STANDARD REFERENCE METHOD FOR THE DETERMINATION OF LEAD IN MOTOR FUEL (ATOMIC ABSORPTION)

Air Pollution Control Directorate
Environmental Protection Service

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1 SCOPE AND FIELD OF APPLICATION

1.1 Applicability

The method is applicable to the determination of total lead in gasoline or other motor fuels. It compensates for variations in gasoline composition and is independent of the lead alkyl type.

1.2 Measurement Range

Concentrations in the range 0.010 – 0.10 g lead/Imp. gal can be determined. Gasolines with a higher lead content require a dilution with isooctane before measurement.

2 PRINCIPLE

The gasoline sample is diluted with methyl isobutyl ketone and the alkyl lead compounds are stabilized by reaction with iodine and a quaternary ammonium salt. The lead content of the sample is determined by atomic absorption flame spectrometry at 283 nm. Standards prepared from reagent grade lead chloride are used for calibration.

3 REAGENTS

3.1 Methyl Isobutyl Ketone (MIBK)

Certified, lead free.

3.2 Iodine Solution

Dissolve 3.0 g of reagent grade iodine crystals in toluene and dilute to 100 ml with the same solvent.

3.3 Aliquat 336 (Tricaprylmethylammonium Chloride)

Available from the General Mills Corporation, Minneapolis, Minnesota, U.S.A.

3.4 Aliquat 336/MIBK Solution (10% v/v)

Dilute 100 ml of Aliquat 336 to 1 litre with MIBK.

3.5 Aliquat 336/MIBK Solution (1% v/v)

Dilute 10 ml of Aliquat 336 to 1 litre with MIBK.

3.6 Lead Chloride ($PbCl_2$)

Reagent grade.

3.7 Standard Lead Solution (5.0 g Lead/Imp. gal)

Dissolve 0.3694 g of lead chloride (3.6), previously dried at 105 °C for 3 h, in about 200 ml of 10% Aliquat/MIBK solution (3.4) in a 250 ml volumetric flask. Dilute to the mark with the 10% Aliquat solution, mix, and store in a brown bottle having a polyethylene- or Teflon-lined cap.

3.8 Standard Lead Solution (1.0 g Lead/Imp. gal)

By pipette, accurately transfer 50 ml of the 5.0 g lead/gal solution (3.7) to a 250 ml volumetric flask and dilute to volume with 1% Aliquat/MIBK solution (3.5). Store in a brown bottle having a polyethylene- or Teflon-lined cap.

3.9 Standard Lead Solutions (0.02, 0.05, and 0.10 g Lead/Imp. gal)

Transfer 2, 5, and 10 ml of the 1.0 g lead/gal solution (3.8) by pipette to 100-ml volumetric flasks; add 5.0 ml of 1% Aliquat 336 solution (3.5) to each flask and dilute to the mark with MIBK (3.1). Mix well and store in bottles having polyethylene- or Teflon-lined caps.

3.10 Isooctane (2, 2, 4-Trimethylpentane)

Certified, lead free.

3.11 Air, Compressed

In pressure cylinders or online.

3.12 Acetylene, Compressed

In pressure cylinders.

4 APPARATUS

4.1 Spectrophotometer, Atomic Absorption

With meter, recorder or digital readout, and monochromator with wavelength dial reading to 0.1 nm.

4.2 Pipettes, Glass

Millilitre capacities, 'to deliver'.

4.3 Volumetric Flasks

Borosilicate with ground-glass stoppers, with capacities 50, 100, and 250 ml.

4.4 Micropipette

Eppendorf type or equivalent, 100 µl capacity.

4.5 Storage Bottles

Glass and brown glass, 250 ml, with polyethylene- or Teflon-lined screw caps.

5 SAMPLING AND SAMPLES

Gasoline samples must generally be diluted before measurement. Dilute with isooctane so that the concentration is less than 0.1 g lead/Imp. gal. Dilution by a factor of 50 is necessary for most commercial gasolines. Test solutions should be measured promptly to

avoid errors from evaporation. If gasoline samples are kept for long periods, they must be stored in vapour-tight bottles (4.5), preferably in a refrigerator.

6 PROCEDURE

6.1 Safety Precautions

Follow normal precautions for the handling of compressed gases. *TEST THE GAS SUPPLY SYSTEM FOR LEAKS BEFORE USE AND EACH TIME A NEW CYLINDER IS INSTALLED.* Observe the manufacturer's instructions on lighting and extinguishing the flame. Gasoline and the other solvents used are highly flammable and should be handled accordingly.

