
INTERNATIONAL STANDARD



2083

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Gasoline — Determination of lead content — Volumetric chromate method

First edition — 1973-12-01

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To be withdrawn

UDC 662.75 : 546.815 : 543.242

Ref. No. ISO 2083-1973 (E)

Descriptors : petroleum products, gasoline, determination of content, lead (metal), volumetric analysis.

FOREWORD

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International Standard ISO 2083 was drawn up by Technical Committee ISO/TC 28, *Petroleum products*, and circulated to the Member Bodies in February 1971.

It has been approved by the Member Bodies of the following countries :

Australia	Germany	South Africa, Rep. of
Austria	India	Spain
Belgium	Italy	Sweden
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Egypt, Arab Rep. of	Portugal	U.S.A.
France	Romania	U.S.S.R.

No Member Body expressed disapproval of the document.

Gasoline – Determination of lead content – Volumetric chromate method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a method for the volumetric determination of the total lead content of gasoline and other volatile distillates blended with lead alkyls (tetraethyl lead, tetramethyl lead, trimethylethyl lead, dimethyldiethyl lead, methyltriethyl lead, or mixtures thereof) within the concentration range of 0,05 to 1,1 g of lead per litre.

2 PRINCIPLE

The lead alkyl is converted to lead chloride and extracted from the gasoline by refluxing with hydrochloric acid. The acid extract is evaporated to dryness, and any organic matter present is removed by oxidation with nitric acid. The lead is precipitated as lead chromate and determined by an iodometric method.

3 REAGENTS

All reagents used shall be of recognized analytical reagent quality. Lead-free distilled water, or water of equivalent purity, shall be used throughout.

3.1 Potassium iodide (KI).

3.2 Acetic acid solution (1 + 1).

Mix 1 volume of glacial acetic acid with 1 volume of water.

3.3 Hydrochloric acid (HCl), concentrated (ρ 1,19 g/ml).

3.4 Nitric acid (HNO₃), concentrated (ρ 1,42 g/ml).

3.5 Nitric acid solution (1 + 20).

Dilute 1 volume of the concentrated nitric acid (3.4) with 20 volumes of water.

3.6 Ammonium hydroxide solution (1 + 1).

Mix 1 volume of concentrated ammonium hydroxide (NH₄OH, ρ 0,90 g/ml) with 1 volume of water.

3.7 Lead acetate trihydrate, 100 g/l solution.

Dissolve 100 g of lead acetate trihydrate [Pb(CH₃COO)₂·3H₂O] in water and dilute to 1 l.

3.8 Potassium dichromate, 100 g/l solution.

Dissolve 100 g of potassium dichromate (K₂Cr₂O₇) in water, dilute to 1 l, and filter.

3.9 Potassium chlorate, nitric acid solution.

Dissolve 78 g of potassium chlorate (KClO₃) in 550 ml of the concentrated nitric acid (3.4).

3.10 Solvent for lead chromate.

Prepare two separate solutions as follows :

- solution A : 200 ml of the concentrated hydrochloric acid (3.3) in 350 ml of water;
- solution B : 300 g of sodium chloride (NaCl) in 1 l of water.

Combine solutions A and B.

3.11 Lead, standard solution.

Place 3,197 g of lead nitrate [Pb(NO₃)₂] in a 1 l, one-mark volumetric flask, dissolve in water, and dilute to the mark.

1 ml of this standard solution contains 2 mg of Pb.

3.12 Sodium thiosulphate, 0,05 N standard volumetric solution.

Weigh about 12,4 g of sodium thiosulphate pentahydrate (Na₂S₂O₃·5H₂O) and dissolve it in 1 l of water contained in a dark (amber-coloured) bottle.

In prolonged storage the titre of the solution should be checked at least once a month. Before establishing the titre of the solution, add 0,5 g of sodium carbonate as a preservative, shake vigorously and allow to stand for 3 days before standardizing. Standardize and calculate the lead factor as follows :

3.12.1 Pipette 25 ml of the lead standard solution (3.11) into a 400 ml beaker, add 10 ml of the nitric acid (3.5) and dilute the solution by adding 250 to 300 ml of water. Complete the standardization in accordance with 5.6 to 5.9.

