A study comparing the use of oxygen and ambient air as the combustion gas in a sulfur analysis with the Antek 6200 Series Analyzer

Abstract

Burning fossil fuels like diesel causes sulfur to penetrate the atmosphere as gaseous sulfur dioxide. Because of this, sulfur levels in diesel fuels are strictly regulated in many of the industrialized countries throughout the world, including in North America, the European Union, and Asia.

This has created a challenge for refiners, who must adjust their processes to meet a 15 ppm standard for sulfur in on-road diesel fuel, while other products may have a 500 ppm standard for sulfur. As refineries take steps to meet tight regulations, there are a number of considerations they must make. First, they must take steps to avoid cross-product contamination, which has made the requirement for fast, accurate sulfur data even more important. They need to optimize their process to keep it as close to the specification limits as possible, so a quick analysis time and the ability to handle process variability is important. Also, accuracy and correlation to standards is essential. Finally, controlling maintenance costs is important.

PAC's Antek 6200 Series Analyzer addresses these considerations by delivering sulfur measurements with excellent repeatability and reproducibility at various stages of production and blending. One of the differences that the 6200 incorporates is the ability to use either air or oxygen as the combustion gas, depending on the best choice for the application.

This technical paper highlights a study, conducted by PAC, to demonstrate that air as the combustion gas is as accurate as oxygen as the combustion gas for the analysis of sulfur in fuels.

Introduction

Antek's 6200 Series Analyzer monitors sulfur in diesel at full-scale range from 0 - 2 ppm S (w/w) to % levels S (w/w) with results in under a minute. It is rugged and reliable, and capable of dual-stream and dual-range analysis.

The 6200 Series Analyzer correlates to ASTM D5453 using UV-Fluorescence (UVF) Spectrometry technology, a fast and accurate quantification method. This clean, instrumental methodology is more stable than lead acetate tape methods, without the associated consumables or lead waste disposal issues.

A recent study was conducted to analyze the sulfur content in gasoline and diesel using air or oxygen as the combustion gas. It was shown that both combustion gases demonstrate accurate results within the stated specification.

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6200 Series Analyzer Specifications

The 6200 Series Analyzer is designed to deliver accurate measurements using either air or oxygen as the combustion gas for numerous samples, including gasoline, diesel, LPG, or gaseous hydrocarbons. For the purposes of this study, gasoline and diesel were tested. The stated specifications of the analyzer are provided in Table 1 below.

Matrix	Density @60F (g/ml)	Sulfur Dynamic Range	Application Range	LOD
Gasoline Naphtha	0.70-0.75	250 ppb - 4%	0-2 ppmv	250 ppbv
			0-20 ppmv	2 ppmv
			20-ppmv - 4%	~5% of full scale
Diesel	0.82-0.86	200 ppb - 4%	0-2 ppmv	200 ppbv
			0-20 ppmv	2 ppmv
			5000-ppmv - 4%	~5% of full scale

Table 1

Test Results – Sulfur in Diesel

In the first test, diesel was used as the sample. This was a traditional analysis, with argon being used as the carrier gas to move the sample from the injection valve to the pyrotube. Oxygen was used for the combustion process. Three tests were conducted – 7 ppm sulfur in diesel, 4 ppm sulfur in diesel, and 2 ppm sulfur in diesel samples. The results are provided in Figure 1. The testing process ran for 24 hours and consisted of 500 injections. The data provided within this document is an average of the results of the 500 injections. To establish a benchmark, a sample that was part of ASTM proficiency testing program with an accepted reference value was used.

As seen in Figure 1, the results of the tests with a 7 ppm sample, a 4 ppm sample, and a 2 ppm sample were well within the expected specifications of the analyzer. In each test, the standard deviation was well within the limits of expected variability, and the repeatability factor, as shown by %

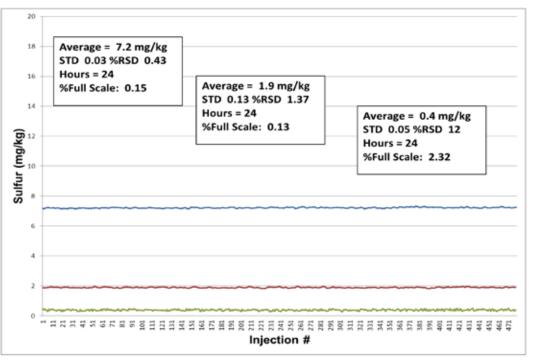


Figure 1. An analysis of diesel using oxygen as the combustion gas

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relative standard deviation, (%RSD), is excellent.

