How Oil Companies can use EDXRF Technology to comply with the EPA Tier 3 Standard Requirement of Low Sulfur Fuel and other Key Applications

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Abstract

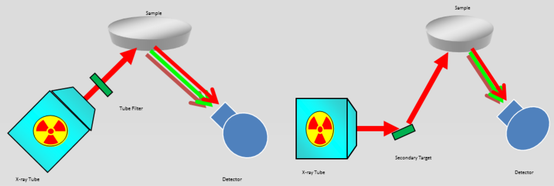
Energy Dispersive X-ray Fluorescence (EDXRF) is a fast, simple, and non-destructive elemental analysis technique for the measurement of liquids, powders, and solids. It is widely applied throughout the petroleum industry: upstream at the well site, mid-stream at pipelines, storage facilities and blending operations, and down-stream at the refinery. In 2017, the US Environmental Protection Agency (EPA) implemented new regulations on the composition of fuel, which included changing the maximum allowable sulfur content from 30 parts per million (ppm) on an annual average basis down to 10 parts per million (ppm). With more stringent requirements, better tools and technology are needed to test the sulfur content of fuels, namely, gasoline and diesel. The EDXRF is the ideal analytical tool to accurately determine the sulfur content in fuel samples, conforming to not only ASTM D7220, but also meeting the requirements for the EPA Tier 3 program.

Furthermore, the EDXRF can be used to determine concentration of some elements such as manganese, lead, zinc, phosphorous, and calcium. The determination of manganese and lead content gives an indication of the anti-knock agent added to motor gasoline and Avgas to improve octane rating. Whilst the determination of zinc, phosphorous, calcium, and sulfur give an indication of the antioxidant, and anti-wear agents in lubricating oils. This poster discusses the versatile application of the EDXRF which allows end-users to effectively ascertain correct results for this desired use, and conform to international testing standards.

Koehler EDXRF Systems

Sulfur (S) measurement is one of the most important measurements to make in the petroleum industry. The Koehler line of benchtop EDXRF systems are designed with unique features to give best sulfur results from crude oil, diesel and middle distillates by ASTM D4294, to ULSD and U.S. EPA Tier 3 gasoline by ASTM 7220. Features include simple software operation for the non-technical and technical operators alike. Koehler uses high performance Si PIN diode and SDD detectors giving the ability for multi-element analysis as well, measuring not only S but other petro apps as well, including Mn and Pb in gasoline, metals in crude and resid, and Cl measurement from high levels to ultra-low levels.

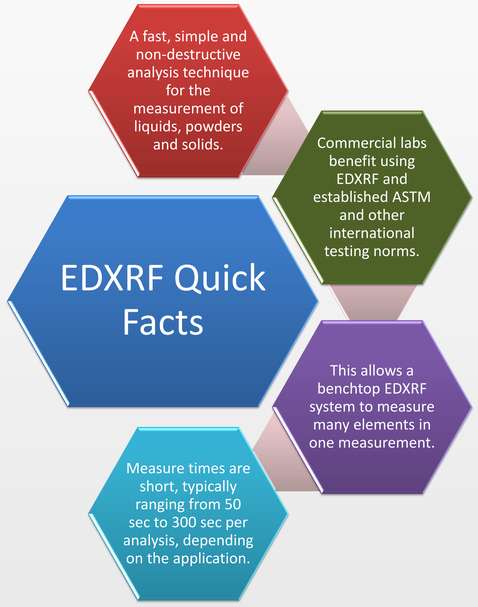
To achieve this range of performance, Koehler system employ either direct excitation or indirect excitation. Koehler direct excitation systems produce polychromatic source X-rays and background removal is achieve with a unique multi-layer filters which remove extra amounts of background X-rays. Indirect excitation provides monochromatic polarized source X-rays for the near complete removal of all background.



Koehler EDX1000 and EDX2000 analyzers use direct excitation and special filters to provide optimum polychromatic excitation.

The Koehler EDX3000 uses indirect excitation using secondary targets and full Cartesian polarization providing monochromatic excitation for optimal background removal.

