

Analysis of Sulfur-Containing Compounds in Diesel and Residual Fuel Oil with Heart-cutting Multidimensional GC

Using the Agilent 8890 GC System

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Abstract

An Agilent 8890 GC coupled with flame photometric detection (FPD) and flame ionization detection (FID) was used to analyze the distribution of hydrocarbons and sulfur-containing compounds in diesel and residual fuel oil (RFO). Multidimensional heart-cutting GC was performed using an Agilent capillary flow technology Deans switch to sample regions from a nonpolar primary column to a midpolarity secondary column to aid in the separation of sulfur-containing compounds, mainly alkylated dibenzothiophenes. The midpolarity column helps reduce quenching of the analytes when detected with the FPD. A calibration curve of 4,6-dimethyldibenzothiophene demonstrated linearity across two orders of magnitude from 1 to 100 ppm with the FPD Plus. An electronic pneumatic control (EPC) module called the pneumatic switching device (PSD) was used to control the flows for the Deans Switch. The PSD also provided the system with enhanced backflushing.

Introduction

For several decades, worldwide environmental regulations have consistently lowered the allowable sulfur content in hydrocarbon fuels used in road, agricultural, locomotive, and maritime applications. This will likely continue to decrease in the future^{1,2}. Producing adequate quantities of these low-sulfur fuels in an economical fashion is an ongoing challenge in the hydrocarbon processing industry. Understanding the distribution of sulfur-containing compounds in hydrocarbon feedstocks is critical for optimal catalytic cracking performance. It is also important with refined products to ensure consistency, optimal performance, and regulatory compliance. Gas chromatography (GC) coupled with FPD is a commonly used tool for the speciation of sulfur in complex hydrocarbon samples. The redesigned flame photometric detector (the FPD Plus) from Agilent has a deactivated transfer line and separate thermal zones to ensure transfer of active and high-boiling-point compounds from the column to the flame emission region³. Multidimensional GC (MDGC) uses multiple columns connected in series to increase the resolving power and selectivity of the system. The Deans switch is used to cut a region of interest, known as a heart-cut, from the primary column to the secondary column. The secondary column has a different stationary phase that ideally will separate unresolved components from the first dimension. In this Application Note, the primary column was a nonpolar Agilent J&W DB-1ms Ultra Inert (100 % dimethylpolysiloxane), and column two was a moderate polarity Agilent J&W DB-17ht (50 % phenylmethylpolysiloxane).

To reduce the possibility of quenching in the FPD Plus, the midpolar J&W DB-17ht aids in separating the sulfur-containing compounds. The Deans switch is also compatible with backflush to remove high-boiling-point compounds from the system at the end of a run without excessive bake-out periods. The PSD was used as the auxiliary pressure source for Deans switching and backflushing.

This Application Note used the 8890 GC system with an Agilent capillary flow technology (CFT) Deans switch coupled to FID and FPD Plus. The system was tested with a middle distillate and a heavy distillate, diesel and RFO, respectively.

Experimental

Figure 1 shows a schematic of the 8890 GC system used. The Deans switch was configured for the effluent of column 1 to pass through the restrictor (to the FID) when the actuating valve was off. The flow was switched to column 2 (to the FPD Plus) when the valve was actuated. The Agilent Deans switch calculator was used to calculate the appropriate length of the restrictor. A multimode inlet (MMI) was used, and operated in temperature-programmed mode in both split and splitless modes. 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.

