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# XRF1083 - Analysis of ultralow sulfur in automotive fuels according to ASTM D2622-16

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## Introduction

Recent developments in ultra low sulfur (ULS) fuel have improved fuel efficiency and created cleaner exhaust gases. Globally, the permitted sulfur limit in fuel oils has been decreased to 10ppm in many countries and regions.

For compliance verification, X-ray fluorescence (XRF) spectrometry is the definitive analysis tool for use at distribution terminal and refineries, as well as mobile or stationary testing laboratories.

In recent years, there has been an increasing need for an instrument which does not require the use of helium gas, for instances, when acquisition or delivery of helium to the analysis site is difficult

The Micro-Z ULS (ultralow sulfur) is a newly developed sulfur analyzer which does not require helium gas in operation.

This application note demonstrates that Micro-Z ULS can meet the requirements of ASTM D2622-16.

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## Instrument

The Micro-Z ULS is a benchtop wavelength dispersive X-ray fluorescence (WDXRF) spectrometer with fixed optics optimized for sulfur analysis. The atmosphere in the optics path of the Micro-Z ULS, is a vacuum, so that helium gas is not required. The spectrometer is designed to minimize the restrictions in installation such as cooling water, special power supply, installation space, etc. The Micro-Z ULS is equipped with an air-cooled 40 W Cr-target X-ray tube and a doubly curved RX-9 analyzing crystal optimized for low concentration sulfur.

The Micro-Z ULS has a built-in operation panel, which enables simple and easy operation for daily analysis. The counting time was 300 seconds for peak and background measurements in this experiment.

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## Sample preparation

Four mL of each sample was poured into a liquid cell (inner diameter 35 mm) with sample film of 2.5  $\mu\text{m}$  Mylar® film (Chempex® 100).

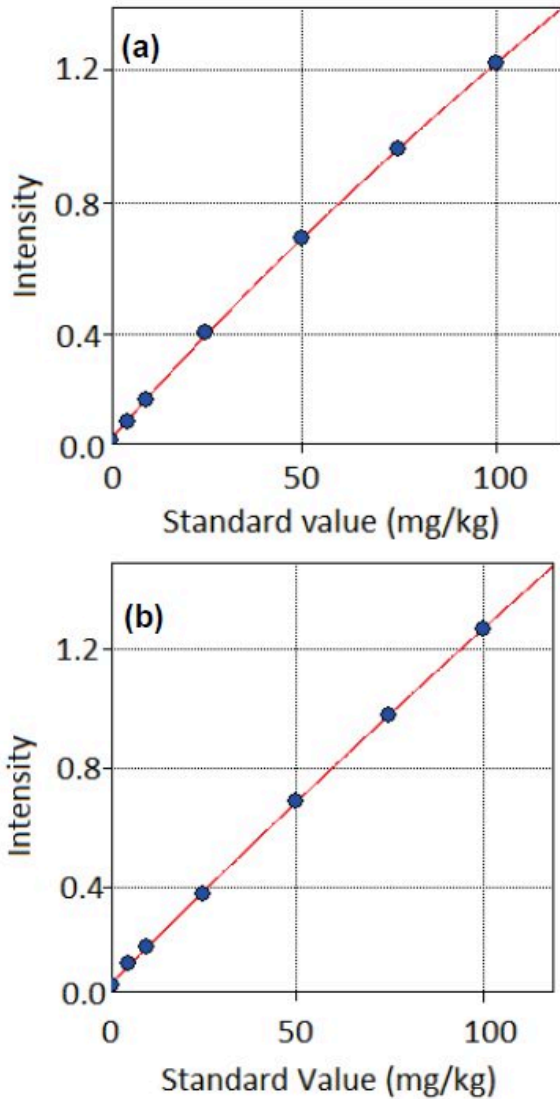
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## Standard and calibration

"Number 2 diesel fuel" standards and isooctane-based standards provided by VHG Labs, inc. were used for calibrations of diesel fuel and gasoline respectively. The calibration results are listed in Table 1 and the calibration curves are shown in Figure 1.

