HORIBA Scientific

Low Sulfur Analyzer
SLFA AB204

ASTM D7220 Method for Analyzing Low Sulfur Concentrations in Fuel

Introduction

ASTM D7220 is an EDXRF sulfur analysis method that has evolved over the years to meet changing regulatory testing requirements for low concentrations of sulfur in fuel. It was developed by a consensus based methods committee within ASTM International that is comprised of regulators, fuel suppliers, analytical instrument manufacturers and other interested parties. The committee works together to develop methods to ensure that the fuel industry has access to appropriate testing technologies with guidance on using them properly. The Instruments group at HORIBA Scientific has been directly involved with this effort and at the forefront of providing EDXRF technology innovations that are cost-effective, accurate and precise for the analysis of sulfur in fuels at low concentration levels.

Background

Unless removed, sulfur which is present in crude oil ends up in the fuels we use. The detrimental pollution effects from sulfur in fuels continue to drive regulators to lower its allowable levels. In the early 1990s, the US EPA limited sulfur to 500 ppm in highway diesel fuel. By 2004, they limited it in gasoline to an average of 120 ppm with a cap of 300 ppm. In 2007, they further reduced it to an average of 30 ppm with a cap of 80 ppm. In conjunction with these regulations, EPA stipulated specific ASTM sulfur test methods for reporting compliance with the restrictions. ASTM D4294 was the EDXRF method specified for these restriction levels as it met the analysis needs for concentrations from 15 mg/kg to 5 wt% sulfur in fuel.

HORIBA Scientific developed two sulfur-in-fuel-analyzers (SLFAs) that comply with ASTM D4294. The benchtop SLFA 2100/2800, capable of automating multiple samples, analyzes sulfur from 5 ppm to 9.999%. The lightweight, ultra-compact, transportable SLFA 20/60 analyzes sulfur from 15 ppm to 9.999%.

In 2006, ASTM published an EDXRF method to meet US EPA's Tier 2 Vehicle and Gasoline Standards. This EPA Ruling restricted highway diesel fuels to an average of 15 ppm sulfur, and was phased in from 2004 to 2010. These even lower levels were referred to as ultra-low sulfur in diesel, or ULSD. The new EDXRF method EPA specified for reporting

EPA / ASTM / HORIBA Sulfur in Fuel Timeline

	US EPA Average Sulfur Level Restriction in Fuel	ASTM D02 Committee Method Published	HORIBA Scientific Sulfur Analyzer Developed
Early 1990's	500 ppm in highway diesel		
2004	120 ppm in highway gasoline, cap of 300 ppm	EDXRF Method D4294 (15 ppm - 5% S)	SLFA 2100/2800 (5 ppm - 9.999% S) & SLFA 20/60 (15 ppm -9.999% S) EDXRF analyzers
2006		EDXRF Method D7220-06 (6-50 ppm S)	MESA 6000 EDXRF analyzer (1.25 ppm - 10% S)
2007	30 ppm in highway gasoline; cap of 80 ppm		
2010	Tier-2, 15 ppm in highway diesel (ULSD)		
2012			MESA-7220 EDXRF analyzer (1 ppm - 10% S)
2014		EDXRF Method D7220-12 (3-942 ppm S)	
2017	Tier-3, 10 ppm in highway gasoline (ULSG)		
Future	Lower sulfur levels		

compliance was ASTM D7220-06 which met the ULSD analysis requirements for 6 to 50 mg/kg of sulfur in fuel.

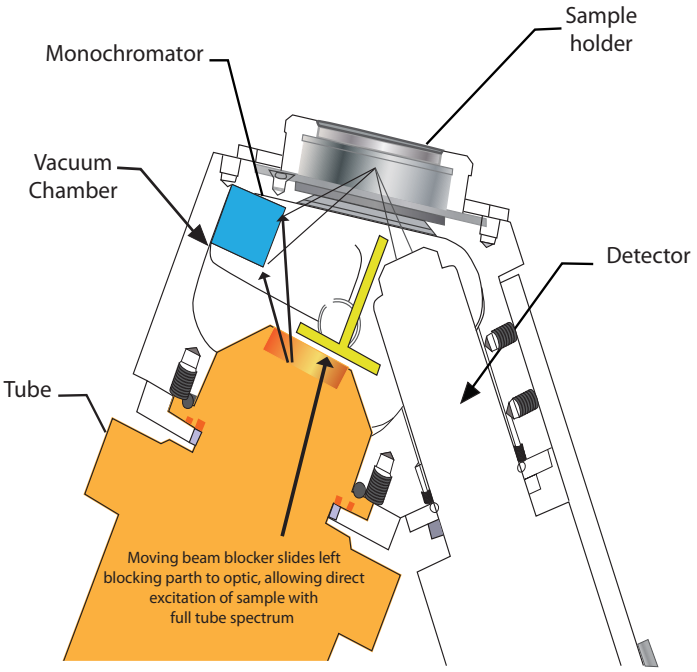
Method D7220-06 was very specific in terms of the excitation technology for EDXRF and was entitled "Standard Test Method for Sulfur in Automotive Fuels by Polarization Energy Dispersive X-ray Fluorescence". Polarized excitation geometry improves the detection limits of sulfur by producing a focused energy excitation for sulfur while reducing interfering signals from the X-ray tube background as well as other elements in the sample. This method provided a sulfur determination range of 6-50 mg/kg in gasoline and diesel with a pooled limit of quantification (PLOQ) of 6 mg/kg sulfur.

