching and backflushing in a single chromatographic method.

Introduction

The use of backflushing in gas chromatography (GC) is essential for obtaining reproducible results in a timely manner when analyzing complex samples containing high boiling point compounds. The benefits of backflushing have been documented extensively¹⁻³. Backflushing is growing in popularity due to ease-of-use improvements such as Agilent capillary flow technology (CFT) devices⁴. The recently released Agilent Intuvo 9000 GC system delivers easy-to-use backflush capability as a standard option^{5,6}.

With the release of the Intuvo 9000 GC system came a newly designed EPC module (available on the 8890 GC) called the PSD. The PSD has two pneumatic control channels. The primary channel is a forward pressure-controlled channel. This would typically be used to supply pressure for a backflush or CFT device, similar to the AUX EPC or PCM. The second channel of the PSD (called the purge flow) is an engineered bleed restrictor for the first channel. The purge flow is a user-controlled setpoint with a range of 3 to 30 mL/min with a default setpoint of 3 mL/min.

The purge flow has two main functions. First, it allows for better pneumatic control when the PSD is providing low volumetric flow. To supply the engineered bleed, a minimum amount

of supply pressure from the primary channel is required. The requisite primary channel pressure ensures that the EPC proportioning valve functions in a stable regime. For example, in a midcolumn backflush configuration, the midpoint pressure source may only provide a few tenths of mL/min of total flow to the second column. Without this purge flow, the valves would not be able to control the flow accurately due to having to control a low supply pressure. To address this issue in previous pneumatic configurations, a bleed restrictor had to be constructed manually by cutting into the pressure line and installing a tee and restrictor. The purge flow engineered into the PSD provides a built-in bleed restrictor.

The second function of the purge flow is that it can be held at constant flow with varying input pressures, which helps conserve carrier gas. For example, a typical backflush system uses a fixed restrictor, such as 1 m of 250 μm fused silica tubing. At high pressures (that is, during backflush), the fixed restrictor can have hundreds of mL/min of wasted flow. The PSD will stay at the user-defined setpoint (default 3 mL/min) even at high pressures.

Experimental

Figure 1 shows a schematic of the 8890 GC system used. The Deans switch was configured to cut between 20.1 and 20.4 minutes. This cuts 4,6-dimethyldibenzothiophene from column 1 to column 2 for detection with FPD Plus. The multimode inlet (MMI) was used. All analyses used helium as the carrier gas in constant flow mode. See Table 1 for additional instrumental parameters used. Table 2 gives the backflush settings. A simulated distillation separation was performed to analyze the carbon chain distribution in the residual fuel oil. An Agilent J&W DB-HT Sim Dis column (5 m \times 530 μm , 0.15 μm) was used. This experiment did not use the Deans switch apparatus. Table 3 lists the parameters used for the simulated distillation method. Table 4 lists relevant consumables used in the experiment.

Samples

The heavy distillate analyzed was NBS 1622c – 2 % sulfur in residual fuel oil (RFO). This was diluted 1:40 in toluene, then injected 1 μL splitless. The polyethylene standard (Polywax 500) was diluted to 0.1 % in toluene, and injected 1 μL splitless.

