INTERNATIONAL STANDARD

ISO 3830

Third edition
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Petroleum products — Determination of lead content of gasoline — Iodine monochloride method

Produits pétroliers — Détermination de la teneur en plomb de l'essence — Méthode au monochlorure d'iode

Reference number
ISO 3830:1993(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 3830 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This third edition cancels and replaces the second edition (ISO 3830:1981), which has been technically revised.

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Petroleum products — Determination of lead content of gasoline — Iodine monochloride method

WARNING — The use of this International Standard 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.

1 Scope

This International Standard specifies a method for the determination of total lead content in gasolines containing lead alkyls at concentrations between 0,026 g and 1,300 g of lead per litre.

This International Standard is not applicable to gasoline containing manganese anti-knock additives.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 835-1:1981, *Laboratory glassware — Graduated pipettes — Part 1: General requirements.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1770:1981, *Solid-stem general purpose thermometers.*

ISO 3007:1986, *Petroleum products — Determination of vapour pressure — Reid method.*

ISO 3170:1988, *Petroleum liquids — Manual sampling.*

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 3839:1978, *Petroleum distillates and commercial aliphatic olefins — Determination of bromine number — Electrometric method.*

ISO 4788:1980, *Laboratory glassware — Graduated measuring cylinders.*

ISO 4800:1977, *Laboratory glassware — Separating funnels and dropping funnels.*

3 Principle

A known volume of the test sample is diluted with heavy distillate and shaken with aqueous iodine monochloride reagent. Any tetraalkyl lead compounds present react with the iodine monochloride and are extracted into the aqueous phase as the dialkyl lead compounds. The aqueous extract is separated from the gasoline and evaporated to low bulk to decompose free iodine monochloride. Any organic matter present is removed by oxidation with nitric acid, which also serves to convert the dialkyl lead compounds into inorganic lead compounds. The residue is dissolved in water and buffered to pH 5 with sodium acetate/acetic acid buffer. The lead content of the buffered solution is determined by titration with Na_2EDTA using xylenol orange as indicator.

4 Reagents

During the analysis described in this International Standard, use only reagents of recognized analytical reagent grade and only water complying with the requirements of Grade 3 of ISO 3696.

4.1 Nitric acid, concentrated [69 % (*m/m*) to 70,5 % (*m/m*)].

4.2 Hydrochloric acid, concentrated [35,4 % (*m/m*)].

4.2.1 Hydrochloric acid solution (1 + 1).

Mix one volume of concentrated hydrochloric acid (4.2) with one volume of water.

4.3 Ammonia solution (1 + 1).

Mix one volume of concentrated ammonia solution [35 % (*m/m*)] with one volume of water.

4.4 Heavy distillate.

A straight-run petroleum distillate having a maximum bromine number of 1,5 with approximately 10 % distilling at 205 °C and 90 % at 240 °C. It shall also be lead-free, having been, if necessary, previously extracted with the iodine monochloride solution (4.6).

4.5 Sodium acetate/acetic acid buffer solution (pH 5).

Dissolve 23,0 g of anhydrous sodium acetate (CH_3COONa) in approximately 500 ml of water. Using a burette or graduated pipette, add 7,2 ml of glacial acetic acid. Dilute to the mark with water in a 1 000 ml one-mark volumetric flask and shake to mix thoroughly.

4.6 Iodine monochloride reagent, 1,0 mol/l solution.

Dissolve 111,0 g of potassium iodide (KI) in approximately 400 ml of water. Add 445 ml of concentrated hydrochloric acid (4.2) and allow to cool to ambient temperature. Add 75,0 g of potassium iodate (KIO_3) slowly and with stirring, until all free iodine initially formed has just redissolved to give a clear, orange-red solution. Allow to cool to ambient temperature and dilute to 1 000 ml with water. Store in a glass-stoppered bottle.

WARNING — Iodine monochloride will react with ammonium ions under certain conditions to yield explosive nitrogen tri-iodide. Care shall be taken, therefore, that this reagent does not come into contact with ammonia or ammonium salts.

Never use rubber bungs to stopper vessels containing iodine monochloride solutions.

NOTE 1 The amounts of KI and KIO_3 are calculated to give a slight excess of iodate; if a greater excess is present, this will lead to precipitation of lead and indifferent end-points in the Na_2EDTA titration.

