



X-RAY FLUORESCENCE

Analysis of Lead in Gasoline

ASTM D5059

Lab Report 184

Introduction

Adding Lead (Pb) to gasoline seemed to be a great enhancement, when first discovered in the 1920s. Early concerns about environmental and health safety began shortly after.

A long and in the end heated battle between the governmental institutions and the strong industrial lobby followed, until the Clean Air Act was passed in 1963 as one of the first measures for environmental protection.

Soon after, unleaded gasoline was available and catalytic converters were adjusted to the new standard. Finally, in 1996 Pb in gasoline was banned in the US and is now absent in common fuel in most of the world.

Some aviation and specialty fuels however still use Pb and need to report the concentrations to the authorities. Additionally, it sometimes is required to test for Pb in gasoline to ensure it is below the regulated limits.

The ASTM Standard Test Method D5059 describes how to measure high (0 - 5 g Pb / US gal or 0 - 1.3 g Pb / L) and low (0 - 0.3 g Pb / US gal or 0 - 0.079 g Pb / L) levels of Pb in gasoline with X-ray Fluorescence (XRF) spectrometry using Bi as an internal standard.

Instrumentation

The Wavelength-Dispersive XRF (WDXRF) spectrometer S6 JAGUAR is equipped with Bruker's 400 W HighSense™ Technology (Figure 1). This makes the S6 JAGUAR the most powerful benchtop WDXRF unit on the market!

Modern software with built-in audit-tracking and state-of-the-art hardware enables best-in-class analytical performance. The S6 JAGUAR achieves outstanding sensitivity for a wide range of elements (F to U) and the various configuration options allow us to optimize the system for your needs.

When using the S6 JAGUAR for gasoline analyses, you get the full performance of a WDXRF system that fits in a benchtop unit. Also when measuring only a few elements, the S6 JAGUAR is an excellent fit.

In contrast to other methods like AAS (Atomic Absorption Spectroscopy) and ICP-OES (Induced Coupled Plasma – Optical Elemental Spectroscopy), a simple one-time calibration makes the S6 JAGUAR ready for your application.

S6 JAGUAR is the ideal choice for liquid sample analysis:

- Dedicated liquid cups for simple and rapid loading of liquid samples
- SampleCare™ technology, protecting critical system components for low maintenance
- (optional) Cup-in-cup technology for additional protection
- Intuitive software SPECTRA.ELEMENTS with “one button” solutions
- Sturdy design and robust, high quality components for long lifetime
- (optional) Ergonomic TouchControl™ display for operation without PC peripherals

Norm Compliance

Precision testing as stated in ASTM D5059 has been tested by running appropriate check samples 20 times on each method. The results are listed in Table 3 and Table 4. For each measurement a fresh sample was prepared.

For method A, the allowed difference between two consecutive measurements must be within $0.029+0.008C$, where C is the concentration of the test sample. For a 2.5 g/gal test sample, this leads to a permitted difference of 0.049 g/gal.

For method C, the limit is set by $0.007+0.14C$, which gives 0.020 g/gal for a 0.09 g/gal sample.

