

Methods for

# Analysis and testing of coal and coke —

Part 106: Ultimate analysis of coal and  
coke —

Section 106.4 Determination of total  
sulfur content —

Subsection 106.4.2 High temperature  
combustion method.

ICS 75.160.10

# Committees responsible for this British Standard

The preparation of this British Standard was entrusted to Technical Committee SFI/3 Analysis and testing of coal and coke, upon which the following bodies were represented:

British Cement Association  
 British Coal Corporation  
 British Iron and Steel Producers' Association  
 Electricity Association  
 GAMBICA (BEAMA Ltd.)  
 Power Generation Contractors' Association (PGCA (BEAMA Ltd.))

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## National foreword

This British Standard has been prepared by SFI/3 and is identical to ISO 351:1996 *Solid mineral fuels — Determination of total sulfur — High temperature combustion method*, including Corrigendum 1:1996, published by the International Organization for Standardization (ISO) and in the preparation of which the UK played a full part.

BS 1016-106 will form a revision of Parts 6 to 11 of BS 1016. This Subsection supersedes the following.

In BS 1016-6:1977, clause 5, subclause 8.3 and those parts of clause 11 which refer to sulfur;

In BS 1016-7:1977, clause 5, subclause 8.3 and those parts of clause 10 which refer to sulfur.

Principal differences are the allowance of an alternative layout for the absorbers, recommendation of an alternative rate of combustion for certain types of coal and coke and modification of the precision requirements for the method with respect to higher sulfur content coals.

An alternative method is given in BS 1016-106.4.1 *ESHKA method*.

BS 1016-106 is part of a rationalized and restructured BS 1016. The Parts numbered from 1 to 21 are gradually being withdrawn and replaced by Parts in the new series. The full list of Parts in the new series, together with corresponding numbering of the old series and related international standards is given in BS 1016 *Analysis and testing of coal and coke Part 100:1994 General introduction and methods for reporting results*.

The Technical Committee has reviewed the provisions of ISO 1015:1975, ISO 5068:1983 and ISO 5069-2:1983 to which normative reference is made in the text, and has decided that they are acceptable for use in conjunction with this standard.

British Standards related to ISO 331:1983, ISO 587:1981, ISO 687:1974, ISO 1170:1977, ISO 1988:1975 and ISO 2309:1980 are BS 1016 *Methods for analysis and testing of coal and coke Section 104.1:191 Determination of the moisture content of the general analysis sample of coal*, Part 8:1977 *Chlorine in coal and coke*, Section 104.2:1991 *Determination of the moisture content of the general analysis sample of coke*, Part 100:1994 *General introduction and methods for reporting results*, BS 1017 *Sampling of coal and coke Part 1:1989 Methods for sampling of coal* and Part 2:1994 *Methods for sampling of coke* respectively.

ISO 2309 is being revised in conjunction with ISO 1988 *Hard coal — Sampling*, ISO 9411 *Solid mineral fuels — Mechanical sampling from moving streams Part 1: Coal* and Part 2: *Coke*. This revision will be published in eight Parts, and it is intended to implement these Parts as identical British Standards, superseding BS 1017.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

**Compliance with a British Standard does not of itself confer immunity from legal obligations.**

### Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 6 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.

## Introduction

An alternative method to that specified in this International Standard is given in ISO 334:1992, *Solid mineral fuels — Determination of total sulfur — Eschka method*.

## 1 Scope

This International Standard specifies a method of determining the total sulfur content of hard coal, brown coal and lignite, and coke by high temperature combustion.

## 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 331:1983, *Coal — Determination of moisture in the analysis sample — Direct gravimetric method*.

ISO 587:1981, *Solid mineral fuels — Determination of chlorine using Eschka mixture*.

ISO 687:1974, *Coke — Determination of moisture in the analysis sample*.

ISO 1015:1992, *Brown coals and lignites — Determination of moisture content — Direct volumetric method*.

ISO 1170:1977, *Coal and coke — Calculation of analyses to different bases*.

ISO 1988:1975, *Hard coal — Sampling*.

ISO 2309:1980, *Coke — Sampling*.

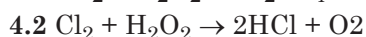
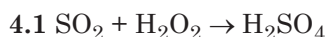
ISO 5068:1983, *Brown coals and lignites — Determination of moisture content — Indirect gravimetric method*.

