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Reaffirmed
March 2017

National Standard of Canada

Methods of testing petroleum and associated products

Determination of lead in automotive gasoline (Atomic absorption)

Canadian General Standards Board CGSB

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CETTE NORME NATIONALE DU CANADA EST DISPONIBLE EN VERSIONS FRANÇAISE ET ANGLAISE.

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Preface to the National Standard of Canada

This National Standard of Canada has been reaffirmed by the CGSB Committee on Petroleum Test Methods. An editorial change has been made by the correction of the following paragraph:

14.2.1 The publications referred to in par. 2.1.1 and 14.1.1 may be obtained from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, U.S.A., telephone 610-832-9585, fax 610-832-9555, or from IHS Markit, 200-1331 MacLeod Trail SE, Calgary, Alberta T2G 0K3, telephone 613-237‑4250 or 1‑800‑267‑8220, fax 613-237‑4251, Web site www.global.ihs.com.

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CANADIAN GENERAL STANDARDS BOARD

METHODS OF TESTING PETROLEUM AND ASSOCIATED PRODUCTS

Determination of Lead in Automotive Gasoline (Atomic Absorption)

1. SCOPE

1.1 This method is used to determine the lead content of gasolines, including those containing ethanol. Lead in the range of 1 to 1100 mg/L can be measured.

1.2 The testing and evaluation of a product against this method may require the use of materials and/or equipment that could be hazardous. This document does not purport to address all the safety aspects associated with its use. Anyone using this method has the responsibility to consult the appropriate authorities and to establish appropriate health and safety practices in conjunction with any applicable regulatory requirements prior to its use.

2. REFERENCED PUBLICATIONS

2.1 The following publications are referenced in this method:

2.1.1 ASTM International

D4057 — Standard Practice for Manual Sampling of Petroleum and Petroleum Products

D6299 — Standard Practice for Applying Statistical Quality Assurance Techniques to Evaluate Analytical Measurement System Performance

E969 — Standard Specification for Glass Volumetric (Transfer) Pipets.

2.2 A dated reference in this method is to the issue specified. An undated reference in this method is to the latest issue, unless otherwise specified by the authority applying this method. The sources are given in the Notes section.

3. SUMMARY OF TEST METHOD

3.1 The gasoline sample is diluted with methyl isobutyl ketone, the lead alkyl compounds are stabilized by a reaction with iodine, and the resultant lead alkyl iodide is complexed with a quaternary ammonium salt. The lead content of the sample is determined by atomic absorption spectrophotometry at 283.3 nm. Standards prepared from reagent-grade lead chloride are used for calibration. The method compensates for variations in gasoline composition and is independent of the lead alkyl type.

4. SIGNIFICANCE AND USE

4.1 This method is used to ensure compliance of automotive gasolines with product or regulatory standards.

5. APPARATUS

Note: *It is good laboratory practice to segregate apparatus that will be reused, such as sample bottles, volumetric flasks and pipettes, into two sets. Reserve one set for leaded gasoline and another set for unleaded gasoline.*

5.1 **Spectrophotometer:** atomic absorption, capable of scale expansion and nebulizer adjustment and equipped with a slot burner and premix chamber for use with an air-acetylene flame.

5.2 **Pipettes:** glass, with capacities of 0.5, 1, 2, 3, 4, and 5 mL, "to deliver" and Class A volume accuracy in accordance with ASTM E969.

5.3 **Volumetric flasks:** borosilicate with ground-glass stoppers, with capacities of 25, 50, 100, 250 and 1000 mL.

5.4 **Micropipette:** Eppendorf type or equivalent, 100 µL capacity.

5.5 **Sample bottles:** brown glass with polyethylene or polytetrafluoroethylene-lined (PTFE-lined) caps, or amber polypropylene bottles and caps, with nominal capacities of 50, 100, 250 and 1000 mL.

6. REAGENTS

Reagent-grade chemicals are required for this method.

6.1 **Methyl isobutyl ketone (MIBK):** certified lead free 4-methyl-2-pentanone.

6.2 **Iodine solution:** dissolve 3.0 g of iodine crystals in toluene and dilute to 100 mL.

