CURRENT APPLICATION TRENDS IN THE PETROLEUM INDUSTRY USING EDXRF AND PROCESS XRT GAUGE

Energy Dispersive X-ray Fluorescence (EDXRF) is a robust, simple and fast analytical technique for the elemental analysis of liquids, powders and solids designed for use upstream and midstream for in-field use, as well as downstream at the refinery and at commercial labs.

Simply put, EDXRF irradiates a sample with source X-rays causing the atoms in the sample to fluoresce their own characteristic X-rays to a detector. The particular energy of a fluorescent X-ray corresponds to a particular element. These characteristic X-rays are collected and sorted by energy creating a spectrum of elemental peaks where the number of counts per second for each element is compared to a stored calibration that determines the concentration of each element in the sample.

In EDXRF the unwanted background X-rays coming from the source X-ray tube are reduced or removed in one of two ways called direct excitation and indirect excitation.

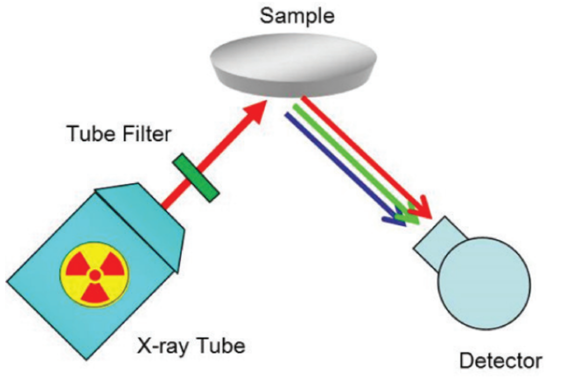


Image 1: Direct Excitation

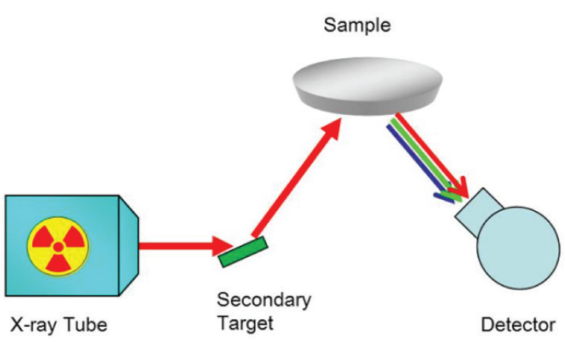


Image 2: Indirect Excitation

Direct excitation creates polychromatic source X-rays by removing unwanted parts of the background using thin filters between the tube and sample. Indirect excitation virtually removes all the background creating monochromatic source X-rays.

While accuracy in XRF is determined by the goodness of the reference materials and calibration standards, measurement precision and detection limits are determined by many factors including background removal and measurement time. Measurement times shown here are for demonstration of optimum performance and shorter measurement times can be used if such tight precision and low detection limits are not required.

X-ray transmission (XRT) uses the principle of X-ray attenuation rather than fluorescence. A monochromatic X-ray beam is directed through the oil to a detector on the opposite side. A portion of the source X-ray beam is absorbed by sulfur atoms, and so by collecting the attenuated beam at the detector the sulfur concentration is determined. In this way the sulfur content of the crude or other heavy hydrocarbon oils is determined in-line in real time as the oil flows between source and detector.

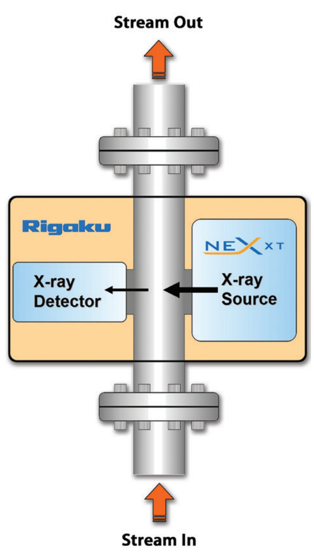


Image 3. Schematic of Rigaku NEX XT in-line sulfur gauge using XRT technology

Current Application Trends in the Petroleum Industry

ULSD and Tier 3 Gasoline

EDXRF has been used for over twenty-five years for the measurement of sulfur in crude, fuels and petroleum-based oils by standard test method ASTM D4294 (Sulfur in Petroleum and petroleum Products by Energy Dispersive X-ray Spectrometry, 17 mg/kg to 4.6 mass% S). Testing ULSD (ultra-low sulfur diesel) and meeting U.S. EPA Tier 3 gasoline requirements are met by EDXRF and ASTM standard test method D7220 (Sulfur in Automotive, Heating and Jet Fuels by Monochromatic Energy Dispersive X-ray Spectrometry, 3-942 mg/kg S). The following demonstrates the use of EDXRF for measuring ultra-low sulfur.

