The Determination of Lead in Unleaded Gasoline Using the Agilent 55 AA Atomic Absorption Spectrophotometer

Application Note

Atomic Absorption

Author

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Introduction

The reduction of lead levels in gasoline has been a priority of environmental agencies around the world since the early eighties.

In this paper we describe the use of Agilent's 55B AA atomic absorption spectrophotometer when applied to the analysis of unleaded gasoline for trace lead levels.

The methodology used in sample preparation was taken from the ASTM D3237-79 [1], with a change in the sample solvent from methyl isobutyl ketone (MIBK) to di-isobutyl ketone (DIBK).

A National Institute of Standards and Technology (NIST, Gaithersburg, MD, U.S.A.) Standard Reference Material (SRM) 2712 Pb in Reference Fuel was used to establish the accuracy and precision of the method.

Experimental

Instrumentation

An Agilent 55B AA atomic absorption spectrometer, air/acetylene burner, organics solvent "O" ring kit for the spray chamber, and a serial printer.

This system was also operated with a simulated LIMS connection through Hyperterminal under Windows®95.

A series of analyses was also conducted using the Agilent 55 AA software.

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The instrument operating conditions are shown in Table 1.

Table 1. Instrument operating conditions

Element	Pb
Instrument mode	Absorbance
Active current mA	10.0
Standby current mA	0.0
D_2 background correction	Yes
Flame type	Air acetylene
Wavelength nm	217.0
Slit nm	1.0
Measurement parameters	
Measurement mode	Integration
Read time sec	5.0
Replicates sec	3
Pre-read delay sec	3.0
Calibration parameters	
Standard concentrations	
Cal 0	0.000
Std 1	20 mg/USgal
Std 2	50 mg/USgal
Std 3	100 mg/USgal
Nebulizer uptake rate	5 mL/min

Reagents and Solutions

All reagents were Analytical Reagent grade.

- Di-isobutyl ketone, DIBK (818831, Merck, Schuchardt, Germany)
- Lead free gasoline: Retail grade (containing less than 0.005 g/USgal)
- Aliquat 336 (tricaprylylmethylammonium chloride, Aldrich, Milwaukee, WI, U.S.A.)
- 10% (v/v) Aliquat 336/DIBK solution Dissolve Aliquat 336 (88 g) in DIBK and dilute to 1000 mL
- 1% (v/v) Aliquat 336/DIBK solution: Dissolve Aliquat 336 (8.8 g) in DIBK and dilute to 1000 mL
- Iodine Solution: Dissolve iodine crystals (3.0 g) in toluene and dilute to 100 mL
- 5g/USgal lead standard solution: Dissolve anhydrous lead chloride ($PbCl_2$, 0.4433 g), previously dried at 105 °C for 3 hours, in about 200 mL of 10% Aliquat 336/DIBK solution in a 250-mL volumetric flask. Dilute to the mark with 10% Aliquat 336/DIBK. This solution contains 1321 ig Pb/mL and is equivalent to 5.0 g Pb/USgal
- 1g/USgal lead standard solution: Accurately pipette 50.0 mL of the 5.0 g Pb/USgal solution to a 250-mL volumetric flask and dilute to the mark with 1% (v/v) Aliquat 336/DIBK
- Lead standard solutions: (0.02, 0.05, and 0.1 g Pb/USgal.) Accurately pipette 2.0, 5.0, and 10.0 mL of the 1 g/USgal Lead Standard solution to 100-mL volumetric flasks respectively and add 5.0 mL of 1% (v/v) Aliquat 336 solution to each flask. Dilute to the mark with DIBK.

Calibration Solutions

Prepare working standards and a blank using the 0.02, 0.05 and 0.10 g Pb/USgal standard lead solution.

1. Add 30 mL DIBK and 5.0 mL of lead free gasoline to each of four 50-mL volumetric flasks. add 5.0 mL of standard solution respectively to three flasks. The last flask represents a blank.
2. Add immediately 0.1 mL of iodine/toluene solution by means of a 100 µL Eppendorf pipet, mix well and allow to stand for 5 minutes.
3. Add 5 mL of 1% (v/v) Aliquat 336/DIBK solution and mix well.
4. Dilute to volume with DIBK and mix well.

Sample Preparation

1. To each of four 50 mL volumetric flasks containing 30 mL DIBK add 5.0 mL the gasoline sample.
2. Add immediately 0.1 mL of iodine/toluene solution using a 100 µL digital (Eppendorf or similar) pipette, mix well and allow to stand for 5 minutes.
3. Add 5 mL of 1% (v/v) Aliquat 336/DIBK solution and mix well.
4. Dilute to volume with DIBK and mix well.

