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International Standard



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## Aromatic hydrocarbons — Determination of sulphur content — Pitt-Ruprecht reduction and spectrophotometric method

*Hydrocarbures aromatiques — Dosage du soufre — Méthode par réduction et spectrophotométrie de Pitt-Ruprecht*

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## Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 5282 was developed by Technical Committee ISO/TC 78, *Aromatic hydrocarbons*, and was circulated to the member bodies in September 1979.

It has been approved by the member bodies of the following countries :

Austria	Italy	Romania
Czechoslovakia	Korea, Rep. of	South Africa, Rep. of
France	Libyan Arab Jamahiriya	United Kingdom
Germany, F. R.	Netherlands	USSR
Hungary	Philippines	
India	Poland	

No member body expressed disapproval of the document.

# Aromatic hydrocarbons — Determination of sulphur content — Pitt-Ruprecht reduction and spectrophotometric method

## 1 Scope and field of application

This International Standard specifies a method for the determination of the sulphur content of aromatic hydrocarbons boiling below 200 °C.

The method is directly applicable to sulphur contents of 0,1 to 30 mg/kg; higher contents may be determined by suitable dilution of the sample.

Alkylsulphones, arylsulphonic acids and arylsulphonates all give incomplete recovery of sulphur.

## 2 Reference

ISO 1995, *Aromatic hydrocarbons — Sampling*.

## 3 Principle

Reduction of the sulphur compounds to nickel sulphide with Raney nickel.

Stripping of the hydrogen sulphide in hydrochloric acid medium and absorption in an alkaline zinc acetate solution. Formation of methylene blue with *N,N*-dimethyl-*p*-phenylenediamine sulphate and iron(III) ammonium sulphate.

Determination of the absorbance of the blue coloured solution at a wavelength of 667 nm.

## 4 Reagents

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

### 4.1 Glycol-potassium hydroxide solution.

Dissolve 4 g of potassium hydroxide in 100 ml of ethylene glycol.

### 4.2 Sodium hydroxide solution, $c(\text{NaOH}) = 2,5 \text{ mol/l}$ .

### 4.3 Hydrochloric acid solution, $c(\text{HCl}) = 5 \text{ mol/l}$ .

### 4.4 Zinc acetate [zinc di(acetate)], 10 g/l solution.

**4.5 Propan-2-ol**, of such quality that the use of different quantities for the blank test (for example 25 and 50 ml) should give no difference in absorbance. Otherwise, the blank test shall be carried out using sulphur-free toluene, instructions for the preparation of which are given in the annex.

### 4.6 Raney nickel.

Raney nickel consists of a mixture of  $50 \pm 5 \%$  nickel and  $50 \pm 5 \%$  aluminium.

The reducing power of the Raney nickel shall be checked regularly, for example by means of a standard sample.

### 4.7 Sulphur, standard solution.

Weigh, to the nearest 1 mg, about 320 mg of thiophene (purity  $> 99 \%$ ), transfer quantitatively to a 500 ml one-mark volumetric flask containing 250 ml of the propan-2-ol (4.5), dilute to the mark with the propan-2-ol and mix.

Pipette 25,0 ml of this solution into a second dry 500 ml one-mark volumetric flask, dilute to the mark with the propan-2-ol and mix.

1 ml of this standard solution contains  $3,81 \times 10^{-5} m$  mg of S, where  $m$  is the actual mass, in milligrams, of thiophene taken.

### 4.8 Iron(III) ammonium sulphate [ammonium iron bis(sulphate)] solution.

Dissolve 120,6 g of iron(III) ammonium sulphate dodecahydrate  $[\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}]$  in 750 ml of water; while cooling and stirring, add 27 ml of sulphuric acid ( $\rho = 1,84 \text{ g/ml}$ ), dilute with water to 1 000 ml and mix.

### 4.9 *N,N*-dimethyl-*p*-phenylenediamine sulphate (4-amino-*N,N*-dimethylaniline sulphate) solution.

Dissolve 930 mg of *N,N*-dimethyl-*p*-phenylenediamine sulphate in 75 ml of water; while cooling and stirring, add 187 ml of sulphuric acid ( $\rho = 1,84 \text{ g/ml}$ ), dilute with water to 1 000 ml and mix.

