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# Steel and iron — Determination of total carbon and sulfur content — Infrared absorption method after combustion in an induction furnace (routine method)

*Aciers et fontes — Dosage du carbone et du soufre totaux — Méthode par absorption dans l'infrarouge après combustion dans un four à induction (méthode pratique)*

Reference number
ISO 15350:2000(E)

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## Contents

# Foreword

SO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15350 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

Annexes A to D of this International Standard are for information only.

# Steel and iron — Determination of total carbon and sulfur content — Infrared absorption method after combustion in an induction furnace (routine method)

## 1 Scope

This International Standard specifies an infrared absorption method, after combustion in an induction furnace, for the determination of the total carbon and sulfur content in steel and iron.

The method is applicable to carbon contents of mass fraction between 0,005 % and 4,3 % and to sulfur contents of mass fraction between 0,000 5 % and 0,33 %.

This method is intended to be used in normal production operations and is intended to meet all generally accepted, good laboratory practices of the type expected by recognized laboratory accreditation agencies. It uses commercially available equipment, is calibrated and calibration verified using steel and iron certified reference materials, and its performance is controlled using normal statistical process control (SPC) practices.

This method can be used in the single element mode, i.e., determination of carbon and sulfur independently or in the simultaneous mode, i.e., determination of carbon and sulfur concurrently.

## 2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 437:1982, *Steel and cast iron — Determination of total carbon content — Combustion gravimetric method*.

ISO 4934:1980, *Steel and cast iron — Determination of sulfur content — Gravimetric method*.

ISO 4935:1989, *Steel and iron — Determination of sulfur content — Infrared absorption method after combustion in an induction furnace*.

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*.

ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*.

ISO 5725-3:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*.

ISO 9556:1989, *Steel and Iron — Determination of total carbon content — Infrared absorption method after combustion in an induction furnace*.

ISO 10701:1994, *Steel and iron — Determination of sulfur content — Methylene blue spectrophotometric method*.

ISO 13902:1997, *Steel and iron — Determination of high sulfur content — Infrared absorption method after combustion in an induction furnace*.

ISO 14284:1996, *Steel and iron — Sampling and preparation of samples for the determination of chemical composition*.

# 3 Principle

## 3.1 Carbon

The carbon is converted to carbon monoxide and/or carbon dioxide by combustion in a stream of oxygen. Measurement is by infrared absorption of the carbon monoxide and carbon dioxide carried by a current of oxygen.

## 3.2 Sulfur

The sulfur is converted to sulfur dioxide by combustion in a stream of oxygen. Measurement is by infrared absorption of the sulfur dioxide carried by a current of oxygen.

# 4 Reagents

**4.1 Acetone,** the residue after evaporation shall have a mass fraction less than 0,000 5 %.

**4.2 Cyclohexane,** the residue after evaporation shall have a mass fraction less than 0,000 5 %.

**4.3 Inert ceramic,** attapulques clay impregnated with sodium hydroxide and having particle sizes from 0,7 mm to 1,2 mm for absorption of carbon dioxide.

**4.4 Pure iron,** used as an accelerator, 0,4 mm to 0,8 mm size with carbon and sulfur contents with a mass fraction of less than 0,001 % respectively.

**4.5 Magnesium perchlorate,** reagent grade, having particle size from 0,7 mm to 1,2 mm for absorption of moisture.

**4.6 Oxygen,** ultra high purity (mass fraction minimum 99,5 % )

An oxidation catalyst [copper(II) oxide or platinum] tube heated to 600 °C followed by suitable carbon dioxide and water absorbents shall be used when the presence of organic contaminants is suspected in the oxygen.

**4.7 Platinum or platinized silica,** heated to 350 °C for the conversion of carbon monoxide to carbon dioxide.

**4.8 Accelerator,** copper, tungsten-tin or tungsten for carbon determination and tungsten for sulfur determination, 0,4 mm to 0,8 mm size with carbon and sulfur contents of mass fraction less than 0,001 % and 0,000 5 % respectively.

**4.9 Cellulose cotton,** for the collection of sulfur trioxide

**4.10 Steel and iron certified reference materials (CRMs),** all reference materials used for calibration and calibration verification shall be certified by internationally-recognized bodies and validated by adequate performance on one or more national or international interlaboratory test programmes. Preference shall be given to materials that were certified using referee methods, e.g. ISO 437 and ISO 9556 for carbon, and ISO 4934, ISO 4935, ISO 10701 and ISO 13902 for sulfur, traceable to SI units as opposed to those based on other certified reference materials.

**4.11 Steel and iron reference materials (RMs),** those used for statistical process control of the method need not be certified, but adequate homogeneity data shall be available, either from the certifying body or from the laboratory that uses the material, in order to ensure the validity of the control data generated.

## 5 Apparatus

Ordinary laboratory equipment plus the following shall be used.

**5.1 C and/or S determinator,** consisting of an IR energy source, a separate measuring chamber and reference chamber, and a diaphragm acting as one plate of a parallel plate capacitor.

**5.2 Ceramic crucible,** as specified by the manufacturer of the instrumentation used and capable of withstanding combustion in an induction furnace without evolving carbon- and sulfur-containing chemicals so that achieving and maintaining blank values within specification is possible.

NOTE Carbon and sulfur contamination can usually be removed by igniting the crucibles in an electric furnace in air for not less than 40 min at 1 000 °C or not less than 15 min at 1 350 °C. After treatment, remove them from the heat, allow them to cool for 2 min to 3 min on an appropriate clean heat-resistant tray and then store them in a desiccator.

**5.3 Crucible tongs,** capable of handling recommended crucibles (5.2).

## 6 Test method

This test method is written for use with commercial analysers, equipped to carry out the included operations automatically and calibrated using steels and irons of known carbon and sulfur contents.

The analyser used will be satisfactory if it meets the criteria listed in clause 8.

### 6.1 Infrared (IR) absorption for carbon — Method A

The amount of carbon dioxide is measured by infrared absorption. Carbon dioxide ($CO_2$) absorbs IR energy at a precise wavelength within the IR spectrum. Energy of this wavelength is absorbed as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is prevented from reaching the detector by use of a precise wavelength filter. Thus, the absorption of IR energy can only be attributed to $CO_2$ and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measuring chamber. Total carbon, as $CO_2$, is monitored and measured over a period of time. See Figure A.1.

### 6.2 Infrared (IR) absorption for carbon — Method B

During specimen combustion, the flow of $CO_2$ with its oxygen gas carrier is routed through the measuring chamber (see 5.1) while oxygen alone passes through the reference chamber. Energy from the IR source passes through both chambers, simultaneously arriving at the diaphragm (capacitor plate). Part of the IR energy is absorbed by the $CO_2$ present in the measuring chamber while none is absorbed passing through the reference chamber. This creates an IR energy imbalance reaching the diaphragm, thus distorting it. This distortion alters the fixed capacitance creating an electric signal change that is amplified for measurement as $CO_2$. Total carbon, as $CO_2$, is monitored and measured over a period of time. See Figure A.2.

### 6.3 Infrared (IR) absorption for carbon — Method C, closed loop

The combustion is performed in a closed loop, where CO and $CO_2$ are detected in the same infrared cell. Each gas is measured using a solid state energy detector. Filters are used to pass the appropriate IR wavelength to each detector. In the absence of CO and $CO_2$, the energy received by each detector is maximum. During combustion, the IR absorption properties of CO and $CO_2$ gases in the chamber cause a loss of energy; therefore a loss in signal results which is proportional to concentrations of each gas in the closed loop. Total carbon, as $CO_2$ plus CO, is monitored and measured over a period of time. See Figure A.3.

### 6.4 Infrared absorption for sulfur — Method A

Sulfur dioxide ($SO_2$) absorbs infrared (IR) energy at a precise wavelength within the IR spectrum. Energy of this wavelength is absorbed as the gas passes through a cell body in which the IR energy is transmitted. All other IR energy is prevented from reaching the detector by use of a precise wavelength filter. Therefore, the absorption of

IR energy can only be attributed to $SO_2$ and its concentration is measured as changes in energy at the detector. One cell is used as both a reference and a measure chamber. Total sulfur, as $SO_2$, is monitored and measured over a period of time. See Figure A.4.

### 6.5 Infrared absorption for sulfur — Method B

During specimen combustion, the flow of $SO_2$ with its oxygen gas carrier is routed through the measuring chamber (see 5.1) while oxygen alone passes through the reference chamber. Energy from the IR source passes through both chambers, simultaneously arriving at the diaphragm (capacitor plate). Part of the IR energy is absorbed by the $SO_2$ present in the measuring chamber while none is absorbed passing through the reference chamber. This creates an IR energy imbalance reaching the diaphragm, thus distorting it. This distortion alters the fixed capacitance creating an electric signal change that is amplified for measurement as $SO_2$. Total $SO_2$ is monitored and measured over a period of time. See Figure A.5.

