# Determination of Lead in Unleaded Gasoline by ICP–OES with the Use of Oxygen and a Cooled Spray Chamber

Application Note

Inductively Coupled Plasma-Optical Emission Spectrometers


## Author

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## Introduction

In nature, lead is not highly abundant in the earth's crust. However, large amounts of lead have been released into the environment by human activities in the last few decades. The effects of lead on human health have been widely reported [1–3]. The major contribution of lead into the atmosphere results from the combustion of gasoline. To improve the octane number, organo-lead compounds such as tetraethyl lead and/or tetramethyl lead have been used as anti-knock additives in gasoline. Since gasoline engines are the most common internal combustion engines for vehicles, the amount of lead released into the atmosphere from the exhaust gases of vehicles using leaded gasoline is high.

In 1986, the United States Environmental Protection Agency (USEPA) reported [4] that 90% of the total lead released into the environment in the United States was the result of lead emission from gasoline combustion. In recent years, unleaded gasoline has been introduced in order to reduce lead pollution into the environment, and therefore, lead contamination in unleaded gasoline is closely monitored.

The determination of lead in gasoline has been described by various analytical techniques, such as X-Ray Fluorescence spectrometry (XRF) [5,6], Colorimetry [7], Volumetry [8], Titrimetry [9,10] and Atomic Absorption Spectrometry (AAS) [11–13]. However, such analysis by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-OES) has not yet been described. ICP-OES is a technique that offers large linear dynamic range, relative freedom from chemical interferences, and multi-element capability.

Gasoline is a highly volatile liquid with a very low boiling point and extremely high vapor pressure, and its continuous aspiration into the plasma can lead to the rapid build up of carbon on the rim of the intermediate tube as well as the injector tip of the torch. The plasma can be rapidly extinguished.


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To reduce carbon build up and maintain a stable plasma, oxygen is added and mixed with the auxiliary argon gas flow to assist the oxidation of carbon molecules. Unleaded gasoline can then be introduced into the plasma, and no more carbon build up is observed on the torch. On the other hand, the extreme high vapor pressure from the gasoline results in gradual accumulation inside the spray chamber with time, which causes the plasma to flicker and affects signal stability. By lowering the temperature of the gasoline (using a cooled spray chamber), the solvent vapor loading in the plasma is reduced – this results in a much more stable plasma.

This work describes the determination of Pb in unleaded gasoline by ICP-OES with the addition of oxygen and using a cooled spray chamber. The accuracy and validity of the method has been as¬sessed by the use of a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2712 Pb in Reference Fuel, which contains tetraethyl lead.

# Experimental

## Instrumentation

An Agilent Liberty 220 Inductively Coupled Plasma Atomic Emission Spectrometer was used for all the measurements. The resolution of the spectrometer is typically 0.018 nm in 1st order, 0.009 nm in 2nd order, 0.007 nm in 3rd order and 0.006 nm in 4th order. The operating conditions used are listed in Table 1.

**Table 1. ICP Operating Parameters**

| | |
|---|---|
| Power | 1.5 kW |
| Plasma gas flow | 15.0 L/min |
| Auxiliary gas flow | 2.25 L/min |
| Torch type | Demountable torch with a 0.8 mm I.D. injector tube |
| Nebulizer type | Concentric glass type K |
| Nebulizer pressure | 80 kPa |
| Sample uptake rate | 0.2 mL/min |
| Integration time | 5 s |
| Viewing height | 8 mm |
| Background correction | Dynamic |
| Grating order | 2nd |
| Filter | Default |
| PMT voltage | 650 V |

An oxygen accessory AGM 1 (Agilent Technologies, Inc., Mulgrave, Australia) was used to introduce oxygen into the auxiliary argon gas flow before entering the torch, with its flow controlled by a high precision needle valve and the oxygen settings displayed on the front panel of the accessory.