4.7 Lead nitrate, 0,005 mol/l standard solution.

Weigh, to the nearest 0,001 g, approximately 1,7 g of lead nitrate [$Pb(NO_3)_2$] that has been dried at 105 °C and allowed to cool in a desiccator. Dissolve it in water and add 10 ml of the concentrated nitric acid (4.1). Dilute to the mark with water in a 1 000 ml one-mark volumetric flask and shake thoroughly to mix.

Calculate the concentration, c_0, of the lead nitrate solution, in moles per litre, according to the equation:

$$c_0 = \frac{m}{331{,}23}$$

where m is the mass, in grams, of lead nitrate dissolved.

4.8 Disodium dihydrogen ethylenediaminetetraacetate, $[-CH_2N(CH_2COOH)CH_2COONa]_2.2H_2O$ (Na_2EDTA), 0,005 mol/l standard volumetric solution.

4.8.1 Preparation

Dissolve approximately 3,75 g of the Na_2EDTA in 2 000 ml of water.

4.8.2 Standardization

Using a pipette, transfer 25,0 ml of the standard lead nitrate solution (4.7) to a 250 ml conical flask. Dilute to approximately 75 ml with water and add several drops of the bromothymol blue indicator solution (4.10). Titrate with the ammonia solution (4.3) until the colour of the solution just changes from yellow to blue, then add 10 ml of the sodium acetate/acetic acid buffer solution (4.5) and five drops of the xylenol orange indicator solution (4.9).

NOTE 2 In the presence of lead the solution will have a plum-red colour.

Titrate with the Na_2EDTA solution (4.8) until the end-point is reached. This is indicated by a sharp change from orange to a permanent bright lemon-yellow. Record the volume used and calculate the concentration of the Na_2EDTA solution.

NOTE 3 The addition of excess Na_2EDTA solution produces no further colour change at the end-point.

4.8.3 Calculation

Calculate the concentration, c_1, of the Na_2EDTA solution to the nearest 0,000 01 mol/l according to the equation

$$c_1 = \frac{25c_0}{V}$$

where

c_0 is the concentration, in moles per litre, of the standard lead nitrate solution (4.7);

V is the volume, in millilitres, of the Na_2EDTA solution used in the standardization.

4.9 Xylenol orange indicator solution.

Dissolve 0,2 g of xylenol orange, sodium salt, in 100 ml of water and add 1 drop of 1 + 1 hydrochloric acid (4.2.1).

Prepare a fresh solution each week.

4.10 Bromothymol blue indicator solution.

Dissolve 0,1 g of bromothymol blue in 80 ml of 95 % (V/V) ethanol and dilute to 100 ml with water.

5 Apparatus

5.1 Burette, 25 ml capacity, Class A in ISO 385-1.

5.2 Pipette, 25 ml capacity, Class A in ISO 835-1.

5.3 Volumetric flasks, one-mark, 1 000 ml and 2 000 ml capacities, Class A in ISO 1042.

5.4 Conical flasks, wide neck, borosilicate glass, 250 ml and 500 ml capacities.

5.5 Measuring cylinders, 100 ml and 500 ml capacities, in accordance with ISO 4788.

5.6 Separating funnel, 250 ml capacity, borosilicate glass, glass-stoppered, to ISO 4800.

5.7 Watch glass, borosilicate glass, of a size sufficient to cover the mouth of the 500 ml conical flask (5.4).

NOTE 4 Ribbed watch glasses are recommended but may not be readily available in all countries. They have been found to significantly reduce the time required for evaporation of aqueous phases containing the extracted lead.

5.8 Thermometer, general purpose, nominal range 0 °C to 50 °C or 0 °C to 100 °C, in accordance with ISO 1770 Type L or Type M.

5.9 Balance, single or double pan, capable of weighing to ± 0,001 g.

5.10 Desiccator, glass, of sufficient capacity, with desiccant.

6 Sampling

Test samples shall be taken in accordance with ISO 3170, ISO 3171 or an equivalent national standard. Gasoline samples having a Reid vapour pressure (ISO 3007) above 50 kPa shall be cooled in the sealed sample container to below 15 °C before removing the test sample for analysis. The sampling procedure shall be recorded in the test report.

7 Test procedure

7.1 Transfer 50 ml of the iodine monochloride reagent (4.6) and 25 ml of the heavy distillate (4.4) to the separating funnel (5.6). Measure the temperature of the test sample to the nearest 0,5 °C (see clause 6). Using the pipette (5.2), transfer 25 ml of the test sample of gasoline to the same separating funnel. Immediately stopper the funnel and shake the contents for 1 min. Allow the funnel to stand for several minutes, until the two phases have separated, and run the lower aqueous phase into the 500 ml conical flask (5.4). Wash the gasoline phase by shaking with three separate 20 ml portions of water and add the washings to the conical flask.