### 6.6 Infrared absorption for sulfur — Method C, closed loop

The combustion is performed in a closed loop where $SO_2$ is detected in an infrared cell. The $SO_2$ is measured using a solid state energy detector, and filters are used to pass the appropriate IR wavelength to the detector. During combustion, the IR absorption properties of the $SO_2$ gas in the chamber causes a loss of energy, therefore a loss in signal results which is proportional to the concentration of the gas in the closed loop. Total sulfur, as $SO_2$, is monitored and measured over a period of time. See Figure A.6.

## 7 Sampling

Carry out sampling in accordance with ISO 14284 or appropriate national standards for iron and steel.

## 8 Procedure

**WARNING — The risks related to combustion analysis are mainly burns in pre-igniting the ceramic crucibles and in effecting fusion. Use crucible tongs at all times and suitable containers for the used crucibles. Normal precautions for handling oxygen cylinders shall be taken. Oxygen from the combustion process shall be effectively removed from the apparatus since a high concentration of oxygen in a confined space can present a fire hazard.**

### 8.1 Preparation of apparatus

Assemble the apparatus and prepare it for operation according to the manufacturer's instructions. Test the furnace and analyser to ensure the absence of leaks. Make a minimum of five determinations using a specimen with measurable concentrations of carbon and sulfur and accelerator as directed in 8.3 before attempting to calibrate the system or determine the blank.

### 8.2 Test portion

**8.2.1** The sample shall be uniform in size, but not finer than 0,4 mm. It shall also be free of oil, grease and other contaminants, particularly those that could augment the carbon and sulfur contents of the sample. The same size of portion of test material shall be taken for both calibration and analysis and shall be in accordance with the manufacturer's instructions.

Wash contaminated samples and those which contain a mass fraction of less than 0,02 % carbon in acetone, cyclohexane or other suitable solvent, and dry at 70 °C to 100 °C.

Weigh, to the nearest 1 mg, a suitable amount of test sample depending on the capability of induction furnace and analyte content.

**8.2.2** The laboratory should ensure that its samples are not contaminated with carbon- and/or sulfur-containing materials. Specific sample preparation methods are not included in this International Standard. It is recommended that from time to time the laboratory conduct controlled, replicate determinations on portions of analysis-ready and analysis-ready/solvent-cleaned samples at different concentrations in order to detect contamination. If there are statistically significant differences between the analysis-ready and the analysis-ready/solvent-cleaned portions, sample preparation procedures should be reviewed and revised, as appropriate.

## 8.3 Calibration

### 8.3.1 Carbon

### 8.3.1.1 Establishing calibration ranges and selecting CRMs

Establish the total range of carbon contents to be analysed in the laboratory using this method and then divide it into sub-parts as given in the Table 1.

**Table 1 — Calibration range of carbon**

| Instrument range designation | Calibration range mass fraction % |
|---|---|
| I | 0,005 to 0,120 |
| II | 0,10 to 1,25 |
| III | 1,0 to 4,3 |

The instrument ranges given in Table 1 were selected to achieve optimum instrument performance and to set parameters for interlaboratory testing. They overlap slightly to provide operating flexibility. It is important to note that carbon contents with a mass fraction below 0,005 % or above 5 % are outside the tested range and therefore such results cannot be claimed to have been determined in compliance with this standard method. In like manner, laboratories are not obliged to calibrate over all three ranges if these are not required to meet the workload requirements.

Finally, reasonable deviations from these ranges may be made to accommodate to workload requirements the need for flexibility in matching the calibration ranges for both carbon and sulfur in simultaneous determinators.

Select a set of CRMs (4.10) for calibration and verification which, at a minimum, fall at the bottom, top, and quartile points of each operational operating range. In addition, select a CRM very low in carbon content for use in establishing the blank.

### 8.3.1.2 Adjust response of measurement system

If the instrument has more than one carbon detector (measurement system) perform the adjustment described in this section on each one.

NOTE 1 The sole purpose of this section is to provide a calibration of sufficient accuracy to establish the blank.

Establish all experimental parameters for all ranges of carbon. If simultaneous carbon and sulfur determinations are to be made, make sure that all parameters for the corresponding channels are the same. Parameters to be specified include:

- crucible: to pre-burn or not;
- accelerator: type and mass;
- sample size: mass.

It is highly recommended that crucibles be pre-burned to minimize the magnitude and variability of the blank.

Transfer the selected mass of an RM (4.11) containing about 0,05 % carbon by mass fraction, weighed to the nearest 1 mg and the selected mass of accelerator, weighed to the nearest 5 mg, to a crucible (5.2). Place the crucible on the furnace pedestal and raise the pedestal into position. Use crucible tongs (5.3) to handle pre-burned crucibles.

Start the analysis cycle; referring to the manufacturer's recommended procedure regarding entry of specimen weight and blank value.

Repeat the analysis of the RM (4.11) until the absence of drift is indicated. Following the manufacturer's instructions adjust the signal to provide a reading within 0,003 % mass fraction carbon value for the RM.

#### 8.3.1.3 Determination of blank reading

For each instrument range, transfer the selected mass of accelerator, to the nearest 0,005 g, into a crucible. Add the selected mass of the CRM (4.10) to be used to measure the carbon blank. Enter the mass of the CRM into the instrument's weight compensator. Place the crucible on the furnace pedestal and analyse. Repeat the determination three more times. Average the results. Subtract the carbon content of the CRM from the average to determine the blank value. If the blank is greater than 0,002 % by mass fraction and the standard deviation is greater than 0,000 5 % by mass fraction, find the cause of the problem, fix it, and repeat the experiment. Enter the average blank value into the analyser in accordance with the manufacturer's instructions.

The mass of accelerator taken should be adjusted, if necessary, to match the amount specified in 8.3.1.2. If the analyser does not have automatic blank correction, the blank value should be subtracted from the total result prior to any calculation.

#### 8.3.1.4 Establish calibration curves

Using CRMs (4.10) selected appropriately from the list created in 8.3.1.1, calibrate the instrument for the ranges indicated in 8.3.1.1, using the blank values determined in 8.3.1.3 in accordance with the manufacturer's instructions. If the software supplied with the instrument does not allow curve-fitting with multiple calibrants, calibrate it as instructed by the manufacturer and then immediately analyse all the calibrants as unknowns. Evaluate the results against the manufacturer’s requirements. Correct any non-compliant conditions before continuing to the next step.

### 8.3.2 Sulfur

#### 8.3.2.1 Establishing calibration range and selecting CRMs

Establish the total range of sulfur contents to be analysed in the laboratory using this method and then divide it into subparts along the following Table 2.

**Table 2 — Calibration range of sulfur**

| **Instrument range designation** | **Calibration range** mass fraction % |
|---|---|
| I | 0,000 5 to 0,050 0 |
| II | 0,03 to 0,33 |

The instrument ranges given in Table 2 were selected to achieve optimum instrument performance and to set parameters for interlaboratory testing. They overlap slightly to provide operating flexibility. It is important to note that sulfur contents below 0,000 5 % mass fraction or above 0,4 % mass fraction are outside of the tested range and therefore such results cannot be claimed to have been determined in compliance with this standard method. In like manner, laboratories are not obliged to calibrate over both ranges if these are not needed to meet the workload requirements.

Finally, reasonable deviations from these ranges may be made to accommodate to workload requirements the need for flexibility in matching the calibration ranges for both carbon and sulfur in simultaneous determinations.

Select a set of CRMs (4.10) for calibration and verification which, at a minimum, fall at the bottom, top and quartile points of each operational operating range. In addition, select a CRM which is very low in sulfur content for use in establishing the blank.

#### 8.3.2.2 Adjust response of measurement system

Follow the procedure given in 8.3.1.2 but use a reference material containing about 0,03 % mass fraction sulfur.

#### 8.3.2.3 Determination of blank readings

Follow the procedure given in 8.3.1.3, but use an appropriate CRM (4.10) containing sulfur.

#### 8.3.2.4 Establish calibration curves

Using CRMs (4.10) selected appropriately from the list created in 8.3.2.1, calibrate the instrument for the ranges indicated in 8.3.2.1, using the blank values determined in 8.3.2.3, in accordance with the manufacturer's instructions. If the software supplied with the instrument does not allow curve-fitting with multiple calibrants, calibrate it as instructed by the manufacturer and then immediately analyse all of the calibrants as unknowns. Evaluate the results against the manufacturer’s requirements. Correct any non-compliant conditions before continuing to the next step.

