Technical Notes
015

Exceeding Expectations

S stands for **Sulfur**

The total sulfur concentration is determined by a variety of techniques and is used for a wide range of petroleum products. To learn more about this line of testing, let's apply the **AmSpec** approach.

A = Application

Figure 1 - Elemental Sulfur

The Environmental Protection Agency regulates the amount of sulfur added to gasoline and diesel. Ultra-low-sulfur diesel fuel was proposed by the EPA as a new standard for the sulfur content of diesel fuel sold in the United States. After December 1, 2014 all highway, non-road, locomotive and marine diesel fuel produced and imported will be ULSD. The allowable sulfur content for ULSD (15 ppm) is much lower than the previous U.S. on-highway standard for low sulfur diesel (LSD, 500 ppm). This allows advanced emission control systems to be fitted that would otherwise be poisoned by these compounds. These systems can greatly reduce emissions of oxides of nitrogen and particulate matter.

The Tier 2 Gasoline Sulfur program reduced the sulfur content of gasoline by up to 90 percent from uncontrolled levels. Phased in from 2004–2007, and now in effect, the program allows refiners to produce gasoline with a range of sulfur levels as long as their annual corporate average does not exceed 30 parts per million (ppm). In addition, no individual batch can exceed 80 ppm.

Crude oil may be characterized as sweet or sour. Sweet crude oil contains less than 0.42% total sulfur, while sour crude oil contains more than 0.5% total sulfur. The sweet crude oil has small amounts of hydrogen sulfide and therefore has a pleasant smell. Sour crude may contain a higher level of hydrogen sulfide which will cause the oil to smell like rotten eggs. The toxicity of the oil increases as the hydrogen sulfide content increases. Sour crude also costs more to process into gasoline as more sulfur needs to be removed. Sour crude is usually processed into heavy crude oil, diesel, and fuel oil while sweet crude is used for gasoline.

To determine the total amount of sulfur in a sample, 3 different types of instrumentation are commonly used: Wavelength Dispersive X-Ray Spectrometry, Energy-Dispersive X-Ray Spectrometry, and Ultraviolet Fluorescence.

Wavelength Dispersive X-Ray Spectrometry

Wavelength dispersive X-ray spectrometry (WDXRF or WDS) is a method used to count the number of X-rays of a specific wavelength diffracted by a crystal. WDS reads or counts only the x-rays of a single wavelength at a time, not producing a broad spectrum of wavelengths or energies simultaneously.

Energy-Dispersive X-Ray Spectrometry

Energy-dispersive X-ray spectrometry (EDS, EDX, or XEDS) relies on the investigation of an interaction of X-ray excitation and a sample. Each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays are characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Ultraviolet Fluorescence

In Ultraviolet Fluorescence Spectroscopy, the light from an excitation source passes through a filter and strikes the sample. A proportion of the incident light is absorbed by the sample, and some of the molecules in the sample fluoresce. The fluorescent light is emitted in all directions. Some of this fluorescent light passes through a second filter and reaches a detector.

M = Methods

These are the most common methods that AmSpec uses to determine total sulfur content:

D2622 - Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

D4294 - Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-ray Fluorescence Spectrometry

D5453 – Determination of Total Sulfur in Light Hydrocarbons, Spark Ignition Engine Fuel, Diesel Engine Fuel, and Engine Oil by Ultraviolet Fluorescence

D6667 - Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence

D7039 – Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry

S = Scope

Method	Products	Scope
D2622	diesel fuel, jet fuel, kerosene, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol and biodiesel	3 mg/kg to 4.6 weight% *Samples above 4.6 weight% may be diluted in mineral oil
D4294	diesel fuel, jet fuel, kerosine, other distillate oil, naphtha, residual oil, lubricating base oil, hydraulic oil, crude oil, unleaded gasoline, gasohol, biodiesel, and similar petroleum products.	17 mg/kg to 4.6 mass% *Samples above 4.6 mass% may be diluted in mineral oil
D5453	naphthas, distillates, engine oil, ethanol, Fatty Acid Methyl Ester (FAME), and gasoline, biodiesel, diesel/biodiesel blends, and jet fuel.	1.0 to 8000 mg/kg
D6667	gaseous hydrocarbons and liquefied petroleum (LP) gases	1 to 100 mg/kg
D7039	gasolines, diesel fuels, and refinery process streams used to blend gasoline and diesel	2 to 500 mg/kg *Samples above 500 mg/kg may be diluted with appropriate solvent.

*** Please note below, **Turnaround Time** is defined as the actual length of time, on average, it takes to perform a particular method once the sample has arrived and logged in the lab, and prepared for testing.*

P = Procedure Notes

Method	Limitations	Instrumentation	Turnaround Time
D2622	N/A	WDXRF	15 minutes
D4294	N/A	EDX	30 minutes
D5453	Sample must contain less than 0.35 mass% of halogens	UV	30 minutes
D6667	1) Samples must vaporize under the conditions of the test. 2) Sample must contain less than 0.35 mass% of halogens	UV	30 minutes
D7039	If the sample composition differs drastically from the calibration standards, corrections must be applied	WDXRF	15 minutes

E = Equivalents

ASTM	IP	ISO	DIN	JIS	AFNOR
D2622			51400T6	K 2541	
D4294					
D5453					
D6667					
D7039					

C = Cause & Effect

Sulfur is used to increase film strength in certain lubricating and cutting oils. Sulfur chemically reacts with the metal surfaces to form a film, or surface compound, which gently wears away rather than allowing the mating surfaces to weld and tear loose, causing surface destruction. After this film has developed on the metal surface, it has lower shear strength than the base metal, thus reducing friction. However, because of sulfur's corrosive properties, copper, brass, and other nonferrous metals cannot be used when the lubricating oil contains sulfur. In gasolines and diesel fuels, sulfur causes corrosion to engine parts and produces sulfur dioxide when burned. Sulfur reduces catalyst efficiency in modern vehicles, and vehicles operating with higher sulfur gasoline have higher emissions than vehicles operating on lower sulfur gasoline. There is evidence that in some instances, sulfur in gasoline may degrade the performance of oxygen sensors, which may also result in high emissions.

For any questions about these methods, please contact Jennifer Nesci at JNesci@amspecllc.com

Also, please download the new & improved AmSpec Smart Phone app for a number of useful conversion tools and information.