Discussion of Energy Dispersive X-ray (EDXRF) Technology's Application to Measure the Absolute Fuel Parameter of Gasoline Sulfur to Comply with the Tier 3 Gasoline Standards

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Abstract

The adoption of the new Tier 3 Program by the Environmental Protection Agency (EPA) has resulted in the need for increased sensitivity in instruments to meet the updated testing requirements. The new program has mandated revised regulations on the composition of fuel, scaling down the maximum allowable sulfur content to 10 parts per million (ppm). The EPA considers vehicles, and the fuel it uses, as a major contributor of adverse effects to the environment and to public health. It is predicted that 10% to 30% of air toxins will be mitigated due to the new policy, this will improve both the environment and overall public health.

Moreover, the burden of oversight on monitoring the sulfur content in fuels has been placed on global field refiners, and it is their incentive to be confident that the reported data to the EPA is reliable and accurate. The EPA accepts the ASTM D7220: "Standard Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry," to verify the absolute fuel parameter of gasoline sulfur. This poster discusses a new benchtop analyzer which is a simple, compact, and versatile analytical tool that utilizes polarized X-ray technology to accurately determine the sulfur content of samples in question, and presents experimental data with related statistics for a variety of samples. This unique analyzer has the necessary precision and accuracy to meet the requirements for testing set by the EPA Tier 3 program for ultra-low sulfur fuels such as gasoline and diesel, while complying with ASTM D7220.

EDXRF Overview

EDXRF is a fast, simple and non-destructive analysis technique for the measurement of liquids, powders and solids. It is 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. Commercial labs also benefit using EDXRF and established ASTM and other international testing norms.

The technique is simple to use. An X-ray source safely irradiates the sample, causing the atoms in the sample to fluoresce their own characteristic X-rays in a process called fluorescence. The energy of a characteristic X-ray is unique to the element that produced it, and so by summing These fluorescent X-rays are collected by a detector and compared to a calibration to provide precise concentration results from single digit ppm to the higher percent levels.

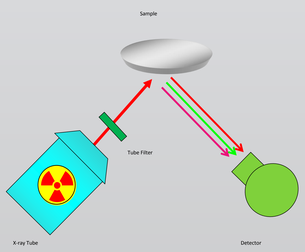
The EDXRF detection system is simple, collecting all energy X-rays at the same time. This allows a benchtop EDXRF system to measure many elements in one measurement. The typical element range for EDXRF measurement is Na through U in a single, low-cost, compact system. No special sample preparation is required using EDXRF. Simply ensure sample is homogeneous and stable and measure directly using standard 32mm XRF sample cups. Measure times are short, typically ranging from 50 sec to 300 sec per analysis, depending on the application.

Calibration is achieve by empirical best-fit gression using a set of calibrations standards. Certified calibration standards are commercially available.

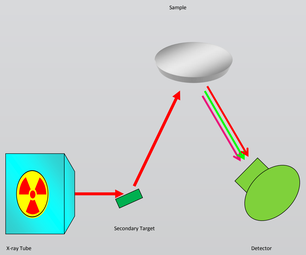
Koehler EDXRF Systems

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 distallates, to ULSD and U.S. EPA Tier 3 gasoline. 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 exciatation 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 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.

Koehler EDX-Series

EDX1000 with Si PIN Diode Detector
EDX2000 with SDD Detector

Technical Specifications	
Type	Direct Excitation using Filters
X-ray Tube	Ag Anode End-window Transmission
Voltage (max)	50kV
Power	4W
Detector	High Performance Semiconductors
Atmosphere	Air
Optional	Helium Purge

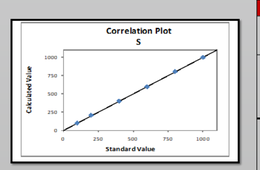
EDX3000 Indirect Excitation with Cartesian Geometry Polarization

Technical Specifications	
Type	Indirect Excitation with Secondary Targets & Polarization
X-ray Tube	Pd Anode
Voltage (max)	50kV
Power	50W
Detector	High Performance SDD
Atmosphere	Helium Purge

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



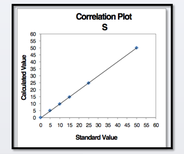
Typical calibration low range 100 – 1000 ppm S

Typical Repeatability S in Diesel Units: ppm					
Koehler System	**Atmosphere**	**Standard Value**	**Average Value**	**Std Dev**	**% Relative**
EDX1000 120 sec measurement time	Air	1000	51.5	2.6	5.2
	Air	100	1002	7.2	0.7
EDX2000 300 sec measurement time	Helium	50	50.9	0.50	1.0
	Helium	10	10.2	0.48	4.8

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

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, where r is the repeatability shown in ASTM D7039
- Example: 10 ppm sulfur: s≤1.75/2.77=0.95 ppm

EDX3000 Test Sample: Certified Gasoline Sample 10.0 ppm S			
Average	**Standard Deviation (s)**	**Criteria**	**Determination**
9.8 ppm S	0.4 ppm	**0.4≤0.95 ppm**	**PASS**

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

EDX3000 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**

Sulfur Detection Limits:
Lower Limit of Detection (LLD) is the 3-sigma precision in measuring the background. LLD is dependent on instrument used, calibration range, atmosphere (helium or air) and measurement time. The following typical LLDs are shown using helium purge and 300 sec measurement time. S levels above 100 ppm do not require the use of helium.

Koehler	EDX1000	EDX2000	EDX3000
S LLD @ 300 sec	5 ppm	1.3 ppm	0.24 ppm

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**

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

	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	✓	✓	✓	✓	✓

Conclusion:

The Koehler line of benchtop EDXRF systems are demonstrated to give accurate readings of sulfur content in crude oil, diesel and middle distallates, to ULSD and U.S. EPA Tier 3 gasoline. With its unique features the EDXRF line provides end-users with an effective instrument to follow ASTM 7220 test method allowing to yield results that meet the new EPA requirements.

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"

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