## 8.4 Verification of calibration

### 8.4.1 Linearity

For each calibration range for carbon and sulfur, pick two CRMs (4.10) which are known to be homogeneous below the 0,1 g sample size level. One should be lower (A), and the other above the upper (B) extremities of the calibration range. Mix these into the nine different blends, analyse them, and assess the linearity of the calibration as described below.

If more than one calibrated range uses the same combination of hardware, including detector, then these ranges may be combined for the linearity test. In such cases samples A and B shall be at the extreme ends of the combined ranges.

Prepare a series of nine crucibles according to the procedure to be used in the laboratory to analyse unknown samples. Using a four-place analytical balance, weigh a portion of each of the RMs (4.11) into each crucible, according to Table 3. Weigh, to the nearest 0,000 1 g, each portion and record the results. In Table 3, $M$ designates the mass of total sample, normally 1 g, to be taken for analysis.

Calculate the concentration of the element to be determined using the formula:

$$c_{\mathrm{E}} = \frac{M_{\mathrm{A}} \times c_{\mathrm{A}} + M_{\mathrm{B}} \times c_{\mathrm{B}}}{M_{\mathrm{A}} + M_{\mathrm{B}}}$$

where

$M_{\mathrm{A}}$ is the mass of A in grams;

$c_{\mathrm{A}}$ is the concentration of A in grams per cubic centimetre;

$M_{\mathrm{B}}$ is the mass of B in grams;

$c_{\mathrm{B}}$ is the concentration of B in grams per cubic centimetre.

Analyse the samples in random order without any undue delay and plot the determined values on the Y axis versus the calculated values on the X axis. The plot should be a straight line with a slope of very nearly 45°. If it is not, find the source of the problem, eradicate it, and repeat the experiment.

Calculate the slope of the line defined by crucibles 1 to 3 and the slope of the line defined by crucibles 7 to 9. Subtract the two slopes and calculate the percentage difference between the two slopes. If the percentage difference is greater than 0,2, consider fine-tuning the linearity of the detector or taking other appropriate corrective action and repeating the experiment. If no corrective action is taken at this time, and one or more other performance specifications are not met, then the linearity of the system shall be improved. Record the linearity test data.

An example of a linearity test, with data, is given in annex B.

**Table 3 — Series of samples for checking linearity**

| Sample No. | Mass of A<br>g | Mass of B<br>g |
|---|---|---|
| 1 | $M$ | 0 |
| 2 | $0,875 \times M$ | $0,125 \times M$ |
| 3 | $0,75 \times M$ | $0,25 \times M$ |
| 4 | $0,625 \times M$ | $0,375 \times M$ |
| 5 | $0,5 \times M$ | $0,5 \times M$ |
| 6 | $0,375 \times M$ | $0,625 \times M$ |
| 7 | $0,25 \times M$ | $0,75 \times M$ |
| 8 | $0,125 \times M$ | $0,875 \times M$ |
| 9 | 0 | $M$ |

### 8.4.2 Agreement with CRMs

For each range of each element, pick a set of CRMs (4.10) that were not used in either the calibration or the linearity check and that cover at least the low, top and mid-quartile points of the calibration range and analyse them three times each in rapid succession and in random order. Average the found values for each material. Compile the data and obtain the average of the determinations for each CRM and create a table along the following lines:

| Instrument range | CRM | Certified value | Found value |
|---|---|---|---|
| | | | |

Plot the average of the found values versus the certified values and draw a best-fit straight line through the points. Then draw an ideal straight line that would result if all found values were exactly the same as their corresponding certified values. If the differences between these lines (not individual data points) exceed the values in Table 4, recalibrate and take other corrective action as needed to bring the performance of the instrument into this specification. This test ensures that the instrument's calibration is sufficiently bias-free over its calibration range and that its calibration is traceable to a number of reliable CRMs.

**Table 4 — Target maximum allowed difference**

| **Concentration** mass fraction | **Target maximum allowed difference** % |
|---|---|
| 0,000 5 | 0,000 1 |
| 0,005 0 | 0,000 2 |
| 0,008 0 | 0,000 3 |
| 0,010 5 | 0,000 4 |
| 0,012 0 | 0,000 8 |
| 0,030 | 0,001 |
| 0,100 | 0,002 |
| 0,170 | 0,003 |
| 0,250 | 0,004 |
| 0,300 | 0,005 |
| 0,400 | 0,007 |
| 0,600 | 0,008 |
| 0,800 | 0,009 |
| 0,900 | 0,010 |
| 2,000 | 0,020 |
| 3,000 | 0,030 |
| 4,000 | 0,040 |
| 5,000 | 0,045 |

## 8.5 Set-up of statistical process control (SPC) parameters

### 8.5.1 Selection of RMs for SPC

For each element and each concentration range defined in 8.3.1.1 and 8.3.2.1, select an RM (4.11) which falls in the mid-portion of the range. The RM need not be certified, but homogeneity data shall be available to demonstrate short-term precision, at the 95 % confidence level, at least within the target maximum allowed differences given in 8.4.2. The laboratory shall provide sufficient material to last well past the start-up period so that the method's performance can be reliably tracked over an extended period of time.

### 8.5.2 Establishment of control limits

Laboratories shall establish written SPC data-generating and operating protocols that are consistent with good laboratory practice and are capable of controlling the performance of the instrument to be in compliance with 8.4.2. Minimum operating control requirements are given in 8.6.

## 8.6 Document operating procedure

Following the instructions given in the preceding sections, the manufacturer's instructions and laboratory-specific protocols, document the specific operating procedure to be followed in the laboratory for performing this method. Be sure to include all within-laboratory specified details of the procedure which might influence the performance of the method.

### 8.7 Analysis of samples

At the beginning of each shift, whenever there is a change of personnel assigned to operate the equipment, or whenever there is reason to believe that calibration may have changed, verify the calibration of each range of the instrument to be used according to the following procedure. Analyse one CRM (4.10) at the bottom of the calibration range and another at the top of the calibration range. If the results do not agree within the target maximum values given in 8.4.2, identify the source of the problem, eradicate it and repeat the steps in 8.3 to 8.4.2. When the daily calibration verifiers have been satisfactorily analysed, analyse the SPC material and, if it is within control, document the results and proceed with the analysis of unknown samples. Analyse an SPC sample at least every 2 h during the analysis campaign. At the end of the campaign, repeat the analysis of the two daily calibration verifiers. If any of the daily verification samples are out of control, identify the problem, eradicate it and re-analyse those samples shown to be in possible error. If all verifiers are within control, report the results.

## 9 Expression of results

### 9.1 Method of calculation

Carbon and sulfur content $W$, expressed as a mass fraction, are given by the following equation:

$$W = 100 \times \frac{(m_\mathrm{T} - m_0) \times C}{m}$$

where

$m_\mathrm{T}$ is the mass, in grams, of the element in the test portion;

$m_0$ is the mass, in grams, of the element in the blank test portion;

$C$ is the weight compensator setting;

$m$ is the mass, in grams, of the test portion.

NOTE Since most commercially available instruments calculate percent concentrations directly, including corrections for blank and sample weight, calculations by the analyst are not required.

### 9.2 Precision

#### 9.2.1 Carbon

A planned trial of this method was carried out by 31 laboratories, at 20 levels of carbon, each laboratory making three determinations of carbon content at each level.

NOTE 1 Two of the three determinations were carried out under repeatability conditions ad defined in ISO 5725-1; i.e., one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

NOTE 2 The third determination was carried out at a different time (on a different day), by the same operator as in note 1 of 8.2.1, using the same apparatus with a new calibration.

The test samples used and mean results obtained are listed in table C.1.

The results obtained were treated statistically in accordance with ISO 5725, Parts 1, 2 and 3.

The data obtained showed a logarithmic relationship between carbon content and repeatability ($r$) and reproducibility ($R_\mathrm{W}$ and $R$) of the test results (see note 3) as summarized in table 5. The graphical representation of the figures is given in Annex D.

NOTE 3 From the two values obtained on day 1 the repeatability ($r$) and reproducibility ($R$) were calculated using the procedure specified in ISO 5725. From the first value obtained on day 1 and the value obtained day 2, the within laboratory reproducibility ($R_W$) was calculated.

**Table 5 — Results for repeatability limit and reproducibility limits of carbon**

| Mass fraction of carbon | Repeatability limit | Reproducibility limits | |
|---|---|---|---|
| % | $r$ | $R_W$ | $R$ |
| 0,002 | 0,000 27 | 0,000 29 | 0,001 07 |
| 0,005 | 0,000 46 | 0,000 52 | 0,001 76 |
| 0,01 | 0,000 70 | 0,000 81 | 0,002 58 |
| 0,02 | 0,001 04 | 0,001 26 | 0,003 76 |
| 0,05 | 0,001 79 | 0,002 27 | 0,006 21 |
| 0,10 | 0,002 68 | 0,003 55 | 0,009 07 |
| 0,20 | 0,004 03 | 0,005 55 | 0,013 25 |
| 0,50 | 0,006 90 | 0,010 02 | 0,021 87 |
| 1,0 | 0,010 36 | 0,015 65 | 0,031 95 |
| 2,0 | 0,015 56 | 0,024 47 | 0,046 66 |
| 4,3 | 0,024 38 | 0,040 07 | 0,070 90 |

### 9.2.2 Sulfur

A planned trial of this method was carried out by 31 laboratories, at 20 levels of sulfur, each laboratory making three determinations of sulfur content at each level (see notes 1 and 2 of 9.2.1).