A cooled glass spray chamber (Agilent Technologies, Inc., Mulgrave, Australia) and a glass concentric nebulizer were used. The cooled spray chamber was operated at a temperature of –10 °C with 1:1 ethylene glycol used as coolant and controlled by a refrigerated circulator. A schematic diagram of the cooled spraychamber is shown in Figure 1.

A demountable torch with a 0.8 mm id injector tube was used. A small bore injector can give better tolerance to volatile organics compared with the 1.4 mm id of a standard torch.

## Reagents

Analytical reagent grade organic solvents and chemi-cals were used.

- Iso-octane, Merck

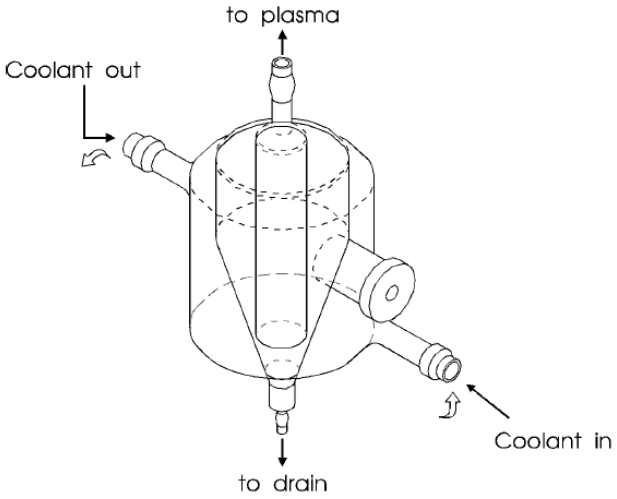


*Figure 1. Schematic diagram of the cooled spray chamber.*

- Toluene, BDH
- Dekalin (decahydronaphthalene), BDH
- Aliquat 336 (tricaprylmethylammonium chloride), Aldrich Chemicals
- Iodine, Univar, Ajax Chemicals
- 10% v/v Aliquat 336/dekalin solution: dissolve 10 mL (or 8.8 g) of Aliquat 336 into 100 mL of dekalin
- 3% w/v Iodine solution: dissolve 3 g of iodine crystals in toluene and dilute to 100 mL volume
- The unleaded gasoline sample was obtained from a service station

Dekalin was also used as the rinse solution.

### Standard Preparation

Stock standard was a 5000 mg/Kg Conostan Pb standard in hydrocarbon oil (Conostan division, Continental Oil Company, Ponca City, Oklahoma, USA).

100 mg/L Pb secondary standard solution was prepared by accurately weighing 2 g of the 5000 mg/Kg Pb standard into 100 mL of iso-octane.

Working standards were prepared by pipetting 1.25 mL and 2.50 mL of the 100 mg/L Pb standard solution into 25 mL volumetric flasks, then 20 mL of the unleaded gasoline sample was added to each flask, followed immediately by the addition of 0.3 mL of 3% iodine solution. This was allowed to stand for 5 minutes and mixed well. Then 0.5 mL of the 10% Aliquat 336/dekalin solution was added. It was made up to volume with dekalin and mixed well. The final solutions contained 5 mg/L Pb addition and 10 mg/L Pb addition, respectively.

### Sample Preparation

20 mL of the unleaded gasoline sample was transferred to a 25 mL volumetric flask. 0.3 mL of 3% iodine solution was immediately added and allowed to react for 5 minutes. Then 0.5 mL of 10% Aliquat 336/ dekalin solution was added, the solution was made up to volume with dekalin then mixed well.

For the NIST 2712 sample, 3 mL of the sample was transferred to a 25 mL volumetric flask, 20 mL of the unleaded gasoline sample was added, immediately followed by 0.3 mL of 3% iodine. This was allowed to stand for 5 minutes. Then 0.5 mL of 10% Aliquat 336/ dekalin solution was added, made up to volume with dekalin, and mixed well.

