

Trace Sulfur Impurities in Petroleum Liquids Using the Sulfur Chemiluminescence Detector

Introduction

PerkinElmer-Arnel offers a family of turnkey analyzers that measure trace levels of sulfur compounds in liquid-phase petrochemicals, including liquefied petroleum gas (LPG), naphtha and gasoline. Analyzer Models 4026, 4027 and 4227 incorporate a sulfur chemiluminescence detector (SCD) for analysis of these liquids.

Key performance features of the SCD for these petrochemicals include high sensitivity, $> 10^4$ dynamic range, equimolar sulfur response, lack of carbon interference and simple calibration.

Features of SCD

- Trace-level analysis of H_2S , COS , SO_2 , mercaptans, aromatic sulfur compounds and sulfides
- Typical samples include LPG, gasoline, naphtha and liquid olefins
- Programmable Pneumatic Control (PPC) and non-PPC configurations

- Additional PID channel for aromatics and FID channel for hydrocarbons and oxygenates or total hydrocarbons such as methane are available
- Worldwide service and support

Analyzer models

Model 4026

The Model 4026 (Figure 1) analyzes liquids and compressed gas liquids such as LPG using a liquid sampling valve (LSV) connected directly to a capillary column and configured with the SCD for trace-sulfur measurement. This design provides the highest reliability and, especially for the lightest most active sulfur compounds, the best chromatography.

The valve is shown in the off or fill position. Sample is injected by turning the valve rotor clockwise. When the rotor turns, the liquid contained in the groove between ports "S" and "W" is placed in the carrier flow path or ports "C" and "P". Pressurized liquids immediately flash to a gas in a vaporization zone and then enter the column.

It is important to keep pressurized liquids as liquid when they are in the LSV's sample groove. If the sample vaporizes while in the groove, sampling precision is very poor. The LSV is mounted outside the column oven in order to keep the liquid as cool as possible and a spring-regulated check valve provides backpressure to the sample while in the sampling groove. This pressure prevents low vapor pressure components from vaporizing in the groove.

A secondary particulate filter, which is included, helps to prevent valve damage and is designed to be a backup filter should the operator's primary filter fail.

Model 4027

The Model 4027 (Figure 2) analyzes liquid samples via syringe injection to a capillary column.

Model 4227

The Model 4227 (Figure 3) adds an LSV and capillary column system to Model 4027 to also analyze pressurized liquids.

Column-temperature programs

The actual starting temperature and temperature program used in the analyzer depend upon the components to be analyzed. The liquid sampling valve is at ambient temperature and not in the analyzer's column oven. Therefore, the column oven temperature can be programmed to whatever is required to accomplish the analysis.

If a separation of COS and SO₂ is required, the analyzer must be configured with either the liquid nitrogen or liquid CO₂ cryogenic-oven cooling option.

Minimum detection limit (MDL)

Practical sulfur compound detection limits are < 10 ppb for liquid samples. Figure 4 presents an example chromatogram of a liquid standard comprising trace level sulfur compounds in toluene.

The SCD has a selectivity of > 10⁸ gS/gC i.e., one gram of sulfur generates a signal that is 10⁸ greater than the signal generated by a gram of carbon. Even with this great

selectivity, a very high concentration of a single hydrocarbon will generate a small signal.

For example, consider analyzing a sample of 10 ppb (molar) methylmercaptan in propane. The weight of the sulfur in the methylmercaptan (32) and the weight of the carbon in propane (3 x 12 = 36) are such that this sample contains ~10⁸ more carbon than sulfur on a weight basis. With a selectivity of > 10⁸, pure propane will generate a peak of the same size as the sulfur impurity. With more carbon in the component, pure butane would generate a larger peak.

Specifying a custom analyzer

Although the Model 4026, 4027 and 4227 analyzers cover most common samples, some sample combinations are better served by a custom adaptation of a standard model. Some examples include: the analysis of a sample with heavy components that might condense, a requirement to add an autosampler or the inclusion of an FID channel for another analysis to be combined with the SCD channel. These models all have an

unused detector location and, depending upon the samples to be analyzed, it is possible to add a second analysis or a second application.

Routine maintenance

The SCD is a trace-level detector with remarkable characteristics. This remarkable performance requires extremely clean gases, a working vacuum pump and a clean, active burner. All of these SCD analyzers require sulfur filters. Filter use depends upon the quality of your supply gases.

The SCD generates ozone and this gas is pulled to the vacuum pump. The chemical traps supplied in the optional one-year maintenance kit protect the pump by trapping the ozone.

Over long periods of use, SCD burner ceramics can deactivate. The ceramics are also deactivated if exposed to a hydrogen-rich atmosphere, due to loss of burner air. Sensitivity is recovered by the replacement of the SCD's ceramics. The best way to assure optimum system performance is to hold to a rigorous preventative maintenance schedule.