HORIBA Scientific developed the MESA 6000 multi-element and sulfur analyzer which met these EPA and ASTM requirements. The MESA benchtop EDXRF analyzer utilizes a unique and patented design with close-coupled, doubly curved HOPG (highly oriented pyrolytic graphite) X-ray optics. It simultaneously polarizes, focuses, and monochromates the X-ray beam for ultra-low sulfur in fuel measurements as well as for the simultaneous analysis of other elements in the sample.

Current

At the beginning of 2014, the US EPA enacted their Tier 3 Regulation which further reduced the allowable sulfur content in gasoline to an average of 10 ppm by 2017. These even lower levels for gasoline are referred to as ultra-low sulfur in gas, or ULSG. EPA did not specify a method for this regulation; instead, it enacted use of a PBMS (Performance Based Measurement System) approach to allow reporting laboratories new flexibility regarding the sulfur test method they may use. However, use of consensus group standardized test methods with mandatory quality control practices, such as ASTM's revised Method D7220-12, validate adequate measurement quality.

ASTM published Method D7220-12 in 2014 to meet these ULSG analysis levels. The revision, entitled "Standard Test Method for Sulfur in Automotive, Heating & Jet Fuels by Monochromatic EDXRF Spectrometry", has a sulfur determination range of 3-942 mg/kg with a PLOQ of 3mg/kg and unified a single precision for all sample types for repeatability and reproducibility. It allows more flexibility in the excitation technology by not specifying polarized EDXRF spectrometry, but instead requiring that the EDXRF technology irradiate the sample surface with



MESA-7220 Monochromatic EDXRF

Key Differences Between ASTM Methods D7220-6 and D7220-12		
	ASTM Method D7220-06	ASTM Method D7220-12
Title	Standard Test Method for Sulfur in Automotive Fuels by Polarization Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF)	Standard Test Method for Sulfur in Automotive, Heating & Jet Fuels by Monochromatic EDXRF Spectrometry
Excitation Technology	Polarized EDXRF Spectrometry	EDXRF that irradiates the sample surface with an indirect monochromatic X-ray beam
Sulfur Determination Range	6 - 50 mg/kg S	3 - 942 mg/kg S
PLOQ: Pooled Limit of Quantification	6 mg/kg	3 mg/kg
Sample Types	Automotive fuels - gasoline & diesel	Gasoline, oxygen enriched gasoline (RFG), diesel, diesel/biodiesel blends containing up to 50% by voume. Biodiesel, kerosene, jet fuel, jet fuel/ biodiesel blends containing up to 5% by volume biodiesel, #2 home heating oil.

an indirect monochromatic X-ray beam. Method D7220-12 also expands the sample types it can be used for to beyond just automotive gasoline and diesel fuels. An ASTM Interlaboratory Study (ILS) measured results and found no significant bias in a comparison of NIST SRM data and ASTM Interlaboratory Study (ILS) measured results.

HORIBA Scientific updated the MESA multi-element and sulfur analyzer for these requirements and renamed it the MESA-7220 to reflect more accurately the ASTM method revision for ULSG and ULSD. HORIBA's MESA-7220 meets the ASTM D7220-12 (3-942 ppm) method as well as ASTM D7220-06 (6 – 50 ppm S), D4294 (16ppm-5%), IP 532 (6-50 ppm), EN ISO 8754 (100mg/kg-5%), and EN ISO 20847 (30- 500mg/kg). It can also be used to meet US EPA performance-based testing requirements for ULSD.

D7220-12's improved low level sulfur measurement method has a PLOQ (pooled limit of quantification) of 3 mg/kg with an extended analytical range of 3-942 mg/kg S

Sulfur Content mg/kg	r = Repeatability mg/kg	R = Reproducitility mg/kg
3	1.1	1.9
5	1.4	2.5
10	2.1	3.5
25	3.3	5.6
50	4.6	8.0
100	6.5	11.3
250	10.4	18.0
500	14.7	25.5
942	20.3	35.1

Where r = same lab, difference between two results;
R = different labs, difference between two results

ASTM interlaboratory study repeatability estimates based on average measured mg/kg sulfur

	NIST 2770	NIST 2299	NIST 1616b
Sulfur mg/kg NIST	41.57 (±0.39)	13.6 (±1.5)	8.4 (±0.12)
Matrix	Diesel	Gasoline	Kerosene
Average Measured mg/kg Sulfur ASTM ILS	41.8	12.5	8.9
Observed Difference mg/kg Sulfur	0.2	-1.1	0.5
Statistically Significant (95% Confidence Level)?	No	No	No

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