

### Abstract

The Energy Dispersive X-ray Fluorescence Spectrometry (EDXRF) is a fast, simple, and non-destructive analysis technique, used for the measurement of liquids, powders, and solids. It is widely applied throughout the petroleum industry for various purposes, including but not limited to upstream at the well site, mid-stream at pipelines, storage facilities and blending operations, and down-stream at the refinery.

Recently, with the Environmental Protection Agency (EPA) mandating new regulations on the composition of fuel, the maximum allowable sulfur content has been scaled down to 10 parts per million (ppm). Therefore, the EDXRF is an ideal analytical tool for refiners - with good lab practices- to accurately determine the sulfur content in fuel samples, conforming to not only ASTM D7220, but also meeting the testing requirements for the EPA Tier 3 program for ultra-low sulfur fuels such as gasoline and diesel.

Furthermore, the EDXRF can be used to determine concentration of some elements such as manganese, lead, zinc, phosphorous, and calcium. EDXRF is also ideal for the measurement of S, Ca, V, Fe, and Ni in crude, resid, and bunker fuel. 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 antiwear agents in lubricating oils. The versatile application of the EDXRF 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.

# EDXRF Technology's Applications to Measure the Sulfur Content in Ultra-Low Sulfur Fuels and to **Measure Organometallic Additives in Lubrication Oils and Motor Gasoline**

A fast, simple and nondestructive analysis technique for the measurement of liquids powders and solids

> Commercial labs benefit using EDXRF and established ASTM and other international testing norms.

EDXRF Quick Facts

> his allows a benchtop EDXRF system to measure many elements in one measurement.

Measure times are short, typically ranging from 50 sec to 300 sec per analysis, depending on the application.

## **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<sup>™</sup> 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<sup>™</sup> is a registered trade mark of Chemplex Industries.)

### **Other Applications Using Koehler EDX-Series**

- Metals in Crude and Resid
- ➢ Ultra-low Cl in Crude by ASTM 4929
- Mn in Gasoline
- Pb in Gasoline
- Lube Oils
- > Metalworking Fluids



	<b>ASTM D4294</b>	<b>ASTM D7220</b>	ISO 13032	ASTM D4929	
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	
EDX1000	$\checkmark$				
EDX2000	$\checkmark$		$\checkmark$		
EDX3000	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	

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> 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: 0.9999				
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.



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		0.150	Correlat F	rrelation f Pb	
Standard I.D.	Assay Values	Measured Values	٩	0.120 -			
1	0.0013	0.0018	ed Valu	0.090 -			/
2	0.0026	0.0032	Aeasun	0.060 -			×
3	0.0053	0.0055		0.030 -	_		
4	0.009	0.0088		0.000	0.030	0.050	
5	0.0132	0.0122		0.000	0.050	Assa	y Value

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

### **Usages in the Petroleum Industry**

#### Crude Oil

- Diesel
- > ULSD
- Gasoline
- Bunker Fuel
- Jet Fuel & AvGas
- Kerosene & Heating Oil
- > Pipelines
- > Tank Farms
- > Gathering Points
- > Blending Operations
- Refineries
- Commercial Labs
- Bunkering Stations



## **Popular EDXRF Standard Test Methods**



U.S.EPA Tier 3 Gasoline

10 ppm S in Gasoline

### 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.
- The EDXRF 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 Heating, and Jet Fuels by Automotive, 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"

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