The test samples used and mean results obtained are listed in Table C.2.

The results obtained were treated statistically in accordance with ISO 5725, parts 1, 2, and 3.

The data obtained showed a logarithmic relationship between sulfur content and repeatability ($r$) and reproducibility ($R$ and $R_W$) of the test results (see note 3 of 8.2.1) as summarized in Table 6. The graphical representation of the figures is given in annex D.

## 10 Test report

The test report shall include the following information:

a) all information necessary for the identification of the sample, the laboratory and the date of the analysis;

b) the method used, by reference to this International Standard;

c) the results, and the form in which they are expressed;

d) any unusual features noted during the determination;

e) any operation not specified in this International Standard, or any optional operation which may have influenced the results.

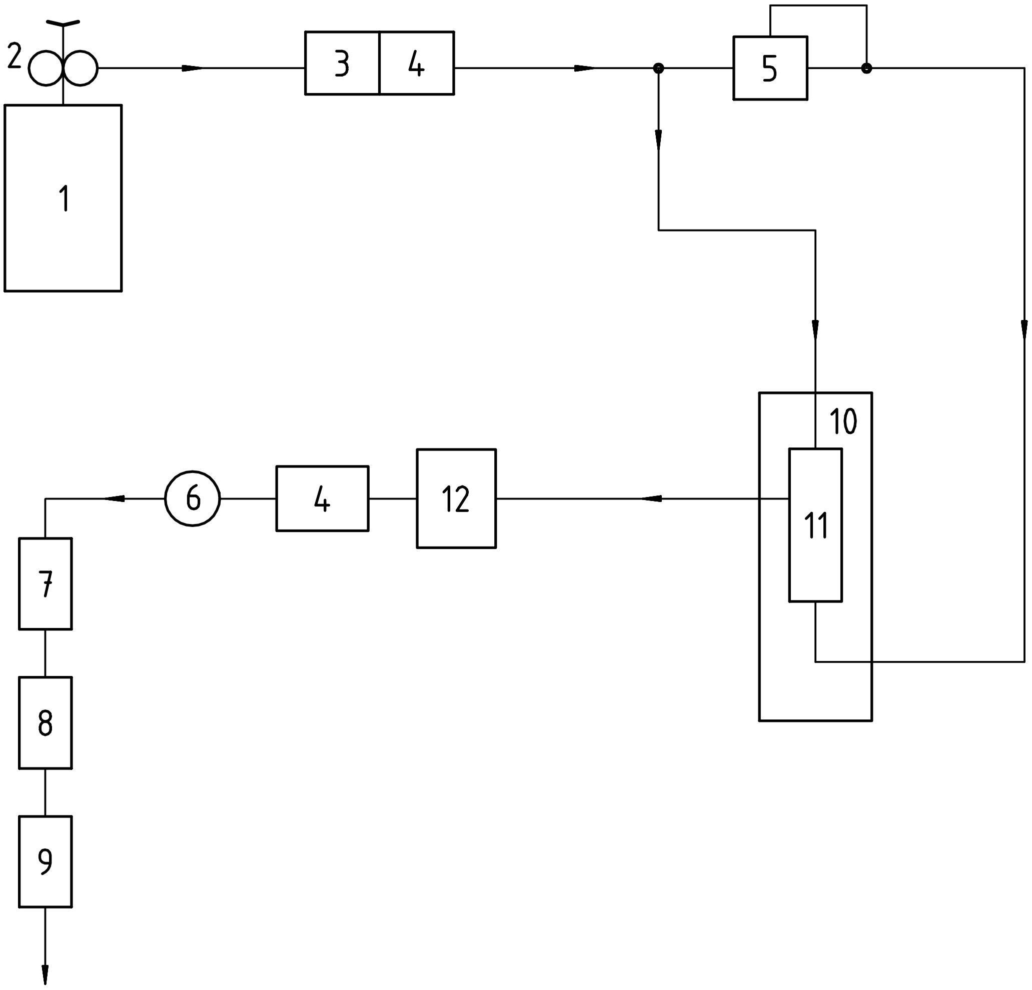
**Table 6 — Results for repeatability limit and reproducibility limits of sulfur**

| Mass fraction of sulfur | Repeatability limit | Reproducibility limits | |
|---|---|---|---|
| % | $r$ | $R_W$ | $R$ |
| 0,000 5 | 0,000 11 | 0,000 15 | 0,000 29 |
| 0,001 | 0,000 18 | 0,000 23 | 0,000 48 |
| 0,002 | 0,000 28 | 0,000 36 | 0,000 78 |
| 0,005 | 0,000 53 | 0,000 65 | 0,001 48 |
| 0,010 | 0,000 85 | 0,001 02 | 0,002 43 |
| 0,02 | 0,001 36 | 0,001 60 | 0,003 96 |
| 0,05 | 0,002 55 | 0,002 91 | 0,007 59 |
| 0,10 | 0 004 09 | 0,004 56 | 0,012 40 |
| 0,2 | 0,006 56 | 0,007 15 | 0,020 27 |
| 0,3 | 0,008 65 | 0,009 30 | 0,027 02 |

# Annex A

(informative)

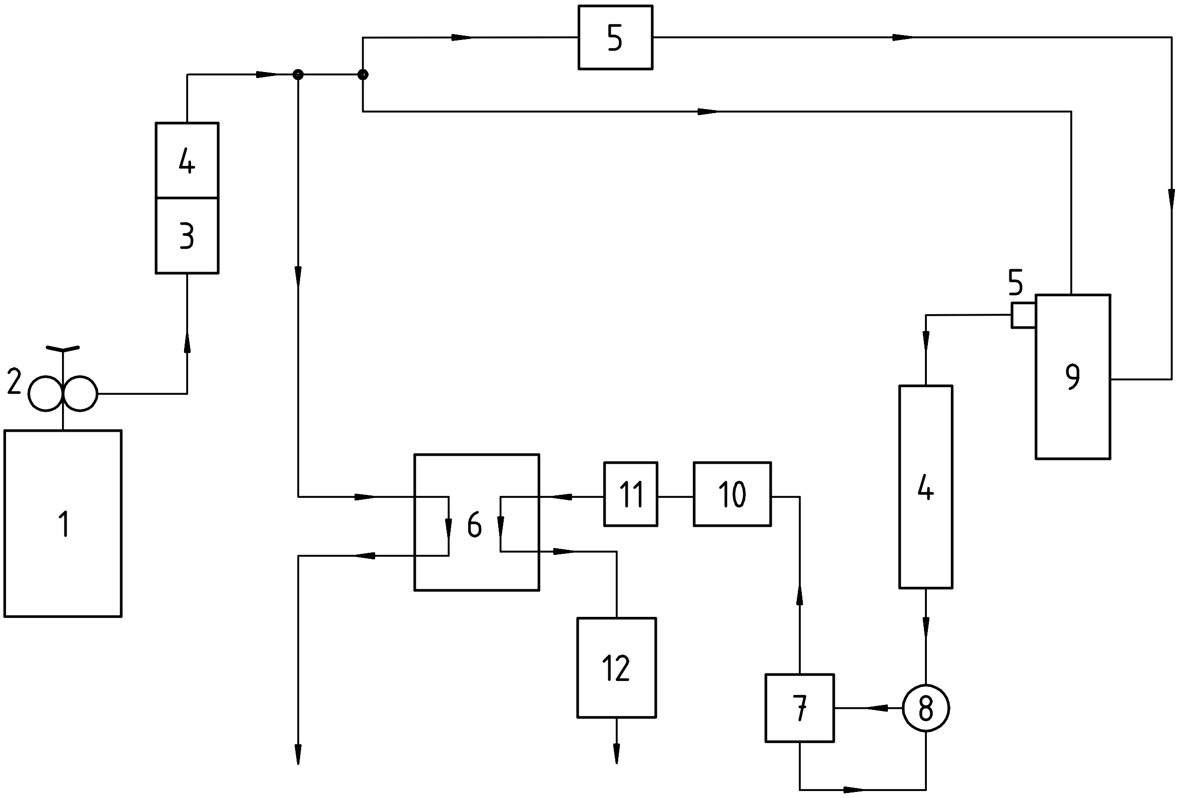
## Examples of diagram for analytical principles



