EDXRF Application Note
Sulfur in Diesel

#1135 REV1

SCOPE

The analysis of sulfur in diesel fuel as per ASTM D4294 is demonstrated.

BACKGROUND

Sulfur will always be an important element in crude oils and fuels oils. Sulfur content is regulated in many products, and plays an important role in fuel quality and control of polluting emissions. Around the world regulations are limiting the amount of sulfur allowable in diesel fuels, kerosene, heating oils, etc. Jet fuels also rely on the sulfur content to ensure optimum fuel properties, in addition to emission concerns. Therefore, from characterizing, blending and refining crude oil to the production of various fuel oils, monitoring sulfur content will continue to be a very important measurement. To meet the needs of the industry, Rigaku offers NEX QC, a simple and versatile benchtop EDXRF analyzer for the analysis of sulfur and other elements in petroleum oils and fuels.

INSTRUMENTATION

Model:	Rigaku NEX QC
X-ray tube:	4 W Ag-anode
Detector:	Semiconductor
Sample Type:	Diesel fuel
Film:	Mylar or Prolene
Analysis Time:	120 sec – Standard Range, in Air
	(240 sec during calibration)
	300 sec – Low Range, in Helium
Environment:	Air or Helium
Optional:	Autosampler

SAMPLE PREPARATION

To measure a sample, gently shake the sample bottle, allow bubbles to settle and fill a 32mm XRF sample cup 3/4 full (5g). Mylar film is used for the standard range and higher levels, and Prolene film is used to optimize the low sulfur range of 20-100 ppm S.

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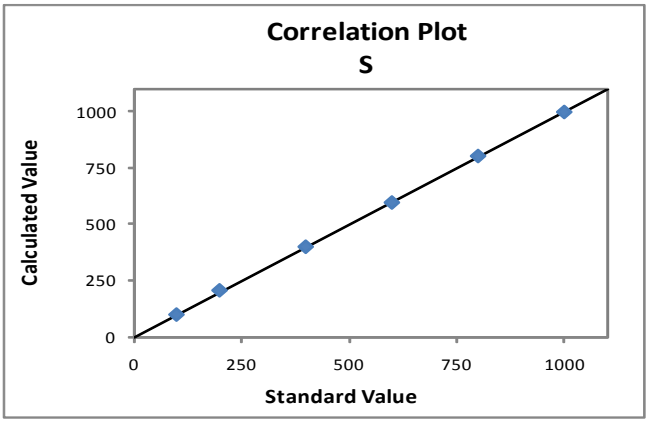
CALIBRATION – Standard Range

An empirical calibration was built using a set of commercially available certified diesel fuel standards. Separate calibration methods can be built for different sulfur ranges, if needed. A summary of the calibration is shown here, using a measurement time of 240 sec in air atmosphere.

Element: S		Std Error of Est: 4
Units: ppm		Correlation: 0.99991
Sample I.D.	Standard Value	Calculated Value
STD 1	100	97
STD 2	200	205
STD 3	400	399
STD 4	600	596
STD 5	800	803
STD 6	1000	999



REPEATABILITY – Standard Range

To demonstrate repeatability (precision), the select samples were chosen from the set of calibration standards. Each sample was measured in static position for ten repeat analyses using a total analysis time of 120 sec per measurement in air atmosphere, with typical results shown below.

Element: S	Units: ppm			
Sample ID	Standard Value	Average Value	Std Dev	% Relative
STD 1	100	98	3.4	3.5
STD 6	1000	1002	7.2	0.7

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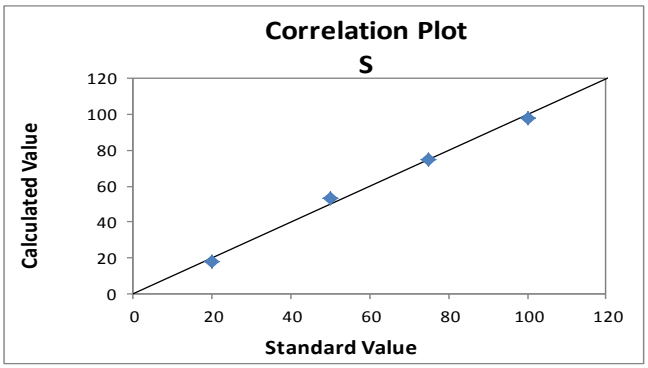
CALIBRATION – Low Range