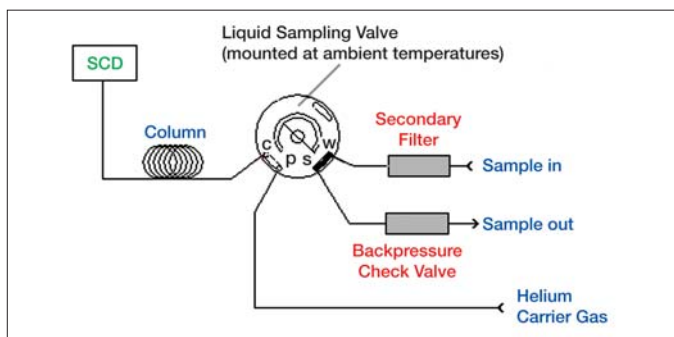


Figure 1. Model 4026 analyzer, incorporating a liquid sampling valve.

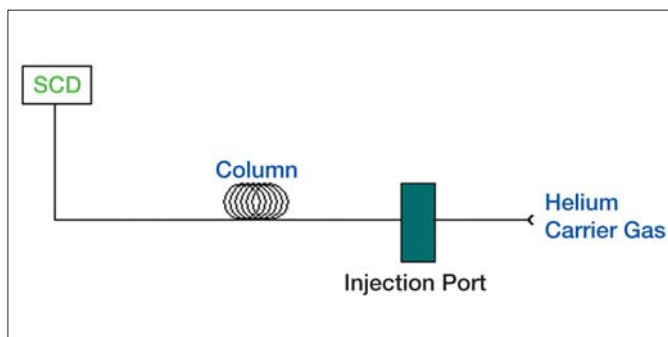


Figure 2. Model 4027 analyzer, incorporating an injection port.

Model 3062 reporting software

Model 3062 reporting software can be utilized to provide customized reports and calculations using the full capabilities of Microsoft® Excel® and TotalChrom® data-handling software. It can also be used to translate the resulting report into many languages. Model 3062 is an Excel workbook that must be customized by the user. It requires knowledge of Excel. Excel and TotalChrom are not included and must be purchased separately.

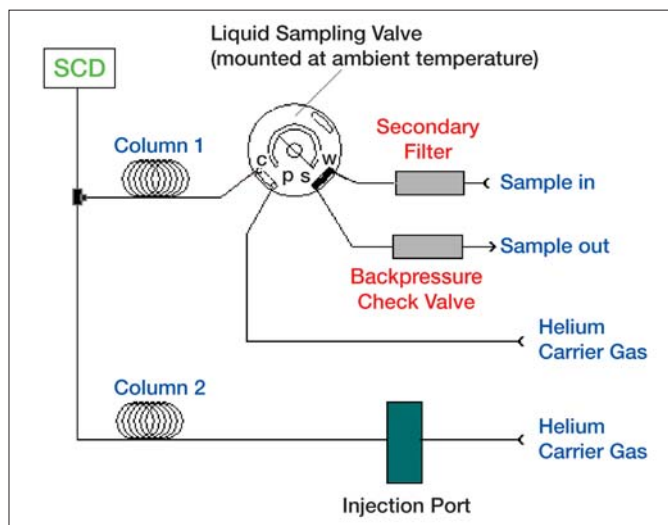


Figure 3. Model 4227 analyzer, incorporating a liquid sampling valve and injection port.

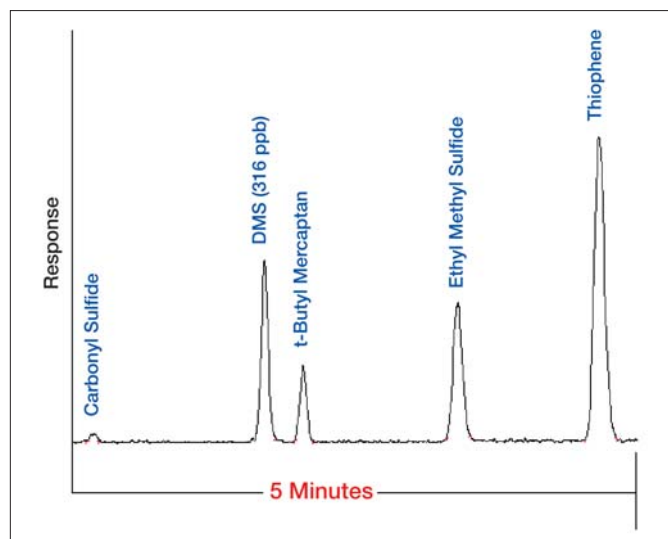


Figure 4. Liquid standard of sulfur compounds in toluene.

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