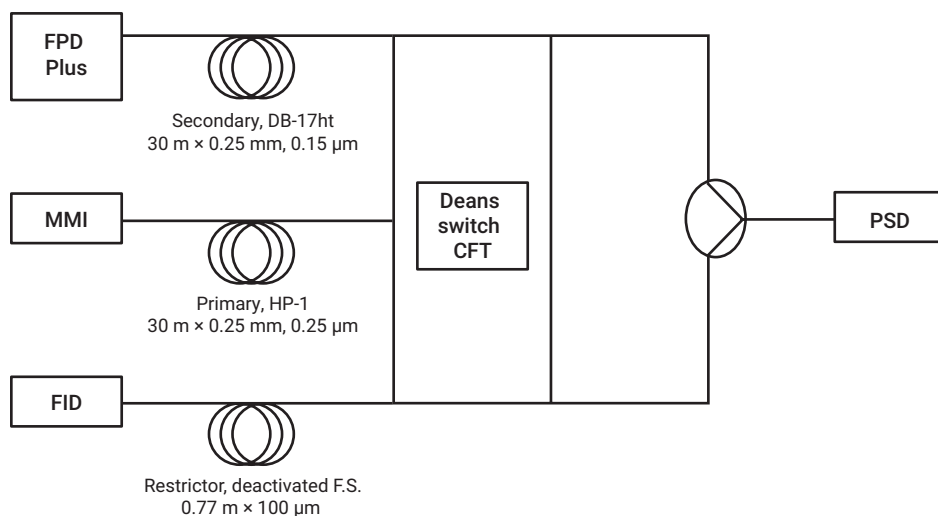


Figure 1. Schematic of the 8890 GC system configured with Deans switch with the PSD.

Table 1. Instrumental parameters.

| Parameter | Value |
|--------------------------|---|
| Gas chromatograph | 8890 Series GC |
| Automatic liquid sampler | Agilent 7693A automatic liquid sampler (1 μ L injection) |
| Inlet type | MMI |
| MMI program | 100 °C (0.02 minutes), 900 °C/min to 450 °C |
| Oven program | 50 °C (1 minute), 10 °C/min to 350 °C (1.5 minutes) |
| Column 1 | Agilent J&W DB-1ms UI, 30 m \times 250 μ m, 0.25 μ m, 2 mL/min (helium) |
| Column 2 | Agilent J&W DB-17ht, 30 m \times 250 μ m, 0.15 μ m, 3 mL/min (helium) |
| Restrictor | 0.77 m \times 100 μ m deactivated fused silica, 3 mL/min (helium) (controlled through column 2) |
| Aux. pressure source | Pneumatic switching device (PSD) |
| PSD purge flow | 3 mL/min (default) |
| FPD+ | Sulfur filter (394 nm) Transfer line: 350 °C Emission block: 150 °C Air: 60 mL/min Hydrogen: 60 mL/min Nitrogen: 60 mL/min |
| Deans switch window | 20.1 to 20.4 minutes |

Table 2. Backflush parameters.

| Parameter | Value |
|-------------------|--------------------------------|
| Oven (post run) | 360 °C (5 minutes) |
| Inlet temperature | 450 °C |
| Inlet purge flow | 100 mL/min |
| PSD | 70 psi (4.5 mL/min column 2/3) |
| Inlet | 2 psi (4.5 mL/min column 1) |

Table 3. Simulated distillation parameters.

| Parameter | Value |
|--------------|---|
| Column | Agilent J&W DB-HT Sim Dis, 5 m \times 530 μ m, 0.15 μ m |
| Carrier flow | 5 mL/min helium (constant flow) |
| Inlet (MMI) | 100 °C (0.02 minutes), 900 °C/min to 450 °C |
| Oven program | 40 °C (no hold), 10 °C/min to 430 °C (5 minutes) |
| FID | 450 °C Air: 450 mL/min Hydrogen: 40 mL/min Nitrogen: 30 mL/min |

Table 4. Consumables used.

| Parameter | Value |
|-----------|--|
| Syringe | Blue Line, 5 μ L, tapered (p/n G4513-80206) |
| Liner | Ultra Inert, split, glass wool (p/n 5190-2295) |
| Ferrules | Flexible metal ferrules, UltiMetal Plus, 0.4 mm id (p/n G3188-27501) |
| Column 1 | J&W DB-1ms UI (p/n 122-0132UI) |
| Column 2 | J&W DB-17ht (p/n 122-1831) |
| Software | Agilent OpenLab 2.3 |

Results and discussion

Figure 2 shows an overlay of the NBS 1622c RFO and the Polywax 500 calibration standard obtained with the SIMDIST parameters. The carbon chain distribution of the RFO appears to tail off at the end of the Polywax distribution near C_{70} , which has a boiling point of 647 °C⁷. If this sample were analyzed with a typical chromatographic setup using standard capillary columns, there would be significant carryover, as much of the heavy hydrocarbon backbone would not elute. The full range of boiling points in a sample is often not known prior to beginning analysis, but in this case, it shows the need for backflushing.