6.3 **Aliquot 336 (tricaprylmethylammonium chloride).**

6.4 **Aliquot 336/MIBK solution (10% v/v):** dissolve 100 mL (88.0 g) of Aliquot 336 in MIBK and dilute to 1 L.

6.5 **Aliquot 336/MIBK solution (1% v/v):** dissolve 10 mL (8.8 g) of Aliquot 336 in MIBK and dilute to 1 L.

6.6 **Lead chloride:** ($PbCl_2$).

6.7 **Isooctane (2,2,4-trimethylpentane):** certified lead free.

6.8 **Air:** compressed.

6.9 **Acetylene:** compressed.

6.10 **Stock lead solution** (1000 mg lead/L): dissolve 0.3356 g of lead chloride previously dried at 105°C for 3 h, in approximately 200 mL of 10% Aliquot 336/MIBK solution in a 250 mL volumetric flask. Dilute to the mark with the 10% Aliquot 336/MIBK solution, mix and store in a sample bottle. The most serious potential source of error in this method lies in the preparation of this solution. Therefore, the utmost care is required in its preparation and handling.

6.11 **Working standard lead solutions** (5, 10, 20, 30, 40 and 50 mg lead/L): transfer 0.5, 1, 2, 3, 4 and 5 mL of the 1000 mg lead/L solution by pipette to 100 mL volumetric flasks and dilute to the mark with MIBK. Mix well and store in sample bottles. These solutions should be prepared and used within one day.

7. SAFETY PRECAUTIONS

7.1 Gasolines are flammable and explosive. All appropriate safety precautions should be observed.

8. PROCEDURE

8.1 **Sampling —** Sampling is to be carried out in accordance with ASTM D4057 in recognition that test results are dependent upon the integrity of the samples provided. Samples that must be stored for more than one day should be refrigerated between 0 and 4°C to minimize losses. Allow the samples to warm to room temperature just prior to analysis.

8.2 **Analysis**

8.2.1 Optimize the atomic absorption spectrophotometer for lead at 283.3 nm. Light the air-acetylene flame. Using the reagent blank (par. 9.1.5) adjust the gas mixture and the sample aspiration rate to obtain an oxidizing flame. MIBK solutions should be aspirated at about one-third the rate of aqueous solutions so that the flame remains blue.

8.2.2 In order to achieve the lower detection limits of this method, optimization of the atomic absorption operating parameters and equipment is recommended. The absorbance of the 30 mg/L calibration standard should be optimized to its maximum value, which is typically greater than 0.15.

8.2.3 Dilute the gasoline sample, if necessary, in accordance with Table 1. Samples with a lead concentration exceeding 50 mg/L must first be diluted with isooctane to bring the lead concentrations below this level. Table 1 shows the necessary dilutions for concentrations up to 1000 mg/L. Dilutions have been chosen so that the concentration to be measured lies in the middle to upper range for the method.

8.2.4 Pipette 5 mL of the gasoline sample into a 50 mL volumetric flask containing approximately 30 mL of MIBK and mix.

8.2.5 Add 100 µL of iodine solution using the micropipette, mix well and allow the mixture to react for one minute.

8.2.6 Add 5 mL of 1% Aliquot 336/MIBK solution using a pipette, mix well and dilute to volume with MIBK. Mix again. Allow the sample to stabilize for five minutes.

8.2.7 Aspirate the sample into the calibrated atomic absorption spectrophotometer (see section 9) and record the absorbance value. Frequently check the zero reading with the reagent blank.

9. CALIBRATION

9.1 Gasoline standards and samples should be at the same temperature. It is necessary to prepare six working standards (5, 10, 20, 30, 40 and 50 mg/L) and a blank to cover the full measurement range of the method. For unleaded gasolines with a lead content of less than 30 mg/L, only four working standards (5, 10, 20 and 30 mg/L) are required. These standards are prepared as described in par. 6.11.

Note: *To maximize accuracy, matrix matching may be necessary for gasolines containing ethanol. When matrix matching is required, prepare calibration standards and blanks to contain approximately the same concentration of ethanol as the samples of interest.*

9.1.1 To each of six 50 mL volumetric flasks containing 30 mL of MIBK add, with a pipette, 5 mL of the working standard lead solutions prepared as specified in par. 6.11.