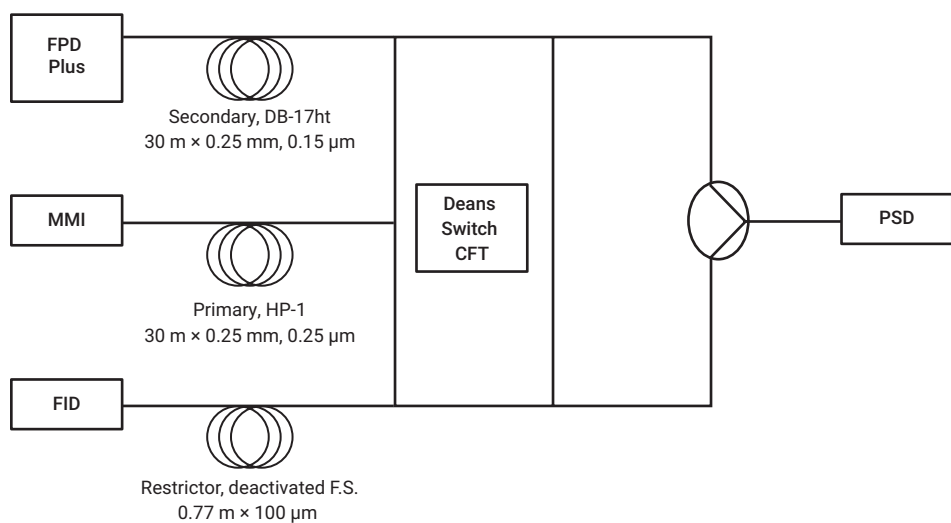


Figure 1. Schematic of the 8890 GC system configured with a Deans switch to FID and FPD Plus.

A simulated distillation separation was performed to analyze the carbon chain distribution in the RFO. A DB-HT Sim Dis column (5 m × 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.

Samples

The middle distillate tested was NIST SRM 2724–sulfur (425 μg/g) in diesel fuel oil. One microliter was injected neat at a split ratio of 100:1. The heavy distillate was NBS 1622c–2 % sulfur in RFO. This was diluted 1:40 in toluene, then injected 1 μL splitless. Serial dilutions of 4,6-dimethyldibenzothiophene (4,6-DMDBT) in toluene were made to 1, 5, 10, 25, 50, and 100 ppm. These had an injection volume of 1 μL at a split ratio of 25:1. The polyethylene standard (Polywax 500) was diluted to 0.1 % in toluene, and injected 1 μL splitless. Table 4 lists the consumables used.

Table 1. Instrumental parameters.

Parameter	Value
Gas chromatograph	8890 Series GC
Automatic liquid sampler	Agilent 7693A automatic liquid sampler (1 μL 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	DB-1ms UI (30 m × 250 μm, 0.25 μm), 2 mL/min (He)
Column 2	DB-17ht (30 m × 250 μm, 0.15 μm), 3 mL/min (He)
Restrictor	0.77 m × 100 μm deactivated fused silica, 3 mL/min (He) (controlled using column 2)
Auxiliary pressure source	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	18 to 24 minutes for diesel 20.1 to 20.4 minutes for 4,6-DMDBT

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	J&W DB-HT Sim Dis (5 m × 530 μm, 0.15 μm)
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	5 μL tapered (Blue Line) (p/n G4513-80206)
Liner	Ultra Inert, split, wool (p/n 5190-2295)
Ferrules	Flexible metal ferrules (p/n G3188-27501)
Column 1	DB-1ms UI (p/n 122-0132UI)
Column 2	DB-17ht (p/n 122-1831)
Software	Agilent OpenLab 2.3

Results and discussion

The first sample analyzed was the NIST 2724 sulfur in diesel fuel oil sample. The total sulfur is certified at 0.0425 % (425 ppm). Figure 2A shows the entire separation of the diesel without heart-cutting any regions detected with the FID. This sample eluted fully within the temperature program and did not require backflushing. Figure 2B shows the separation of the diesel with the Deans switch heart-cut from 18 to 24 minutes. This contrasts with the traditional operation of a Deans switch, where a single compound (or small window) is cut from a complex matrix to resolve nearby interferences. In this case, a large region of the separation was sampled to reveal a family of compounds. Figure 2C shows the heart-cut region from Figure 2B separated on the secondary column, DB-17ht, detected with the FPD Plus. There is a distribution of alkylated dibenzothiophenes in this region. This family of compounds, especially those with substitutions at the 4 or 6 positions (or both) are sterically hindered during the hydrodesulfurization process and remain present in higher concentrations⁴. Thus, to ensure low enough sulfur levels after treatment to pass regulatory requirements, it is advantageous to monitor these slowly reacting compounds. The United States Environmental Protection Agency (US EPA) allows highway diesel to have no more than 15 ppm total sulfur².

