



Monochromatic EDXRF Analysis of Gasoline (Petrol)

Measuring and controlling sulfur concentrations in gasoline (Petrol) is important to the petroleum industry. A fast, easy-to-operate and reliable method of determining and monitoring sulfur throughout the gasoline production and distribution process is of vital importance.

Introduction

Since the implementation of US EPA Tier II directives early in the century and European based “sulfur-free” requirements at the end of the last decade, the sulfur content in gasoline consumed on a global basis has continued to spiral downward. Accordingly, regulated sulfur content at levels required to be less than 10 mg/kg levels are becoming common worldwide. The HORIBA MESA-7220 utilizes break through monochromatic EDXRF technology that can readily determine the “near-zero” sulfur contaminations found in many contemporary spark ignition (gasoline) fuels.

Within the global community, various jurisdictions often adopt unique fuel programs to meet local air quality needs. This combination of state-controlled and regional fuel quality programs has resulted in diverse RFG requirements sometimes referred to as “boutique fuels.” Because of potential spectral interferences, of primary importance to the analyst of the various compositional make-ups of these boutique gasolines is oxygen content. The HORIBA MESA-7220 monochromatic EDXRF technology readily enables the analysis gasoline containing up to 5 volume % (E15) gasoline without concern of classic oxygen interference.

Sample Preparation

Ensure each sample is stable and homogeneous. Shake the room temperature sample gently and allow any entrained air (bubbles) to dissipate. To ensure consistent sample depth of at least 5 mm, transfer a 5 mL aliquot to an X-ray sample cup. Mylar film (2-6 um) is typically used to provide the sample cup seal. Carefully avoid contamination of the X-ray cup film testing surface and start the sulfur analysis immediately after sealing the sample cup. Provide a small X-ray cup vent hole whenever gasoline-type or volatile sample materials are analyzed.

ASTM and International Normatives

The HORIBA MESA-7220 monochromatic EDXRF analyzer complies with several international standard test methods for the determination of sulfur in petroleum oils, fuels and ULSD using EDXRF based technology.

Standard Test Method	Sulfur Range
ASTM D7220	3 - 950 mg/kg
ASTM 4294	16 mg/kg - 5 wt%
EN ISO 20847	30-500 mg/kg
EN ISO 8754	300 mg/kg - 5 wt%
Pr EN ISO 13032	8mg - 50 mg/kg

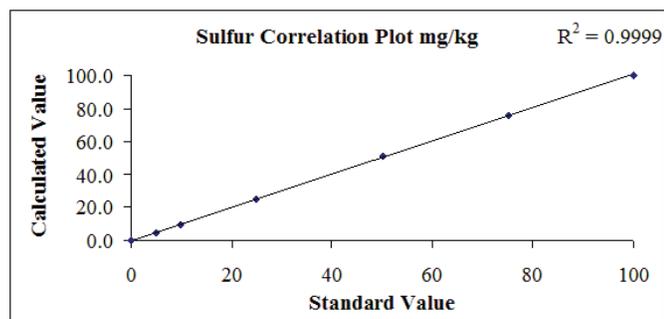
Calibration

Construct a calibration curve that will include (bracket) the range of sulfur to be measured. For routine RFG screening and quality control purposes a 0 - 100 mg/kg calibration curve is often employed. Below an empirical calibration was built using seven certified calibration standards.

Element	Units: mg/kg Correlation: 0.9999	
Sample ID	Standard Value	Calculated Value
1	Zero (Blank)	0
2	5	4.8
3	10	9.9
4	25	25.0
5	50	51.0
6	75	75.4
7	100	99.9

Calibration Curve Information: Gravimetrically prepared:

Sulfur Source: N, Butyl Sulfide
Matrix; Synthetic Gasoline



Precision

The above calibration curve was used to establish MESA-7220 repeatability by evaluating nine repeated analyses of each calibration check sample shown below. A single result is derived by the automatic (user controlled) reporting of the average of two consecutive 180 s determinations taken on the same test specimen placed in the analysis position. Analyses are then repeated with a new sample cup containing a fresh test specimen.

Gasoline Sample #	Assigned Value mg/kg	Avg. Value mg/kg	Std. Dev.	% Relative
Certified Ref. (Gas)	5.0	4.8	0.7	14%
Certified Ref. (Gas)	30.0	31.8	1.7	5%
NIST 2299	13.6	13.4	0.8	6%
Certified Ref. (Gas)	60.0	61.1	2.0	3%

Unique One Analysis - Two Results Capability

Detection Limit – Nine repeat analyses of a blank synthetic gasoline sample containing no sulfur or chlorine. Analyses are repeated as described in the precision study above, fresh test specimen for each repeat.

Sulfur and Chlorine Detection Limits:		
Element	LOD Mg/kg	Analysis Time
Sulfur	0.71	180 s x 2
Chlorine	0.59	180 s x 2

No Oxygen Interference

Oxygenated Fuels – Gasoline reformulations containing 3.5 to 5 volume % oxygen (E10-E15) are common in many global regions. The table below demonstrates no oxygen interference with MESA-6000 sulfur determination capability when oxygen is present at levels up to 5%, because all values meet D7220 repeatability requirements (agree within 2.1 mg/kg) at the 10 mg/kg sulfur.

D7220 Repeatability Requirement at 10 mg/kg equals 2.1 mg/kg		
Standard value sulfur mg/kg	Volume % oxygen added	Sulfur Determined
10.0	1%	10.2
10.0	2%	9.4
10.0	3%	10.8
10.0	4%	9.9
10.0	5%	9.6

Discussion

Sample handling, sample preparation and measurement protocols are very important for the analysis of gasoline and Naphtha. Calibrations for sulfur only, chlorine only and simultaneous sulfur and chlorine determinations can be readily constructed and maintained by the user. Simultaneously measurement of chlorine and sulfur content from weight percent down to part per million levels with the MESA-7220 are readily achieved.

Conclusion

Results shown here in this application note indicate that the HORIBA MESA-7220 provides exceptional performance for the determination of sulfur in gasoline (Petrol) in the less than 10 mg/kg commercial range.

The wide range of analyzable material types, large sulfur concentration range and chlorine determination capabilities make the HORIBA-6000 an ideal tool for the measurement of many petroleum-based matrices, such as light hydrocarbons, middle distillates, crude oils, lube oils and used/waste oils found throughout the petroleum industry.

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