6.2 Preparation of Test Portions

6.2.1 To a 50 ml volumetric flask containing 30 ml MIBK, add with a pipette 5 ml of gasoline sample and mix.

6.2.2 Add 0.1 ml (100 μl) of iodine/toluene solution (3.2) and allow the mixture to react about 1 min.

6.2.3 Add with a pipette 5 ml of 1% Aliquat solution (3.5) and mix.

6.2.4 Dilute to volume with MIBK and mix.

6.2.5 For the preparation of the blank, follow steps 6.2.1 to 6.2.4, but substitute *isooctane* (3.10) *for gasoline in* 6.2.1.

6.3 Treatment of Test Portions

6.3.1 Prepare the atomic absorption instrument in accordance with the guidelines set out in section 8, Notes on Procedure.

6.3.2 Zero the instrument by aspirating blank solution (6.2.5).

6.3.3 Introduce the test portion into the flame by *CONTINUOUS* aspiration, through polyethylene tubing, of an *UNMEASURED* portion of the test sample. Record the absorbance after the reading has become constant. Aspirate MIBK between the introduction of each test portion to prevent cross contamination.

6.4 Calibration Procedure

Prepare three working standards by using the 0.02, 0.05, and 0.10 g lead/gal standard lead solutions (3.9).

6.4.1 To each of three 50 ml volumetric flasks containing 30 ml of MIBK, add with a pipette 5 ml of the lead standard solutions (3.9).

6.4.2 Add by pipette 5 ml isooctane (3.10) and 0.1 ml iodine solution (3.2) with the micropipette (4.4). Mix well.

6.4.3 Add with a pipette 5 ml of 1% Aliquat solution (3.5) and mix.

6.4.4 Dilute to volume with MIBK and mix.

6.4.5 Measure the absorbance of each standard dilution and record the results. Zero the instrument using the blank solution (6.2.5). A plot of absorbance versus concentration should yield a straight line.

7 EXPRESSION OF RESULTS

7.1 Instrumental Precision

This should be checked by running repeat determinations on a number of prepared samples. Preliminary results of an eight-laboratory round robin indicate a repeatability of 0.002 g/gal.

7.2 Conversion Factors

1 g lead/Imp. gal = 0.8333 g/U.S. gal
= 0.2201 g/l
= 220.1 μg/ml

8 NOTES ON PROCEDURE

8.1 Operating Conditions, Spectrophotometer

The optimum operating conditions are:

wavelength	=	283.3 nm
slit opening	=	1 mm
spectral bandwidth	=	0.7 nm
source	=	hollow cathode
source current	=	as recommended
oxidant	=	air
fuel	=	acetylene
flame	=	oxidizing, lean, blue

8.1.1 The flame should be set as lean as possible. Compared with an aqueous solution, the MIBK solution should be aspirated at about one-third the rate so that the flame remains blue on aspirating the organic mixture.

8.1.2 The burner position should be adjusted to give the maximum response. An absorbance of 0.12 – 0.14 can be expected for the 0.1 g/gal working standard. Some instruments may require scale expansion.

8.2 Storage

Because the light fractions of gasoline can easily be lost by evaporation, store the samples under refrigeration in vapour-tight bottles (4.5). The samples should be allowed to attain room temperature just before analysis and must not remain uncovered except to obtain the portions required for analysis.

8.3 Standard Solutions

It is preferable to prepare the 0.02, 0.05, and 0.10 g/gal standard solutions (3.9) daily to check the linearity of response.

8.4 Comparison with Other Methods

The literature gives a number of different atomic absorption methods that can be used for lead in gasoline analysis. These may be broadly classed into three groups.

(*a*) The gasoline (or a dilution) is aspirated directly into the atomic absorption flame. Standards are prepared using lead alkyls in isooctane (1, 2).

(*b*) Gasoline is diluted in a polar solvent and free halogen is added to produce inorganic lead. Organic or inorganic lead standards may be used. This reference method falls in this category (3).

(*c*) The lead in gasoline is converted to an inorganic form and extracted into an aqueous medium. Measurements are made on the aqueous phase and inorganic aqueous standards can be used (4, 5, 6).

Methods of group *a* are perhaps the simplest and fastest. Claims have been made (3, 4) that these methods give different responses for different lead alkyls. However, the proper choice of operating parameters overcomes these problems (1, 2) (see also Table 1), and analyses can be done with confidence. The only drawback is that hazardous lead alkyls are needed for calibration purposes.

Methods of group *b* are still quite rapid and less hazardous inorganic standards can be used.

