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Methods of test for petroleum and its products —

BS 2000-428: Liquid petroleum products — Petrol — Determination of low lead concentrations by atomic absorption spectrometry

(Identical with IP 428:2004)

The European Standard EN 237:2004 has the status of a
British Standard

ICS 75.160.20

British Standards

National foreword

This British Standard is the official English language version of EN 237:2004. It supersedes BS EN 237:1996, BS 2000-428:1996 which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology, which has the responsibility to:

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Further information is available from:

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Liquid petroleum products - Petrol - Determination of low lead concentrations by atomic absorption spectrometry

Produits pétroliers liquides - Essence - Détermination des basses teneurs en plomb par spectrométrie d'absorption atomique

Flüssige Mineralölerzeugnisse - Ottokraftstoff - Bestimmung von niedrigen Bleigehalten durch Atomabsorptionspektrometrie

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Contents

Foreword

This document (EN 237:2004) has been prepared by Technical Committee CEN/TC 19 “Petroleum products, lubricants and related products”, the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by March 2005, and conflicting national standards shall be withdrawn at the latest by March 2004.

This document supersedes EN 237:1996.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Cyprus, Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

1 Scope

This document specifies an atomic absorption spectrometric test method for the determination of the lead content of petrol in the range 2,5 mg/l to 10,0 mg/l. This test method is independent of the lead alkyl type.

NOTE 1 Annex A describes an alternative procedure but with a poorer precision for the determination of the lead content of petrol in the range 3,0 mg/l to 10,0 mg/l. This procedure is also independent of the lead alkyl type.

NOTE 2 For the purposes of this document, the term "% (*V/V*)" is used to represent the volume fraction.

WARNING – The use of this document may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 1042, *Laboratory glassware – One-mark volumetric flasks (ISO 1042:1998)*.

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170:2004)*.

EN ISO 3171, *Petroleum liquids - Automatic pipeline sampling (ISO 3171:1988)*.

ISO 385-1, *Laboratory glassware - Burettes - Part 1: General requirements*.

ISO 648, *Laboratory glassware – One-mark pipettes*.

3 Principle

The sample, diluted to the tenth (*V/V*) with methyl isobutyl ketone and treated with iodine, is aspirated into the air/acetylene flame of an atomic absorption spectrometer. The absorbance is measured at a wavelength of 217,0 nm and is compared with that of calibration solutions of known lead concentrations.

NOTE Annex A describes an alternative procedure, but with a poorer precision, that may be used when the spectrometer is not stable enough in the wavelength region of 217,0 nm to obtain correct results according to the above.

4 Reagents and materials

Use only reagents of recognised analytical grade.

4.1 Air, oil free, under pressure in a steel cylinder, or compressed air.

4.2 Acetylene, under pressure in a steel cylinder.

WARNING – Compressed gases shall be stored outside the laboratory.

4.3 Toluene

4.4 2,2,4-Trimethylpentane (iso-octane)

4.5 Methyl isobutyl ketone (MIBK)

4.6 50 %/50 % *(V/V)* mixture of toluene and iso-octane

4.7 Aliquat 336 (tricapryl methyl ammonium chloride)

4.8 10 % (*V/V*) Aliquat 336/MIBK Solution

Dissolve 100 ml (88,0 g ± 0,1 g) of Aliquat 336 with MIBK and make up to 1 l.

4.9 1 % (*V/V*) Aliquat 336/MIBK Solution

Dissolve 10 ml (8,80 g ± 0,05 g) of Aliquat 336 with MIBK and make up to 1 l.

4.10 Iodine solution.

Dissolve 3,0 g ± 0,1 g of iodine crystals with toluene and make up to 100 ml.