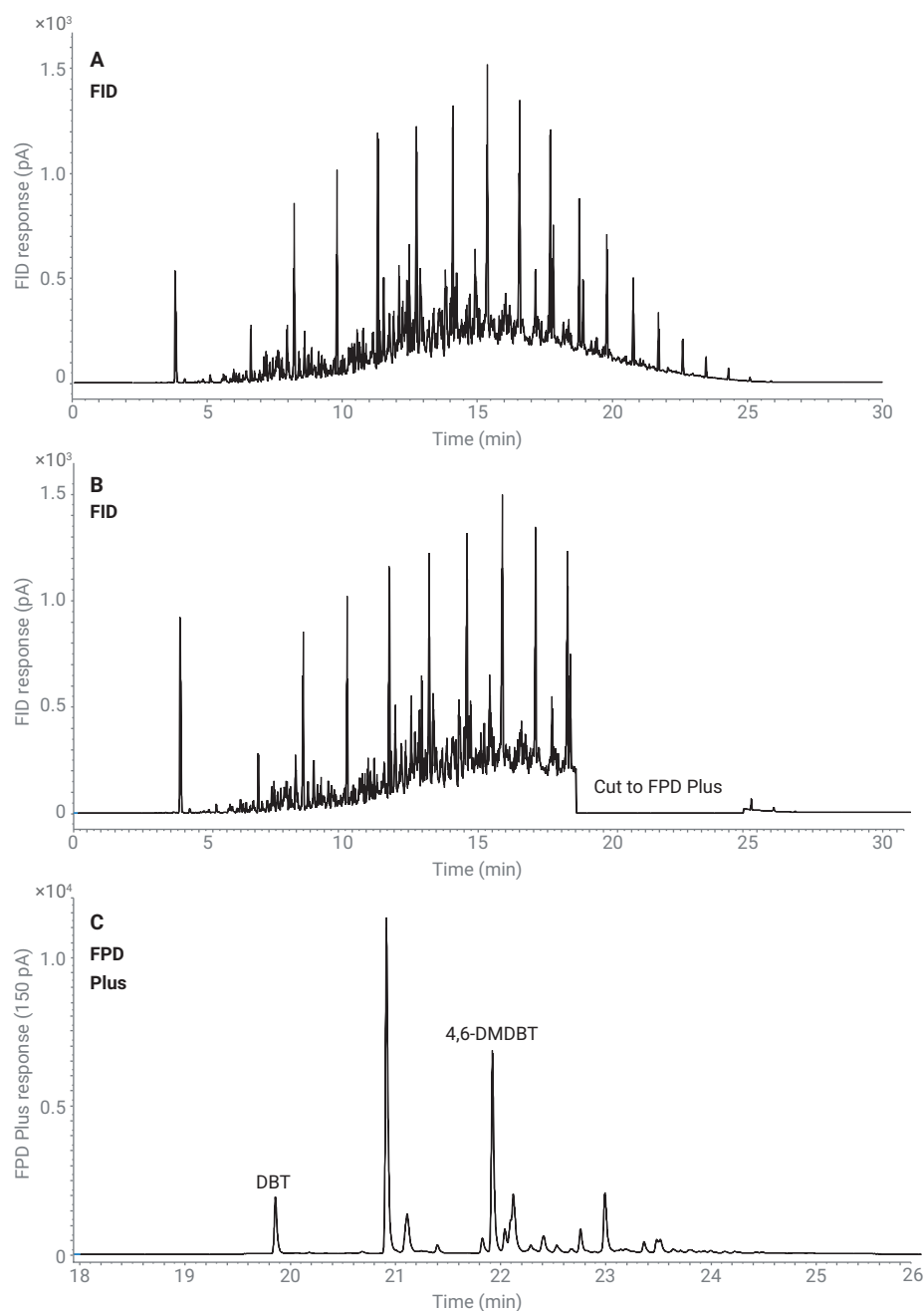


Figure 2. A) Separation of NIST 2724 (sulfur in diesel fuel) detected with FID. B) Separation of NIST 2724 with region 18 to 24 minutes cut to the FPD Plus. C) Region from (B) separated on the secondary column, J&W DB-17ht, and detected with the FPD Plus.

