PAC | Application Note

Determination of Low Sulfur in Diesel (ULSD) by Gas Chromatography and Sulfur Selective Detection (SCD)

- Sulfur in Diesel (Total & Distributed)
- Robust Solution using PAC SeNse Detector
- Excellent Recovery
- No matrix interference

Keywords: SeNse, Sulfur, ULSD

INTRODUCTION

Refinery streams contain many contaminants including sulfur, nitrogen and heavy metals. These contaminants reduce the quality of the product and degrade equipment and catalysts in reformers, catalytic crackers and hydrocrackers. Sulfur is the least tolerable of the impurties and present in the greatest quantity. It lowers the quality of finished products and affects the performance of refinning processes. Current regulatory limitations specify a maximum amount of 10 (mg/kg S) in ULSD (region depended).

The ULSD application provides sulfur distribution in diesel samples together with the total sulfur amount down to 1 mg/kg S (LDL distribution depended). The distribution of sulfur allows refineries to study their process streams indicated differences between feed and final product specifications.

INSTRUMENTAL

The sample is introduced by syringe (ALS) into the split/splitless inlet. The polydimethylsiloxane (methylsilicone) capillary column separates the Diesel components in a temperature-programmed run. The capillary column is coupled to a SCD *furnace* where the sulfur compounds are combusted to SO_2. Sulfur dioxide is reduced, in the presence of excess hydrogen to various reduced sulfur species. These species are transferred to a reaction cell. Ozone produced in the ozonator is added to the reaction cell where it reacts with the reduced sulfur species to create exited state sulfur dioxide. Relaxation of sulfur dioxide to the ground state releases a photon. The emitted light is measured using a photomultiplier tube and converted to a voltage.

RESULTS

This application note briefly illustrates the capability of gas chromatography with sulfur Chemiluminescence detection using the Analytical Controls SeNse SCD for the analysis of sulfur in a low-sulfur diesel fuel.

The column outlet is attached to a two-way splitter with make-up gas. The two outlets of the splitter are connected to the SeNse SCD and an FID to compare the hydrocarbon and sulfur signal.

Two NIST diesel fuel oil standards (SRM 2723a and SRM 2770 containing 10.9 mg/kg and 41.57 mg/kg sulfur respectively) are used to check the linearity of the system for Sulfur response. NIST 2723a SCD and FID chromatograms are displayed in figure 1 and 1a. NIST 2770 SCD signal is displayed in figure 2. The system shows very good linearity with $R^2 > 0.999$ (figure 3).