**Key**

| | | | | | |
|---|---|---|---|---|---|
| 1 | Oxygen cylinder | 5 | Regulator | 9 | $CO_2$ IR cell/readout |
| 2 | Two stage regulator | 6 | Flow controller | 10 | Induction furnace |
| 3 | Sodium hydroxide impregnated clay | 7 | CO to $CO_2$ converter | 11 | Combustion area |
| 4 | Magnesium perchlorate | 8 | $SO_3$ trap | 12 | Dust trap |

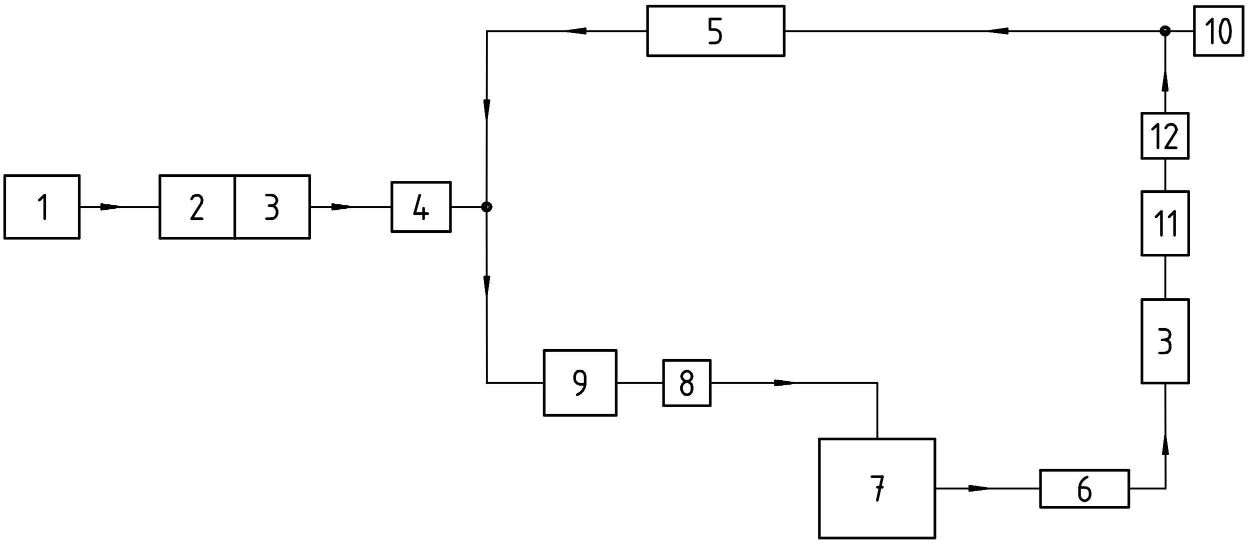
**Figure A.1 — Infrared absorption for carbon — Method A**



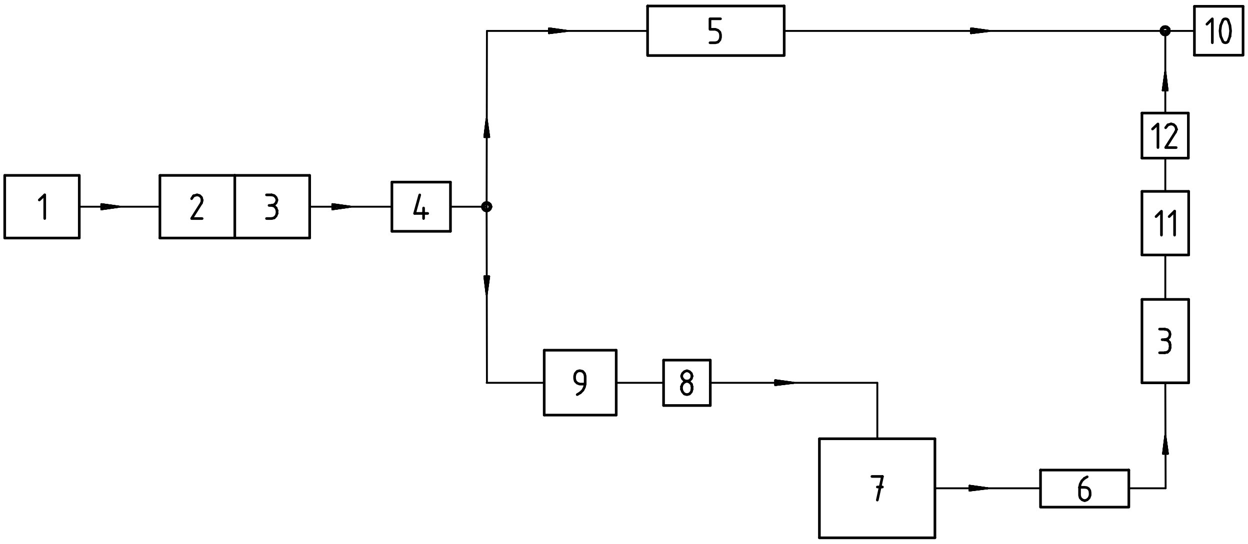
**Key**

| | | | | | |
|---|---|---|---|---|---|
| 1 | Oxygen cylinder | 5 | Dust trap | 9 | Combustion chamber |
| 2 | Two stage regulator | 6 | IR cell/readout | 10 | CO to $CO_2$ converter |
| 3 | Sodium hydroxide impregnated clay | 7 | Orifice | 11 | $SO_3$ trap |
| 4 | Magnesium perchlorate | 8 | Pressure regulator | 12 | Measure flow rotameter |

Figure A.2 — Infrared absorption for carbon — Method B



a) **Operate mode**

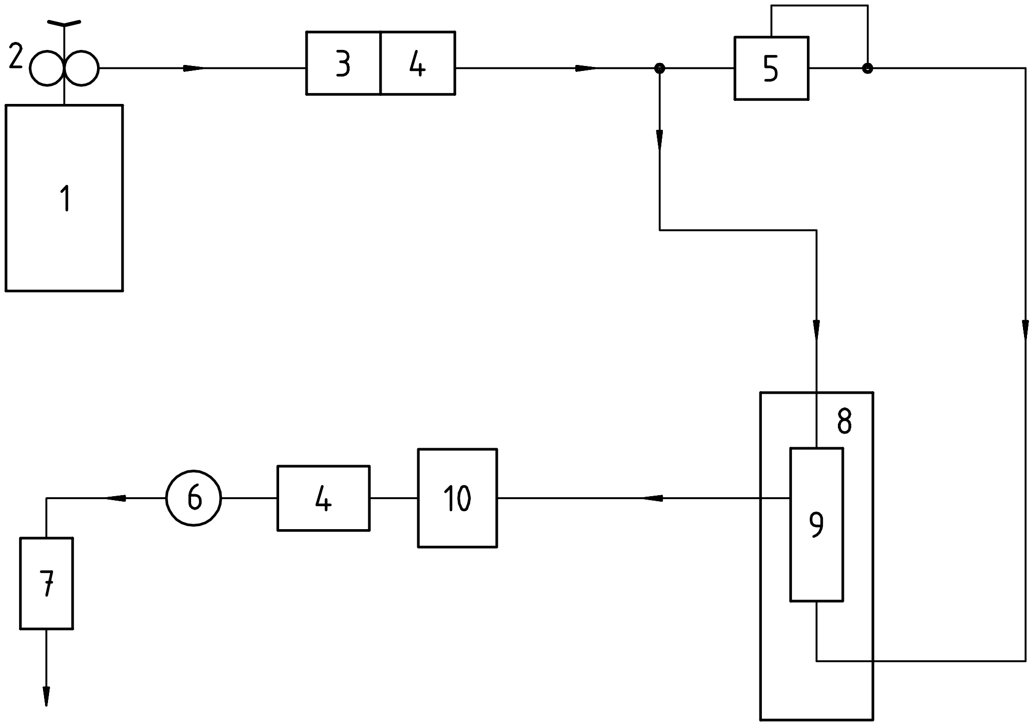


b) **Purge mode**

**Key**

| | | | | | |
|---|---|---|---|---|---|
| 1 | Oxygen cylinder | 5 | IR cell/readout | 9 | Flowmeter |
| 2 | Sodium hydroxide impregnated clay | 6 | Dust trap | 10 | Exhaust |
| 3 | Magnesium perchlorate | 7 | Furnace | 11 | CO to $CO_2$ convertor |
| 4 | Pressure regulator | 8 | Pump | 12 | $SO_3$ trap |

