

Determination of the sulphur content of petroleum products by the Wickbold combustion method

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CAUTION. The procedure described in this standard includes the combustion of hydrogen in glass apparatus, which is potentially hazardous and all precautions should be carefully observed.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the EN title page, pages 2 to 18, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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English version

Determination of the sulphur content of petroleum products by the Wickbold combustion method

Détermination de la teneur en soufre des
produits pétroliers par la méthode de
combustion selon Wickbold

Bestimmung des Schwefelgehaltes von
Mineralölerzeugnissen durch Verbrennung
nach Wickbold

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

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Brief history

This standard, drawn up by CEN working group CEN/WG 19 “Methods of test for petroleum products” (secretariat BSI), was submitted to the ballot of CEN members in June 1974, with a view to its adoption as a European Standard.

It was adopted as such by CEN on 1 November 1975 on the strength of its acceptance by the following member countries:

Belgium, Denmark, Finland, France, Germany, Italy, Netherlands, Spain, United Kingdom.

It was subsequently accepted also by Austria.

1 Scope and field of application

This European Standard describes a method for the determination of total sulphur in petroleum products. The method may be applied to products having sulphur contents in the range 1 mg/kg to 50 000 mg/kg and is particularly suitable for distillates with total sulphur contents of less than 300 mg/kg. Samples which are viscous, highly aromatic, or of high sulphur content may be first diluted with a solvent.

The method can be used for the determination of the total sulphur content of natural and refinery gases, also for substances supplied to the burner in the liquid state and for the determination of volatile sulphur in substances supplied to the burner in the gaseous state after vaporization from the liquid phase.

When viscous or solid materials, such as bitumen or heavy fuel oils, are burnt in a combustion boat some of the sulphur may be bound to the ash retained in the boat. In this case the bound sulphur shall be determined on the residue.

NOTE 1 Organically bound chlorine in petroleum products can be determined by the usual volumetric, gravimetric or potentiometric determination of the chloride ions present in the absorption solution after combustion.

2 Principle of method

Gaseous or liquid samples are passed to the oxy-hydrogen flame of a suction burner where they are burnt with considerable excess of oxygen.

Viscous or solid samples are preferably dissolved in light petroleum/toluene blend and treated as liquid samples or may be burnt in a stream of oxygen in a combustion boat.

The resulting sulphur oxides are converted into sulphuric acid by absorption in hydrogen peroxide solution. Depending on the sulphur content of the sample, the sulphate ions in the absorption solution are determined in accordance with Table 1.

3 Reagents and materials

(See additionally under individual finishes for the appropriate volumetric solutions and other reagents required.)

3.1 Purity. All reagents, unless otherwise specified, shall be of recognized analytical reagent quality. References to water shall be taken to mean distilled water or water, otherwise produced, of equivalent quality.

3.2 Reagents. The following reagents are required:

- 1) *Hydrogen peroxide* solution, 3 % (m/m), free from sulphur.
- 2) *Ethanol*, 96 % (v/v), free from sulphur.
- 3) 80 %/20 % (v/v) *blend of light petroleum*, boiling range 60 °C to 80 °C and *toluene* free from sulphur (in the following referred to as "light petroleum/toluene blend").
- 4) *Oxygen*, compressed gas, commercial grade, free from sulphur.
- 5) *Hydrogen*, compressed gas, commercial grade, free from sulphur.
- 6) *Hydrochloric acid*, concentrated ($\rho_{20} = 1.19$ g/ml).
- 7) *Mercury*.
- 8) *Dihexyldisulphide reference blend*. Dissolve a known mass of dihexyldisulphide weighed to the nearest 0.1 mg in the light petroleum/toluene blend [3.2 3)]. The concentration of dihexyldisulphide should be chosen from the sulphur concentration in the range shown in column 1 of Table 1 according to the finish which will be used. Dihexyldisulphide contains 27.36 % (m/m) S.

CAUTION. It is recommended that gas cylinders are not stored in the laboratory.

4 Apparatus

(See additionally under individual finishes for the appropriate apparatus.)

NOTE 2 In order to provide a detailed description of the mode of operation this European Standard has been based on a single type of silica Wickbold burner and absorption train. Other types of burner using the principle of combustion of a test portion in an oxy-hydrogen flame with excess oxygen may also be used. These should be operated as described in the manufacturers' instructions and checked by the combustion of samples of the standard sulphur-containing reference blends (see clause 9).

4.1 Combustion apparatus. Figure 1 shows the schematic layout of the apparatus for the combustion of gaseous or liquid samples and Figure 2 shows that for the combustion of viscous or solid samples.

Table 1 — Relation between expected sulphur content, mass of test portion and finish recommended

Expected sulphur content	Mass of test portion	Sulphur in absorber solution	Aliquot portion of 100 ml absorber solution	Sulphur in the aliquot	Finish recommended for different levels of S content			Precision	
								Repeatability	Reproducibility
(absolute)									
mg/kg	g	µg		µg	Conductimetric	Turbidimetric	Nephelometric	mg/kg	
1	100	100	1/2	50				0.3	0.6
	50	50	1/1	50					
	20	20	1/1	20					
5	20	100	1/2	50				0.8	1.5
	50	250	1/5	50					
	50	250	1/1	250					
10	5	50	1/1	50				1	2
	10	100	1/2	50					
	20	200	1/2	100					
	50	500	1/2	250					
30	5	150	1/2	75				2	4
	10	300	1/2	150					
	20	600	1/2	300					
	50	1 500	1/5	300					
50	5	250	1/2	125	3	6			
	10	500	1/2	250					
	30	1 500	1/5	300					
100	2	200	1/2	100	6	12			
	5	500	1/2	250					
	10	1 000	1/5	200					
1 000	1	1 000	1/5	200	20	40			
	2	2 000	1/5	400					
20 000	1	20 000	1/10	2 000	600	1 000			

NOTES

The volume of gas required may be calculated with sufficient accuracy from the mass and density of the gas.

The precision values were derived from statistical examination of inter-laboratory test results on liquid samples containing 0.4 mg/kg, 3.1 mg/kg, 203 mg/kg and 4 400 mg/kg of sulphur; the analysis involved results from 9, 13, 17 and 17 laboratories, respectively, after discarding outliers.

The combustion apparatus consists essentially of the following components (see Figure 1 and Figure 2).

Reducing valve (1). With gauge, range 0 bar to 5 bar (0 kPa to 500 kPa)¹⁾, for oxygen.

Reducing valve (2). With gauge, range 0 bar to 2 bar (0 kPa to 200 kPa)¹⁾, for hydrogen.

Flowmeter (3). Range 20 l/h to 300 l/h, operating on the floating element principle, with precision control valve, for the secondary oxygen line.

Flowmeter (4). Range 20 l/h to 200 l/h, operating on the floating element principle, with precision control valve, for the hydrogen line.

Flowmeter (5). Range 200 l/h to 2 000 l/h, operating on the floating element principle, with precision control valve, for the primary oxygen line.

Excess pressure vessels (6). e.g. Wash-bottles, containing mercury [3.2 7]) and white oil (see 7.2) or metal pressure safety valves. Three are required. The inlet valves must be of the non-return type.

Flame arrester (7). With metal connections.

Flow indicator (8). Glass.

Vacuum gauge (11). Range from approximately 0.6 bar to 1.1 bar (60 kPa to 110 kPa)¹⁾ absolute.

¹⁾ The SI unit of pressure is the pascal (Pa)
1 Pa = 1 N/m² = 10⁻⁵ bar