## Results and Discussion

The use of oxygen to improve the tolerance of the plasma to organic solvents has been reported [14–16]. In this work, oxygen was mixed with the auxiliary Ar gas flow. Carbon tends to form a deposit on the intermedi-ate tube as well as the injector tip of the torch. The use of a high auxiliary flow of 2.25 L/min lifts the plasma up and when combined with the added oxygen prevents the build up of carbon. A stable plasma is achieved and, in addition, no safety hazard is presented by oxygen introduction in this manner. The use of a cooled spray chamber can reduce the solvent vapor loading in the plasma, resulting in a much more stable plasma for long term measurements on a routine basis.

### Effect of Oxygen on Pb Emission Intensity

It is essential to add oxygen to the argon gas flow to minimize carbon build up and sustain the plasma while gasoline is aspirated. In the experiment, oxygen was added before the gasoline was introduced in order to prevent the plasma from being extinguished. The amount of oxygen added to the auxiliary Ar flow to prevent carbon deposition on the torch, and provide optimum Pb emission intensity was studied. As can be seen in Figure 2, an oxygen flow rate of 0.035 L/min was found to be the optimum.

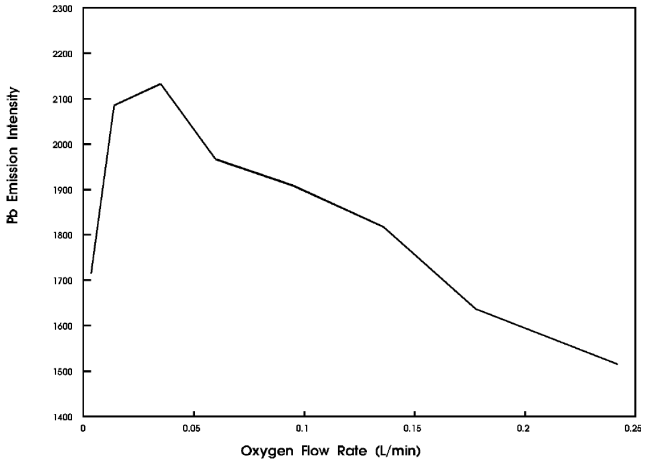


*Figure 2. Effect of oxygen flow rate on Pb emission intensity.*

### Effect of the Addition of Iodine and Aliquat 336 on Pb Emission Intensity

Experiments have shown that when iodine and Aliquat 336 were added, both the tetraethyl lead (from NIST 2712) and Conostan Pb standard give similar emission intensity at the same concentration. However, without the addition of those reagents, an apparent decrease in Pb signal was obtained with the NIST 2712 sample.

This is apparently because the alkyl lead compounds react with iodine to form iodo lead alkyl anions which then are stabilized by the addition of a quaternary ammonium salt such as Aliquat 336 [7,11,13]. The stabilized iodo lead alkyl compounds are then analyzed by ICP.

## Selection of Pb Wavelength

The important criteria for the Pb wavelength selection is based upon the best detection limit and relative freedom from spectral interferences.

The most intense Pb line is 220.353 nm. However, at this Pb wavelength, a severe structural background is present when running organics. Therefore, other Pb lines such as those at 283.306 nm and the Pb 261.418 nm line were studied.

The Pb 283.306 nm line has a detection limit of 0.050 mg/L and a background equivalent concentration of 5.3 mg/L, whereas the Pb 261.418 nm line has a detection limit of 0.075 mg/L and a background equivalent concentration of 4.1 mg/L. The Pb 283 line was preferred because of its better detection limit and the closeness of the background equivalent concentration to the Pb 261 line. Similar analytical results were obtained on both wavelengths. Figures 3 and 4 show wavelength scans of 5 mg/L and 10 mg/L of Pb addition standards, and the unleaded gasoline sample in the vicinity of the Pb 283.306 nm line and Pb 261.418 nm line, respectively.