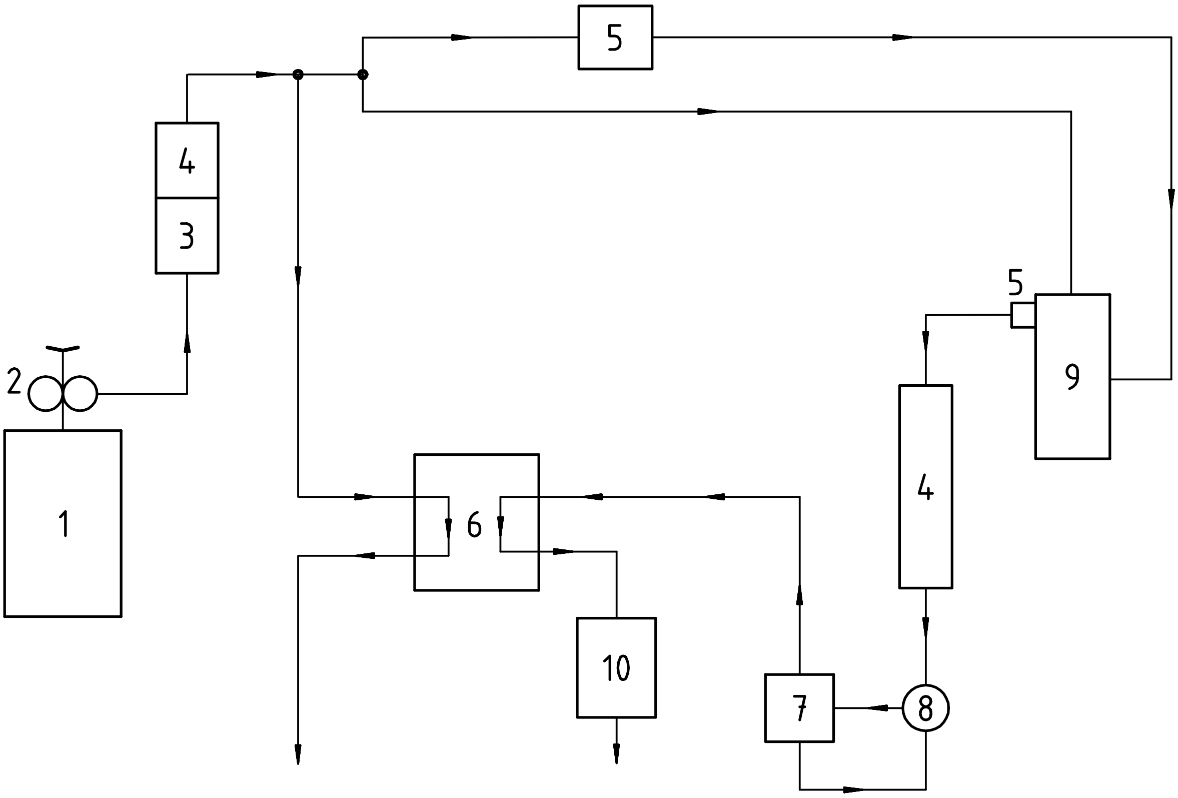
**Figure A.3 — Infrared absorption for carbon — Method C, closed loop**



**Key**

1 Oxygen cylinder
2 Two stage regulator
3 Sodium hydroxide impregnated clay
4 Magnesium perchlorate
5 Regulator
6 Flow controller
7 IR cell/readout
8 Induction furnace
9 Combustion area
10 Dust trap

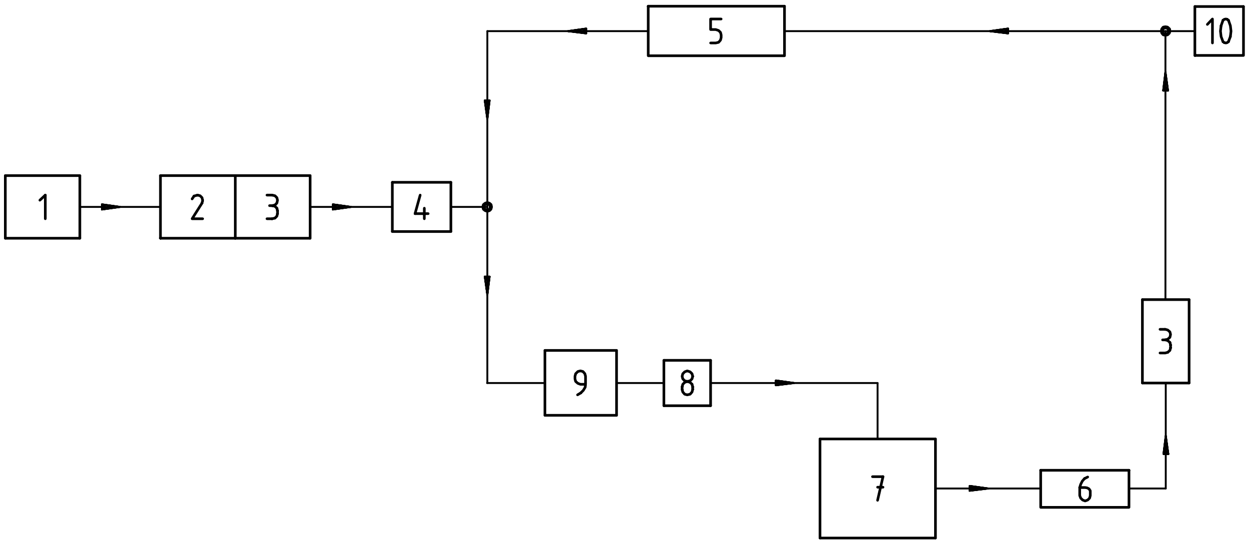
Figure A.4 — Infrared absorption for sulfur — Method A



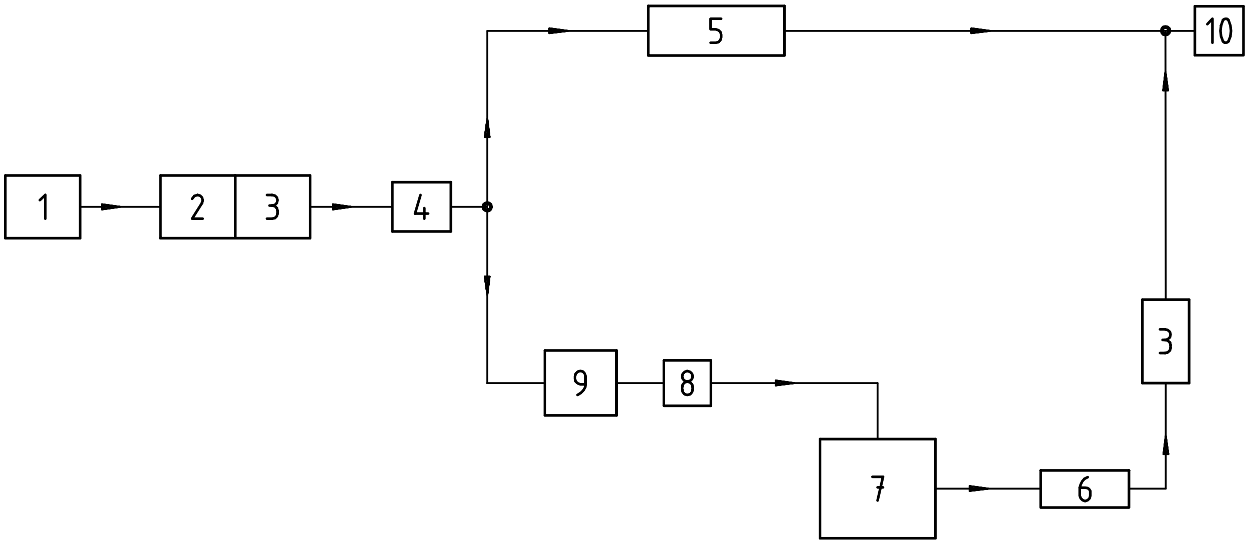
**Key**

1 Oxygen cylinder
2 Two stage regulator
3 Sodium hydroxide impregnated clay
4 Magnesium perchlorate
5 Dust trap
6 IR cell/readout
7 Orifice
8 Pressure regulator
9 Combustion chamber
10 Measure flow rotameter

Figure A.5 — Infrared absorption for sulfur — Method B



a) **Operate mode**



b) **Purge mode**

**Key**

| | |
|---|---|
| 1 | Oxygen cylinder |
| 2 | Sodium hydroxide impregnated clay |
| 3 | Magnesium perchlorate |
| 4 | Pressure regulator |
| 5 | IR cell/readout |
| 6 | Dust trap |
| 7 | Furnace |
| 8 | Pump |
| 9 | Flowmeter |
| 10 | Exhaust |

Figure A.6 — Infrared absorption for sulfur — Method C, closed loop

# Annex B
(informative)

# Example calculation of a linearity check

Test: Carbon over the mass fraction range 0,005 % to 0,12 %

Reference materials:

A: Euronorm CRM 088-1, 0,002 5 % carbon

B: Analysen Kontrolprobe 038-1, 0,159 % carbon

Data are shown in table B.1.