4.11 Lead chloride ($PbCl_2$), of 99 % mass purity grade.

4.12 Concentrated lead standard stock solution, *c*(Pb) = 1 000 mg/l.

Dissolve 335,6 mg of lead chloride (4.11) previously dried at about 105 °C for at least 3 h in about 200 ml of 10 % Aliquat 336/MIBK solution (4.8) in a 250 ml volumetric flask (5.4). Dilute to the mark with the 10 % Aliquat solution, mix, and store in a brown bottle having a polyethylene-lined cap. This solution contains 1 000 mg/l of lead.

NOTE 1 The concentrated lead standard stock solution is stable for at least 6 months.

NOTE 2 Smaller volumes may be prepared, e.g. 100 ml, however the precision statement as given in clause 10 has been established using 250 ml volumetric flasks.

4.13 Diluted lead standard stock solution, *c*(Pb) = 100 mg/l.

Using a pipette (5.5), transfer accurately 25,0 ml of the concentrated lead standard stock solution (4.12) into a 250 ml volumetric flask (5.4), and dilute to the mark with the 1 % Aliquat 336/MIBK solution (4.9). Store in a brown bottle having a polyethylene-lined cap. This solution contains 100 mg/l of lead.

NOTE Smaller volumes may be prepared, e.g. 100 ml, however the precision statement as given in clause 10 has been established using 250 ml volumetric flasks.

4.14 Lead standard solutions, 2,5 mg/l, 5,0 mg/l, 7,5 mg/l and 10,0 mg/l of lead

Using a pipette (5.5) or a micro-burette (5.3), transfer accurately 2,5 ml, 5,0 ml, 7,5 ml and 10,0 ml of the diluted lead standard stock solution (4.13) to 100 ml volumetric flasks; add 5 ml of 1 % Aliquat 336/MIBK solution (4.9) to each flask; dilute to the mark with MIBK (4.5). Mix thoroughly and store in bottles having polyethylene-lined caps.

5 Apparatus

Usual laboratory apparatus and glassware, together with the following:

5.1 Flame atomic absorption spectrometer, suitable for measurements at a wavelength of 217,0 nm, and fitted with a burner feed with acetylene and air, suitable for use with organic solutions.

NOTE The attention of the user is drawn that the alternative procedure as described in Annex A requires the use of a flame absorption spectrometer that is suitable for measurements at a wavelength of 283,3 nm.

5.2 Lead hollow-cathode lamp.

5.3 Micro-burette, capacity 10 ml, conforming to class A of ISO 385-1.

5.4 One-mark volumetric flasks, capacity 50 ml, 100 ml, 250 ml and 1 l conforming to class A of EN ISO 1042.

5.5 One-mark pipettes, capacity 2 ml, 5 ml, 10 ml, 20 ml, 25 ml and 50 ml, conforming to class A of ISO 648, with suction ball.

5.6 Micropipette, 100 µl Eppendorf type or equivalent.

5.7 Analytical balance, capable of weighing to the nearest 0,1 mg.

6 Sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171, and/or in accordance with the requirements of national standards or regulations for the sampling of petrol.

7 Procedure

7.1 General preparation

Note and record the temperature, T_x, at which all volumetric measurements are made. The volumetric glassware is usually calibrated at 20 °C.

Prepare the calibration solutions and the test solution on the same day and measure on that day.

7.2 Preparation of calibration solutions (0,25 mg/l, 0,50 mg/l, 0,75 mg/l, and 1,0 mg/l of lead)

7.2.1 To a 50 ml volumetric flask containing 30 ml of MIBK (4.5), add 5,0 ml of low lead standard solution (4.14) and 5,0 ml of the toluene/iso-octane mixture (4.6). Repeat this operation for each of the low lead standard solutions (2,5 mg/l, 5,0 mg/l, 7,5 mg/l, and 10,0 mg/l of lead). In the case of blank, add only 5,0 ml of the toluene/iso-octane mixture.

7.2.2 Add immediately 0,1 ml of the iodine solution (4.10) by means of a micropipette (5.6). Mix thoroughly and allow to react for at least 1 min.