Table 1. ULSD, Tier 3 gasoline and ultra-low Cl EDXRF instrument configuration

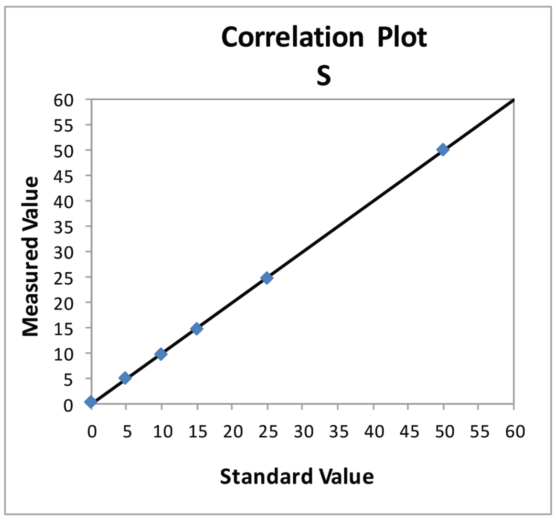
EDXRF Instrumentation	Rigaku NEX CG
Type	Monochromatic EDXRF Indirect Excitation with Cartesian Geometry Polarization
X-ray tube	50W Pd Anode
Detector	High Performance SDD
Atmosphere	Helium Purge
Analysis Time	300 sec

Sample preparation is simple. Ensure each sample is homogeneous and stable. Shake the sample gently and allow bubbles to settle. Fill a 32mm diameter XRF sample cup with 4.0g of sample to ensure consistent sample depth. It is recommended to make the measurement immediately after filling the cup and remove the sample immediately when measurement is complete.

Calibration is achieved using commercially available certified reference standards.

The following demonstrates precision and sulfur detection limit

Element: S	RMS Dev: 0.25	
Units: ppm	Correlation: 0.99993	
Sample I.D.	Standard Value	Measured Value
1	0.0	0.3
2	5.0	5.0
3	10.0	9.8
4	15.0	14.9
5	25.0	24.8
6	50.0	50.2



Plot 1. Typical calibration for ultra-low sulfur in gasoline using Rigaku NEX CG

using monochromatic Cartesian geometry polarization. Ten repeat measurements are taken without moving the sample. The standard deviation (s) is considered the precision, while 2.77s is considered repeatability, called "little r" in ASTM.

Table 2. Typical precision and repeatability at 10 mg/kg S using Rigaku NEX CG

Element: S	Units: mg/kg			
Standard Value	Average Value	Std Dev (s)	2.77s	ASTM D7220 r value
10	10.1	0.2	0.6	2.1

Detection limit, also called LLD (lower limit of detection), is determined by at least 10 repeat measurements of a blank sample containing no sulfur. The detection limit is based on the precision in measuring background signal and shown by the standard deviation, s, of the ten measurements of the blank. LLD is then defined as 3s.

Table 3. Typical S LLD in gasoline using Rigaku NEX CG

Element	LLD (mg/kg)	Analysis Time per Measurement
S	0.24	300 sec

The U.S. EPA recently implemented performance-based testing criteria for the measurement of ultra-low sulfur in gasoline. The following results show NEX CG performance using the EPA testing criteria as per U.S. code of federal regulations 40 CFR 80.47.

Tier 3 Gasoline Precision 80.47 13.b.1 –

- Use a commercially available certified gasoline sample with sulfur content between 5-15 ppm
- Measure 20 aliquots over 20 days and calculate standard deviation (s)
- Criteria: Maximum allowable s ≤ 1.5*r/2.77
- Example: 10 ppm sulfur: s≤1.75/2.77=0.95 ppm

Table 4. Passing Tier 3 precision criteria using Rigaku NEX CG

Test Sample: Certified Gasoline Sample 10.0 ppm S			
Average	Standard Deviation (s)	Criteria	Determination
9.8 ppm S	0.4 ppm	0.4≤0.95ppm	PASS

Tier 3 Gasoline Accuracy 80.47 13.b.2(i) –

- Use a commercially available certified gasoline sample with sulfur content between 1-10 ppm
- Measure a continuous series of at least 10 tests and calculate the average of the results (AVG)
- Criteria: The AVG cannot deviate from the accepted reference value (AVR) by more than 0.71 ppm
- |AVR-AVG|≤0.71 ppm