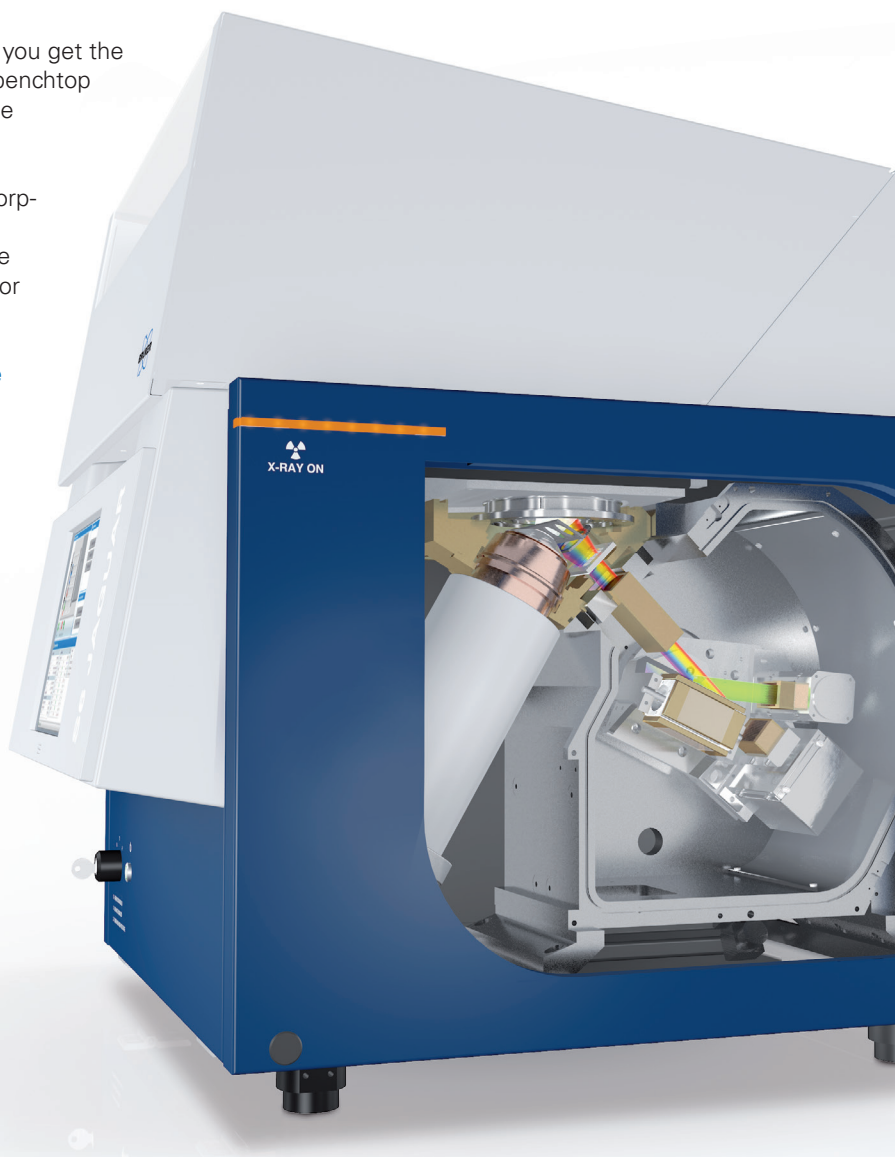


Figure 1
S6 JAGUAR HighSense™ Technology.

Sample Preparation and Standards

Two sets of standards – six samples for ASTM D5059 A and seven samples for D5059 C – were prepared. The internal standard Bi was in a separate bottle and was mixed with the other samples according to the ratio defined in ASTM methods D5059 A and C. The standards and their concentrations are listed in Table 1.

After mixing Bi and the standards, 7 g per sample were filled into liquid cups sealed with a thin film window, see Figure 2. For heavy analytes like Pb and Bi the foil thickness does not affect the measured intensities.

Table 1

Calibration standards for ASTM D5059 method A and C.

Std.	Concentration		Ratio w. Bi int. std.
	[g Pb / US gal]	[mg Pb / L]	
#1	0.000	0.00	20:2
#2	0.001	0.26	20:2
#3	0.005	1.32	20:2
#4	0.010	2.64	20:2
#5	0.050	13.21	20:2
#6	0.100	26.42	20:2
#7	0.300	78.52	20:2
#8	0.100	26.42	10:10
#9	1.000	264.2	10:10
#10	2.000	528.3	10:10
#11	3.000	792.5	10:10
#12	4.000	1056.7	10:10
#13	5.000	1320.9	10:10



Figure 2

Preparation of liquid samples.

Measurement Parameters

The analytical conditions for the D5059 methods are listed in Table 2. The total measurement time for method A was under 2 minutes. For method C longer times were chosen due to the lower concentrations.

Table 2

Measurement Parameters.

Element	Voltage [Kv]	Current [mA]	Filter	Crystal	Detector	Collimator	Method A Peak/BG [s]	Method C Peak/BG [s]*
Pb	50	8	None	LiF200	HighSense XE	0.66°	30 / -	200 / 200
Bi	50	8	None	LiF200	HighSense XE	0.66°	30 / -	200 / 200

* Background is shared, therefore only measured once.

Calibration

The calibration curves for ASTM D5059 method A and C are shown in Figure 3 and Figure 4, respectively. Both curves show excellent linearity with a low standard deviation s and squared correlation coefficient R^2 better than 0.999.