7.2.3 Add 5 ml of the 1 % Aliquat 336/MIBK solution (4.9) and mix thoroughly.

7.2.4 Dilute to volume with MIBK (4.5) and mix thoroughly.

7.3 Preparation of the test solution

7.3.1 Transfer approximately 30 ml of MIBK (4.5) into a 50 ml volumetric flask (5.4), add 5,0 ml of the sample by means of a pipette (5.5) and mix.

7.3.2 Add immediately 0,1 ml of the iodine solution (4.10) by means of a micropipette (5.6). Mix thoroughly and allow to react for at least 1 min.

7.3.3 Add 5 ml of 1 % Aliquat 336 Solution (4.9) and mix thoroughly.

7.3.4 Dilute to volume with MIBK (4.5) and mix thoroughly.

7.4 Preparation of instrument

7.4.1 Install the lead hollow-cathode lamp (5.2) in the spectrometer (5.1) and leave the apparatus switched on for the time necessary to achieve stability.

7.4.2 Adjust the lamp current, the attenuation and the slit, to suit the characteristics of the apparatus. Adjust the wavelength to the region of 217,0 nm in order to obtain the maximum intensity.

7.4.3 Install the burner-head for acetylene-air and ignite the flame.

7.4.4 Using pure MIBK, adjust the flow rates of acetylene (4.2) and air (4.1) and the sample aspiration to obtain an oxidising flame, which is fuel lean and light blue in colour.

7.4.5 Aspirate pure MIBK (4.5) to set the zero of the instrument.

7.4.6 Aspirate the 1,0 mg/l calibration solution and adjust the burner position to get a maximum response.

7.4.7 Aspirate pure MIBK (4.5) to set the zero of the instrument and check the blank and the four calibration solutions (7.2) for linearity.

7.5 Determination

Aspirate the calibration solutions (7.2) and the test solution (7.3) and record the absorbance values.

NOTE The stability of the instrument should be checked by analysing the 0,50 mg/l calibration solution every five samples. If the lead concentration as determined is lower than 0,48 mg/l or higher than 0,52 mg/l, a new calibration is necessary and the last five samples should be re-analysed.

8 Calculation

Plot the absorbance values versus the concentration of the calibration solutions and determine the concentration of the test solution, ρ(Pb), expressed in milligrams per litre, from the graph. Modern analysers have internal calibration and calculation procedures giving direct results, in such case it is unnecessary to draw calibration graphs.

Calculate the lead content of the sample, *C*(Pb), expressed in milligrams per litre, using the equation:

$$C(\mathrm{Pb}) = 10 \times \rho(\mathrm{Pb}) \times (1 + 0{,}001\,2(T_x - 15)) \tag{1}$$

where

ρ(Pb) is the concentration of lead, in milligrams per litre;

T_x is the temperature at which the measurements are made, in degrees Celsius.

NOTE The coefficient of expansion of motor gasoline per degree Celsius at 15 °C is 0,001 1, and that of aviation gasoline 0,001 3. As a reasonable compromise 0,001 2 is selected in the above equation as the factor to apply. This corresponds to using a factor intermediate between Groups 3 and Groups 4 in Table 7 of the Abridged Volume Correction Tables of ASTM D 1250 [1]) .

9 Expression of results

Report the lead concentration to the nearest 0,1 mg/l.

NOTE 1 If results are required in grams per litre, they should be divided by 1 000.

NOTE 2 This also applies to the alternative procedure described in Annex A.

10 Precision

10.1 General background

The precision statement as given in this standard is based on an inter-laboratory test performed by 11 laboratories on a single sample. The average lead value was chosen at about 5,0 mg/l. Possible variation of *r* and *R* with the concentration over the range is not expected to be significant.

10.2 Repeatability, *r*

The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values given in Table 1 only in one case in twenty.

10.3 Reproducibility, *R*

The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values given in Table 1 only in one case in twenty.