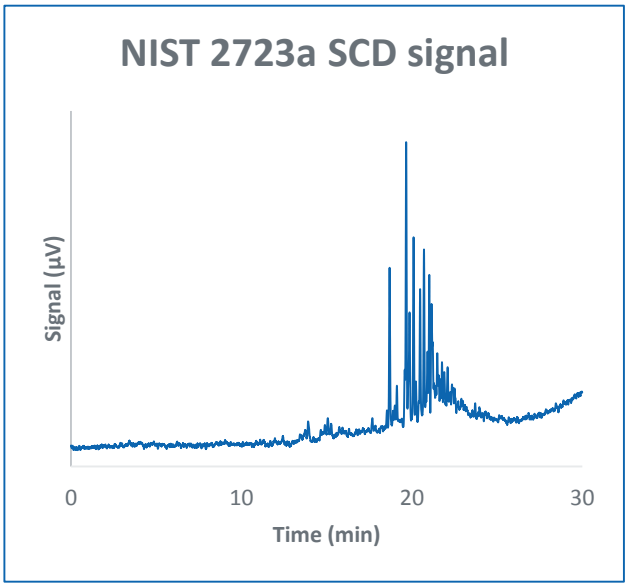

Figure 1: SCD signal of NIST 2723 SRM standard containing 10.9 mg/kg S

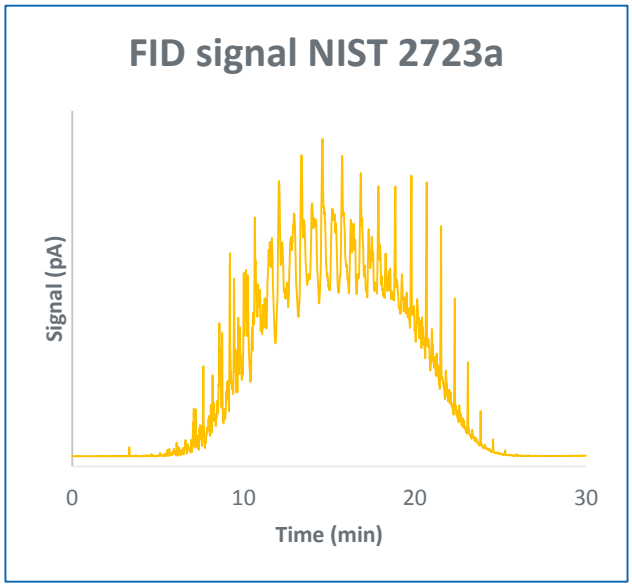

Figure 1a: FID signal of NIST 2723a

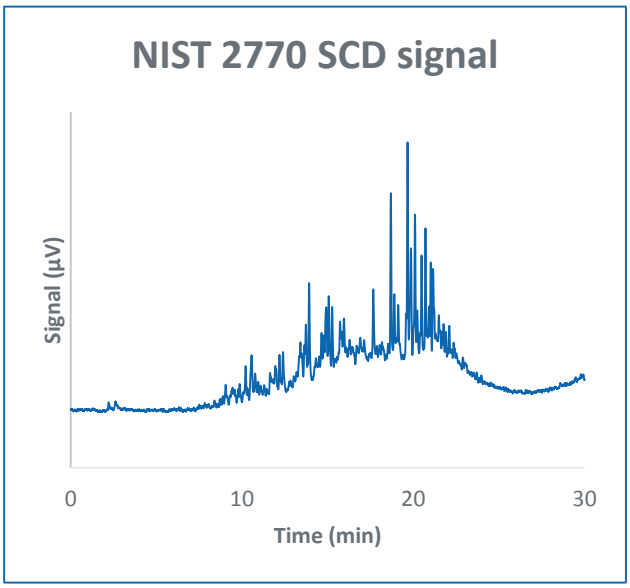

Figure 2: SCD signal of NIST 2770 SRM standard containing 41.57 mg/kg S

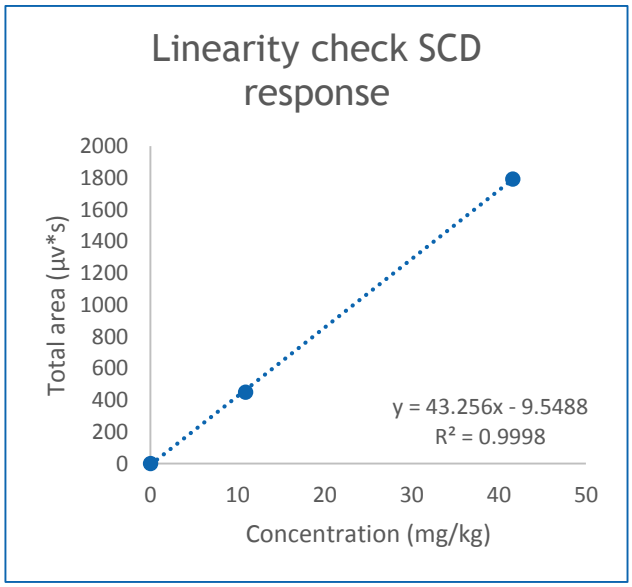

Figure 3: Linearity check based **SRM 2723a and SRM 2770**

A “Sulfur free” Diesel sample which contains virtually no Sulfur is analyzed as “Blank” to check the Selectivity of the detector. The SCD signal is displayed in figure 4. For illustration purpose, the FID signal is displayed in figure 4a. The sulfur response is negligible which illustrates the very good selectivity of sulfur over hydrocarbons.