Methods of group *c* are generally quite lengthy and often require the handling of corrosive chemicals, e.g. bromine (4, 5) and strong acids (5, 6). One danger in the methods of group *c* is that the organic to aqueous extraction may be incomplete, especially where only strong acids are used. Cold extraction using concentrated (40%) nitric acid (6) was found by us to be incomplete, especially when mixed lead alkyls were present.

TABLE 1 COMPARISON OF METHODS

Method		Sample (μg/ml)		Ratio (MLA/TEL)
Group	Reference	TEL	MLA	
a	2	624*	806	1.29
b	3	624*	808	1.29
c	4, 5	628	818	1.30

*Used as the standard in groups *a* and *b*.

Table 1 shows that the same results can be obtained using a variety of methods. One method from each group is presented. The samples were prepared by diluting tetraethyl lead (TEL) and mixed lead alkyls (MLA) (designated MLA 500 by Ethyl Corp.) in isooctane. Concentrations were typical of commercial gasolines.

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REVISION NO.1 TO EPS 1-AP-73-3 (DEC. 1975)

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This amendment to the analytical procedure extends the range of the method to include normal leaded gasolines.

1. Delete Section 1.2 and replace with the following:

1.2 Measurement Range

Concentrations in the range 0.003 - 5.0 g lead/Imp. gal can be determined.

2. Delete Section 3.8

3. Delete Section 3.9 and replace with the following:

3.9 Standard Lead Solutions (0.05, 0.10, 0.15, 0.20, 0.25 g lead/Imp. gal)

Transfer 1, 2, 3, 4 and 5 ml of the 5.0 g lead/Imp. gal solution (3.7) by pipette to 100-ml volumetric flasks and dilute to the mark with MIBK (3.1). Mix well and store in brown bottles having polyethylene or Teflon-lined caps.

4. Delete Section 5

5. Delete Sections 6.2, 6.3 and 6.4 and replace with the following:

6.2 Calibration Procedure - Preparation of Working Standards

It is necessary to prepare five working standards and a blank to cover the full measurement range of the method. For lead-free gasolines with a lead content of less than 0.15 g/Imp. gal, only the first three working standards are required. The working standards are prepared with 0.05, 0.10, 0.15, 0.20 and 0.25 g/Imp. gal standard lead solutions (3.9).

6.2.1 To each of five 50-ml volumetric flasks containing about 30 ml of MIBK (3.1), add with a pipette 5 ml of the standard lead solutions (3.9).

6.2.2 Add by pipette 5 ml isooctane and mix.

6.2.3 Add by micropipette 0.1 ml iodine solution (3.2) and mix.

6.2.4 Add by pipette 5 ml of 1% Aliquat solution (3.5) and mix.

6.2.5 Dilute to volume with MIBK and mix.

6.2.6 To prepare the blank, repeat steps 6.2.1 to 6.2.5, but omit the standard lead solution added in 6.2.1.

6.2.7 Aspirate the reagent blank (6.2.6) to zero the instrument. (The absorbance of the blank differs from the absorbance of pure MIBK.) Measure the absorbances of the working standards and plot a graph of absorbance versus concentration. The plot should yield a straight line.

6.3 Preparation of Test Portions

6.3.1 Samples with a lead concentration exceeding 0.25 g/Imp. gal

must first be diluted with isooctane to reduce the lead concentrations below this level. Table 1 shows the necessary dilutions for concentrations up to 5 g/Imp. gal. Dilutions have been chosen so that the concentration to be measured lies in the middle to upper range of the calibration.

TABLE 1 DILUTIONS

Concentration (g Pb/Imp.gal)	Sample aliquot (ml)	Final volume (ml)	Dilution factor
0 – 0.25	-	-	-
0.25 – 0.60	10	25	2.50
0.60 – 1.5	4	25	6.25
1.5 – 5.0	5	100	20.00

6.3.2 Make a dilution, if necessary, in accordance with Table 1. Use only calibrated pipettes and volumetric flasks.

6.3.3 Pipette 5 ml of the gasoline sample into a 50-ml volumetric flask containing about 30 ml of MIBK and mix.

6.3.4 With the micropipette add 0.1 ml iodine solution (3.2). Mix well and allow the mixture to react about one minute.

6.3.5 With a pipette add 5 ml of 1% Aliquat solution (3.5) and mix.

6.3.6 Dilute to volume with MIBK and mix.

6.4 Treatment of Test Portions

6.4.1 Prepare the instrument as outlined in Section 8

6.4.2 Aspirate the test portions and working standards and record the absorbance values with frequent checks of the zero.

6.4.3 Read the concentrations of the test portions from the calibration curve obtained using the working standards. If a prior dilution has been made (6.3.1) calculate the lead concentration by applying the appropriate dilution factor from Table 1.