9.1.2 Add 5 mL of isooctane, using a pipette, and mix.

9.1.3 Add 100 µL of iodine solution using the micropipette, and mix.

9.1.4 Add 5 mL of 1% Aliquot 336/MIBK solution using a pipette, mix and dilute to volume with MIBK. Mix again.

9.1.5 To prepare a reagent blank, repeat the steps described in par. 9.1.1 to 9.1.4 omitting the standard lead solution added in par. 9.1.1.

9.1.6 Aspirate the most concentrated working standard for the range of interest and adjust the burner position to give maximum response.

9.1.7 Aspirate the reagent blank to zero the instrument.

Note: *The absorbance of the blank differs from the absorbance of pure MIBK.*

9.1.8 Measure the absorbances of the working standards and plot a graph of absorbance versus concentration. This should show a linear relationship. For instruments with digital readout, concentration in grams per litre can be read directly.

10. CALCULATIONS

10.1 Read the concentrations of the test portions from the calibration curve obtained using the working standards or directly from the spectrophotometer readout. The calibration curve should be linear and calibration checks can therefore be made with only one standard.

10.2 If a prior dilution has been made (par. 8.2.3), calculate the lead concentration by applying the appropriate dilution factor from Table 1.

TABLE 1

Dilutions

Concentration mg lead/L	Sample Aliquot mL	Final Volume mL	Dilution Factor
0 – 50	—	—	—
50 – 130	10	25	2.5
130 – 350	4	25	6.25
350 – 1000	5	100	20

11. QUALITY CONTROL

11.1 Analyze a quality control (QC) sample after each calibration and after a minimum of ten sample runs. The QC sample shall be representative of the test samples and shall contain approximately the same concentration of ethanol if applicable.

11.2 Statistical quality control assurance techniques shall be used to maintain control of this test method. Techniques described in ASTM D6299 or other recognized techniques shall be used.

12. REPORT

12.1 Report the result in milligrams of lead per litre to the nearest whole integer.

13. PRECISION AND BIAS

13.1 **Bias —** Preliminary intralaboratory studies with NBS reference standards suggest that there is no bias.

Note: *Bias has not been determined for gasolines containing ethanol.*

13.2 **Precision** — The following criteria, based on co-operative studies (par. 14.1.2) should be used for judging the acceptability of results (95% confidence).

Note: *Precision has not been determined for gasolines containing ethanol.*

13.2.1 ***Repeatability*** — Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

Lead Level, mg/L	Repeatability, mg/L
10	1
50	5
440	10
660	15

13.2.2 ***Reproducibility*** — Results submitted by each of two laboratories should be considered suspect if they differ by more than the following amounts:

Lead Level, mg/L	Reproducibility, mg/L
10	3
50	10
440	41
660	61

14. NOTES

14.1 Related Publications

14.1.1 ASTM International

D3237 — Test Method for Lead in Gasoline by Atomic Absorption Spectroscopy.

14.1.2 National Research Council of Canada

Results of a precision study for leaded gasoline, co-ordinated by the Fuels and Lubricants Laboratory, National Research Council of Canada, Division of Mechanical Engineering Report No. LTR-FL-167, August 1980

Letter from P.L. Strigner, Program Coordinator to the Subcommittee on Test Methods of the CGSB Committee on Petroleum, National Research Council of Canada File No. 1491-78-21, August 8, 1975.

14.2 Sources of Referenced Publications

The following addresses were valid at the date of publication.

14.2.1 The publications referred to in par. 2.1.1 and 14.1.1 may be obtained from ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, U.S.A., telephone 610-832-9585, fax 610-832-9555, Web site www.astm.org, or from IHS Canada, 1 Antares Drive, Suite 200, Ottawa, Ontario K2E 8C4, telephone 613-237-4250 or 1-800-267-8220, fax 613-237-4251, e-mail gic@ihscanada.ca, Web site www.canada.ihs.com.

14.2.2 The publications referred to in par. 14.1.2 may be obtained from the National Research Council of Canada, Ottawa, Canada K1A 0R6.