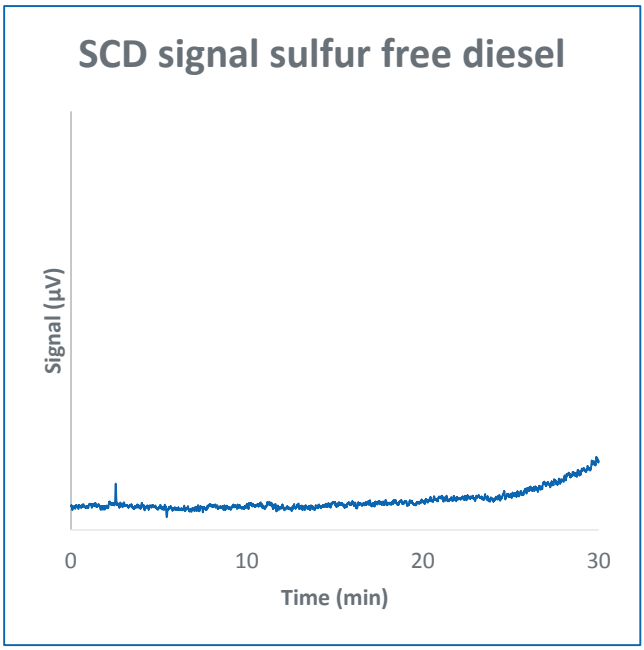

Figure 4: SCD signal of sulfur free diesel

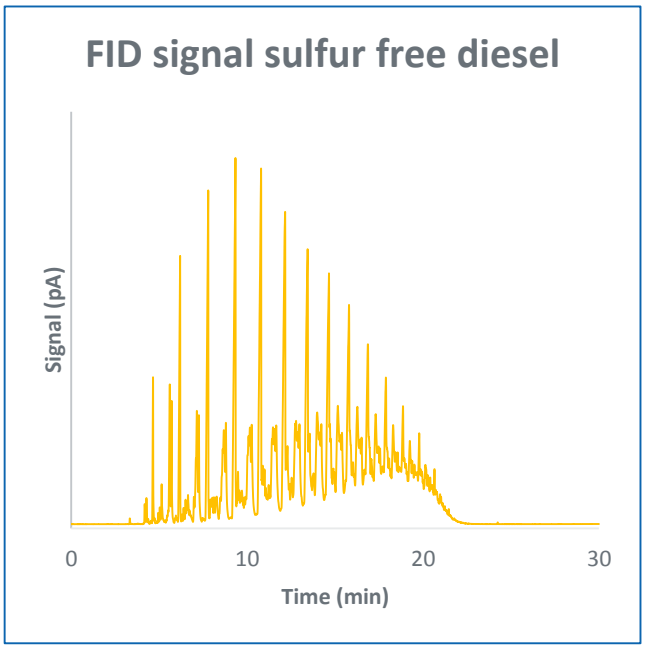

Figure 4a: FID signal of Sulfur Free Diesel

Two different ULSD samples (with and without FAME’s) have been analyzed on the system to check recovery values on low level. The values obtained by this application can be compared with the total sulfur values which have been obtained by a round robin test (RFA-wd and UVF). Two examples are displayed in figures 5 and 6.