The low sulfur range 20-100 ppm uses typical ULS technique protocol:

- Prolene film
- Helium purge
- 300 sec measurement time
- 5.0g of sample
- Prepare fresh sample in new cup, set on Kim-wipe or similar to check for leaks
- Measure sample immediately

An empirical calibration was built using a set of commercially available certified diesel fuel standards. A summary of the low range calibration is shown here, using a measurement time of 300 sec in helium atmosphere.

Element: S		Std Error of Est: 3.5
Units: ppm		Correlation: 0.99309
Sample I.D.	**Standard Value**	**Calculated Value**
STD 1	20	18
STD 2	50	53
STD 3	75	75
STD 4	100	98



REPEATABILITY – Low Range

To demonstrate repeatability (precision), the select samples were chosen from the set of calibration standards. Each sample was measured in static position for ten repeat analyses using a total analysis time of 300 sec per measurement in helium atmosphere, with typical results shown below.

Element: S	Units: ppm			
Sample ID	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
STD 1	20	18	3.7	19
STD 2	50	52	2.0	4.0
STD 4	100	102	3.0	3.0

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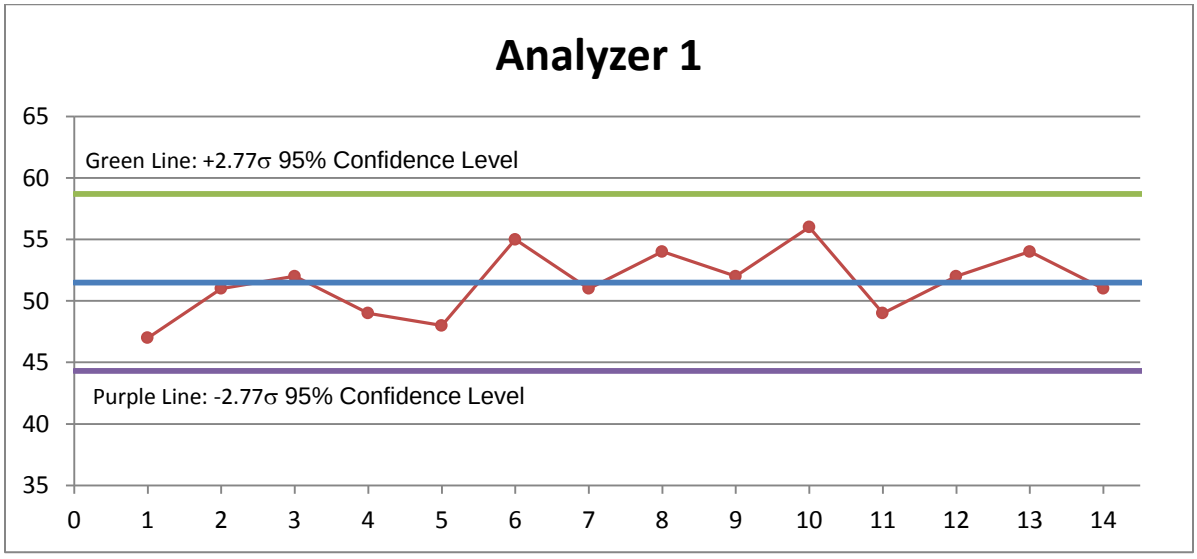
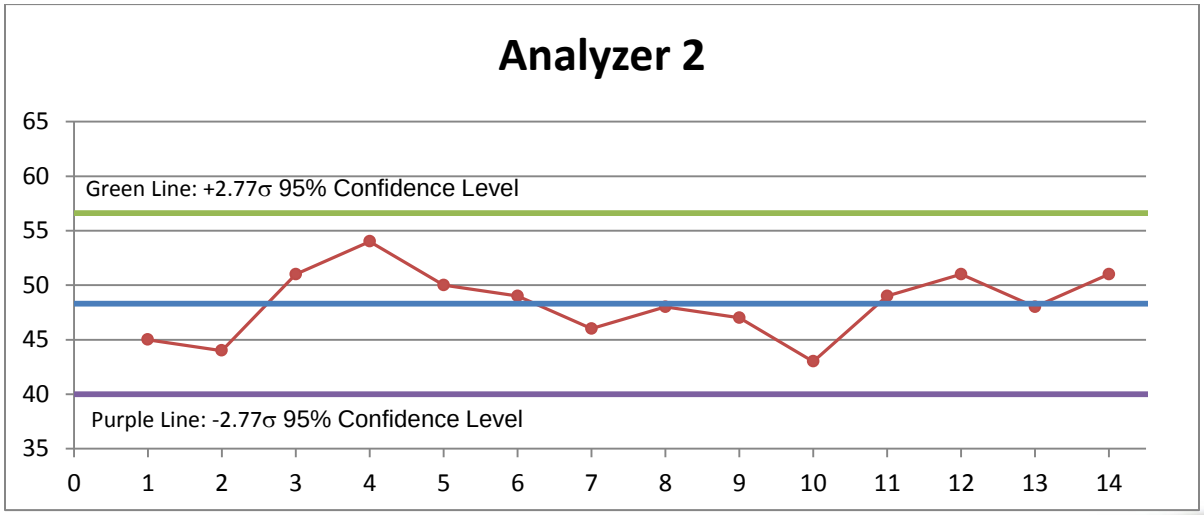
REPRODUCIBILITY – Low Range

