Technical Paper

PAC Antek On-line Total Sulfur Analysis in Process Streams for FCC Gasoline Selective Desulfurization

Introduction:

Total sulfur is an important parameter to monitor and control intermediates and/or final products for process optimization and blending in refineries, pipelines, and petrochemical plants. An online sulfur analysis can be deployed at many points in the process and provides the means to monitor conversion processes to produce the most valuable products without giveaway. The Antek Sulfur Process Analyzers have a strong heritage of being among the best in class for the online analysis of various levels of sulfur in a wide range of these matrices including naphtha, diesel, gasoline, LPG and gas.

One such application is for the Residue Fluid Catalytic Cracker (RFCC). The RFCC enables the conversion of low value residual feeds and de-asphalted oils from heavy crudes to high valued light olefins, gasoline and distillates. The process is economically favorable because of dwindling supply of light sweet crude, availability of large reserves of unconventional extra-heavy crude in Canada and Venezuela, and decline in fuel oil demand. Recent reports show that virtually every FCC unit licensed since 2005 is being used for this purpose.

Antek Process Sulfur Analyzers have been sold for a major refinery project for one of the largest RFCC units in the world to monitor and optimize the process at eleven different points. In this paper, the parameters and results for the analyzers will be provided to demonstrate the wide ranging capabilities of the Antek Process Sulfur Analyzer.

Instrumentation and Experimental Conditions:

Each analyzer was configured for a specific working range and matrix except two which were deployed as dual range and dual stream. The products to be monitored ranged from LPG to gasoline. This resulted in nine of the analyzers with gas phase sample introduction and two with liquid phase sample introduction.

Analyzer Number	Application Range (mg/kg S)	Phase
1	0-115	gas
2	0-165	liquid
3	0-300	gas
4	0-300	gas
5	0-20	gas
6	0-10	gas
7	0-5,000	gas
	0-10	gas
8	0-10	gas
9	0-5,000	liquid
10	0-10	gas
11	0-1000	gas
	0-10	gas

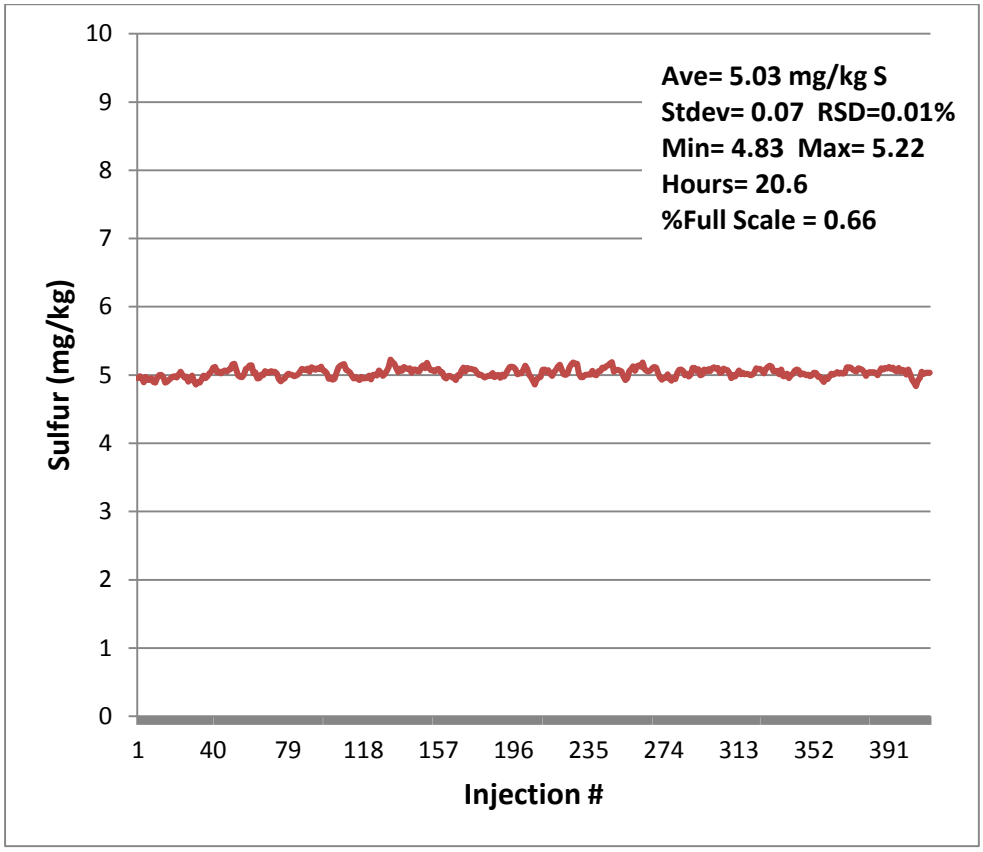
The analysis parameters, including flows, sample size, gain and voltage, were optimized for each analyzer and stream to ensure complete combustion and stable results based on expected sample matrix, composition and sulfur concentration. The following are examples of the parameters used for the analysis of the gas and liquid phases. The voltage and gain was concentration dependent and not included in the tables.