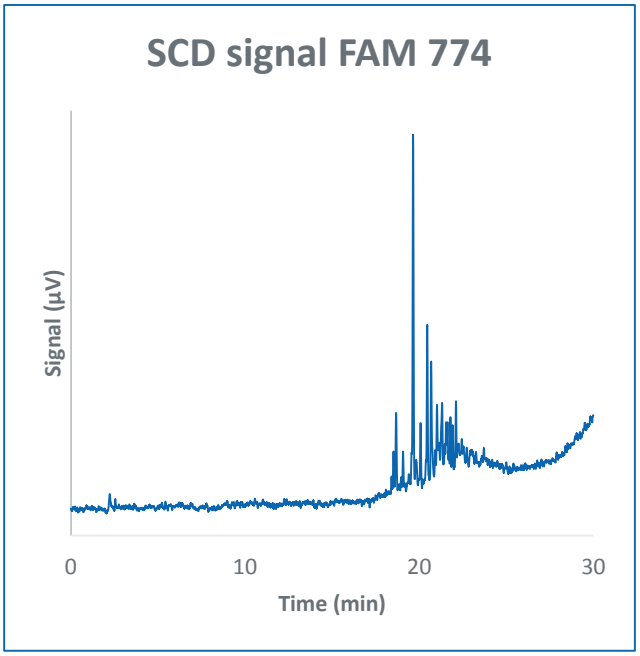

Figure 5: SCD signal of FAM 774

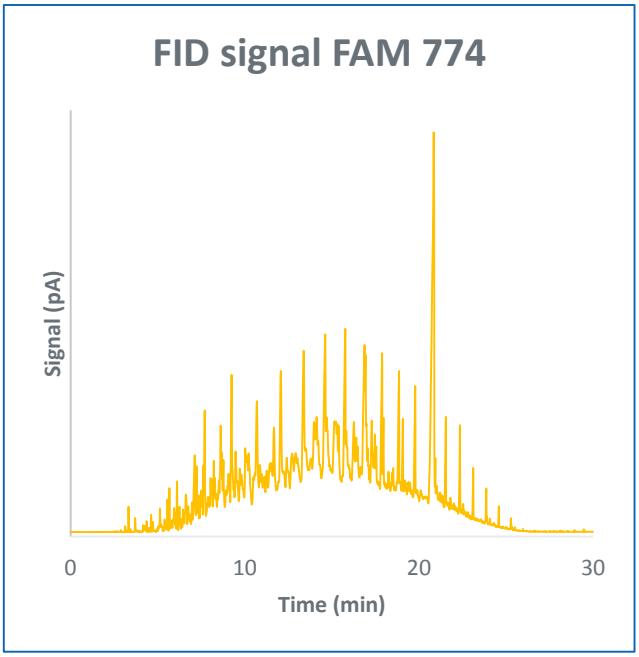

Figure 5a: FID signal of FAM 774

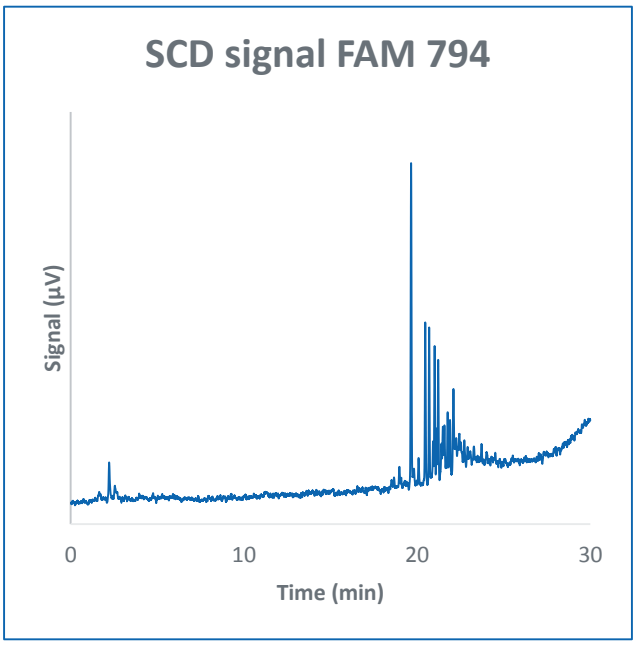

Figure 6: SCD signal of FAM 794

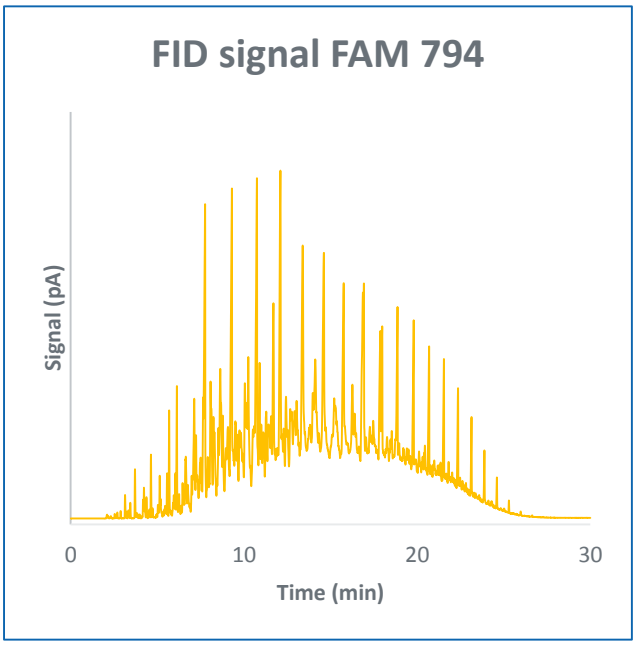

Figure 6a: FID signal of FAM 794

Recovery of the samples is calculated after response calibration with the NIST SRM sample. The recovery is compared with the total Sulfur results by RFA-wd (EN ISO 20884) and UVF method (EN ISO 20846) (table 1).

	EN ISO 20884 RFA-wd (mg/kg S)	EN ISO 20884 UVF (mg/kg S) Reproducability	EN ISO 20846 UVF (mg/kg S)	EN ISO 20846 UVF (mg/kg S) Reproducibility	PAC GC_SCD (mg/kg S)
FAM 774	6.86	2.72	6.93	1.90	6.52
FAM 794	5.16	2.52	5.55	1.74	5.21

Table 1: Recovery calculation

CONCLUSION

The AC Low sulfur in Diesel analyzer is a dedicated solution for accurate determination of Sulfur in diesel. Recovery values of Sulfur corresponds to total sulfur methods RFA-wd and UVF.

The application with the novel AC SeNse detector, already well known for its stability and ruggedness, makes the AC low sulfur in diesel system very robust and easy to use in routine environments. The analyzer provides low detection levels, stability and recovery values every time.

AC Analytical Controls® has been the recognized leader in chromatography analyzers for gas, naphtha and gasoline streams in crude oil refining since 1981. AC also provides technology for residuals analysis for the hydrocarbon processing industry. Applications cover the entire spectrum of petroleum, petrochemical and refinery, gas and natural gas analysis; ACs Turn-Key Application solutions include the AC Reformulyzer® , DHA, SimDis, NGA, Hi-Speed RGA and Customized instruments.