Table 1 — Repeatability and reproducibility

Mass concentration of lead in sample mg/l	**Repeatability** ***r*** mg/l	**Reproducibility** ***R*** mg/l
between 2,5 and 10,0	0,12	0,62

11 Test report

The test report shall contain at least the following information:

a) type and complete identification of the product under test;

b) reference to this document;

c) sampling procedure used (see clause 6);

d) procedure used (basic or alternative);

e) result of the test (see clause 9);

f) any deviation, by agreement or otherwise, from the procedure described;

g) date of the test.

Annex A
(informative)

Alternative procedure

When the spectrometer is not stable enough in the wavelength region of 217,0 nm to obtain correct results, the following alternative method can be used for the determination of lead content in petrol in the range from 3 mg/l to 10 mg/l. This method is independent of the lead alkyl type.

The differences in relation to the procedure given in the main body are:

- The sample, diluted to the fifth (*V/V*) with MIBK (4.5) and treated with iodine, is aspirated into the air/acetylene flame of an atomic absorption spectrometer. The absorbance is measured at a wavelength of 283,3 nm and is compared with that of calibration solutions of known lead concentrations.
- The flame atomic absorption spectrometer should be suitable for measurements at a wavelength of 283,3 nm;
- The preparation of the calibration solutions (0,50 mg/l, 1,0 mg/l, 1,5 mg/l and 2,0 mg/l of lead) should be done as given below:
  - To a 50 ml volumetric flask containing 10 ml of MIBK (4.5), add 10 ml of low lead standard solution (4.14) and 10 ml of the toluene/iso-octane mixture (4.6). Repeat this operation for each of the low lead standard solutions (2,5 mg/l, 5,0 mg/l, 7,5 mg/l and 10 mg/l of lead). In the case of blank, add only 10 ml of the toluene/iso-octane mixture.
  - Add immediately 0,2 ml of iodine/toluene solution (4.10) by means of a micropipette (5.6). Mix thoroughly and allow to react for at least 1 min.
  - Add 10 ml of 1 % Aliquat 336/MIBK solution (4.9) and mix thoroughly.
  - Dilute to volume with MIBK (4.5) and mix thoroughly.
- The test solution should be prepared as follows:
  - Transfer approximately 10 ml of MIBK (4.5) into a 50 ml volumetric flask (5.4) and add 10 ml of the sample by means of a pipette (5.5) and mix.
  - Add immediately 0,2 ml of the iodine solution (4.10) by means of a micropipet (5.6). Mix well and allow to react for at least 1 min.
  - Add 10 ml of 1 % Aliquat 336/MIBK solution (4.9) and mix thoroughly.
  - Dilute to volume with MIBK (4.5) and mix thoroughly.
- For the preparation of the instrument, the wavelength should be adjusted to the region of 283,3 nm and to give maximum response, the burner position should be adjusted by means of the 2,0 mg/l calibration solution.
- For the determination, the stability of the instrument is checked by analysing the 1,0 mg/l calibration solution every five samples. If the lead concentration determined is lower than 0,96 mg/l or higher than 1,04 mg/l, a new calibration is necessary and the last five samples should be re-analysed.

- The lead content should be calculated using the following equation:

$$C(\mathrm{Pb}) = 5 \times \rho(\mathrm{Pb}) \times (1 + 0{,}001\,2 \times (T_x - 15)) \qquad \text{(A.1)}$$

where

ρ(Pb) is the concentration of lead, in milligrams per litre;

T_x is the temperature at which the measurements are made, in degree Celsius.

- The precision statement as given in Table A.1 is based on an inter-laboratory test performed by 11 laboratories on a single sample. The average lead value was chosen at about 5,0 mg/l. Possible variation of *r* and *R* with the concentration over the range is not expected to be significant.

Table A.1 — Repeatability and reproducibility

Mass concentration of lead in sample mg/l	**Repeatability** ***r*** mg/l	**Reproducibility** ***R*** mg/l
between 3,0 and 10,0	0,08	1,40

Bibliography

[1] ASTM D 1250:2004, *Standard Guide for Use of the Petroleum Measurement Tables.*

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