#### 4.10 Potassium dichromate-nitric acid solution.

Dissolve 50 g of potassium dichromate in 500 ml of water; while stirring, add 500 ml of nitric acid ( $\rho = 1,40$  g/ml) and mix.

#### 4.11 Nitrogen, free from oxygen.

#### 4.12 Acetone.

### 5 Apparatus

Usual laboratory apparatus and

#### 5.1 Apparatus for the determination of sulphur in low boiling aromatic hydrocarbons (see figures 1 and 2).

Use PVC or other sulphur-free plastics tubing for the nitrogen supply connections. Rubber tubing is not suitable because it contains sulphur and shall not be used.

Clean new apparatus with the potassium dichromate-nitric acid solution (4.10). Rinse thoroughly with water and dry in an oven; between determinations, clean the apparatus with water and acetone (4.12).

#### 5.2 Spectrophotometer, suitable for measurements at 667 nm, with cells of optical path length 20 mm.

#### 5.3 One-mark volumetric flasks, of capacity 50, 250, 500 and 1 000 ml.

#### 5.4 Heater, with a magnetic stirring device.

### 6 Sampling

Take a representative sample of not less than 1 000 ml from the bulk of the material.

Recommended methods of sampling are given in ISO 1995.

### 7 Procedure

#### 7.1 Test portion

Take, by means of a pipette, a test portion, according to the expected sulphur content, as indicated in table 1.

Table 1 — Volume of test portion

Expected sulphur content	Volume of test portion
mg/kg	ml
0,1 to 1	50
1 to 2	25
2 to 5	10
5 to 10	5
10 to 30	1

#### 7.2 Blank test

At the same time as the determination (7.4), carry out a blank test using the same quantities of all the reagents, but with 50 ml of the propan-2-ol (4.5) in place of the test portion.

#### 7.3 Preparation of calibration graph

##### 7.3.1 Preparation of standard colorimetric solutions relating to measurements carried out with cells of optical path length 20 mm

Into a series of six dry 500 ml one-mark volumetric flasks, place the volumes of the standard sulphur solution (4.7) shown in table 2.

Table 2 — Standard colorimetric solutions

Standard sulphur solution (4.7)	Corresponding concentration of sulphur
ml	mg/l
0*	0
5,0	$m \times 0,381 \times 10^{-3}$
10,0	$2 m \times 0,381 \times 10^{-3}$
15,0	$3 m \times 0,381 \times 10^{-3}$
20,0	$4 m \times 0,381 \times 10^{-3}$
25,0	$5 m \times 0,381 \times 10^{-3}$

\* Calibration blank.

Dilute the contents of each flask to the mark with the propan-2-ol (4.5), mix and proceed as described in 7.4.2, 7.4.3 and 7.4.4, but using 50 ml of the standard colorimetric solutions in place of the test portion.

##### 7.3.2 Plotting the graph

Deduct the absorbance of the calibration blank from that of the other standard colorimetric solutions and plot a graph having, for example, the absorbances as abscissae and the corresponding sulphur concentrations, in milligrams per litre, as ordinates.

#### 7.4 Determination

##### 7.4.1 Preparation of Raney nickel

Transfer  $0,5 \pm 0,05$  g of the Raney nickel (4.6) to the reduction flask A (see figures 1 and 2), add 10 ml of the sodium hydroxide solution (4.2), cover the flask with a watch glass and wait until the violent evolution of hydrogen has ended.

Place the flask on a boiling water bath and swirl the liquid in the flask to assist dissolution of the aluminium and to bring the nickel adhering to the sides of the flask to the bottom.

After about 10 min, when all the aluminium has dissolved, take the flask from the water bath, pass nitrogen (4.11) into the flask via entry tube B and remove the supernatant liquid by suction with a small pointed glass tube.

Wash the neck of the flask with 10 to 15 ml of water.