Table 5. Passing Tier 3 accuracy using Rigaku NEX CG

Test Sample: Gasoline certified ARV 9.0 ppm S				
Average of 10 Tests (AVG)	Standard Deviation	Difference from Certified Value |AVR-AVG|	Criteria	Determination
8.8 ppm S	0.4 ppm	0.2 ppm	0.2≤0.71	PASS

Chlorine in Crude

The EDXRF detection system collects and counts elemental X-rays simultaneously, and so EDXRF is multi-element and a single system can measure elements typically from sodium through uranium. For example, the elimination of background by monochromatic excitation lends itself well to the ultra-low sulfur applications as well as the measurement of chlorine in crude containing high sulfur. And for the best measurement of chlorides in crude monochromatic EDXRF using Cartesian geometry polarization is used with ASTM D4929 Part C to measure chlorine in the range 2-12 mg/kg after the crude sample has been washed by the methodology of the standard test method.

Table 6. Typical detection limits for S and Cl in crude using Rigaku NEX CG

Element	LLD
S	<1.0 ppm
Cl	0.3 ppm in crude up to 1.5% sulfur

In-line Measurement of Sulfur in Crude, Bunker Fuels, and Residuums

As the price of sweet crude grows, crude upgrading, blending of crudes to meet specific market demands and custody transfer monitoring has become increasingly attractive based on fundamental economic principals and foreseeable demand patterns.

In the marine industry, the blending of bunker fuels to meet MARPOL sulfur limits or compliance monitoring of bunker fuels onboard ships is increasing in popularity.

One of the key properties of crude and bunker fuels is the sulfur content, as the sulfur level directly impacts the price. Therefore, precise sulfur measurements are critical when optimizing refining or blending operations.

By optimizing the process with a precise in-line measurement of sulfur content, costs can be minimized, maximum profitability can be achieved and compliance guaranteed.

X-ray transmission lends itself well for the measurement of the sulfur content in carbon-rich highly viscous oils. The following demonstrates typical usage and performance.

Table 7. In-line sulfur measurement instrument configuration

XRT Instrumentation	Rigaku NEX XT
Type	Monochromatic source X-ray Transmission
X-ray tube	Side Window
Detector	Scintillation
Atmosphere	Air
Analysis Time	60 sec

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Calibration is achieved using crude oil samples with known sulfur content in static configuration.

Table 8. Typical sulfur calibration using Rigaku NEX XT

Sample I.D.	Known wt%	Calculated wt%	Deviation	Density	Acq Time
1	0	-0.012	0.013	0.8254	60
2	0.124	0.125	-0.001	0.8517	60
3	0.286	0.285	0.001	0.8514	60
4	0.298	0.305	-0.007	0.8042	60
5	0.616	0.627	-0.011	0.8494	60
6	1.526	1.52	0.006	0.8432	60

The NEX XT system exhibits excellent precision and a sulfur detection limit of 45 ppm. The system also shows excellent agreement with benchtop EDXRF in accordance with ASTM D4294, as shown in these measurement of samples in the field.

Table 9. Agreement of NEX XT with EDXRF D4294 sulfur measurement

Sample I.D.	EDXRF wt%	NEX XT wt%	Deviation	Density	Acq Time
A	0.084	0.084	0	0.8003	60
B	0.482	0.488	0.006	0.8152	60
C	1.85	1.89	0.04	0.8504	60
D	0.37	0.39	0.02	0.8149	60

Measuring Sulfur and Metals in Crude and Resid

This is required for multi-element application so that all elements can be measured in a sample, ensuring proper "alpha" corrections are used that compensate for X-ray absorption/enhancement matrix effects.

To demonstrate EDXRF multi-element analysis the application measuring sulfur, calcium, vanadium, iron and nickel in crude and resid is shown here.