Gas Phase	
Loop Size (cc)	2
Carrier Argon (cc/min)	40
Pyro O_2 (cc/min)	380
Inlet O_2 (cc/min)	10
Dryer Argon (cc/min)	350
Furnace (°C)	1000
Cycle Time (mm:ss)	3:00
S Detector Cooler (°C)	10

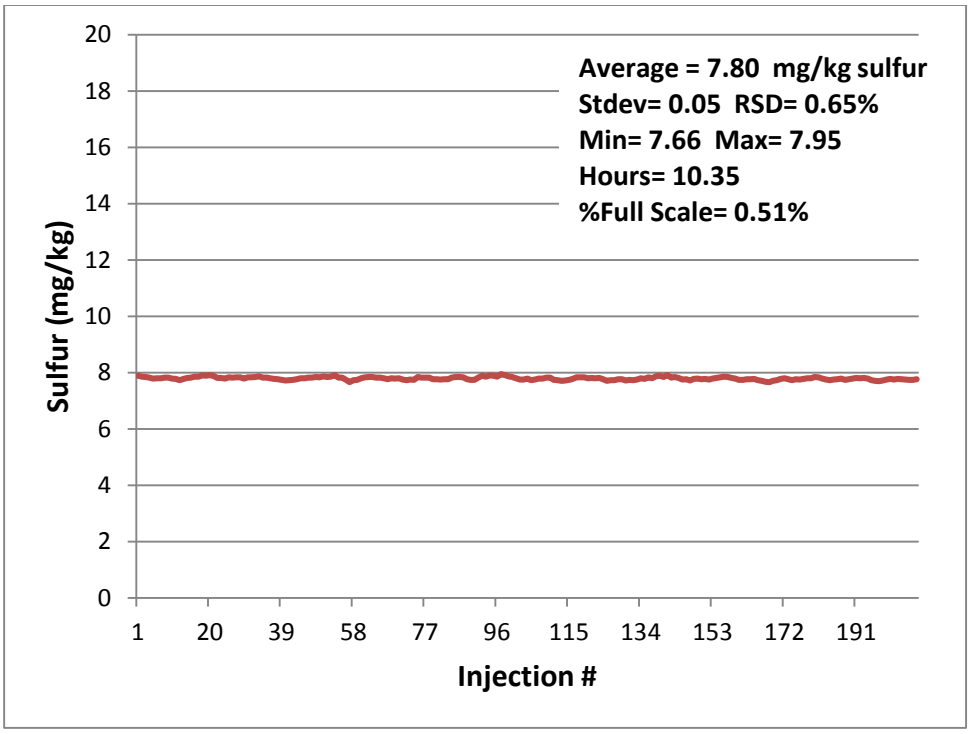
Liquid Phase	
Loop Size (µl)	5
Carrier Argon (cc/min)	5
Pyro O_2 (cc/min)	400
Inlet O_2 (cc/min)	20
Dryer Argon (cc/min)	350
Furnace (°C)	1000
Cycle Time (mm:ss)	3:00
S Detector Cooler (°C)	10