ISO 5069-2:1983, *Brown coals and lignites — Principles of sampling — Part 2: Sample preparation for determination of moisture content and for general analysis*.

## 3 Principle

A known mass of a sample of coal or coke is burnt in a stream of oxygen, in a tube furnace at a temperature of 1 350 °C. The acid gases formed (chlorine and oxides of sulfur) are absorbed in hydrogen peroxide and subsequently determined titrimetrically. A correction is made to take account of any chlorine liberated and a suitable combustion additive prevents the retention of sulfur in the ash.

## 4 Reactions



## 5 Reagents

**WARNING — Care should be exercised when handling reagents, many of which are toxic and corrosive.**

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

**5.1 Aluminium oxide (alumina)**, finely divided.

**5.2 Hydrogen peroxide**, approximately 3 % (m/m) neutral solution.

Dilute 100 ml of 30 % (m/m) hydrogen peroxide solution to 1 litre with water and neutralize with the sodium tetraborate solution (**5.4**) using the mixed indicator (**5.6**).

**5.3 Mercury(II) oxycyanide**, saturated solution at 20 °C, approximately 45 g/l.

Saturate a suitable volume of water with mercury(II) oxycyanide by prolonged agitation; filter and neutralize the filtrate with the sulfuric acid (**5.5**), using bromothymol blue as an external indicator. Store in a dark glass bottle; do not keep for more than 4 d.

**5.4 Sodium tetraborate**, standard volumetric solution,  $c(\text{Na}_2\text{B}_4\text{O}_7) = 0,025 \text{ mol/l}$ .

Dissolve 9,534 2 g of sodium tetraborate decahydrate in water and dilute to 1 litre. Mix thoroughly.

**5.5 Sulfuric acid**, standard volumetric solution,  $c(\text{H}_2\text{SO}_4) = 0,012 5 \text{ mol/l}$ .

**5.6 Mixed indicator solution****5.6.1 Solution A**

Dissolve 0,125 g of 2-(4-dimethylaminophenylazo) benzoic acid, sodium salt (methyl red) in 100 ml of water.

**5.6.2 Solution B**

Dissolve 0,083 g of 3,7-bis(dimethylamino) phenothiazine-5-ylum chloride (methylene blue) in 100 ml of water. Store in a dark bottle.

**5.6.3 Mixed solution**

Mix equal volumes of solution A and solution B. Store in a dark bottle. Discard the mixed solution after 1 week.

**5.7 Oxygen**, laboratory grade, of purity at least 99,6 % (*m/m*).

**5.8 Sodium hydroxide on an inert base**, preferably of a coarse grading, for example 1,2 mm to 1,7 mm, and preferably of the self-indicating type.

**6 Apparatus**

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

**6.2 Graduated glassware**, conforming to the requirements for class A in the International Standards prepared by ISO/TC 48, *Laboratory glassware and related apparatus*.

**6.3 Furnace**, capable of heating a tube, of approximately 28 mm external diameter over a length of 125 mm to 150 mm, to a temperature of 1 350 °C.

The furnace may be heated electrically, using either silicon carbide resistance rods (controlled by a variable transformer) or a resistance wire (controlled by a variable resistance).

**6.4 Combustion tube**, of approximately 28 mm external diameter, 3 mm wall thickness and 650 mm length, made of aluminous porcelain which is impervious to gases up to the working temperature (see Figure 1).

A straight tube is most convenient and may be used in conjunction with an adapter of fused silica having a bell-shaped end, which gives a narrow clearance from the inner wall of the heated tube, and a heat-resistant stopper (acrylonitrile or chloroprene is suitable). Alternatively, the tube may have, a beak end, at the exit, with a tubulure to enable condensation products to be washed out after a test; or a straight tube of aluminous porcelain may be used in conjunction with a borosilicate glass adapter, having a cap-shaped end which fits onto the outer wall of the tube. In this case it will be necessary to lag the end of the combustion tube with a suitable heat-resistant mineral fibre to prevent condensation in the tube.

**6.5 Oxygen cylinder**, fitted with a needle valve to control the rate of flow of oxygen (5.7), and a flowmeter to measure up to 300 ml/min. The oxygen should, as a precautionary measure, be passed through a U-tube packed with sodium hydroxide on an inert base (5.8).