The next sample analyzed was the NBS 1622c RFO with total sulfur present at nearly 2 %. These RFOs, also known as bunker fuel or number 6 fuel oil, can have extremely high sulfur content depending on the source of the crude oil from which they were derived. Global restrictions on sulfur content will soon have major implications. Current regulations for marine use, where most of these fuels are used, allow for a maximum sulfur content of 3.5 %. In 2020, this restriction will fall to 0.5 % (5,000 ppm) with 0.1 % (1,000 ppm) required within Sulfur Emission Control Areas (SECAs). Producing these ultralow sulfur fuel oils (ULSFO) is nontrivial. However, many ocean-going vessels can use sulfur scrubbers to continue using high sulfur fuel oils while staying within sulfur emission limits¹.

Figure 3A shows the separation of the NBS 1622c RFO separated on the DB-1ms UI column and detected with the FID. The sample was diluted 1:40 in toluene and injected splitless. Due to the nature of the Deans switch having an auxiliary pressure source after the outlet of the primary column, it allows for the use of backflushing. The backflush began at 32 minutes (near C₃₆). Table 2 provides the backflush parameters. The PSD is an excellent device for providing backflushing. It has a fixed purge flow (default of 3 mL/min), so for backflush runs with high pressure, the purge flow does not become excessive. Most backflush implementations use a static restrictor (such as a tee coupled to a fixed length of capillary tubing). These systems can have very high purge flows (>500 mL/min) when backflushing at high pressures.