Results and Discussion:

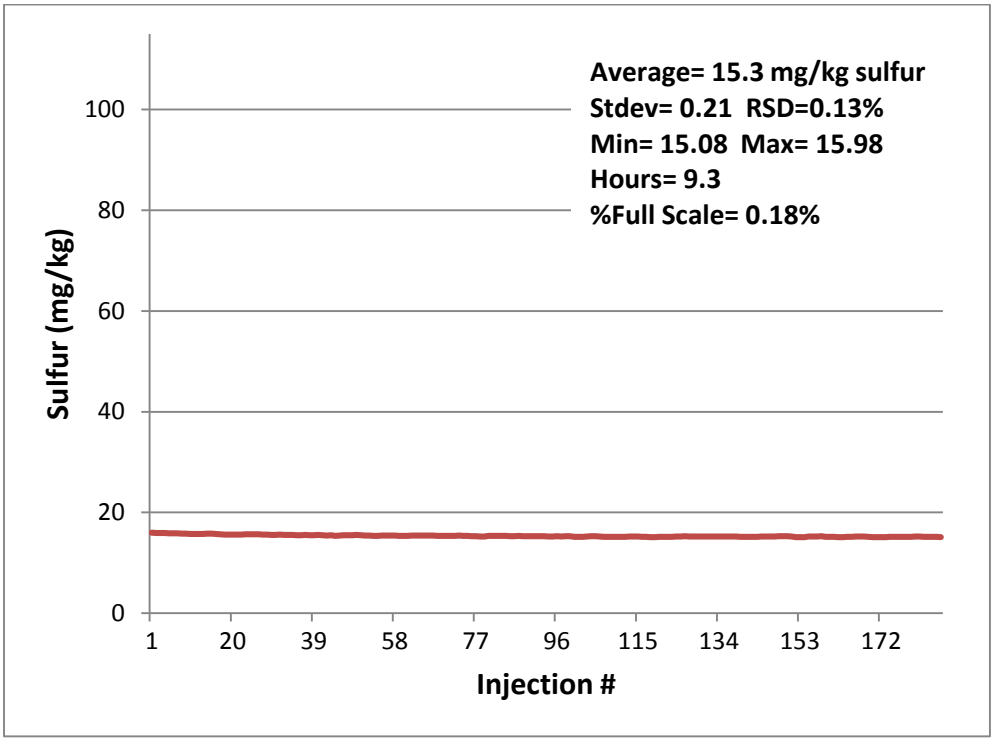
After optimization of the parameters, each analyzer was calibrated with a sample of known concentration near the midpoint of the full scale range. For example, a 0-10 mg/kg sulfur range was calibrated with 5 mg/kg sulfur. In addition, the analyzer was calibrated with either LPG (gas phase introduction) or gasoline (liquid introduction). For brevity, the results for each analytical range will be presented here to demonstrate the repeatability and stability of the analyses.