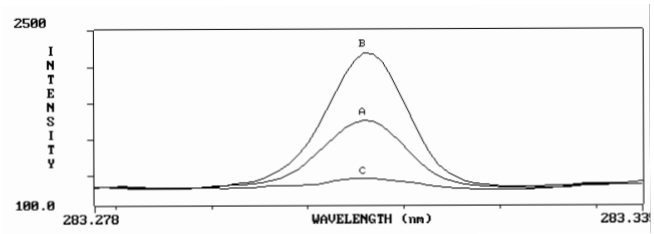


*Figure 3. Spectral scans of (A) 5 mg/L Pb addition standard, (B) 10 mg/L Pb addition standard, and (C) unleaded gasoline sample at the Pb 283.306 nm line.*

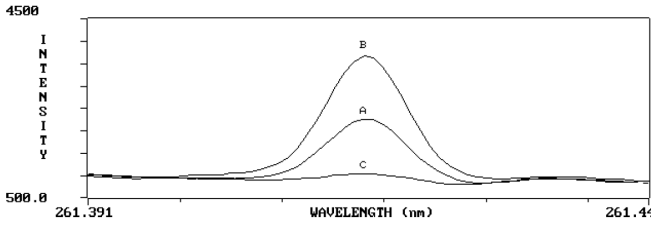


*Figure 4. Spectral scans of (A) 5 mg/L Pb addition standard, (B) 10 mg/L Pb addition standards, and (C) unleaded gasoline sample at the Pb 261.418 nm line.*

## Washout Time of the Cooled Spray Chamber

The washout time of the cooled spray chamber was measured by aspirating a 1000 mg/L Pb in iso-octane for 5 minutes, then rinsing out with iso-octane while monitoring the signal decay of the Pb 283.306 nm line signal intensity. The washout profile is shown in Figure 5. The time required for 1% decay of signal is 33 s, for 0.1% decay is 80 s and decay to background is 130 s. This was achieved with a sample uptake rate of 0.2 mL/min (refer to Table 1).

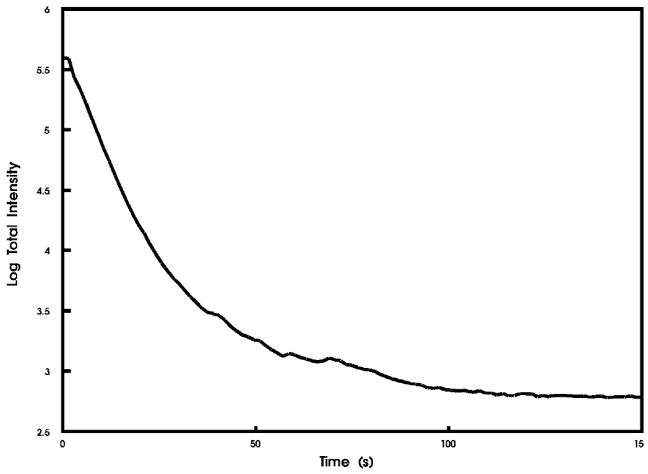


*Figure 5. Washout profile of 1000 mg/L Pb in iso-octane with the cooled spraychamber at –10 °C.*

## Long Term Stability

Long term stability was measured by continuously aspirating a 5 mg/L multi-element standard solution in unleaded gasoline for over an hour. As shown in Figure 6, the reproducibility of the measurements over an hour ranged from 0.7 to 1.1 %RSD.

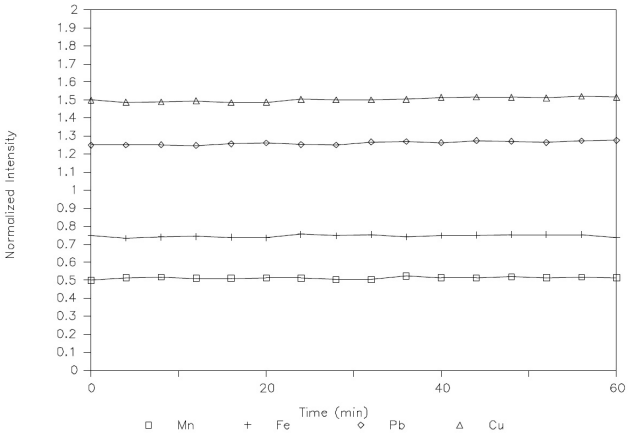


*Figure 6. Signal stability over an hour for 5 mg/L of Mn, Fe, Pb and Cu spiked in unleaded gasoline sample.*

## Results

The standard addition method was used for calibration and the instrument operating conditions are listed in Table 1. The precision of the measurement ranged from 1 to 5 %RSD. The mean results of the triplicate analysis are listed in Table 2. The found value of the NIST SRM 2712 compares well with the certified value confirming the validity of the method and the accuracy of the measurements.