3.12.2 Calculate the lead factor (titre), F , of the sodium thiosulphate solution, expressed in equivalent grams of lead per millilitre of solution, by means of the equation

$$F = \frac{m}{V}$$

where

m is the mass, in grams, of lead contained in 25 ml of the standard lead nitrate solution;

V is the volume, in millilitres, of sodium thiosulphate solution required for the titration.

3.13 Starch, 1 % solution, freshly prepared as follows :

Dissolve 1 g of soluble starch in 100 ml of water, bring to the boil and filter while hot.

To preserve the starch solution, it is recommended that several drops of toluene or chloroform be added.

3.14 Indicator, *p*-nitrophenol solution.

Dissolve 0,5 g of *p*-nitrophenol in 100 ml of water and filter, if necessary, to remove insoluble material.

3.15 Indicator, mixed (methyl red and methylene blue).

Prepare two separate solutions as follows :

– solution C : 0,05 g of methylene blue in 50 ml of ethanol;

– solution D : 0,1 g of methyl red in 50 ml of ethanol.

Combine solutions C and D.

3.16 Heavy distillate.

A straight-run, lead-free, petroleum distillate, of bromine number not greater than 1,5, with approximately 10 % distilling at 205 °C and approximately 90 % at 240 °C.

4 APPARATUS

4.1 Extraction apparatus, conforming to the design and dimensions illustrated in the figure, constructed of heat-resistant glass, and consisting of the following component parts :

4.1.1 Flask, 500 ml capacity.

4.1.2 Funnel, cylindrical dropping, approximately 70 ml capacity.

4.1.3 Heating coil, 250 W, made up of suitable gauge and length of nickel-chromium wire.

4.1.4 Heating tube, with internal tube for increasing convection in the liquid.

4.1.5 Reflux condenser, Hopkins type, having a vapour outlet connected by a rubber tube to an outside vent or exhaust hood.

4.1.6 Rheostat, of suitable resistance and capacity for regulating the heating coil.

4.2 Electric hot-plate, with enclosed heating coil.

4.3 Filter crucible, of approximately 25 ml capacity, porous porcelain or sintered glass, maximum pore size 15 μm.

4.4 Flask, conical, 500 ml capacity, glass stoppered.

5 PROCEDURE

5.1 Measure the temperature of the sample to the nearest 0,5 °C prior to pipetting.

NOTE – For gasoline having a Reid vapour pressure above 0,5 bar the sealed sample container shall be cooled to approximately 15 °C before removing the test portion for analysis.

5.2 Using a pipette (see note), transfer 50 ± 0,05 ml of the sample to the flask (4.1.1) through the funnel (4.1.2) (see figure). Add approximately 50 ml of the heavy distillate (3.16) and 50 ml of the hydrochloric acid (3.3).

NOTE – Leaded gasoline or corrosive liquids should not be sucked into a pipette by the mouth.

5.3 Use the full heat of the heater until boiling commences (usually 0,5 to 1,0 min), and then adjust the rheostat (4.1.6) to regulate the heat to maintain boiling at a vigorous rate, but not at a rate to cause bumping in the flask (see note 1) or to cause the condenser to flood (see note 2).

NOTES

1 A new or thoroughly cleaned extractor has a tendency to induce super-heating, and bumping of the solution may occur. This difficulty will disappear after the apparatus has been used for several analyses.

2 During the heating cycle, hydrochloric acid gas is volatilized and constant boiling hydrochloric acid is obtained. Continuous and vigorous boiling is necessary to obtain intimate mixing of the acid and sample to extract completely the decomposed lead alkyls from the gasoline phase.

5.4 Reflux for 30 min, switch off the heater, allow the sample to cool for a few minutes, and drain the acid layer into a 400 ml beaker. Add 50 ml of water to the sample remaining in the apparatus and reflux the water and

gasoline for 5 min, using the full heat of the heater. Drain the water into the same 400 ml beaker and repeat the water extraction.

5.5 Evaporate the bulk aqueous extract to dryness (see note 1). Add 3 ml of the concentrated nitric acid (3.4) to the residue, cover the beaker with a watch-glass, and heat the residue to oxidize any organic material which is present. Repeat the nitric acid treatment. If a white residue is not obtained after two additions of the nitric acid, oxidize any remaining organic material with the potassium chlorate nitric acid solution (3.9) (see note 2). Add to the residue 4 ml of the dilute nitric acid (3.5) and 25 ml of water and heat the residue until all the lead salt is in solution.

