EDXRF APPLICATION NOTE
MARINE FUELS ANALYZER

#1924

SCOPE

The analysis of sulfur and metals in bunker fuel and marine diesel are demonstrated.

BACKGROUND

Regulations limiting the sulfur content of fuel used in the marine industry continues to evolve. As of January 1, 2015 the revised Annex VI to Marpol 73/78 reduced the maximum sulfur content allowed when entering ECA's (Emission Control Areas) to 0.1 wt%. After January 1, 2020 new IMO regulations require the sulfur content of any fuel used on board ships not to exceed 0.5 wt %. This is a substantial reduction from the 3.5 wt% limit established January 1, 2012.

To meet the needs of the industry, Rigaku offers the NEX QC Marine Fuel Analyzer, a simple, versatile, and portable benchtop EDXRF analyzer for the analysis of sulfur in marine fuels. In addition to sulfur, the unit can be set up to monitor the Nickel (Ni), Vanadium (V) and Iron (Fe) content of residual oils or to ensure fuels have not been adulterated with used engine oil or other undesirable oils. Screening for Zinc (Zn) will help ensure fuels are free of used engine oil.

INSTRUMENTATION

Model:	Rigaku NEX QC
X-ray tube:	4 W Ag-anode
Detector:	Semiconductor
Sample Type:	Bunker Fuel & Diesel
Film:	Mylar
Analysis Time:	100 sec Sulfur
	260 sec Sulfur and Metals
Environment:	Air
Options:	Carrying case, factory calibrations, calibration standards

SAMPLE PREPARATION

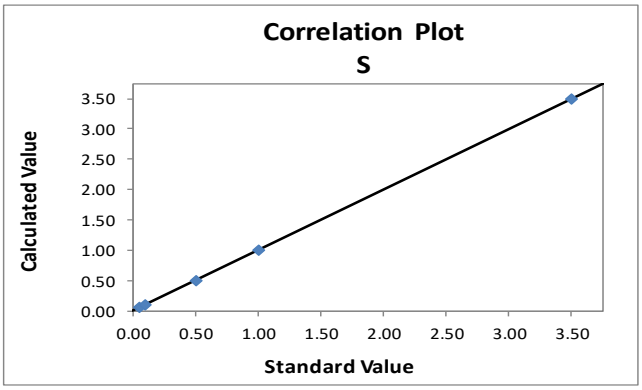
To measure a sample, gently shake the sample bottle, allow bubbles to settle and fill a 32mm XRF sample cup 3/4 full (approximately 5g).

Marine Sulfur-Pak™: 0.05 – 3.50% Sulfur

CALIBRATION

An empirical calibration was built using a set of commercially available mineral oil standards. A summary of the calibration is shown here, using a measurement time of 100 sec.

Element: S		RMS Dev: 0.0017
Units: %		Correlation: 0.99999
Sample I.D.	Standard Value	Calculated Value
STD 1	0.050	0.0495
STD 2	0.100	0.0993
STD 3	0.500	0.5027
STD 4	1.000	0.9980
STD 5	3.500	3.5000



The Marine Sulfur-Pak is ideal for measuring diesel 0.05-1.0% targeting 0.1% sulfur and bunker fuels 0.1-3.5% targeting 0.5% sulfur.

REPEATABILITY

To demonstrate repeatability, samples was measured in static position for ten repeat analyses using a total analysis time of 100 sec per measurement, with typical results shown below.

Element: S	Units: %			
Sample ID	Standard Value	Average Value	Std Dev	% Relative
STD 1	0.100	0.0992	0.0010	1.0
STD 3	0.50	0.4972	0.0021	0.4

INTERNATIONAL STANDARD TEST METHODS FOR SULFUR

The Rigaku NEX QC complies with the following international standards test methods for measuring sulfur in crude, bunker fuel, diesel and other 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%

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Sulfur and Metals in Bunker Fuel

CALIBRATION

Empirical calibrations were built using a suite of 12 commercially available residual oil calibration standards. A summary of the empirical calibrations is shown here.

Element	Concentration Range	RMS Deviation	R^2 Confidence
S	0.24 – 5.50 %	0.014	0.99996
Ni	3 – 100 ppm	1.3	0.99907
V	25 – 500 ppm	7.7	0.99845
Fe	15 – 500 ppm	7.8	0.99822

REPEATABILITY

To demonstrate repeatability, samples was measured in static position for ten repeat analyses using a total analysis time of 260 sec per measurement, with typical results shown below.

Sample: Std 2				
Element	**Standard Value**	**Average Value**	**Std Dev**	**% Relative Dev**
S	0.50 %	0.503	0.007	1.4
Ni	10 ppm	11	0.6	6.0
V	500 ppm	501	5	1.0
Fe	300 ppm	300	3	1.0

DETECTION LIMITS (LLD – Lower Limit of Detection)

The LLDs shown here apply to bunker fuel and diesel over the concentration ranges shown above.

Element	LLD
S	0.0025 %
Ni	1.6 ppm
V	3.6 ppm
Fe	2.7 ppm

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CONCLUSION

The performance shown here demonstrates the ability of the NEX QC to yield excellent results for the measurement of sulfur and metals in bunker fuel and marine diesel. The system also has the capabilities to screen for elements such as Zn, Ni, and V in adulterated fuels.

The simple user interface and low maintenance requirements of the NEX QC allows operators of all skill levels to use and maintain the equipment.

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