Table 10. EDXRF instrument configuration used for measuring S, Ca and metals in crude and resid

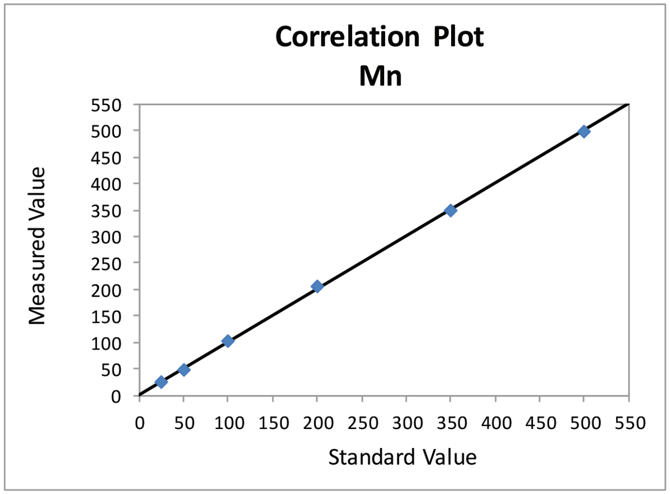
EDXRF Instrumentation	Rigaku NEX DE
Type	Polychromatic EDXRF Direct Excitation using special layered tube filters
X-ray tube	12W Ag Anode
Detector	High Throughput SDD
500,000+ cps	
Atmosphere	Air
Analysis Time	700 sec

As accepted in EDXRF use, calibration is achieved using commercially available certified reference standards. For multi-element application all elements that occur in the unknowns occur in each calibration standard and the concentrations of the element vary independently of other (randomly). This ensures proper "alpha" corrections can be used to compensate for matrix effects in XRF.

Table 11. Typical calibration summary for S and metals in crude using Rigaku NEX DE

Element	Concentration Range	RMS Deviation	R^2 Confidence
S	0.30 – 4.00 %	0.0524	0.99955
Ca	50 – 800 ppm	4.4	0.99990
V	5 – 50 ppm	0.44	0.99966
Fe	5 – 100 ppm	0.88	0.99971
Ni	5 – 50 ppm	0.29	0.99986

Units: mg/kg		RMS Dev: 2.5 Correlation: 0.99982
Standard I.D.	Standard Value	Measured Value
1	25	24.2
2	50	47.4
3	100	101
4	200	204
5	350	349
6	500	499



Plot 2. Typical calibration for Mn in gasoline using Rigaku NEX QC⁺

Detection limits are determined in the same empirical way as discussed in previous section.

Table 12. Typical detection limits in crude and resid using Rigaku NEX DE

700 sec Total Analysis Time	
Element	LLD
S	5 ppm
Ca	0.5 ppm
V	0.3 ppm
Fe	1.1 ppm
Ni	0.4 ppm

Manganese in Gasoline and Avgas

Tetraethyl lead (TEL) is an anti-knock agent added to gasoline but has been phased out in many regions of the world due to the potentially toxic nature of lead. Its replacement is methylcyclopentadienyl manganese tricarbonyl (called MMT or MCMT) using manganese instead of lead as the anti-knock agent.

To illustrate the versatility of EDXRF the measurement of manganese (Mn) in gasoline is demonstrated here.

Table 13. EDXRF instrument configuration used for measuring Mn in gasoline and Avgas

EDXRF Instrumentation	Rigaku NEX QC⁺
Type	Polychromatic EDXRF
Direct Excitation using special layered tube filters	
X-ray tube	4W Ag Anode
Detector	High Performance SDD
Atmosphere	Air
Analysis Time	100 sec

Table 14. Typical precision for Mn in gasoline and Avgas usingRigaku NEX QC⁺

Element: Mn Units: mg/kg				
Sample	Assay Value	Average Measured Value	Standard Deviation	% Relative Deviation
1	25	23.5	0.6	2.6%
3	100	101	1.4	1.4%
6	500	501	4.2	0.8%

Table 15. Typical detection limits for Mn in gasoline and Avgas using Rigaku NEX QC⁺

Element	LLD @ 100 sec mg/kg	LLD @ 300 sec mg/kg
Mn	2.1	1.2

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Conclusion

As screening and testing needs expand throughout the petroleum industry, the EDXRF systems from Applied Rigaku Technologies show versatility in meeting many various needs. While EDXRF is the accepted technique for measuring high sulfur by ASTM D4294, development of background removal by direct and indirect excitation and advanced detection design allows Applied Rigaku Technologies EDXRF analyzers to be used for many petroleum applications, including multi-element applications. The real-time sulfur measurement in crude, bunker oil and other highly viscous oils for trend control, blending, and compliance is achieved using the transmission technique and NEX XT from Applied Rigaku Technologies, Inc.

Author Contact Details

Scott Fess, Applied Rigaku Technologies, Inc.

- 9825 Spectrum Drive, Bldg. 4 Suite 475, Austin, TX 78717 USA • Tel: 00 1 512-225-1796
- Email: Info@RigakuEDXRF.com
- **www.RigakuEDXRF.com**