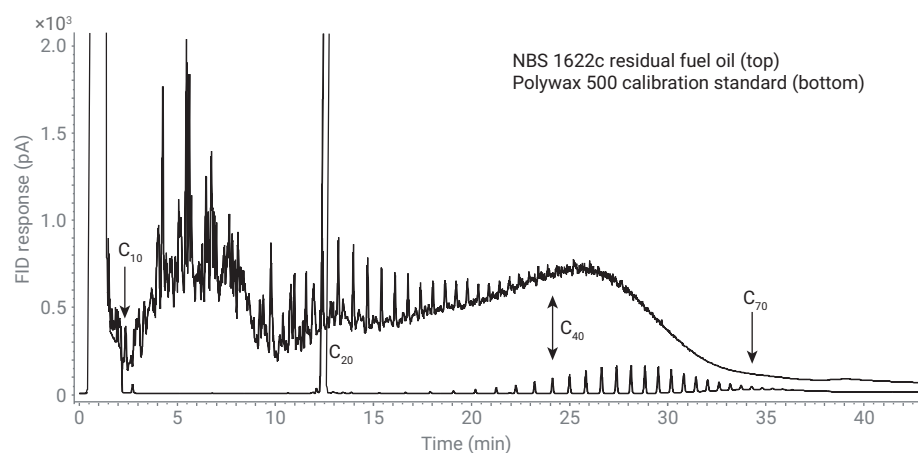
**Figure 2.** Chromatogram of NBS 1622c overlaid with Polywax 500 calibration standard. The NBS RFO sample contains compounds ranging between C_{10} and C_{70} .

Figure 3A shows an overlay of three replicate injections of the NBS 1622c RFO separated on the J&W DB-1ms UI column and detected by FID with the Deans switch configuration. These injections did not use backflush. The separation ended at a final temperature of 350 °C, near the upper operating range of both the J&W DB-1ms UI and J&W DB-17ht columns. The final peak that eluted was C₃₆. Each subsequent injection shows a growing baseline toward the end of the chromatogram, indicating that the sample is not fully eluting from the previous injection, and carryover is occurring. Comparing the chromatograms in Figure 3A to the chromatograms in Figure 2, it is clear that a significant portion of the sample remains on the column (the portion from C₃₆ to C₇₀).

The region from 20.1 to 20.4 minutes marked in Figure 3A was cut to the second column for detection with the FPD Plus. Figure 3B shows the cut region from (A) separated on the secondary column (J&W DB-17ht) and detected with the FPD Plus. The tallest peak is 4,6-dimethyldibenzothiophene (4,6-DMDBT) with two unidentified smaller peaks on either side. The retention time shifts significantly, and the area precision is poor. This is a common side-effect of having a large amount of carryover between runs, as evidenced by the increasing baseline in 3A. Figure 3C shows a no-inject blank after the three injections of the RFO. The heart-cut still occurs at 20.1 to 20.4 minutes, and a small peak of 4,6-DMDBT appears in the FPD Plus channel. There is still significant carryover on the FID channel as evidenced by the growing baseline at the end of the chromatogram.

