Application Note EDXRF2095

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EDXRF2095 - Analysis of ULSD

Scope

Demonstrate the performance for the measurement of sulfur in ULSD (ultra-low sulfur diesel) using the Rigaku NEX CG II monochromatic indirect excitation EDXRF analyzer with polarization.

Background

Regulations around the world have limited the amount of sulfur in various fuels oils. In some regions, sulfur in diesel is limited to 10 - 15 ppm, while other areas of the world are working to bring sulfur levels down to 50 ppm and lower. Aside from automobile, truck, and some bunker fuels, ULSD is also mandated for use as a starter fuel at coal-fired power plants or backup electricity generation at nuclear power plants in some regions. A fast, reliable method of measuring and monitoring sulfur concentration throughout the petroleum industry is vital.

The NEX CG II gives the industry a reliable tool for measuring ULSD using full polarization in 90° Cartesian Geometry EDXRF. Polarization creates extremely low background in the measurement, allowing for very low detection limits for reliable measurement in the ultra-low range to meet international testing norms and EPA testing criteria demands.

ASTM, EPA and international norms

The Rigaku NEX CG II EDXRF analyzer meets several international norms and EPA testing criteria for the measurement of sulfur in petroleum oils, fuels, and ULSD using monochromatic EDXRF.

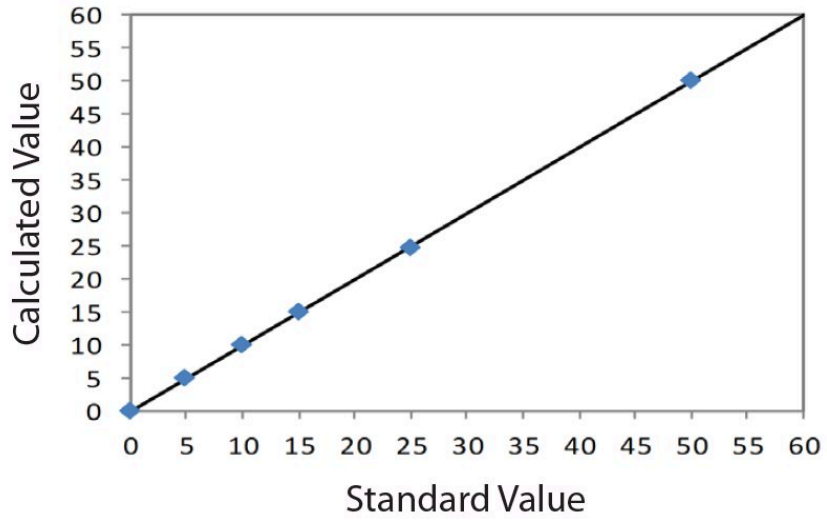
Standard method	Sulfur range
ASTM D7220	3 - 942 mg/kg
U.S. EPA ULSD Testing Criteria	5 - 15 ppm
ISO 13032	8 - 50 mg/kg
ASTM D4294	16 mg/kg - 5%
IP 532	6 - 50 mg/kg
EN ISO 8754	300 mg/kg - 5%
EN ISO 20847	30 - 500 mg/kg

The units ppm and mg/kg can be used interchangeably.

Calibration

Calibration is made using matrix-matched standards that match the fuel oil or biodiesel blend being measured. For demonstration, an empirical calibration was made using a suite of six commercially available certified diesel calibration standards.

Element: S **Units: ppm**		
Sample I.D.	**Standard value**	**Calculated value**
1	0	0.0
2	5	5.09
3	10	9.96
4	15	15.12
5	25	24.74
6	50	50.10



Correlation plot S

Precision

Instrument repeatability (precision) is determined by ten repeat analyses of each sample in static position.

Element: S **Units: ppm**				
Sample	**Standard value**	**Average value**	**Std. dev**	**% Relative**
2	5	5.03	0.04	0.8
3	10	9.93	0.07	0.7
4	15	15.15	0.08	0.5
7	50	49.85	0.14	0.3

U.S. EPA testing criteria 40 CFR 80.584

The following results indicate NEX CG II can be used by a facility to meet EPA ULSD criteria as per 40 CFR 80.584 using ASTM Standard Test Method D7220 and good lab practices.

15 ppm Sulfur Precision Criterion — a standard deviation less than 0.72 ppm, computed from the results of a minimum of 20 repeat tests made over 20 days on samples taken from a single homogenous commercially available diesel fuel with a sulfur range of 5 to 15 ppm. The 20 results must be a series of tests with a sequential record of the analyses and no omissions. A lab facility may exclude a given sample or test result only if the exclusion is for a valid reason under good laboratory practices and it maintains records regarding the sample and test results and the reason for excluding them.

Test Sample: Diesel Certified ARV 10.0 ppm S		
Average	**Standard deviation**	**Pass/Fail**
10.16 ppm S	0.13 ppm	PASS

1 to 10 ppm Accuracy Criterion — the arithmetic average of a continuous series of at least 10 tests performed on a commercially available gravimetric sulfur standard in the range of 1 to 10 ppm sulfur shall not differ from the accepted reference value (ARV) of that standard by more than 0.54 ppm. Individual test results shall be compensated for any known chemical interferences.		
Test Sample: Diesel Certified ARV 10.0 ppm S		
Average	**Standard deviation**	**Pass/Fail**
9.97 ppm S	0.03 ppm	PASS

10 to 20 ppm Accuracy Criterion — the arithmetic average of a continuous series of at least 10 tests performed on a commercially available gravimetric sulfur standard in the range of 10 to 20 ppm sulfur shall not differ from the accepted reference value (ARV) of that standard by more than 0.54 ppm. Individual test results shall be compensated for any known chemical interferences.		
Test Sample: Diesel Certified ARV 15.0 ppm S		
Average	**Standard deviation**	**Pass/Fail**
15.32 ppm S	0.32 ppm	PASS

Conclusion

The results shown here indicate the Rigaku NEX CG II EDXRF analyzer using Cartesian Geometry polarization provides monochromatic excitation to achieve superior performance for the measurement of ULSD for control and certification of 10 – 15 ppm S at the pump, as well as lower levels controlled at the refinery. NEX CG II can also be used for the measurement of ultra-low sulfur in gasoline, RFG, jet fuel, kerosene, #2 heating oil, biodiesel, and biodiesel blends.

Related products

NEX CG II Series

High-performance *indirect excitation* EDXRF for complex ap
plications with trace elements and variable base matrices