**6.6 Combustion boat**, of iron-free, unglazed porcelain, of minimum dimensions 45 mm long, 12,5 mm wide and 10 mm deep, for hard coal and coke samples, and approximately 75 mm long, 15 mm wide and 10 mm deep for brown coal and lignite.

**6.7 Heat-resistant wire**, approximately 2 mm thick and 450 mm long, with a bent end to transfer the used boat from the combustion tube onto a rigid refractory sheet.

**6.8 Silica or steel pusher**, made from rod or sealed tube, approximately 6 mm in diameter and 450 mm long, with a disc end 12 mm in diameter, for pushing the boat into the hot zone of the combustion tube. The pusher passes loosely through a glass or metal T-piece, one end of which fits into the rubber stopper which closes the inlet end of the combustion tube, the other being sealed by a rubber sleeve (see note 1) through which the pusher slides. The sleeve prevents the escape of oxygen, which enters at the stem of the T-piece. The pusher is usually marked from the disc end, for convenience in ascertaining the position of the boat in the combustion tube during pushing.

NOTE 1 The rubber sleeve should be changed periodically to avoid leakage.

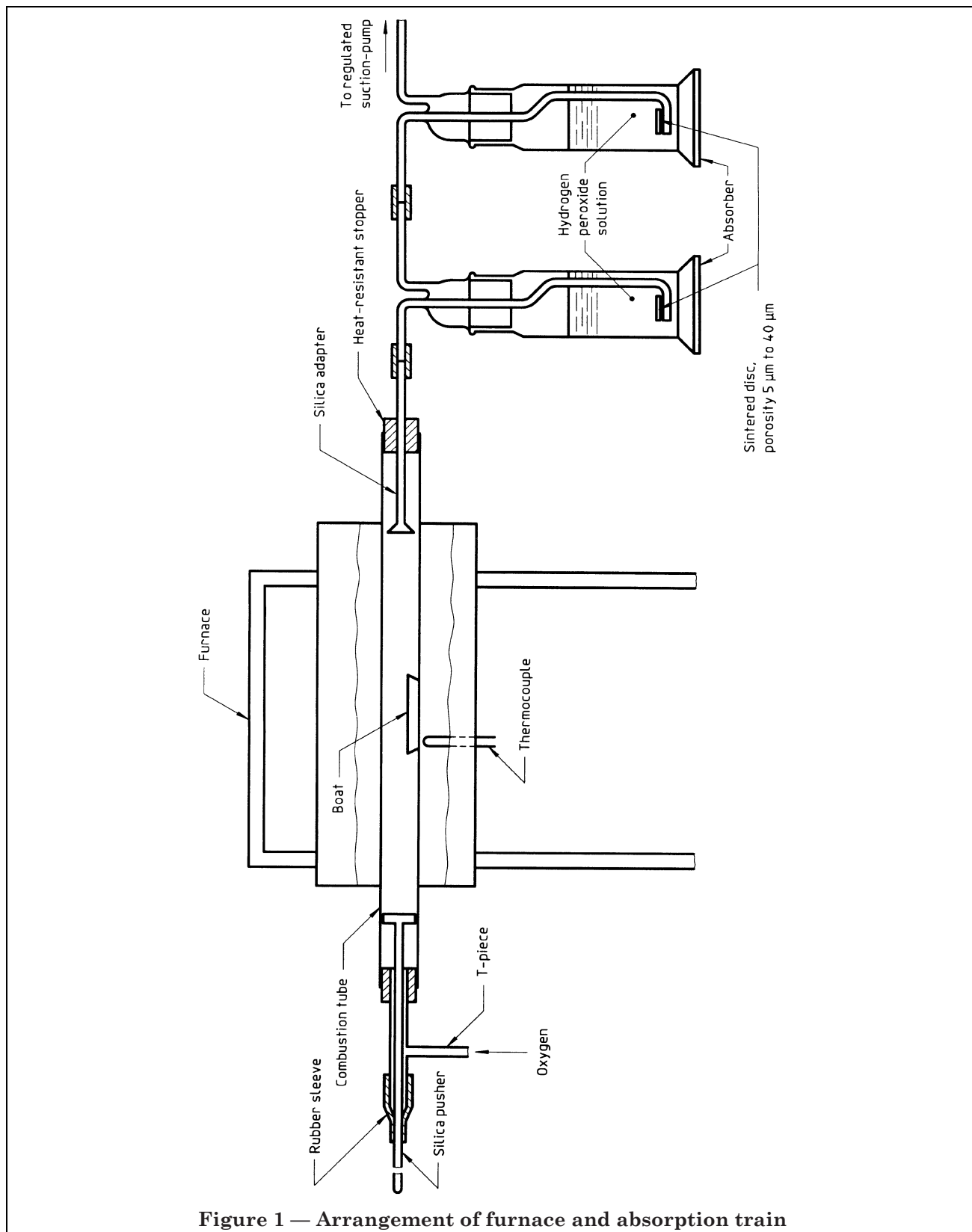


Figure 1 — Arrangement of furnace and absorption train

**6.9** *Two absorbers*, of capacity about 150 ml, which may be large boiling tubes, wide-necked bottles or Dreschel bottles, each containing a sintered glass disc of 0,015 mm to 0,040 mm maximum pore size in the gas distribution tube. The diameter of the absorber shall be such that the disc is covered to a depth of at least 25 mm by the absorbing solution. Connect the silica adapter, or the reaction tube fitted with a tubulure, to the first absorber. Connect this in series with the second absorber.

Alternatively, use a single narrow absorber about 35 mm in diameter and 150 mm deep, so that the bubbler disc (0,015 mm to 0,040 mm maximum pore size) is covered to a depth of at least 90 mm.

To avoid leakage at the rubber sleeve of the inlet end due to the resistance of the sintered glass bubbler, connect the second absorber to a suction-pump through a pressure regulator adjusted to maintain slight suction at the inlet end of the combustion tube.

A convenient assembly of the apparatus is illustrated in Figure 1.

## 7 Preparation of test sample

Prepare the test sample for general analysis in accordance with ISO 1988, ISO 2309 or ISO 5069-2, as appropriate. Ensure that the moisture content of the sample is in equilibrium with the laboratory atmosphere, exposing it, if necessary, in a thin layer for the minimum time required to achieve equilibrium.

Before commencing the determination, thoroughly mix the test sample for at least 1 min, preferably by mechanical means.