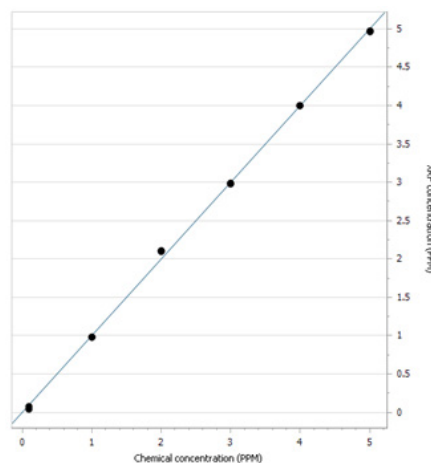


Figure 3

Calibration curve for ASTM D5059 method A.

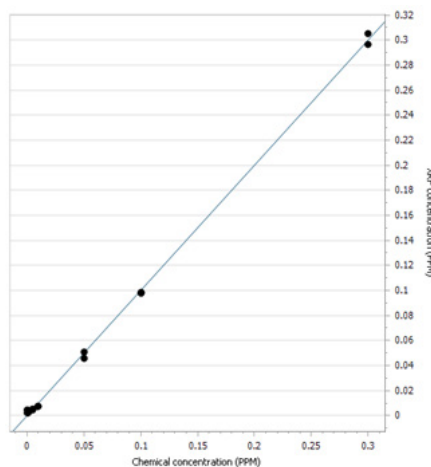


Figure 4

Calibration curve for ASTM D5059 method C.

Table 3

Repetition test for ASTM D5059 method A.

Method A	Pb [g/gal]	Difference [g/gal]
Rep. 1	2.510	
Rep. 2	2.517	0.007
Rep. 3	2.526	0.008
Rep. 4	2.501	0.024
Rep. 5	2.521	0.020
Rep. 6	2.528	0.007
Rep. 7	2.517	0.012
Rep. 8	2.521	0.004
Rep. 9	2.534	0.013
Rep. 10	2.506	0.028
Rep. 11	2.516	0.010
Rep. 12	2.527	0.011
Rep. 13	2.523	0.003
Rep. 14	2.525	0.002
Rep. 15	2.521	0.005
Rep. 16	2.538	0.017
Rep. 17	2.535	0.002
Rep. 18	2.536	0.001
Rep. 19	2.535	0.002
Rep. 20	2.541	0.007
Average	2.524	
Abs. Std. Dev.	0.011	
Rel. Std. Dev.	0.43%	
Certified	2.500 (= 660mg/L)	± 0.049

Table 4

Repetition test for ASTM D5059 method C.

Method C	Pb [g/gal]	Difference [g/gal]
Rep. 1	0.0869	
Rep. 2	0.0868	0.0001
Rep. 3	0.0873	0.0005
Rep. 4	0.0875	0.0002
Rep. 5	0.0875	0.0000
Rep. 6	0.0901	0.0026
Rep. 7	0.0895	0.0006
Rep. 8	0.0905	0.0010
Rep. 9	0.0880	0.0025
Rep. 10	0.0870	0.0010
Rep. 11	0.0882	0.0012
Rep. 12	0.0896	0.0014
Rep. 13	0.0890	0.0006
Rep. 14	0.0888	0.0002
Rep. 15	0.0885	0.0003
Rep. 16	0.0884	0.0001
Rep. 17	0.0886	0.0002
Rep. 18	0.0877	0.0009
Rep. 19	0.0888	0.0011
Rep. 20	0.0877	0.0009
Average	0.088	
Abs. Std. Dev.	0.0011	
Rel. Std. Dev.	1.19%	
Certified	0.090 (= 23.78 mg/L)	± 0.020

Conclusion

The S6 JAGUAR has a wide range of capabilities and this report demonstrates that it is reliable for analysis of Pb in fuels. The system easily fulfils the requirements for the WDXRF norm ASTM D5059 method A and C. The WDXRF spectrometer brings several advantages to your lab, when compared to AAS and ICP-OES, including lower costs of operation and minimal calibration effort.

The S6 JAGUAR enables time-efficient and accurate monitoring of additives, contaminants, and wear metals in fuels, lubricating and engine oils. When installed at refineries and oil-production plants, it can easily test the quality of incoming materials and optimize the used additives from day one. It ensures that all elements in petrochemicals are analyzed with highest accuracy and precision combined with low cost of ownership.

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