Swirl the flask vigorously to agitate the nickel residue, allow to settle and again remove the supernatant liquid by suction.

Repeat this operation three times with water and then with 10 ml of the propan-2-ol (4.5).

Finally add 10 ml of the propan-2-ol.

#### 7.4.2 Reduction

Transfer the test portion (7.1) to the flask and connect the flask to the apparatus. Admit cooling water to the condenser.

Transfer 10 ml of the hydrochloric acid solution (4.3) to the dropping-funnel C. Transfer 5 ml of the zinc acetate solution (4.4) and 0,5 ml of the sodium hydroxide solution (4.2) to the absorption vessel F and place the latter so that the delivery tube E reaches nearly to the bottom of the absorption vessel.

Purge the apparatus with nitrogen (purified by passing first through a gas-washing bottle containing the glycol-potassium hydroxide solution (4.1) and then through a glass wool filter in the second bottle), at a flow rate of about 1,5 to 1,7 l/h; maintain this flow rate throughout the reduction.

By means of the magnetic stirrer (see 5.4), stir at such a rate that the activated nickel is distributed as homogeneously as possible within the liquid. Heat the flask at such a rate that the contents boil in about 10 min.

Maintain the heating, for a further 30 min, so that gentle refluxing occurs.

Allow the hydrochloric acid solution to drop slowly into the flask (10 ml in 5 to 10 min). (The hydrogen sulphide evolved is carried by the nitrogen to the absorption vessel.) Continue refluxing gently for a further 20 min to complete the transfer and absorption of the hydrogen sulphide.

Remove the absorption vessel F plus delivery tube E from the apparatus and turn off the stirrer, the heater and the nitrogen stream.

#### 7.4.3 Colour development

Add 10 ml of water to the absorption vessel (the spiral of the delivery tube should be 10 to 20 mm beneath the liquid surface).

Homogenize the solution by stirring with the delivery tube.

Pipette 5 ml of the *N, N*-dimethyl-*p*-phenylenediamine sulphate solution (4.9) into the delivery tube (this heavy liquid sinks to the bottom of the absorption vessel).

To prevent losses of hydrogen sulphide, add in such a way that a white floating layer (5 to 10 mm deep) remains at the upper surface of the liquid in the absorption vessel.

Pipette immediately 1 ml of the iron(III) ammonium sulphate solution (4.8) into the delivery tube and wash down with as little water as possible.

Mix, with the aid of the delivery tube, such that first the lower part and then the upper part of the liquid is homogenized (during this operation, the entire spiral should be kept beneath the liquid surface).

Stir vigorously for 1 min.

Transfer the blue solution quantitatively to a 50 ml volumetric flask (5.3), dilute to the mark with water and mix.

#### 7.4.4 Spectrophotometric measurement

After 5 min, determine the absorbance ( $E$ ) of the solution at a wavelength of 667 nm in a cell of optical path length 20 mm, having adjusted the apparatus to zero absorbance against water.

Similarly, determine the absorbance ( $E_0$ ) of the blank test solution (7.2).

Determine from the calibration graph the sulphur concentration,  $c_0$ , in milligrams per litre, corresponding to  $E - E_0$ .

## 8 Expression of results

### 8.1 Calculation

The sulphur content  $c_s$ , expressed in milligrams per kilogram, is given by the equation

$$c_s = \frac{c_0 \times V_1}{V \times \rho}$$

where

$c_0$  is the corrected concentration, in milligrams per litre, of sulphur in the test solution, corresponding to  $E - E_0$  (see 7.4.4);

$V$  is the volume, in millilitres, of the test portion (7.1);

$V_1$  is the volume, in millilitres, of the volumetric flask (see 7.4.3) (i.e. 50 ml);

$\rho$  is the density, in grams per millilitre, of the sample.

### 8.2 Precision

#### 8.2.1 Repeatability ( $r$ )

The value below which the absolute difference between two single test results on identical material, obtained by one operator in one laboratory using the same equipment within a short interval of time, using the standardized test method, may be expected to lie with a 95 % probability, is given in table 3.