WARNING — No liquids should be sucked by mouth into a pipette. Release any pressure in the separating funnel during shaking.

7.2 Add a few glass beads, cover the conical flask with the watch glass (5.7) and bring the aqueous solution to a low-boiling condition on a hot-plate in a fume cupboard. When the volume of solution has been reduced to between 15 ml and 20 ml, slowly add, without removing the flask from the hot-plate, 5 ml of the nitric acid (4.1) down the side of the flask and evaporate the contents almost to dryness to oxidise any organic material present. Repeat the nitric acid treatment until a white residue remains. Finally, remove the watch glass and evaporate the solution to dryness. Remove the flask from the hot-plate and allow the contents to cool.

7.3 Add approximately 200 ml of water to the flask and swirl to dissolve the residue.

NOTE 5 The residue may be quickly dissolved by heating the solution.

If the solution has been heated, cool before proceeding. Add several drops of the bromothymol blue indicator solution (4.10) and titrate with the ammonia solution (4.3) until the colour just changes from straw yellow to blue, then add 10 ml of the sodium acetate/acetic acid buffer solution (4.5) and 5 drops of the xylenol orange indicator solution (4.9).

NOTE 6 After addition of xylenol orange, in the presence of lead, the solution will have a plum-red colour. At high lead concentrations, a 1 % (*m/m*) xylenol orange solution may give a better colour indication.

7.4 Titrate the resulting solution with the standard volumetric Na_2EDTA solution (4.8) until the end-point is reached. This is indicated by a sharp colour change from orange to a permanent bright lemon-yellow. Record the volume of Na_2EDTA solution used.

NOTE 7 The addition of excess standard volumetric Na_2EDTA solution produces no further colour change after the end-point.

7.5 Carry out a blank determination using the procedure given in 7.1 to 7.4, omitting the test portion, and record the volume, V_0, of Na_2EDTA in ml.

8 Calculation

Calculate the concentration of lead, c_{lead}, in grams per litre at 15 °C, by means of the following equation (see note 8):

$$c_{lead} = 8{,}288(V_1 - V_0)c_1[1 + 0{,}001\ 2(t - 15)]$$

where

V_0 is the volume, in millilitres, of standard volumetric Na_2EDTA solution used for the blank determination (7.5);

V_1 is the volume, in millilitres, of standard volumetric Na_2EDTA solution used to titrate the test portion;

c_1 is the concentration, in moles per litre, of the standard volumetric Na_2EDTA solution;

t is the temperature, in degrees Celsius, of the gasoline when pipetting the sample;

8,288 is a constant relating the equivalency of Na_2EDTA to grams per litre of lead;

0,001 2 is a compromise coefficient of expansion of gasolines per 1 °C at 15 °C, and is intermediate between that of motor and aviation gasolines.

NOTE 8 For gasoline containing only tetraethyl lead (TEL) or tetramethyl lead (TML), the grams of lead per unit volume can be converted to millilitres per unit volume by multiplying by the following factors:

for TEL = 0,946;

for TML = 0,648.

9 Expression of results

Report the concentration, c_{lead}, obtained to the nearest 0,002 g lead per litre at 15 °C.

10 Precision

The precision of this International Standard was obtained in an ISO cooperative test programme on samples covering a range of 0,3 to 1,0 g of lead per litre. In a subsequent ASTM testing programme, the range was extended down to 0,03 g of lead per litre with equal or better precision. The precision was established using dimethyl yellow indicator solution in place of bromothymol blue. Limited testing has shown that the change of indicator solution does not affect the precision.

10.1 Repeatability

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 following value only in one case in twenty:

$$0{,}003\ 65 + 0{,}007\ 3\bar{c}_{lead}$$

where $\bar{c}_{lead}$ is the average of the results being compared, in grams of lead per litre at 15 °C.

10.2 Reproducibility

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 following value only in one case in twenty:

$$0{,}013\ 5 + 0{,}027\bar{c}_{lead}$$

where $\bar{c}_{lead}$ is the average of the results being compared, in grams of lead per litre at 15 °C.

11 Test report

The test report shall contain at least the following information:

a) sufficient details for complete identification of the product tested;

b) a reference to this International Standard;

c) the sampling procedure used (see clause 6);

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

e) any deviation, by agreement or otherwise, from the procedure specified;

f) the date of the test.

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