

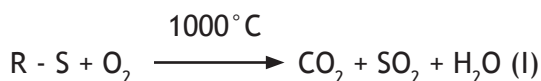
Continuous Monitoring of Total Sulfur in Diesel

INTRODUCTION

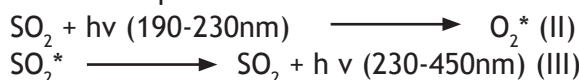
The refining and automobile industries are faced with strict regulatory hurdles for the elimination of sulfur in reformulated gasoline and diesel. Government regulations for maximum sulfur levels in diesel fuel vary depending on the region of the world between 10 to 300 ppm_{wt}. Continuous monitoring is necessary to assure that the maximum allowable level will not be exceeded. From a cost standpoint, it is desirable that the maximum sulfur content be kept as close to this target as possible. This is routinely monitored with NSure. The following will serve to demonstrate the stability and the limit of quantification that can be achieved with the sulfur and nitrogen analyzer.

PRINCIPLE OF OPERATION

When hydrocarbon samples are introduced into a pyrotube at 1000°C, sample components combust to form CO₂ and H₂O. Sulfur compounds are present in hydrocarbon mixtures and fossil fuels in a great variety of forms and chemical nature, however they also form combustion products as described in the general reaction equation (I).



Water in vapor or liquid phase can alter the measurement of sulfur and the combustion product must have the water removed before entering the reaction chamber where SO₂ molecules get excited and relaxed as per equations (II) and (III) below. A PMT set at the appropriate wavelength range will measure the emission signal of the sulfur species.



CALIBRATION

Analyzer was calibrated with an ultra low sulfur diesel of known concentration (8.2 mg/kg S) from the ASTM Proficiency Testing Program (PTP) that was diluted to provide a calibration standard at the mid-range of the full scale value. A 5 mg/kg sulfur standard was used to calibrate the 0-10 mg/kg sulfur full scale, a 2 mg/kg

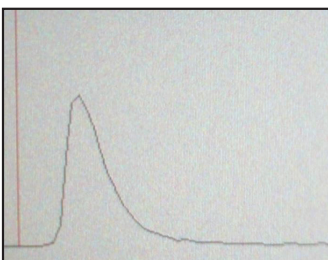


Figure 1. Sulfur peak response on NSure

HIGHLIGHTS

- Rapid and Accurate Determination of Sulfur
- Fully Automated Combustion System
- Excellent sensitivity using UV Fluorescence
- Compliance with D5453

NSure provides accurate sulfur and nitrogen measurements for quality control and regulatory compliance.



EXPERIMENTAL CONDITIONS

INSTRUMENTATION:

NSure with pyrolysis furnace and UV fluorescence detector. Diesel injected using a sample valve.

INSTRUMENT PARAMETERS

Loop Size (μl)	5
Carrier Argon (cc/min)	40
Pyro O ₂ (cc/min)	380
Inlet O ₂ (cc/min)	20
Dryer Argon (cc/min)	350
Furnace (°C)	1000
Cycle Time (mm:ss)	3:00
S Detector Cooler (°C)	10
S PMT High Voltage (V)	600

Parameters can be application and/or concentration dependent.

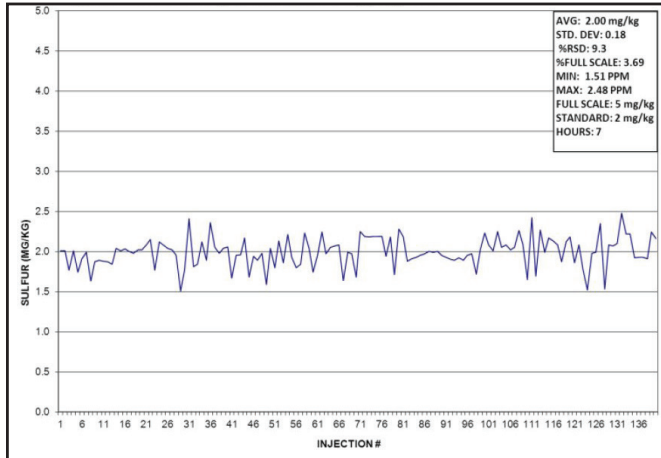


Figure 2. Stability data for 2 mg/kg sulfur

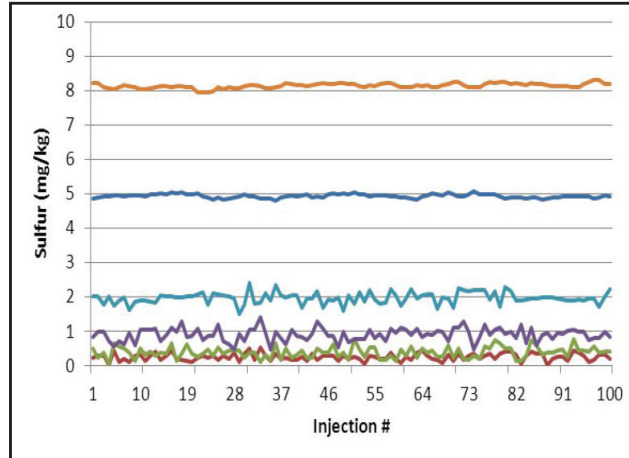


Figure 3. Results of various sulfur concentrations over 8 hours

sulfur standard was used to calibrate the 0-5 mg/kg sulfur full scale and 1 mg/kg S standard was used to calibrate the 0-2 mg/kg sulfur full scale range. A typical peak response is shown below in Figure 1. Figure 2 shows the results of the 2 mg/kg sulfur data over 8 hours and the resulting statistics.

SAMPLE PREPARATION

Samples were prepared by successive dilution starting with the 8.2 mg/kg sulfur ultra low sulfur diesel. The lowest material measured consisted of 0.2 mg/kg sulfur. Each sample was analyzed continuously over 8 hours and the statistics evaluated to determine the lower limit of quantification (LOQ). The results are shown in Figure 3. The calculated statistics demonstrate the repeatability was $\pm 1\%$ (0.2 mg/kg) of the 0-2 mg/kg sulfur full scale range and the limit of quantification (LOQ) was determined to be 200 ppb sulfur.

CONCLUSION

NSure can be used effectively to continuously monitor sulfur in diesel in the refining, pipeline and automotive applications to ensure that regulatory compliance is maintained in the most cost effective manner. The analyzer can not only measure the 10 to 300 ppm_{wt} required limits but also down to 0.2 mg/kg sulfur when the need arises. Engineered for continuous, unattended operation, the NSure Analyzers are ruggedly built for years of reliable performance.

NSure is the only process analyzer on the market that measures sulfur and nitrogen in one instrument. It measures virtually any liquid or gas sample for a variety of applications, including gasoline, naphtha, diesel, gas oils, natural gas, kerosene, and liquefied petroleum gas. It also utilizes the same proven technology of Antek's widely accepted laboratory analyzers, which results in a higher correlation between process and lab analysis. With the NSure, you are able to continually optimize the process and control production to increase productivity.