EDXRF Using ASTM 7220 to Meet EPA Tier 3 Gasoline Testing Requirements

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1. Abstract

As of 2017 the Environmental Protection Agency (EPA) has mandated new regulations on the composition of fuel, scaling down the maximum allowable sulfur content to 10 parts per million (ppm). As a result, this promotes cleaner emissions from passenger vehicles and trucks in the United States. The ASTM D7220: "Standard Test Method for Sulfur in Automotive, Heating, and Jet Fuels by Monochromatic Energy Dispersive X-ray Fluorescence Spectrometry," can be used to check if fuels meet the regulations rolled out by the EPA. The burden of oversight on monitoring the sulfur content 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.

Therefore, the Koehler Instrument's EDX3000 benchtop analyzer is a simple, compact, and versatile equipment that is an ideal analytical tool for refiners - with good lab practices- to accurately determine the sulfur content in fuel samples. Furthermore, the use of the EDX3000 complies with the ASTM D7220 test method, and is also an adequate instrument to meet the requirements of testing for the EPA Tier 3 program for ultra-low sulfur fuels such as gasoline and diesel.

2. ASTM D7220 Test Method Overview

The D7220 test method is a standard internationally accepted that specifies an energy-dispersive X-ray fluorescence (EDXRF) technique to appropriately determine the total sulfur in automotive fuels in the range of 3 mg/kg to 50 mg/kg. Hence, the scope of this test method contains the following:

- The standard and sample matrix is well matched.
- The pooled limit of quantitation (PLOQ), or the smallest concentration of measurement that can be reliably measured by the EDXRF technique is set to 3 mg/kg sulfur.

The sample preparation instructions, as recommended by ASTM, is that a well matched sample matrix is placed in a polarized X-ray beam. The background spectrum is measured with light paraffin oil, or matrix-matching blank sample, with a credited amount of less than 0.2 mg/kg sulfur. The analysis time should be between 200 to 300 seconds. The purpose of this test method is to ascertain the quality of automotive by determining how much sulfur content is present in a given fuel sample.

3. ASTM D7220 Compliance with the EPA Tier 3 Program

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. As such, the Tier 3 program is a build on the implemented Tier 2 program, to effectively reduce the impact by motor vehicles on air quality and public health by stipulating the gasoline sulfur content has to be reduced from 30 ppm average to 10 ppm average. In effect, national emissions of many of the air toxins will reduce on the order of 10% to 30%.

One consequence of implementing this new Tier 3 program is that a reduction in sulfur content essentially leads to a reduction in the fuel's lubricating properties. This affects the fuel's ability to protect parts of the engine's fuel injection system from wear. It is important to note that this is a costly program to embed into the daily lives of everyone. It affects all automotive transport; therefore, it is critical that the sulfur content in gasolines and diesel is detected, both reliably and accurately.

The EPA generally recognizes any voluntary consensus-based body standards to be apt in measuring gasoline properties, and the D7220 is a test method accepted by EPA to satisfy 40 CFR 80.47; which is a Federal Regulation code namely: Title 40 – Protection of Environment, Section 80.47 – Performance-based Analytical Test Method Approach.

4. EDX3000 Benchtop EDXRF Elemental Analyzer

For any instrument intended to be used to measure gasoline properties, it needs to meet the standards set forth by 40 CFR 80.47. The reason for this is that the instruments need to be able to meet a certain precision and accuracy criteria set by the regulation in order to give reliable measurements on the gasoline. . The Koehler EDX3000 is the instrument that not only follows ASTM 7220, but is the exact instrument that refiners can use to meet EPA standards.

Figure 1: EDX3000 Benchtop EDXRF Elemental Analyzer
Description/Features: The following instrument conforms to D7220, and is used for the determination of total sulfur in petroleum, and petroleum products that are single-phase. In the image above the EDX3000 is connected to an external PC computer system, running on the operating system: Microsoft Windows Vista. The EDX3000 can analyze a large array of elements from 11Na to 92U in solids, liquids, alloys, powders, and thin films.

Specifications:

- **X-ray Tube:** 50 W Pd-anode
- **Excitation:** Indirect with polarization
- **Detector:** Silicon Drift Detector (SDD)
- **Analysis Time:** 300 seconds
- **Environment:** Helium Purge
- **Film:** Prolene
- **Sulfur Detection Limit:** 0.54 ppm (3-sigma significance)

5. EDX3000 Test Using on Commercially Available Certified Gasoline Sample

5.1. Testing Standards:

Under section §80.47 in the Code of Federal Regulations, it highlights the requirements of precision and accuracy needed to be met by an instrument, under good lab practices, to accurately measure the absolute fuel parameter of gasoline sulfur:

- As per 80.47 13.b.1 - The agreement from a set of measurements performed on the same instrument, or precision, allows for a maximum standard deviation, s, to equal to at most: $s \leq 1.5*r/2.77$ for a minimum of 20 aliquots, or 20 tests, over 20 days, for a repeatability, r. For example: 10 ppm sulfur: $s \leq 1.75/2.77=0.95$ ppm.
- As per 80.47 13.b.2 - The closeness between an experimentally obtained value and accepted reference value (ARV), or accuracy, can meet either of the following requirements based on the commercially available gasoline's sulfur content: 1) 80.47 13.b.2(i) - If the sulfur range is 1-10 ppm , for at least 10 tests the average of the results (AVG) of the sample cannot differ from the ARV by more than 0.71 ppm; 2) 80.47 13.b.2(ii)- If the sulfur range is 10-20 ppm the average of the results (AVG) of the sample cannot differ from the ARV of the standard by more than 1.00 ppm. For example: $|AVR-AVG| \leq 1.0$ ppm for the sulfur range of 10-20 ppm.

5.2. Purpose of Testing EDX3000:

To test the veracity of the claim that the Koehler EDX3000 can be used by a facility to meet EPA Tier 3 program requirements. The results obtained from the EDX3000, following D7220 test method and good lab practices, testing a commercially available certified gasoline sample will be used to see if it meets the criteria underlined by 40 CFR 80.584.

5.3. Calibration of EDX3000:

For Tier 3 gasoline it is recommended to calibrate with gasoline standards that match the gasoline matrix to be analyzed; in order to obtain the highest degree of accuracy.

5.3.1 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.)

5.3.2 Calibration Model:

Element: S	RMS Dev: 0.25
Units: ppm	Correlation: 0.99993

Sample I.D.	Standard Value	Calculated Value
1	0	0.0
2	5	5.0
3	10	9.8
4	15	14.9
6	25	24.8
7	50	50.1

Figure 2: Table 1-Data tabulated for seven samples of calibration standard.

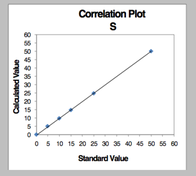

Figure 3: Plotted data of Calculated Value (CV) against Standard Value (SV), with a coefficient of correlation of 0.99993. This follows a linear regression model of: CV = 1.0021*SV – 0.1041. With the units of both CV and SV in ppm of Sulfur.

Element Detected: Sulfur	Units: ppm			
Sample	Standard Value	Average Value	Standard Deviation	Percent Relative
2	5	5.2	0.2	4.0
3	10	10.1	0.2	2.0
4	15	14.6	0.2	1.4
7	50	49.6	0.3	0.6

Figure 4: Table 2 -This table displays the precision of the EDX3000, by returning the measurement of the average value of the different calibrated samples. This table only shows some of the results from all the calibrated samples used, but illustrates the accuracy of detection, by the EDX3000, of the sulfur content in the calibrated samples.

5.4. Results:

5.4.1 Precision

80.47 13.b.1 –

A commercially available certified gasoline sample with a sulfur content between 5-15 ppm is measured to 20 aliquots over 20 days, from which the standard deviation (s) is calculated. The following table presents the results returned from the EDX3000:

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

For an ARV of 10 ppm of Sulfur, the results returned from the EDX3000 has a standard deviation of 0.4 ppm, which is less than the maximum allowable standard deviation of 0.95 ppm, for 10 ppm, which is calculated as follows: $s \leq 1.75/2.77 = 0.95$ ppm. The verdict is the EDX3000 fulfills, or passes, the precision requirements as stipulated by section 80.47 13.b.1.

5.4.2(a) Accuracy

80.47 13.b.2(ii) –

A commercially available certified gasoline sample with sulfur content between 1-10 ppm, for which the AVG is calculated for at least 10 tests. The following table presents the results returned from the EDX3000:

Test Sample: Gasoline certified ARV 19.0 ppm S				
Average of 10 Tests (AVG)	Standard Deviation	Difference from Certified Value |AVR-AVG|	Criteria	Determination
18.6 ppm S	0.9 ppm	0.4 ppm	$0.4 \leq 1.0$	PASS

For an ARV of 19.0 ppm of Sulfur, the results returned from the EDX3000 has a AVG of 18.6 ppm. Taking the absolute value difference against an ARV of 19 ppm of Sulfur the difference returned is 0.4. This is less than the maximum allowable difference of 1.0; or the AVG cannot deviate from the accepted reference value (AVR) by more than 1.0 ppm. The verdict is the EDX3000 fulfills, or passes, the accuracy requirements as stipulated by section 80.47 13.b.2(ii) for a sulfur range between 10-20 ppm.

6. Conclusion:

The results analyzed in the above portion support the claim that the EDX3000 is a sufficient tool to be used for EPA testing for ultra-low sulfur gasoline and diesel fuels. Running the ASTM D7220 Test Method, with good lab practices, will allow refiners, and/or other entities, to properly use the EDX3000 to yield results that meet the new EPA requirements.

7. 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).
- **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.

8. Acknowledgements:

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