

BS 2000-455:2011

Incorporating Corrigendum No. 1



BSI Standards Publication

Methods of test for petroleum and its products

**Part 455: Determination of the
manganese content of gasoline
— Atomic absorption
spectrometry (AAS) method
(Identical with IP 455/12)**

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Summary of pages

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Foreword

Publishing information

This part of BS 2000 is published by BSI Standards Limited under licence from The British Standards Institution and came into effect on 30 June 2011. It was prepared by Technical Committee PTI/13, *Petroleum Testing and Terminology*. A list of organizations represented on this committee can be obtained on request to its secretary.

Supersession

This part of BS 2000 supersedes BS 2000-455:2001, which is withdrawn.

Information about this document

This new edition has been updated to be in line with changes implemented by the Energy Institute.

BS 2000 comprises a series of test methods for petroleum and its products that are published by the Institute of Petroleum (IP) and have been accorded the status of a British Standard. Each method should be read in conjunction with the preliminary pages of "Standard Methods for Analysis and Testing of Petroleum Products and British Standard 2000 Parts" which gives details of the BSI/IP agreement for publication of the series, provides general information on safety precautions, sampling and other matters, and lists the methods published as parts of BS 2000.

Under the terms of the agreement between BSI and the Institute of Petroleum, the revised version of BS 2000-455 will be published by BSI and by the IP (in "Standard Methods for Analysis and Testing of Petroleum Products and British Standard 2000 Parts" and as a separated publication). The numbering of the parts of BS 2000 follows that of the corresponding IP methods. BS 2000-455:2011 is thus identical with IP 455/12.

WARNING. This part of BS 2000 calls for the use of substances and/or procedures that can be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage.

It has been assumed in the preparation of this part of BS 2000 that the execution of its provisions will be entrusted to appropriately qualified and experienced people, for whose use it has been produced.

The start and finish of text introduced or altered by Corrigendum No. 1 is indicated in the text by tags C1 and C1.

Presentational conventions

The provisions of this standard are presented in roman (i.e. upright) type. Its methods are expressed as a set of instructions, a description, or in sentences in which the principal auxiliary verb is "shall".

Commentary, explanation and general informative material is presented in smaller italic type, and does not constitute a normative element.

Contractual and legal considerations

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard cannot confer immunity from legal obligations.

1 Scope

This British Standard¹⁾ specifies a method for the determination of the manganese content of automotive gasoline, when the manganese is present as methylcyclopentadienyl manganese tricarbonyl (MMT®)²⁾. The precision of this test method only applies to the determination of manganese in the range of 10 mg/L to 40 mg/L, but higher concentrations can be measured by prior dilution of the gasoline sample with the specified solvent to bring the test portion within the specified range of the method. The test method may not be applicable to gasoline containing highly cracked components (less than 18% (V/V) olefins as determined by ASTM D1319 non depentanized). Solutions of MMT® in gasoline are chemically unstable when exposed to light, and low and erratic results are expected if the gasoline is exposed to light prior to stabilization during analysis.

NOTE 1 For the purposes of this standard, the terms “% (m/m)” and “% (V/V)” are used to represent the mass fraction and the volume fraction respectively.

WARNING. This part of BS 2000 calls for the use of substances and/or procedures that can be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage.

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.

BS EN ISO 385:2005, *Laboratory glassware – Burettes*

BS EN ISO 648:2008, *Laboratory glassware – Single-volume pipettes*

BS EN ISO 1042, *Laboratory glassware – One-mark volumetric flasks*

BS EN ISO 3170, BS 2000-475, *Methods of test for petroleum and its products – BS 2000-475: Petroleum liquids – Manual sampling (Identical with IP 475)*

BS EN ISO 3171, BS 2000-476, *Methods of test for petroleum and its products. BS 2000-476: Petroleum liquids. Automatic pipeline sampling (Identical with IP 476)*



3 Principle

The gasoline is treated with bromine solution and diluted with methyl isobutyl ketone (MIBK). The manganese content is determined by atomic absorption spectrometry using an air-acetylene flame at 279.5 nm and standards prepared from an organo-manganese standard material.

4 Reagents and materials

4.1 Use only reagents of recognized analytical grade, or of another grade that has been demonstrated to have sufficiently high purity not to affect the accuracy or precision of the determination.

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²⁾  MMT(R) is a trade mark owned by Ethyl Corporation and is the trade name of a product supplied by [supplier]. This information is given for the convenience of users of this standard and does not constitute an endorsement by BSI of the product named. Equivalent products may be used if they can be shown to lead to the same results. 

4.2 Bromine.

CAUTION. Bromine can cause severe and painful burns in contact with skin. Wear protective gloves and prepare, store and use it in a well-ventilated area.

4.3 Cyclohexane.

4.4 Bromine solution. Add reagent grade bromine (4.2) to an equal volume of cyclohexane (4.3).

4.5 Manganese compound, manganese sulfonate or other oil-soluble manganese compound of known high, greater than 99% (*m/m*), purity or certified manganese content.

4.6 Methyl isobutyl ketone (MIBK).

4.7 Manganese stock solution, 400 mg Mn/L concentration. Dissolve the appropriate quantity of manganese compound (4.5) in MIBK (4.6) to give a stock solution of approximately 400 $\frac{C_1}{C_2}$ mg/L $\frac{C_1}{C_2}$ of manganese. Calculate the concentration to the nearest 0.1 mg/L.