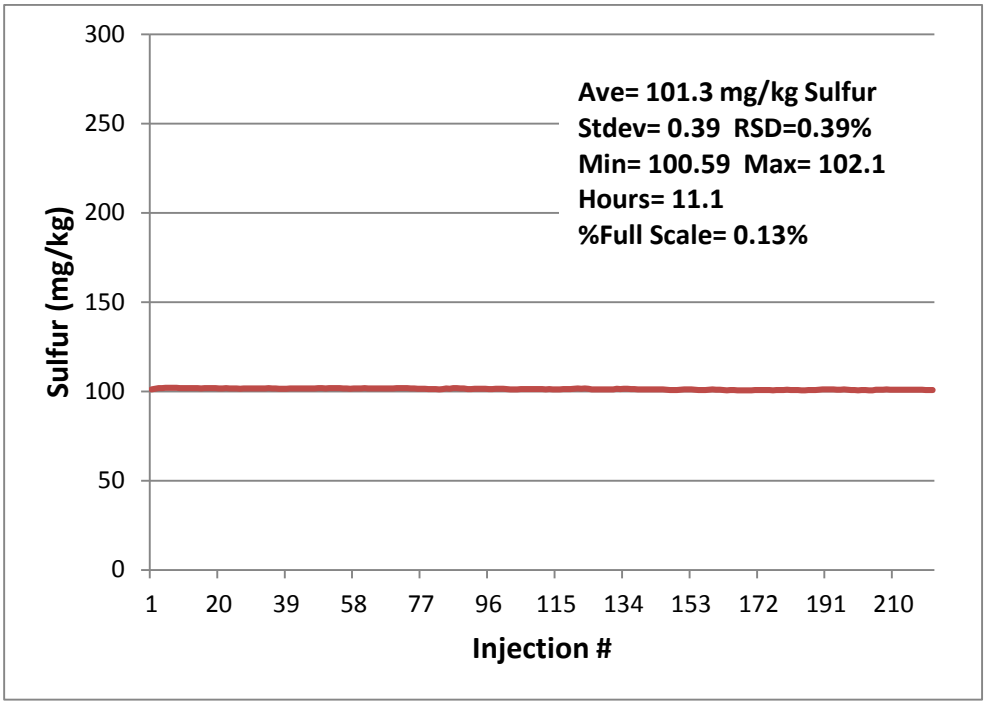
5 ppm on 0-10 mg/kg full scale



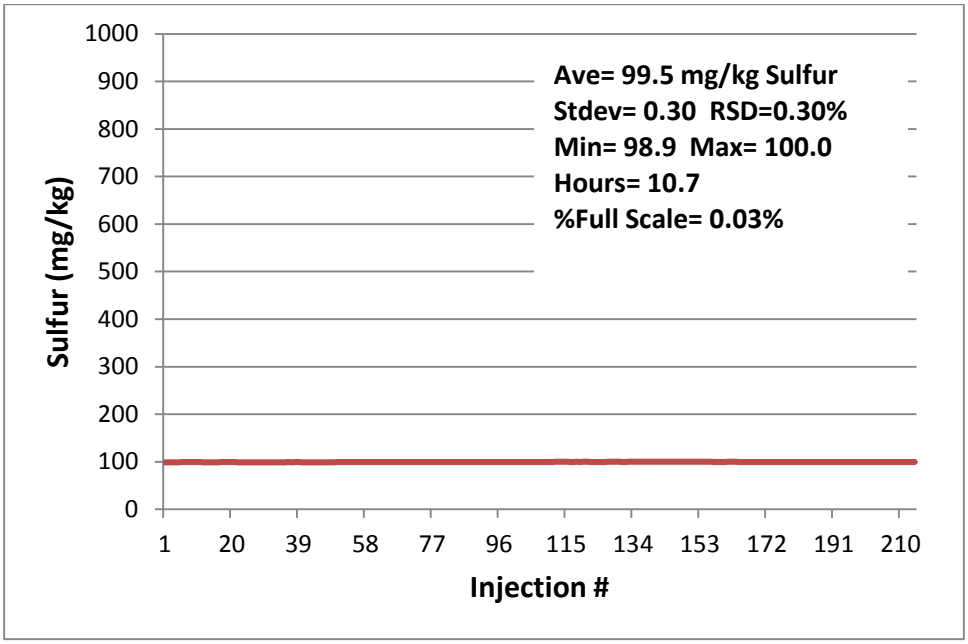
8 ppm on 0-20 mg/kg full scale



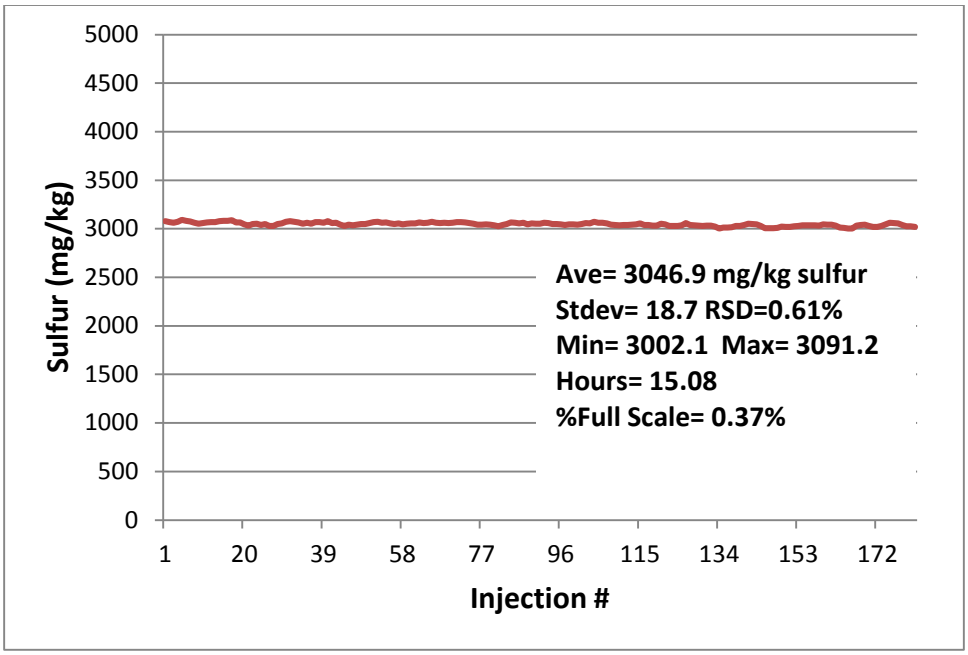
15 ppm on 0-115 mg/kg full scale



100 ppm on 0-300 mg/kg full scale



100 ppm on 0-1000 mg/kg full scale



3000 ppm on 0-5000 mg/kg full scale

Conclusions:

Each analyzer was optimized for the analysis of a specific stream to ensure process optimization of a particular point in the RFCC unit. These analyses resulted in the following repeatabilities:

Analyzer Number	Application Range (mg/kg S)	Repeatability
1	0-115	±1% or better of FSR = 1 ppm
2	0-165	±1% or better of FSR = 2 ppm
3	0-300	±1% or better of FSR = 3 ppm
4	0-300	±1% or better of FSR = 3 ppm
5	0-20	±1% or better of FSR = 0.2 ppm
6	0-10	±1% or better of FSR = 0.1 ppm
7	0-5,000	±1% or better of FSR = 50 ppm
	0-10	±1% or better of FSR = 0.1 ppm
8	0-10	±1% or better of FSR = 0.1 ppm
9	0-5,000	±1% or better of FSR = 50 ppm
10	0-10	±1% or better of FSR = 0.1ppm
11	0-1000	±1% or better of FSR = 10 ppm
	0-10	±1% or better of FSR = 0.1 ppm

In addition, it has been shown that the limit of detection (LOD) is ~5% of full scale and the limit of quantification (LOQ) is ~10% of full scale. Repeatability, LOD and LOQ that can be achieved is a function of the specific application. Contact PAC to discuss your analytical needs.

These data show that Antek Sulfur Process Analyzers can effectively be used to monitor and control intermediates and/or final products for process optimization and blending in refineries, pipelines, and petrochemical plants to produce the most valuable products without giveaway.