#### 8.2.2 Reproducibility ( $R$ )

The value below which the absolute difference between two single test results on identical material, obtained by operators in different laboratories, using the standardized test method, may be expected to lie with a 95 % probability, is given in table 3.

Table 3 — Precision

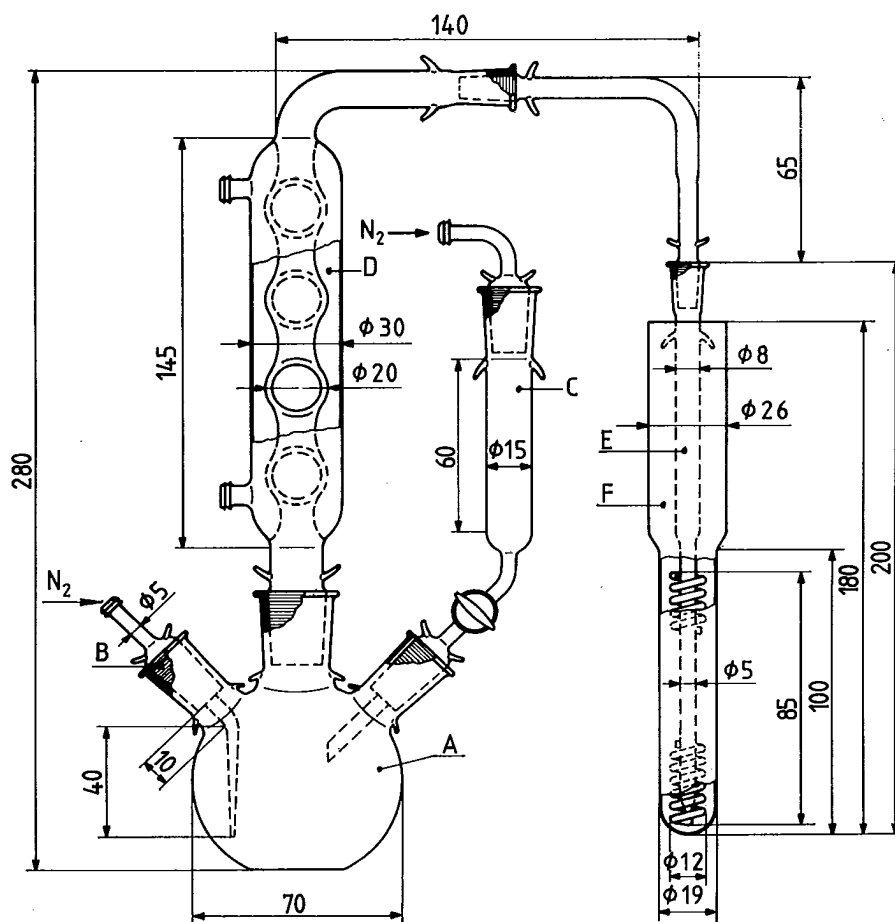
Sulphur content mg/kg	$r$	$R$
0,5	0,05	0,15
1,5	0,15	0,30
5	0,62	0,97

## 9 Test report

The test report shall contain at least the following information :

- |   |  |
|---|--|
| a) the type and identification of the product tested; | c) any deviation, by agreement or otherwise, from the procedure specified; |
| b) a reference to this International Standard;        | d) the result of the test;   |
|   | e) the date of the test.   |