Instrument Optimization

Set up the spectrophotometer and adjust the nebulizer uptake to approximately 5 mL/min.

On the optimize page, maximize the lamp signal intensity and the background lamp intensity.

Then adjust the signal intensity, by adjusting the burner rotation, lateral controls, and the gas flows while continuously aspirating the 0.1 g Pb/USgal standard.

Instrument Measurement

Set the instrument zero while aspirating the blank. Read the calibration solutions from Cal 0 to Standard 3 respectively. Read the samples relative to the calibration.

Results and Discussion

The Agilent 55 AA provides a simple and accurate means of determining lead in unleaded gasoline. Output can be fed either to a LIMS system or to a printer. By using computer control sample identification and data manipulation can be accomplished.

The use of the Agilent 55 AA v2 software and computer control provides access to result storage and archival retrieval.

Table 2 shows the results obtained from this study for the certified reference fuel. The experimental results compare well with the certified values.

Table 2. SRM 2712 Result Summary

SRM 2712	g/USgal
Measured value	0.0302 ± 0.0001
Certified value	0.0297 ± 0.0010

Samples of regular unleaded gasoline and premium grade unleaded gasoline were also analyzed. The results in Table 3 show the lead level in the regular grade was close to the detection limit, while the level in the premium unleaded gasoline was easily measured.

Table 3 expresses the results in mg/USgal. In using these units the Agilent 55B AA provides an increased number of significant figures to enable the results to be expressed to the full capability of the instruments performance.

Table 3. Analytical Results Agilent 55 AA 217.0nm

	mg/USgal	mg/L	Mean Abs
Unleaded regular gasoline	1.0	0.10	0.006
Premium unleaded gasoline	3.0	0.80	0.012
SRM 2712	30.2	8.00	0.071
SRM 2712 certified value	29.7 ± 0.10	7.9 ± 0.3	
Instrument detection limit 3δ	0.28	0.07	

Tables 4 and 5 illustrate the results obtained using the Agilent 55 AA Windows®95 software, using the two common wavelengths for lead. Both wavelengths gave the same result for the analysis.

Table 4. Agilent 55 AA Results Using the 283.3 nm Line

	g/USgal	g/L	Mean Abs
Cal zero	0	0	0.0001
Standard 1	0.0200	0.0053	0.0228
Standard 2	0.0500	0.0132	0.0542
Standard 3	0.1000	0.0265	0.1013
Regular unleaded	0.0002	0.0001	0.0002
Premium unleaded	0.0024	0.0006	0.0027
SRM-2712	0.0303	0.0080	0.0338
SRM-2712 certified value	0.0297 ± 0.0010	0.0079 ± 0.0003	
Instrument detection limit 3δ	0.0007	0.0002	

Table 5. Agilent 55 AA Results Using the 217.0 nm Line

	g/USgal	g/L	Mean Abs
Cal zero	0	0	-0.0019
Standard 1	0.0200	0.0053	0.0508
Standard 2	0.0500	0.0132	0.1217
Standard 3	0.1000	0.0265	0.2262
Regular unleaded	0.0011	0.0003	0.0028
Premium unleaded	0.0028	0.0007	0.0073
SRM-2712	0.0302	0.0080	0.0757
SRM-2712 certified value	0.0297 ± 0.0010	0.0079 ± 0.0003	
Instrument detection limit 3δ	0.0006	0.0002	

No significant difference was found between the values measured at the 217.0 nm and 283.3 nm wavelengths.

The 283.3 nm line is preferred due to the higher signal intensity and lower non-specific background absorbance at the higher wavelength.

Conclusion

The Agilent 55B AA is able to measure lead in unleaded gasoline with precision of better than 0.0001 g/USgal using the ASTM method D3237. Accuracy is excellent and is shown to be better than 0.0005 g/USgal.

Both the 217.0 nm and 283.3 nm lines can be used.

Safety Notice

Solvents used in this methodology present a hazard risk to users; all operators should consult the relevant Material Safety Data Sheet, and local hazardous substances precautions, before carrying out this procedure.

Use of flame atomic absorption systems with gasoline samples requires complete observation of all relevant safety practices for the presence of flammable materials in the presence of flames.

References

1. ASTM D3237-79 (Re-approved 1984); current version D3237-97

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