NOTES

1 To reduce the evaporation time it is permissible to employ an air jet under the following conditions: substitute a 500 ml conical flask for the beaker; evaporate on a hot-plate having a surface temperature between 230 and 260 °C, while impinging upon the surface of the liquid a stream of clean air at about 75 °C, at a rate of about 10 l per minute. The air stream should be led into the flask by means of a glass tube with an orifice about 5 mm in diameter, placed about 60 mm above the surface of the liquid. The air stream should not be used in the nitric acid evaporation.

2 If the residue flashes on being heated with the nitric acid, the sample should be discarded and the hydrochloric acid extraction repeated on another sample. Then evaporate the extract until crystallization commences, but not to complete dryness. Add 10 ml of the potassium chlorate nitric acid solution (3.9), cover the beaker with a watch-glass, and evaporate the mixture almost to dryness. Repeat this treatment, if necessary, to obtain a white residue.

5.6 Cool the solution, add 6 drops of the *p*-nitrophenol indicator solution (3.14) or the mixed indicator (3.15) and neutralize by adding the ammonium hydroxide solution (3.6) until the indicator changes colour; then add an additional 4 to 5 ml of the ammonium hydroxide solution. Add the acetic acid (3.2) to neutralize the ammonium hydroxide, then add 1 to 2 ml in excess. Dilute the solution by adding 300 to 350 ml of water.

5.7 Heat the solution to boiling on a hot-plate and add 10 ml of the potassium dichromate solution (3.8), drop by drop, from a pipette. Continue boiling until the precipitated lead chromate is deep orange in colour (usually 5 to 7 min). Cool the precipitate at room temperature for 3 to 4 h and then filter through a porous filter or filter crucible. Wash the precipitate in the beaker and in the filter crucible with hot water until no turbidity is produced when 1 drop of the lead acetate solution (3.7) is added to 1 drop of the filtrate, indicating that washing is complete.

5.8 Dissolve the washed precipitate of lead chromate in the filter crucible and the residue of lead chromate in the beaker used for precipitation, in 50 ml of the solvent (3.10), adding the solvent in small portions until the sediment is completely dissolved. Wash the beaker and filter crucible several times with small portions of cold water.

Collect the rinsings in a 500 ml conical flask fitted with a ground glass stopper. The final volume of solution should be between 200 and 250 ml.

5.9 Add to the solution 1 g of the solid potassium iodide (3.1) and titrate the liberated iodine immediately with the sodium thiosulphate solution until a faint yellow colour is observed. Add 1 ml of the starch indicator solution (3.13) and continue the titration until the blue-violet colour disappears and does not return in 30 s.

6 EXPRESSION OF RESULTS

Calculate the concentration of lead, in grams per litre at 15 °C, using the equation

$$\text{Pb (g/l) at 15 °C} = 20 F V [1 + 0,0012 (t - 15)]$$

where

F is the lead factor (titre), in grams of lead per millilitre, of the standard sodium thiosulphate solution;

V is the volume, in millilitres, of sodium thiosulphate solution used to titrate the sample;

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

20 is the factor for converting the volume of sample to 1 l;

0,0012 is the coefficient of expansion of motor and aviation gasoline per degree Celsius at 15 °C.

7 PRECISION¹⁾

The following criteria shall be used for judging the acceptability of results (95 % confidence level) when only tetraethyl lead is present in the concentration range of 0,25 to 1,1 g of lead per litre.

7.1 Repeatability

Duplicate results by the same operator using the same apparatus shall be considered suspect if they differ by more than the following amount:

0,014 + 0,007 *X*, where *X* is the lead content in grams per litre at 15 °C.