4.8 Manganese standard solutions. Using the volumetric glassware (5.2) dilute the manganese stock solution (4.7) with MIBK (4.6) to give a series of four standard solutions – 4 mg/L, 10 mg/L, 20 mg/L and 40 mg/L of manganese. Calculate the concentrations to the nearest 0.01 mg/L.

5 Apparatus

5.1 Atomic absorption spectrometer, capable of scale expansion and equipped with a manganese hollow-cathode lamp for monitoring absorption at 279.5 nm, a premix slot-type burner with rotatable burner head, and an adjustable nebulizer.

5.2 Volumetric glassware.

5.2.1 Burettes and/or pipettes, one mark, conforming to class A of BS EN ISO 385:2005 and class A of BS EN ISO 648:2008 respectively.

5.2.2 Volumetric flasks, one mark, conforming to BS EN ISO 1042.

5.3 Glass vials, 40 mL capacity with teflon or polyethylene-lined screw caps.

5.4 Pipette, 1 mL delivery conforming to class A of BS EN ISO 648.

5.5 Micropipette, 100 $\frac{C_1}{C_2}$ μ L $\frac{C_1}{C_2}$ capacity, Eppendorf type or equivalent.

5.6 Automatic pipette, capable of delivering (9.00 \pm 0.01) mL quantities.

NOTE 2 A standard repipette with 950 mL round amber glass bottle and 10 mL dispenser capacity, with its required accuracy, has been found satisfactory.

6 Samples and sampling

6.1 Unless otherwise specified, samples shall be taken as described in BS 2000-475 or BS 2000-476.

6.2 Take samples directly into an all-metal container and analyze as soon as practicable after sampling.

7 Calibration

7.1 General

Measure all volumes for the preparation of working standards and test portions within 5 °C of the temperature at which the volumetric glassware was calibrated.

NOTE 3 This temperature is usually 20 °C.

7.2 Preparation of working standards

7.2.1 Using the micropipette (5.5), add 100 µL of bromine solution (4.4) to each of three separate glass vials (5.3).

7.2.2 Using the pipette (5.4), add 1 mL of each of the four manganese standard solutions (4.8) to each vial. Mix with the bromine solution by swirling.

7.2.3 Using the automatic pipette (5.6), deliver 9.00 mL of MIBK (4.6) to each of the vials. Mix well.

7.3 Preparation of the instrument

7.3.1 Set the spectrophotometer operating conditions to those recommended by the manufacturer for monitoring manganese absorption at 279.5 nm using an air-acetylene flame.

7.3.2 Aspirate MIBK into the flame. Adjust the nebulizer (sample flow rate), acetylene and air flow rates to give a lean non-luminous flame.

7.3.3 Aspirate the highest concentration working standard and note the absorbance. If the absorbance exceeds a value of 0.1, rotate the burner head to decrease the absorbance to approximately 0.1. Zero the instrument with MIBK.

NOTE 4 Using this low absorbance range aids in achieving linearity.

7.3.4 Scale expand the instrument so that the highest concentration working standard gives near full-scale recorder deflection.

7.3.5 With MIBK as a blank, aspirate in turn the four working standards. Record the absorbances and check these data for linearity. If non-linear, readjust the test portion or acetylene flow rates, or both, to slightly leaner conditions and repeat the calibrations until absorbances are linear. Plot the absorbance values against manganese content as the best straight line through the points.

8 Procedure

8.1 Using the micropipette (5.5), add 100 µL of bromine solution (4.4) to a glass vial (5.3).

8.2 Using the pipette (5.4), add a 1 mL test portion of the gasoline sample (see Note 5) to the vial. Mix well.

NOTE 5 If the manganese content of the gasoline is expected to exceed 40 mg/L, the test portion consists of a pre-diluted solution of the gasoline with MIBK in exact known proportions (see 8.5).

8.3 Using the automatic pipette (5.6), add 9.00 mL of MIBK to the vial. Mix well.

8.4 Aspirate the working standards and the test portion solution into the flame and measure the absorbances. Carry out the measurements promptly as absorbances may change with time.

8.5 Read the manganese content of the test portion from the calibration line (7.3.5). If the test portion was diluted, as described in the note under 8.2, calculate the manganese content, M , in mg/L, using the following equation:

$$M = M_C \times V_T/V_G$$

where

M_C is the manganese content read from the calibration line, in mg/L;

V_T is the volume of the test portion (1 mL), in mL;

V_G is the volume of gasoline sample in the test portion, in mL.

9 Expression of results

Report the manganese content of the gasoline, M , to the nearest 0.2 mg/L.

10 Precision

10.1 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 value given below, in absolute value is only one case in twenty.

$$r = 0.3308\%(x + 0.1062)$$

where x is the average of the results being compared, in mg/L.

10.2 Reproducibility, R

The difference between two single and independent test 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 value given below in only one case in twenty.

$$R = 1.650\%(x + 0.1062)$$

where x is the average of the results being compared, in mg/L.

11 Test report

The test report shall contain at least the following information:

- a reference to this standard;
- the type and complete identification of the product tested;
- the result of the test (see Clause 9);
- any deviation, by agreement or otherwise, from the procedures specified;
- the date of the test.

Bibliography

For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ASTM D1319, *Standard test method for hydrocarbon types in liquid petroleum products by fluorescent indicator adsorption*

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