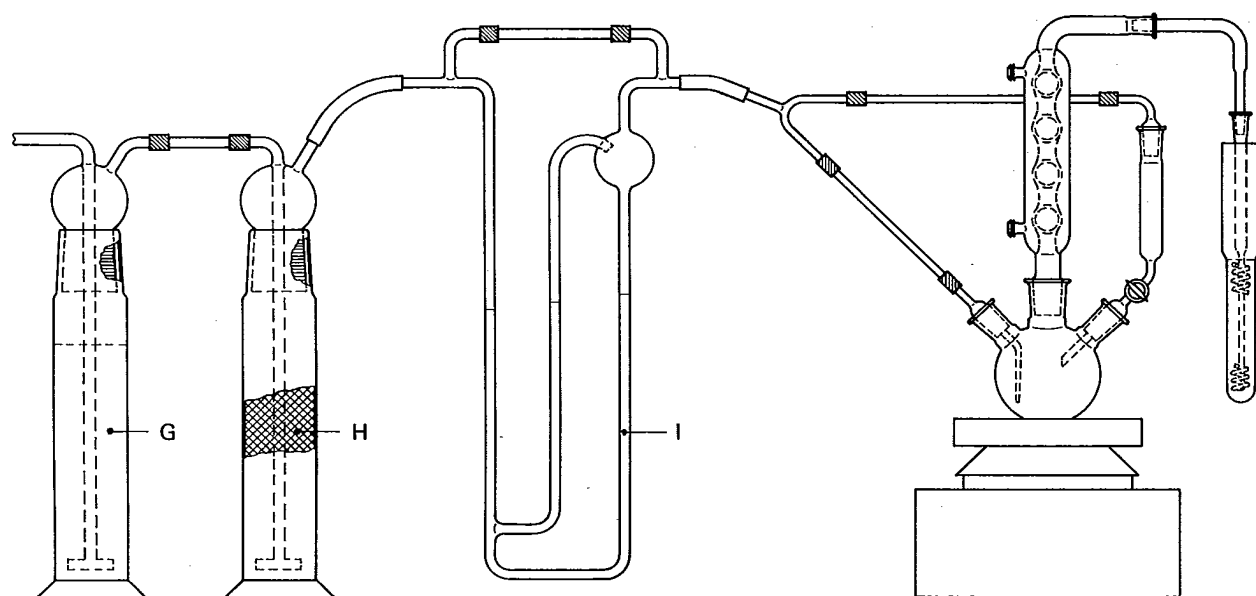
Approximate dimensions in millimetres



A Reduction flask  
B Nitrogen inlet  
C Dropping-funnel

D Reflux condenser  
E Delivery tube with mixing coil  
F Absorption vessel

Figure 1 — Reduction flask and associated equipment



- G Washing bottle with glycol-potassium hydroxide solution (4.1)  
H Washing bottle with glass wool  
I Flowmeter

Figure 2 — Apparatus for reduction

## Annex

### Preparation of sulphur-free toluene

Mix a little more than the required quantity of toluene with a third of its volume of ethanolic potassium hydroxide solution [ $c(\text{KOH}) = 1 \text{ mol/l}$ ], until a homogeneous solution is obtained.

After 1 h, wash three times with an equal volume of water.

Filter the toluene in order to remove undissolved water and transfer the filtrate to a washing device suitable for intensive treatment with concentrated sulphuric acid (for example a mixing vessel with baffles and a turbine stirrer).

Treat the toluene three times with 5 % of its own volume of sulphuric acid ( $\rho = 1,84 \text{ g/ml}$ ) for 30 min. Then wash the toluene with 5 % of its own volume of sodium hydroxide solution (4.2) and then with water.

Filter to remove undissolved water and transfer to a separating funnel.

Add a volume of mercury which is about 1 % of the volume of toluene and shake for 10 min.

**WARNING** — Attention is drawn to the dangers involved in the use of mercury. This element gives off a very poisonous vapour with danger of cumulative effects. Avoid breathing its vapour and avoid contact with eyes and skin.

Decant the toluene and filter into another separating funnel.

Repeat the treatment with successive portions of mercury until no further discoloration of mercury is observed.

Transfer the toluene to a distillation flask containing copper shavings (which have been washed with a sulphur-free solvent and dried) and distil through a Vigreux column.

Discard the first 5 % of distillate and collect the next 90 % of sulphur-free toluene.

### Bibliography

Die Bestimmung von Mikrogrammen Gesamtschwefel in Reinbenzol und anderen niedrigsiedenden Kohlenwasserstoffen, *Erdöl, Kohle, Erdgas, Petrochemie*, **22** pp. 684-687 (1969).