For the second test, a 6200 Series Analyzer that used air as the combustion gas was used to analyze the diesel samples. See Figure 2 for the results below.

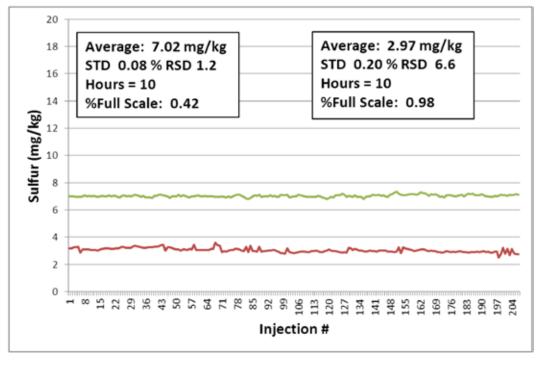


Figure 2

For this test, the diesel sample was tested at concentration levels of 7 ppm and 4 ppm. It was found that analyzing samples with less than 2 ppm of sulfur is not recommended with air as the combustion gas. When testing less than 2 ppm is required, the use of oxygen is the ideal choice to ensure the best performance.

The use of air delivered results that fell within the specifications of the analyzer and were comparable to the first test that used oxygen as the combustion gas. The results were well within the specifications of the analyzer, and repeatability was less than 1% of full-scale range.

This test determined that using air with the 6200 Series Analyzer delivers the equivalent results as using oxygen as the combustion gas.

Test Results – Sulfur in Gasoline Naphtha

For the next test, the analysis of sulfur in gasoline was evaluated. The goal for this test was similar to the diesel testing – to demonstrate that using air as the combustion gas delivers results that are equivalent to using oxygen as the combustion gas. Again, argon was used as the carrier gas, moving the sample from the injection valve to the pyrotube. Oxygen was used for the combustion process. Three tests were conducted – 7 ppm sulfur in gasoline, 4 ppm sulfur in gasoline, and a 2 ppm sulfur in gasoline sample. The results are provided in Figure 3 on the next page.

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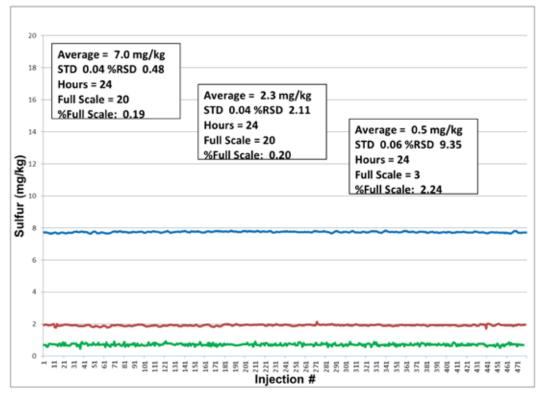
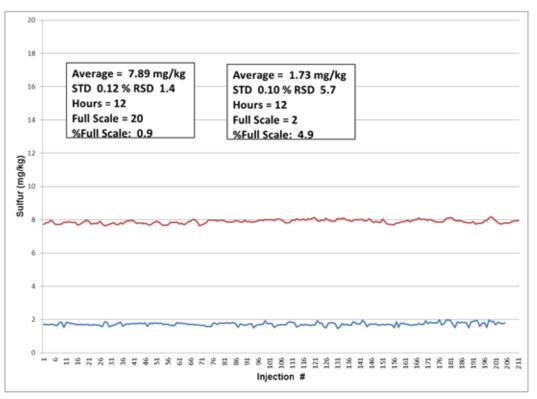
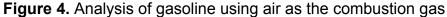


Figure 3

As before, the testing process spanned more than 24 hours and consisted of 500 injections. The results of the tests with a 7 ppm sample, a 4 ppm sample, and a 2 ppm sample were well within the expected specifications of the analyzer. In each test, standard deviation was well within the limits of expected variability, and the (%RSD) was excellent. For the second test, a 6200 Series Analyzer that used air as the combustion gas was used to analyze the diesel sample. See Figure 4 below for the results.





The use of air delivered results that fell within the specifications of the analyzer and were comparable to oxygen as the combustion gas.

Summary

This test concluded that the 6200 Series Analyzer can be used with either oxygen or air as the combustion gas with excellent results. The preferred method will be application dependent. Oxygen is recommended as the combustion gas for sulfur application less than 2 ppm and for higher sulfur concentrations to ensure complete combustion and accurate results.



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