**Table B.1 — Series of calculation for checking linearity**

| Sample No. | Mass of A<br>g | Mass of B<br>g | Mass fraction of calculated carbon<br>% | Mass fraction of determined carbon<br>% |
|---|---|---|---|---|
| 1 | 1,000 0 | 0 | 0,002 5 | 0,002 5 |
| 2 | 0,875 0 | 0,125 0 | 0,022 1 | 0,022 8 |
| 3 | 0,750 0 | 0,250 5 | 0,041 7 | 0,041 8 |
| 4 | 0,625 3 | 0,375 0 | 0,061 2 | 0,061 0 |
| 5 | 0,500 2 | 0,500 5 | 0,080 3 | 0,080 5 |
| 6 | 0,374 9 | 0,625 7 | 0,099 8 | 0,099 2 |
| 7 | 0,250 1 | 0,749 9 | 0,119 8 | 0,117 8 |
| 8 | 0,124 9 | 0,874 8 | 0,139 4 | 0,137 6 |
| 9 | 0 | 0,999 6 | 0,159 0 | 0,157 0 |

Set-up for normal operation — Low carbon channel

Run samples random order

$$c_{\mathrm{E}} = \frac{M_{\mathrm{A}} \times c_{\mathrm{A}} + M_{\mathrm{B}} \times c_{\mathrm{B}}}{M_{\mathrm{A}} + M_{\mathrm{B}}}$$

Calculations:

Slope from sample 1 to sample 3: (0,041 8 – 0,002 5)/(0,041,7 – 0,002 5) = 1,001 3

Slope from sample 7 to sample 9: (0,157 0 – 0,117 8)/(0,159,0 – 0,119 8) = 1,001 8

Difference: 1,001 8 – 1,001 3 = 0,000 5

Percent difference: 100 × 0,000 5/(1,001 8 + 1,001 3)/2 = 0,05 %

0,05 % is smaller than 0,2 % and the linearity is acceptable.

# Annex C
(informative)

## Additional information on international cooperative tests

Tables 5 and 6 were derived from the results of international analytical trials carried out in 1995 on 20 steel samples in 13 countries involving 31 laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 1177, revised in 1998. The precision data are presented in graphical form in annex D.

The test samples used are listed in Table C.1. Detailed results for carbon and sulfur content obtained in international cooperative tests are shown in Table C.2 and Table C.3 respectively.

## Table C.1 — Test samples used

| CRM | C | S | Si | Mn | P | Ni | Cr | Mo | Cu | V | Co | Ti | Others |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| JSS 110-10 | 4,28 | 0,014 9 | 1,74 | 0,39 | 0,068 | 0,013 | 0,019 |  | 0,004 | 0,009 |  | 0,055 | As:0,001 6;<br>N:0,004 7 |
| ECRM 483-1 | 2,46 | 0,103 | 1,75 | 0,596 | 0,615 |  | 0,039 |  |  |  |  |  | Sn:0,13 |
| BCS 402/2 | 1,311 | 0,013 8 | 0,111 | 0,228 | 0,016 1 | 0,808 | 0,652 | 0,140 | 0,302 | 0,194 |  |  | Al:0,161;<br>N:0,069 |
| JSS 601-09 | 1,06 | 0,007 2 | 0,23 | 0,70 | 0,015 | 0,108 | 0,76 | 0,107 | 0,094 | 0,063 |  |  | W:1,13;<br>N:0,016 5 |
| ST604 | 1 | 0,031 | 0,25 | 0,36 |  |  |  |  |  |  |  |  | N:0,003 3 |
| JK 12A | 0,886 | 0,023 | 0,30 | 0,312 | 0,020 | 0,191 | 4,04 | 4,85 | 0,062 | 1,94 | 0,189 |  | W:6,42;<br>Sn:0,007;<br>Pb:0,000 4;<br>N:0,025 9 |
| JSS 606-08 | 0,76 | 0,000 8 | 0,28 | 0,31 | 0,016 | 0,065 | 4,00 | 0,58 | 0,027 | 0,83 | 0,12 |  | W:17,16;<br>N:0,029 |
| ST 642 | 0,68 | 0,031 | 0,083 | 1,26 | 0,035 | 0,21 | 0,15 | 0,19 | 0,086 | 0,048 |  | 0,008 | Sn:0,011;<br>Al:0,15 |
| ST 664 | 0,45 | 0,30 |  |  |  |  |  |  |  |  |  |  |  |
| BCS 410/2 | 0,428 | 0,041 | 1,10 | 0,419 | 0,074 | 2,07 | 1,684 | 0,432 | 0,436 | 0,44 | 0,024 8 |  | Al:0,046;<br>As:0,005 3;<br>N:0,015 5 |
| JSS 503-06 | 0,33 | 0,019 4 | 0,28 | 0,64 | 0,028 | 1,24 | 0,71 | 0,013 | 0,083 |  |  |  | N:0,011 4 |
| ST 639 |  |  |  | 0,001 6 |  | 1,69 | 0,65 |  |  |  |  |  |  |
| NIST SRM 133b | 0,128 | 0,328 | 0,327 | 1,07 | 0,018 | 0,230 | 12,63 | 0,052 | 0,080 | 0,071 |  |  |  |
| ST 608 | 0,12 | 0,016 | 0,49 | 1,06 | 0,014 | 0,49 | 0,28 | 0,036 | 0,021 | 0,034 | 0,027 | 0,015 | Sn:0,019;<br>Al:0,006;<br>B:0,001;<br>Sb:0,000 4 |
| IRSID 024-1 | 0,104 | 0,235 | 0,139 | 0,728 | 0,018 |  |  |  |  |  |  |  | Pb:0,287 |
| ST 651 | 0,062 | 0,048 | 0,035 | 2,10 | 0,012 | 0,034 | 1,27 | 0,79 | 0,043 | 0,004 | 0,23 | 0,004 | Sn:0,049;<br>Al:0,23;<br>B:0,012;<br>Nb:0,005;<br>Zr:0,030:<br>As:0,08;<br>Sb:0,000 8;<br>W:0,027;<br>Ca:0,002 2 |
| ST 629 | 0,033 |  | 1,11 |  | 0,155 |  |  | 0,56 |  | 0,088 |  | 0,25 | Al:0,088 |
| ECRM 287-1 | 0,016 | 0,001 4 | 0,569 | 1,48 | 0,027 | 10,35 | 18,61 | 0,247 | 0,203 |  | 0,148 |  | B:0,89;<br>N:0,019 |
| NIST SRM 2165 | 0,005 9 | 0,003 8 |  | 0,144 | 0,005 2 | 0,155 | 0,050 | 0,005 5 | 0,001 3 | 0,004 | 0,001 2 | 0,005 1 | As:0,001;<br>Sn:0,002;<br>Nb:0,000 4 |
| ST 635 | 0,005 |  |  | 0,006 |  |  |  |  |  |  |  |  |  |

### Table C.2 — Detailed results obtained in international cooperative tests for carbon

| | Mass fraction carbon<br>% | | | Precision data | | |
|---|---|---|---|---|---|---|
| **Sample** | **Certified** | **Found** | **Found** | **Repeatability limit** | **Reproducibility limits** | |
| | $R_w$ | $\bar{w}_1$[a] | $\bar{w}_2$[b] | $r$ | $R_w$ | $R$ |
| JSS 110-10 | 4,28 | 4,226 | 4,226 | 0,040 9 | 0,073 8 | 0,139 6 |
| ECRM 483-1 | 2,46 | 2,465 | 2,465 | 0,036 2 | 0,038 1 | 0,093 5 |
| BCS 402/2 | 1,311 | 1,308 | 1,308 | 0,008 2 | 0,019 8 | 0,021 0 |
| JSS 601-09 | 1,06 | 1,056 | 1,056 | 0,010 3 | 0,018 8 | 0,031 1 |
| ST604 | 1,00[c] | 0,994 | 0,994 | 0,008 2 | 0,010 9 | 0,023 2 |
| JK 12-A | 0,886 | 0,887 | 0,886 | 0,007 8 | 0,013 6 | 0,020 2 |
| JSS 606-08 | 0,76 | 0,767 | 0,767 | 0,005 4 | 0,012 5 | 0,022 2 |
| ST-642 | 0,68[c] | 0,668 | 0,668 | 0,008 6 | 0,011 4 | 0,047 2 |
| ST 664 | 0,45[c] | 0,444 | 0,445 | 0,005 2 | 0,005 9 | 0,015 0 |
| BCS 410/2 | 0,428 | 0,428 | 0,429 | 0,005 1 | 0,008 3 | 0,016 2 |
| JSS 503-06 | 0,33 | 0,330 | 0,330 | 0,004 6 | 0,005 2 | 0,013 6 |
| ST 639 | 0,32[c] | 0,305 | 0,305 | 0,007 4 | 0,008 0 | 0,028 5 |
| NIST SRM 133b | 0,127 | 0,124 | 0,124 | 0,002 8 | 0,004 8 | 0,007 1 |
| ST 608 | 0,12[c] | 0,112 | 0,112 | 0,002 2 | 0,002 9 | 0,008 2 |
| IRSID 024-1 | 0,104 | 0,100 | 0,100 | 0,002 4 | 0,003 1 | 0,007 2 |
| ST 651 | 0,062[c] | 0,053 | 0,053 | 0,002 7 | 0,002 3 | 0,010 0 |
| ST 629 | 0,033[c] | 0,030 | 0,030 | 0,002 5 | 0,002 3 | 0,005 0 |
| ECRM 287-1 | 0,016 4 | 0,016 | 0,016 | 0,000 62 | 0,000 98 | 0,002 2 |
| NIST SRM 2165 | 0,005 9 | 0,006 | 0,006 | 0,000 55 | 0,000 59 | 0,001 9 |
| ST 635 | 0,005[c] | 0,004 | 0,004 | 0,000 46 | 0,000 63 | 0,002 8 |