7.2 Reproducibility

The results submitted by each of two laboratories shall be considered suspect if they differ by more than the following amount:

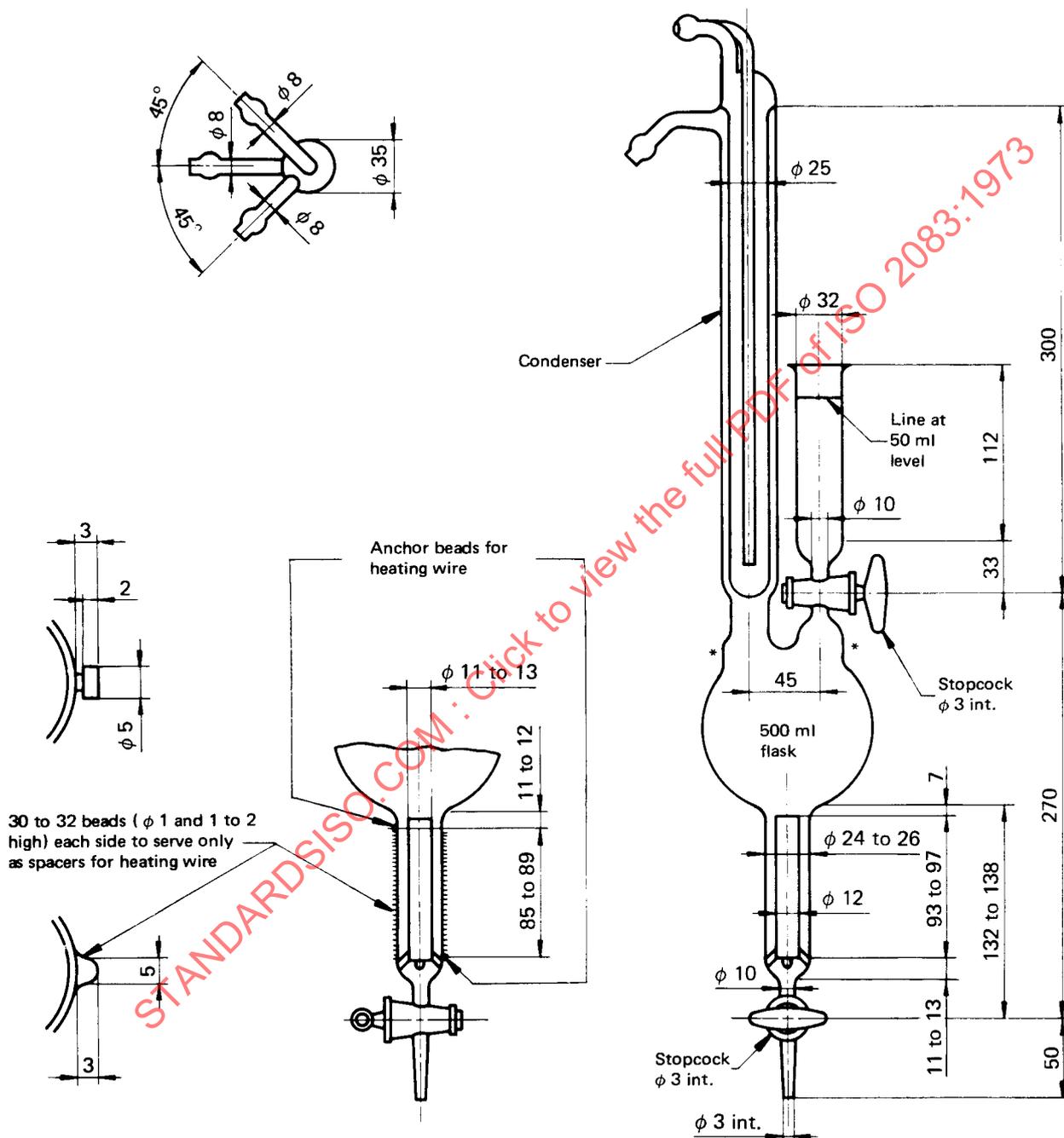
0,040 + 0,019 *X*, where *X* is the lead content in grams per litre at 15 °C.

1) The precision data quoted above were obtained in a cooperative test programme undertaken by Technical Committee ISO/TC 28 on a variety of fuels containing tetraethyl lead only. Precision data have not yet been established for samples containing other lead alkyls.

8 TEST REPORT

Report the result to the nearest 0,01 g of lead per litre at 15 °C and make reference to this International Standard.

Dimensions in millimetres



* Condenser and cylindrical dropping funnel may be fitted to flask by means of 19/26 ground glass joints conforming to ISO/R 383, or equivalent if desired.

NOTE — Hopkins type condenser is used

FIGURE — Extraction apparatus