If the results are to be calculated other than on an "air-dried" basis (see clause 10), after weighing the test portion (see clause 8), determine the moisture content using a further portion of the test sample by the method described in ISO 331, ISO 687, ISO 1015 or ISO 5068, as appropriate. A further portion should be set aside if the determination of chlorine by the Eschka method (ISO 587) is required.

## 8 Procedure

Raise the temperature of the furnace (6.3) to 1 350 °C. Weigh, to the nearest 0,1 mg, about 0,5 g of the test sample (clause 7) and transfer to a combustion boat (6.6), taking care to spread uniformly. Cover evenly with about 0,5 g of the aluminium oxide (5.1). Measure 100 ml of the hydrogen peroxide solution (5.2) and either divide this amount between the two absorbers (6.9) or pour it all into the single absorber.

Adjust the suction-pump and pressure regulator (see 6.9) so that a rapid stream of air is drawn at constant pressure through the absorber(s). Insert the silica adapter into the combustion tube (6.4) and secure the stopper. Adjust the oxygen (5.7) flow to 300 ml/min.

Insert the charged boat from the inlet end of the combustion tube so that its centre is 240 mm from the centre of the hottest zone and secure the stopper carrying the pusher (6.8) and the oxygen inlet. After 1 min, move the boat forward 40 mm. At the end of each of the next five 1 min periods, push the boat forward about 40 mm, pulling back the pusher each time to prevent distortion. After the last push, the boat should be at the centre of the hottest zone. Allow the boat to remain in the hottest zone for a further 4 min. Disconnect the absorber(s) and, using the bent heat-resistant wire (6.7), withdraw the used combustion boat onto a thick sheet of suitable refractory material.

Wash the adapter, collecting the washings in the single absorber or in the first of the two absorbers. Transfer the contents of the absorber(s) into a 250 ml conical filtration beaker, wash out the absorber(s) and collect the washings in the same filtration beaker. Add 2 or 3 drops of the mixed indicator solution (5.6) and titrate with the sodium tetraborate solution (5.4) to a neutral steel-grey colour. Note the titration volume. This procedure gives the total acidity due to oxides of sulfur and chlorine (see the equations in 4.1 to 4.4). Determine the correction for chlorine as described in either 8.1 or 8.2.

For certain coals which liberate volatile matter at a fast rate, the early stages of heating may give a carry-over of unburnt carbon particles. For such coals, and for certain cokes of very low volatile matter (for example foundry cokes), the rate of pushing should be reduced according to the following procedure.