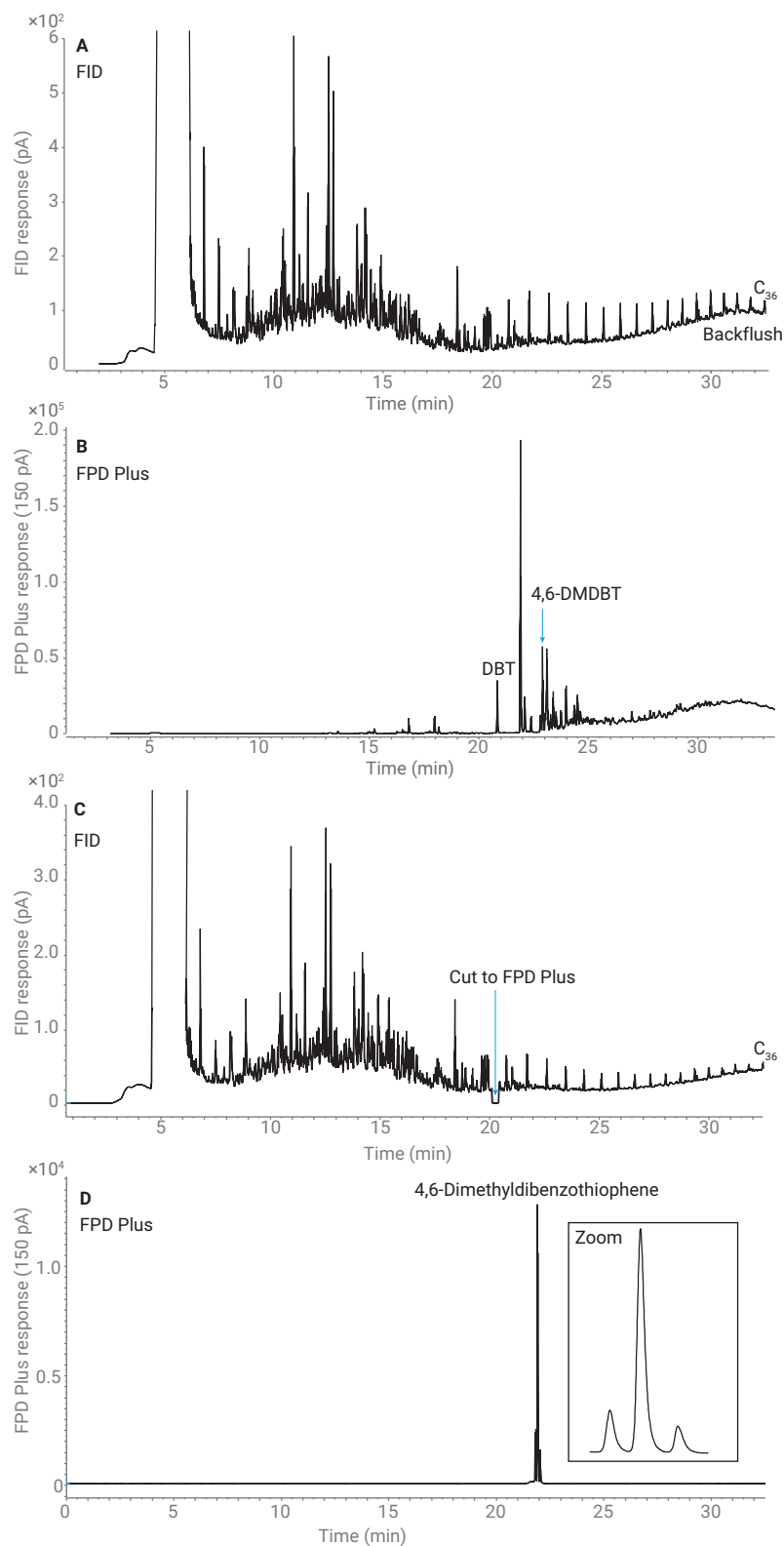


Figure 3. A) Separation of NBS 1622c (sulfur in RFO) detected with FID. Heavy eluting compounds (>C₃₆) were backflushed at 32 minutes. B) Separation of NBS 1622c detected using FPD Plus. The Deans switch delivered the entire sample to the secondary column to view the entirety of the sulfur-containing compounds. C) Separation of NBS 1622c with a narrow heart-cut from 20.1 to 20.4 minutes. D) Cut from (C) of 4,6-DMDBT.

Whereas in Figure 3A, the entire sample was sent to the FID, Figure 3B shows the separation of the Deans switch configured such that the entirety of the sample was sent to the secondary column to the FPD Plus. This is an unusual use of a Deans switch configuration, but allows for great flexibility in the study of unknown samples using different detectors. This method shows the distribution of sulfur compounds in the entire sample, rather than just a small region. It is possible that some quenching of the FPD Plus occurs, but Figure 3A shows that most of the hydrocarbons are separated (from 5 to 20 minutes) before the dibenzothiophenes begin to elute. Similar to the NIST diesel sample, there is a significant amount of alkylated dibenzothiophenes in the sample, albeit in much higher concentrations. Figure 3C shows the NBS 1622c RFO detected through the FID with a small window cut between 20.1 and 20.4 minutes. This method incorporates both a heart-cut window and backflushing. Figure 3D shows that this heart-cut contains 4,6-DMDBT and two other unidentified compounds.

A calibration curve of 4,6-DMDBT was prepared from 1 to 100 ppm in toluene. The sample was injected onto the primary column, and the heart-cut window was 20.1 to 20.4 minutes. To avoid saturating the PMT, the sample was split 25:1. The detector shows a squared response for the sulfur species, so the data are linearized by taking the square root of the response. Figure 4 shows the calibration curve. At the lowest calibration level, 1 ppm (split 25:1), 5.7 pg of sulfur are injected onto the column. The minimum detectable limit (MDL) of the FPD Plus is 2.5 pg S/sec.