Applications and Usage



Usages in the Petroleum Industry

- Crude Oil
- Diesel
- ULSD
- Gasoline
- Bunker Fuel
- Jet Fuel and AvGas
- Kerosene and Heating Oil
- Pipelines
- Tank farms
- Gathering Points
- Blending Operations
- Refineries
- Commercial Labs
- Bunkering Stations

Popular EDXRF Standard Test Methods in the Petroleum Industry

	ASTM D4294	ASTM D7220	ISO 13032	ASTM D4929	U.S. EPA Tier 3 Gasoline
Koehler System:	**16 ppm - 5% Sulfur**	**3 - 942 mg/kg Ultra-low Sulfur**	**8 - 50 mg/kg Ultra-low Sulfur**	**2 - 12 mg/kg Cl in Crude by Naptha Wash**	**10 ppm S in Gasoline**
EDX1000	✓				
EDX2000	✓		✓		
EDX3000	✓	✓	✓	✓	✓

Sample Preparation

First, the user ensures that each sample is homogeneous and stable. Then the user simply shakes the sample gently, allows the bubbles to settle, and fills an XRF sample cup with 4.0 grams of sample to ensure consistent sample depth. Prolene film (or 4µm polypropylene) is used for diesel and other similar fuels, and Etnom™ film is used for gasoline and aromatic hydrocarbons. Cap and vent the cup, and make sure to check for leaks using lab tissue. The measurement should be made immediately after preparing the sample.

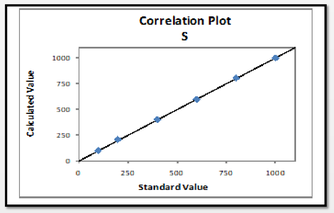
(Etnom™ is a registered trade mark of Chemplex Industries.)

Results

Sulfur Analysis ASTM D4294 & ISO 13032:

EDX1000 provides ASTM D4294 performance 50 ppm S to % levels, while EDX2000 adds ultra-low performance to 8 ppm S by ISO 13032.

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

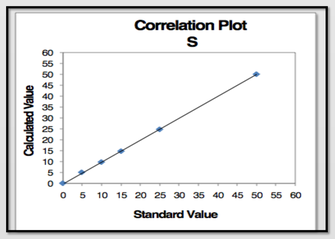


Typical calibration low range 100 – 1000 ppm S

Ultra-low Sulfur ASTM D7220:

ASTM D7220 for monochromatic EDXRF is comparable to the WDXRF methods D2622 and D7039. It can be used for ULSD measurements as well as meeting U.S. EPA Tier 3 gasoline testing requirements as shown here.

Element: S		RMS Dev: 0.25
Units ppm		Correlation: 0.9993
Sample I.D.	**Standard Value**	**Measured Value**
1	0	0
2	5	5
3	10	9.8
4	15	14.9
5	20	24.8
6	25	50.1

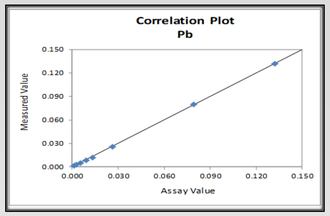


Tier 3 Gasoline Testing Requirements

Lead Analysis ASTM D5059-14:

EDX3000 provides ASTM D5059 performance, determining the total lead content in the gasoline

Units: g/L		RMS Dev: 0.0006
		Correlation: 0.99994
Standard I.D.	**Assay Values**	**Measured Values**
1	0.0013	0.0018
2	0.0026	0.0032
3	0.0053	0.0055
4	0.009	0.0088
5	0.0132	0.0122



Empirical calibration 0.0013 – 0.1321 g/L to satisfy D5059 Part C using a suite of 8 commercially available certified gasoline calibration standards.

Other Applications Using Koehler EDX-Series Analyzers

- Metals in Crude and Resid
- Ultra-low Cl in Crude by ASTM D4929
- Mn in Gasoline
- Lube Oils
- Metalworking Fluids

Conclusions

The Koehler line of benchtop EDXRF systems are demonstrated to give accurate readings of sulfur content in crude oil, diesel and middle distillates, to ULSD and U.S. EPA Tier 3 gasoline.

The EPA Tier 3 program considers vehicles, and the fuels used by them, to be a major contributor to any detrimental effect on the environment and/or public health. Therefore, Running the ASTM D7220 Test Method, with good lab practices, will allow refiners, and/or other entities, to properly use the EDXRF line to yield results that meet the new EPA requirements.

EDXRF technology can be widely used throughout the petroleum industry, upstream at the well site, mid-stream at pipelines, tank farms and gathering points, as well as down-stream at the refinery.

References

- ASTM D7220 “Standard Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry” (West Conshohocken, PA: ASTM International).
- ASTM D5059 “Standard Test Method for Lead in Gasoline by X-Ray Spectroscopy” (West Conshohocken, PA: ASTM International).
- EPA 40 CFR 80.584 “What are the precision and accuracy criteria for approval of test methods for determining the sulfur content of motor vehicle diesel fuel, NRLM diesel fuel, and ECA marine fuel?” Environmental Protection Agency.
- ISO 13032.2012 “Petroleum products -- Determination of low concentration of sulfur in automotive fuels -- Energy-dispersive X-ray fluorescence spectrometric method”

Acknowledgements

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