Reproducibility is the longer term reliability over many days, different aliquots of the same sample, different analyzers and different operators. Reproducibility is expected to be 1.5 – 2.0X repeatability. To demonstrate reproducibility, two NEX QC analyzers were tested over a 10 day period. A 50 ppm sample was measured on each machine, once or twice a day, for a total of 14 measurements over the 10 day period. ULS measurement protocol was used, and no Standardize drift correction was required.

Sample: 50.0 ppm S in Diesel	Units: ppm			
	Standard Value	Average Value	Std Dev	% Relative
Analyzer 1	50.0	51.5	2.6	5.2
Analyzer 2	50.0	48.3	3.0	6.0





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TYPICAL DETECTION LIMITS

To determine the Lower Limit of Detection (LLD) using the empirical method, ten repeat analyses of a diesel fuel standards with <0.1 ppm S were measured and the standard deviation calculated. The LLD is then defined as three times the standard deviation.

Standard Range in Air Atmosphere

Range	S LLD @ 120 sec	S LLD @ 600 sec
100-1000 ppm S	10 ppm	5 ppm

Low Range in Helium Atmosphere

Range	S LLD @ 300 sec	S LLD @ 600 sec
20-100 ppm S	5 ppm	3 ppm

INTERNATIONAL STANDARD TEST METHODS

The Rigaku NEX QC complies with the following international standards test methods for measuring sulfur in crude and petroleum oils. Note that by weight 1 ppm = 1 mg/kg.

ASTM D4294	ISO 20847	ISO 8754	IP 496	IP336	JIS K 2541-4
16 ppm – 5%	**30 -500 mg/kg**	**100 mg/kg – 5%**	**100 mg/kg – 5%**	**100 mg/kg – 5%**	**0.01 – 5%**

FUEL TYPES

The performance shown here for diesel is also applicable to the following fuel and oil types when calibrated over similar ranges:
Diesel ● Kerosene ● Heating oils ● Jet fuel ● Naphtha ● Other middle distillates ● Residual oil ● Crude oil
Unleaded Gasoline ● Gasohol ● Hydraulic oil ● Mineral oil ● Biodiesel (see Note 2 ASTM D4294-10)
And other similar petroleum products.

CONCLUSION

The performance shown here demonstrates the ability of the NEX QC to yield excellent results for the measurement of sulfur in diesel fuel in air, without the need for helium purge. Helium can be used to optimize the low sulfur range. Simple, modern touch screen interface allows for reliable and efficient measurement protocols, and performance meets all international norms for the range 100 ppm into % levels of sulfur, and meets ASTM D4294 and ISO 20847 for measurements below 100 ppm to the ASTM D4294 scope of PLOQ 16 ppm S.

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