A final experiment was performed to study the carbon chain distribution in the NBS 1622c RFO. In this experiment, a short, megabore column (DB-HT Sim Dis, 5 m × 530 μm, 0.15 μm) was used. A polyethylene standard (Polywax 500) was used to verify the carbon number distribution. Polywax 500 contains a distribution of polyethylene chains between C₂₀ and C₇₀. Figure 5 shows an overlay of the NBS 1622c RFO and the Polywax 500 calibration standard. The high end of the RFO appears to tail off at the end of the Polywax distribution, near C₇₀. This shows the necessity (and benefit) of using backflush.

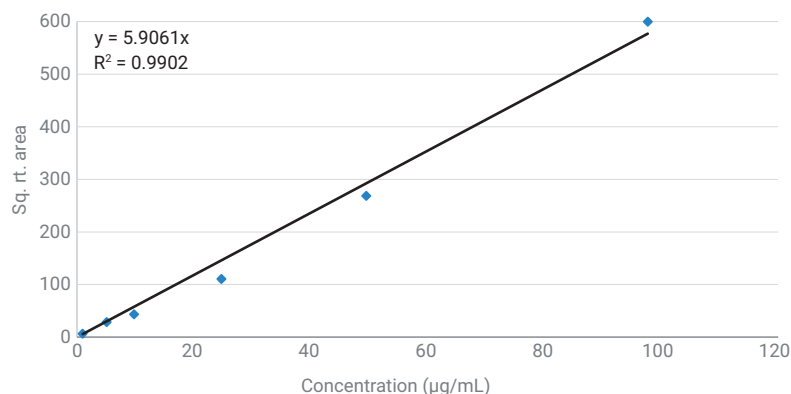


Figure 4. Calibration curve of 4,6-dimethyldibenzothiophene from 1 to 100 ppm.

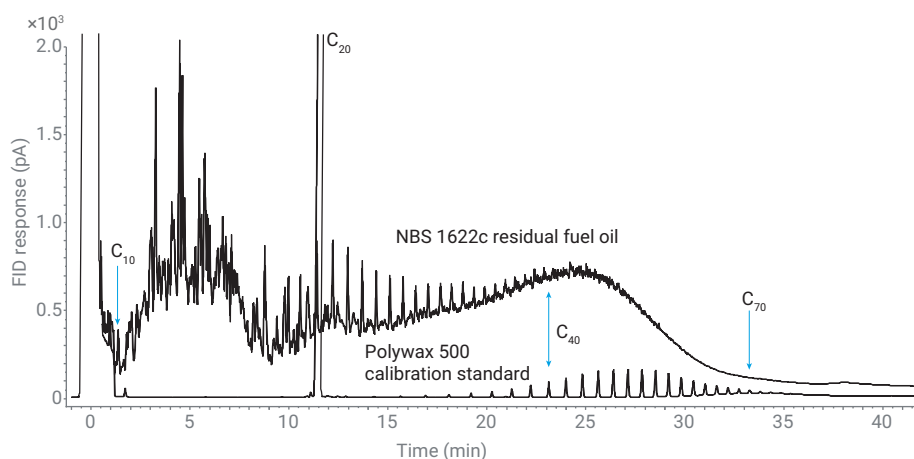


Figure 5. Chromatogram of NBS 1622c overlaid with a polyethylene calibration standard (Polywax 500). The NBS RFO sample contains compounds ranging between C₁₀ and C₇₀.

Conclusion

The 8890 GC system coupled with a Deans switch to FID and FPD Plus was able to separate and identify various sulfur-containing compounds in a middle and heavy distillate hydrocarbon sample. The use of a nonpolar J&W HP-1ms primary column and a midpolar J&W DB-17ht secondary column helped reduce the chance of coelution and quenching in the FPD Plus. The PSD provided backflush capability with significantly reduced carrier gas consumption due to the fixed purge flow. The system was shown to be able to backflush samples with carbon numbers up to C₇₀.

References

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