**Table 1:** Calibration result for each material using Micro-Z ULS (unit: mg/kg)

Material	Diesel fuel	Isooctane (for gasoline)
Calibration range	0 – 100	0 – 100
Accuracy	0.49	0.37
LLD	0.3	0.3



**Figure 1:** Calibration curve for each material of Micro-Z ULS (a) Diesel fuel; (b) Isooctane (for gasoline)

The accuracy of calibration is calculated by the following formula:

$$Accuracy = \sqrt{\frac{\sum_i (C_i - \hat{C}_i)^2}{n-m}}$$

$C_i$ : calculated value of standard sample

$\hat{C}_i$ : reference value of standard sample

n : number of standard samples.

m: degree of freedom (linear 2, quad. 3)

The lower limit of detection (mg/kg) is calculated by the following formula:

$$LLD = 3 \cdot \frac{1}{m} \cdot \sigma_B = 3 \cdot \frac{1}{m} \cdot \sqrt{\frac{I_B}{1000 \cdot t}}$$

$\sigma_B$ : sensitivity of calibration (kcps/mass%)

$\sigma_B$ : standard deviation of blank intensity (kcps)

$I_B$ : blank intensity (kcps)

$t$ : counting time (s); 100 s is used

## Analysis results

Repeatability tests were carried out using a representative sample for each material. For each sample, two aliquots were prepared and analyzed using the calibration Figure 1; this process was repeated twenty times. The test results are tabulated in Table 2 (a) for diesel fuel and (b) for gasoline, in which the average and the difference of two aliquots are shown respectively. "r" represents "repeatability" defined by the following formula in ASTM D2622-16:

$$\text{Repeatability (r)} = 0.1462 \cdot X^{0.8015} \text{ mg/kg} \quad (1)$$

X: total sulfur concentration (mg/kg)

The difference between successive test results obtained by the same operator with the same apparatus under constant operation conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values calculated by Equation (1) only in one case in twenty.

The test results shown in Table 2, where the maximum value for each fuel is smaller than r, prove that the performance of the Micro-Z ULS meets the requirement of ASTM D2622-16 for diesel fuel and gasoline.

**Table 2:** Repeatability test result for Micro-Z ULS (qualification test for ASTM D2622-16)

### (a) Diesel fuel

Run #	Average (mg/kg)	Difference (mg/kg)
1	8.0	0.3
2	8.2	0.1
3	8.1	0.3
4	8.0	0.3
5	8.2	0.1
6	8.1	0.3
7	8.1	0.3
8	8.2	0.1

9	8.1	0.0
10	8.1	0.1
11	8.2	0.5
12	8.5	0.0
13	8.6	0.2
14	8.7	0.0
15	8.4	0.7
16	8.3	0.6
17	8.3	0.5
18	8.0	0.2
19	8.2	0.7
20	8.3	0.5
Avg. 8.2		
Maximum		0.7
r (repeatability)		0.8

**(b) Gasoline**

Run #	Average (mg/kg)	Difference (mg/kg)
1	11.8	0.8
2	11.7	0.7
3	12.1	0.1
4	11.8	0.8
5	11.5	0.1
6	11.5	0.1
7	11.8	0.4
8	12.1	0.4
9	12.1	0.4
10	11.7	0.4
11	11.7	0.4
12	11.9	0.2
13	11.7	0.1
14	12.0	0.6

15	12.1	0.4
16	11.6	0.6
17	11.5	0.3
18	11.6	0.0
19	11.6	0.1
20	11.8	0.4
Avg. 11.8		
Maximum		0.8
r (repeatability)		1.1

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## Conclusion

Low concentration sulfur in petroleum-based fuel can be routinely analyzed with high accuracy and precision on the Micro-Z ULS, a benchtop WDXRF spectrometer with fixed optics, which does not require He gas, external water for cooling the X-ray tube or special power supply. This application note demonstrates that the performance of the Micro-Z ULS meets the requirement of ASTM D2622-16, which has become strict in the recent versions of ASTM D2622.

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## Reference

ASTM D2622-16, Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry, ASTM International, (2016), 12pp.

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## Related products



### Micro-Z ULS

WDXRF ultra low sulfur analyzer for method ASTM D2622