*Table 2. Results of the Analysis*

| | Pb concentration (g/L) | |
|---|---|---|
| **Sample** | **Certified value** | **Measured value** |
| NIST SRM 2712 | 0.0079 ± 0.0003 | 0.0080 ± 0.0002 |
| Unleaded gasoline | – | 0.00039 ± 0.00001 |

## Conclusion

The determination of Pb in unleaded gasoline by ICP-OES with the use of oxygen and a cooled glass spraychamber has been described. The measured Pb value in NIST SRM 2712 is in good agreement with the certified value. The precision of the measurement ranged from 1 to 5 %RSD. The long term stability, which ranged from 0.7 to 1.1 %RSD, is excellent. This study has shown that ICP-OES is a suitable technique for the determination of Pb in unleaded gasoline.

## References


1. U. Ewers and H. W. Schlipkoter, "Metal and their compounds in the environment. Occurrence, analysis and biological relevance". ed. Merian E., VCH **1991**, pp 971-1014.
2. H. S. Posner , T. Damstra, J. O. Nriagu, "The biogeochemistry of lead in the environment". ed. Nriagu J., Elsevier **1978**, pp 173-224.
3. R. R. Russell, R. Stephens, "Lead versus health science and effects of low level lead exposure", eds. Rutter M. and Jones R. R., John Wiley & Sons **1983**, p. 141-177.
4. "Air quality criteria for lead". USEPA, EPA-600/8-83/028, Vols I-IV, US EPA, Triangle Park, North Carolina,**1986**.
5. "Standard test method for lead in gasoline by X-Ray Spectrometry", American Society for Testing & Materials, Method D 2599, **1981**.
6. "Standard test method for low level of lead in gasoline by X-ray spectrometry", American Society for Testing & Materials, Method D 3229, **1983**.
7. "Standard method for testing rapid field test for trace lead in unleaded gasoline (colorimetric method)", American Society for Testing & Materials, Method D 3348, **1985**.
8. "Standard test method for lead in gasoline, volumetric chromate method", American Society for Testing & Materials, Method D 2547, **1982**.
9. "Standard test method for trace amounts of lead in gasoline". American Society for Testing & Materials, Method D 3116, **1982**.
10. "Standard test method for lead in gasoline-iodine monochloride method", American Society for Testing & Materials, Method D 3341, **1980**.
11. M. Kashiki, S. Yamazoe, S. Oshima, "Determination of lead in gasoline by Atomic Absorption Spectrometry", Anal. Chim. Acta, **1971**, 53, pp 95-100.
12. J. B. Sanders, "Lead in gasoline by Atomic Absorption", Varian Techtron publication, **1973**.
13. "Standard test method for lead in gasoline by Atomic Absorption Spectrometry", American Society for Testing & Materials, Method D 3237, **1984**.
14. D. Truitt, J. W. Robinson, "Spectroscopic studies of organic compounds introduced into a radio frequency induced plasma", Anal. Chim. Acta, **1970**, 51, pp 61-67.
15. S. Greenfield, H. McD McGeachin, P. B. Smith, "Inductively coupled plasma discharges for Spectrochemical Analysis". ICP Inf. Newsl., **1976**, 2, pp 167-173.
16. B. Magyar, P. Lienemann, H. Vonmont "Some effects of aerosol drying and oxygen feeding on the analytical performance of an inductively coupled nitrogen-argon plasma". Spectrochim. Acta, **1986**, 41, pp 27-38.


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