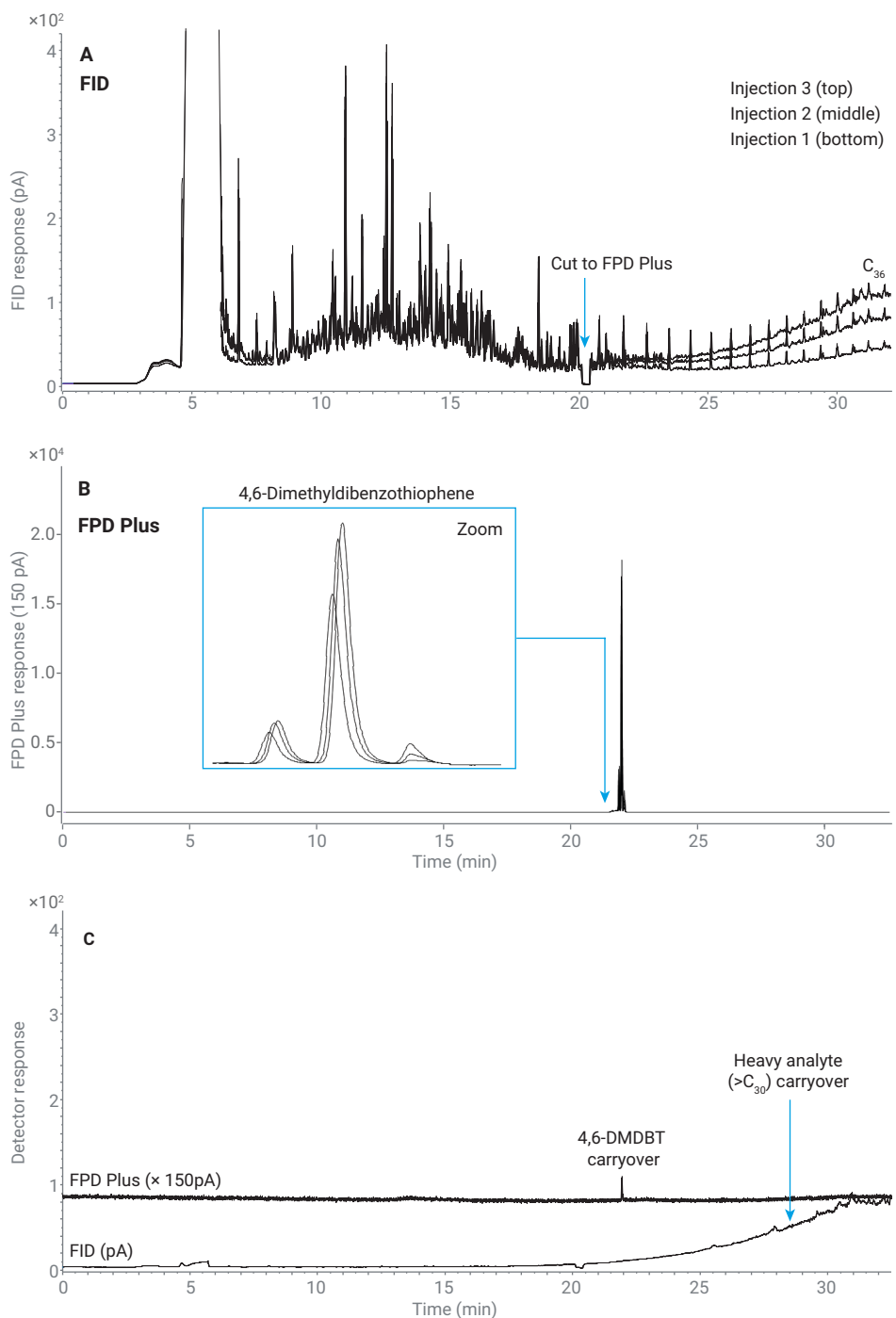


Figure 3. A) Overlay of three injections of NBS 1622c RFO with a narrow heart-cut 20.1 to 20.4 minutes and no backflush. B) Overlay of the three cuts from (A) of 4,6-DMDBT detected with FPD Plus. C) No-inject blank run after three injections of (A).

Figure 4A shows an overlay of three replicate injections of the NBS 1622c RFO with the same experimental parameters as Figure 3, but with backflush. See Table 2 for backflush parameters. During the backflush, the PSD is held at 70 psi to backflush column 1 with 4.5 mL/min of flow (towards the inlet). The purge flow is held at 3 mL/min. A fixed restrictor of 1 m × 250 μm would allow nearly 500 mL/min of flow during the 70 psi backflush. The PSD provides significant savings in gas flow.

The end of the separation, from 25 to 30 minutes in Figure 4A, is very reproducible. There is no increase in baseline, as seen in the nonbackflush chromatogram in Figure 3A.

Figure 4B shows the cut region at 20.1–20.4 minutes from Figure 4A. The retention time and area precision are remarkably improved. Figure 4C shows a no-inject blank following the three injections of the RFO using backflush. There is no visible carryover of heavy analytes in the FID channel. This shows that the backflush works well.