Insert the charged boat so that its centre is about 240 mm from the centre of the hottest zone. After ~min, move the boat forward 20 mm. At the end of each of the next eleven 1 min periods, move the boat forward about 20 mm. Allow the boat to remain in the hottest zone for a further 4 min.

### 8.1 Chlorine correction — Mercury(II) oxycyanide method

After titration with the sodium tetraborate solution (5.4), the chloride ion is present as sodium chloride. Add 20 ml of the mercury(II) oxycyanide solution (5.3) to convert the sodium chloride to sodium hydroxide (see note 2). Titrate the liberated alkali with the sulfuric acid (5.5) (see the equations in 4.5 and 4.6). Note the titration volume.



NOTE 2 For 0,5 g test portions of samples containing up to 1,2 % chlorine, 20 ml of mercury(II) oxycyanide solution is sufficient excess.

### 8.2 Chlorine correction — Eschka method

Determine the chlorine content of the test sample, using a further test portion, according to the procedure described in ISO 587.

### 9 Blank test

Carry out a blank test using the same procedure as described in clause 8, but omitting the test portion.

### 10 Expression of results

The total sulfur content,  $w_S$ , of the sample as analysed, expressed as a percentage by mass, is given by the equation in either 10.1 or 10.2, as appropriate.

Report the result, as the mean of duplicate determinations, to the nearest 0,01 % ( $m/m$ ).

The results of the determination described in this International Standard are reported on the “air-dried” basis. Calculation of results to other bases is dealt with in ISO 1170.

#### 10.1 Calculation using the mercury(II) oxycyanide method for chlorine correction

The total sulfur content,  $W_S$ , of the samples as analysed, expressed as a percentage by mass, is given by the equation.

$$w_S = \frac{3,206[c_1(V_1 - V_2) - c_2(V_3 - V_4)]}{m}$$

where

- $m$  is the mass, in grams, of the test portion;
- $V_1$  is the volume, in millilitres, of the sodium tetraborate solution used in the determination;
- $V_2$  is the volume, in millilitres, of the sodium tetraborate solution used in the blank test;
- $V_3$  is the volume, in millilitres, of the sulfuric acid solution used in the determination;
- $V_4$  is the volume, in millilitres, of the sulfuric acid solution used in the blank test;
- $c_1$  is the concentration, expressed in moles per litre, of the sodium tetraborate solution;
- $c_2$  is the concentration, expressed in moles per litre, of the sulfuric acid solution;

0,032 06 is the mass, in grams of sulfur, equivalent to 1 ml of 1 molar sodium tetraborate solution.

#### 10.2 Calculation using the Eschka method for chlorine correction

The total sulfur content,  $W_S$ , of the samples as analysed, expressed as a percentage by mass, is given by the equation.

$$w_S = \frac{0,032\ 06 \times c_1(V_1 - V_2)}{m} \times 100 - \frac{w_{Cl} \times 32,06}{70,92}$$

where

$w_{Cl}$  is the chlorine content, expressed as a percentage by mass, determined according to the method described in ISO 587 and corrected to the same moisture content as the test portion used for the determination of sulfur;

$\frac{32,06}{70,92}$  is the stoichiometric ratio of the relative molecular masses of sulfur and chlorine.

### 11 Precision

#### 11.1 Repeatability limit

The results of duplicate determinations, carried out at different times, in the same laboratory, by the same operator with the same apparatus, on representative portions taken from the same analysis sample, should not differ by more than the values shown in Table 1.

#### 11.2 Reproducibility critical difference

The means of the results of duplicate determinations, carried out in each of two laboratories, on representative portions taken from the same sample after the last stage of sample preparation, should not differ by more than the values shown in Table 1, at the 95 % confidence level.

### 12 Test report

The test report shall include the following information:

- a) the method used by reference to this International Standard;
- b) the identification of the sample tested;
- c) the results and the method of expression used;
- d) any unusual features noted during the determination;
- e) any operation not included in this International Standard, or regarded as optional;
- f) the date of the test.

Table 1

Sulfur	Maximum acceptable difference between results (calculated for the same moisture content)	
	Repeatability limit	Reproducibility critical difference
≤ 2,5 %	0,05 % absolute	0,10 % absolute
> 2,5 %	2 % relative	4 % relative



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