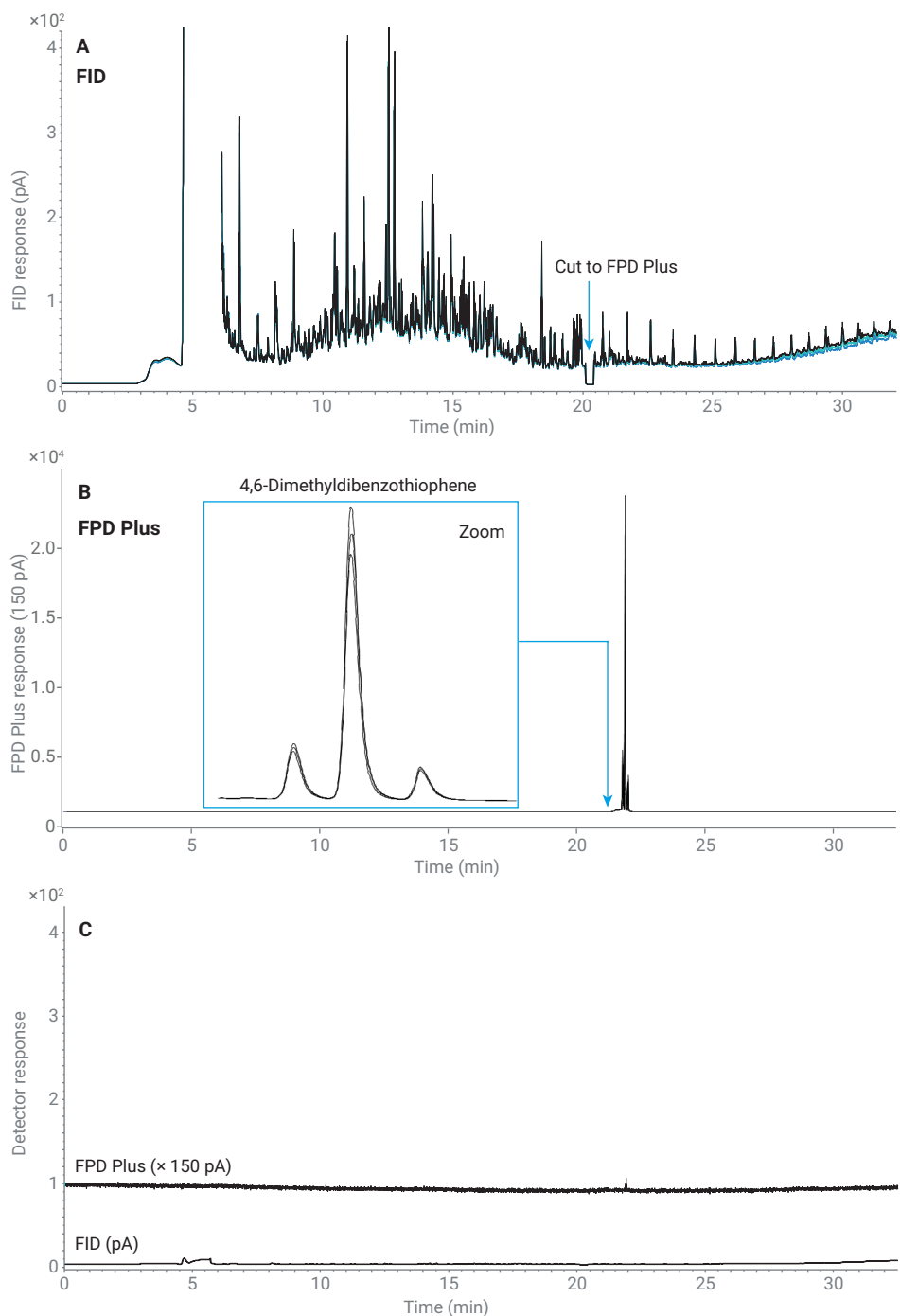


Figure 4. A) Overlay of three injections of NBS 1622c RFO with a narrow heart-cut at 20.1–20.4 minutes with backflush. B) Overlay of the three cuts from (A) of 4,6-DMDBT detected with FPD Plus. C) No-inject blank run following three injections of NBS 1622c RFO from (A).

Conclusion

The 8890 GC system coupled with a Deans switch to FID and FPD Plus with backflushing is shown to provide reproducible analyses of a heavy hydrocarbon distillate: an RFO sample with a carbon chain distribution from C₁₀ to C₇₀. The PSD provided backflush capability with significantly reduced carrier gas consumption due to the fixed purge flow. The use of backflushing can extend column lifetime due to not requiring extended high-temperature bake-outs. This also helps increase sample throughput due to shorter run-to-run times.

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