[a] $\bar{w}_1$ is the general mean within a day.

[b] $\bar{w}_2$ is the general mean between days.

[c] Non-certified value.

**Table C.3 — Detailed Results obtained in international cooperative tests for sulfur**

| | Mass fraction sulfur<br>% | | | Precision data | | |
|---|---|---|---|---|---|---|
| **Sample** | **Certified** | **Found** | **Found** | **Repeatability limit** | **Reproducibility limit** | |
| | $R_\mathrm{w}$ | $\overline{w}_1$[a] | $\overline{w}_2$[b] | $r$ | $R_\mathrm{w}$ | $R$ |
| NIST SRM 133b | 0,330 | 0,328 | 0,328 | 0,008 5 | 0,011 3 | 0,042 |
| ST 664 | 0,30[c] | 0,286 | 0,287 | 0,010 7 | 0,011 7 | 0,026 |
| IRSID 024-1 | 0,235 | 0,238 | 0,239 | 0,007 6 | 0,005 6 | 0,023 |
| ECRM 483-1 | 0,103 | 0,104 | 0,104 | 0,004 8 | 0,006 4 | 0,014 |
| ST 651 | 0,048[c] | 0,041 1 | 0,041 1 | 0,002 1 | 0,002 2 | 0,010 |
| BCS 410/2 | 0,041 | 0,041 0 | 0,041 1 | 0,001 8 | 0,002 5 | 0,008 8 |
| ST 604 | 0,031[c] | 0,030 0 | 0,030 0 | 0,002 4 | 0,002 6 | 0,004 7 |
| ST 642 | 0,031[c] | 0,030 6 | 0,030 6 | 0,001 51 | 0,001 7 | 0,003 8 |
| JK 12-A | 0,023 | 0,022 9 | 0,022 9 | 0,001 12 | 0,001 7 | 0,002 88 |
| JSS 503-06 | 0,019 4 | 0,018 7 | 0,018 6 | 0,001 11 | 0,001 4 | 0,002 58 |
| ST 629 | 0,018[c] | 0,018 0 | 0,018 0 | 0,001 24 | 0,001 5 | 0,003 43 |
| ST 608 | 0,016[c] | 0,016 0 | 0,015 9 | 0,001 20 | 0,001 8 | 0,002 28 |
| JSS 110-10 | 0,014 9 | 0,013 0 | 0,013 1 | 0,000 86 | 0,000 89 | 0,003 87 |
| BCS 402/2 | 0,013 8 | 0,013 1 | 0,013 1 | 0,001 40 | 0,001 26 | 0,003 27 |
| JSS 601-09 | 0,007 2 | 0,006 5 | 0,006 5 | 0,001 18 | 0,000 64 | 0,001 70 |
| ST 635 | 0,006[c] | 0,006 3 | 0,006 3 | 0,000 47 | 0,000 62 | 0,001 340 |
| NIST SRM 2165 | 0,003 8 | 0,003 7 | 0,003 7 | 0,000 30 | 0,000 49 | 0,000 828 |
| ST 639 | 0,001 6[c] | 0,001 7 | 0,001 7 | 0,000 26 | 0,000 37 | 0,000 694 |
| ECRM 287-1 | 0,001 4 | 0,001 2 | 0,001 15 | 0,000 18 | 0,000 20 | 0,000 862 |
| JSS 606-08 | 0,000 8 | 0,000 8 | 0,000 75 | 0,000 19 | 0,000 32 | 0,000 526 |

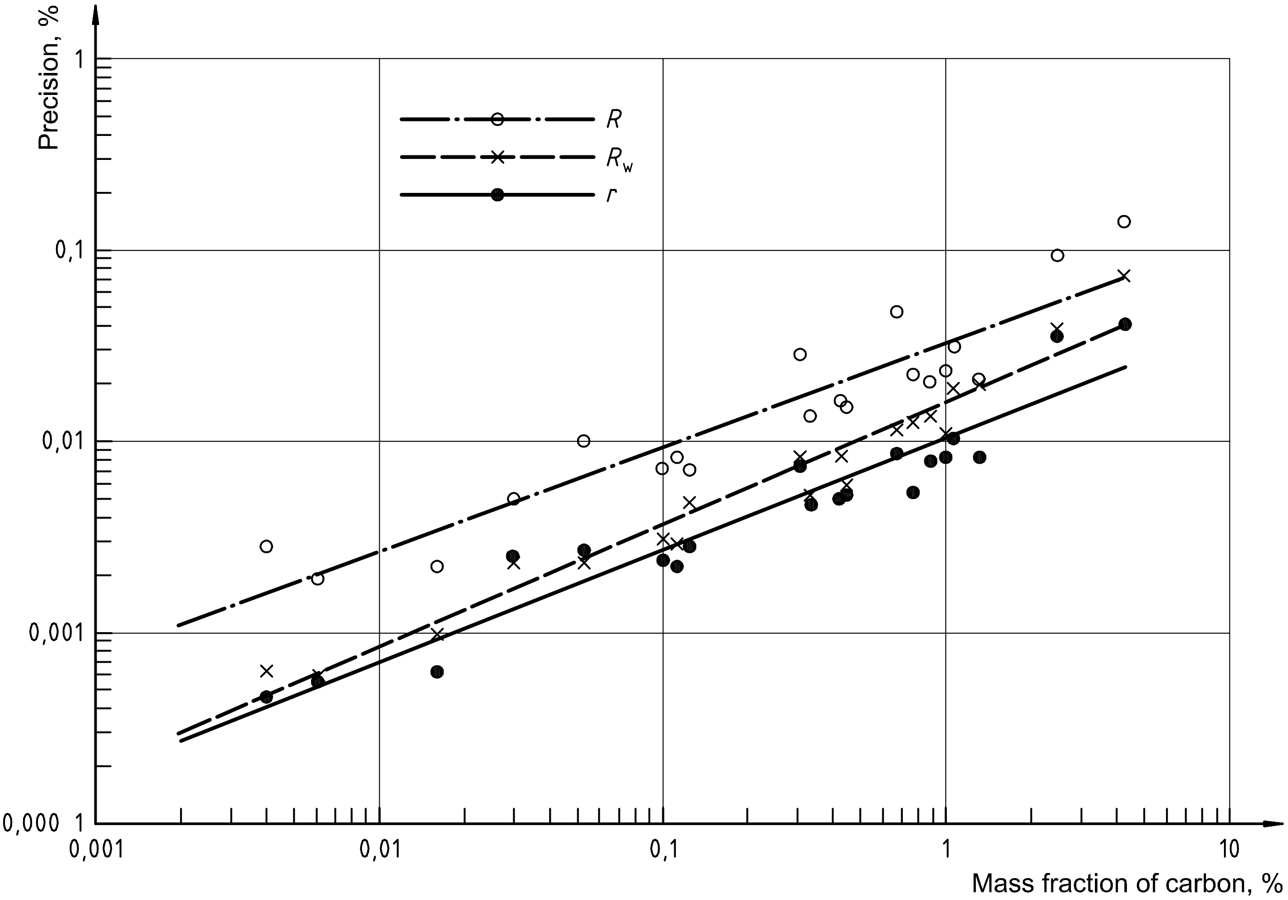
[a] $\overline{w}_1$ is the general mean within a day.

[b] $\overline{w}_2$ is the general mean between days.

[c] Non-certified value.

# Annex D
(informative)

## Graphical representation of precision data



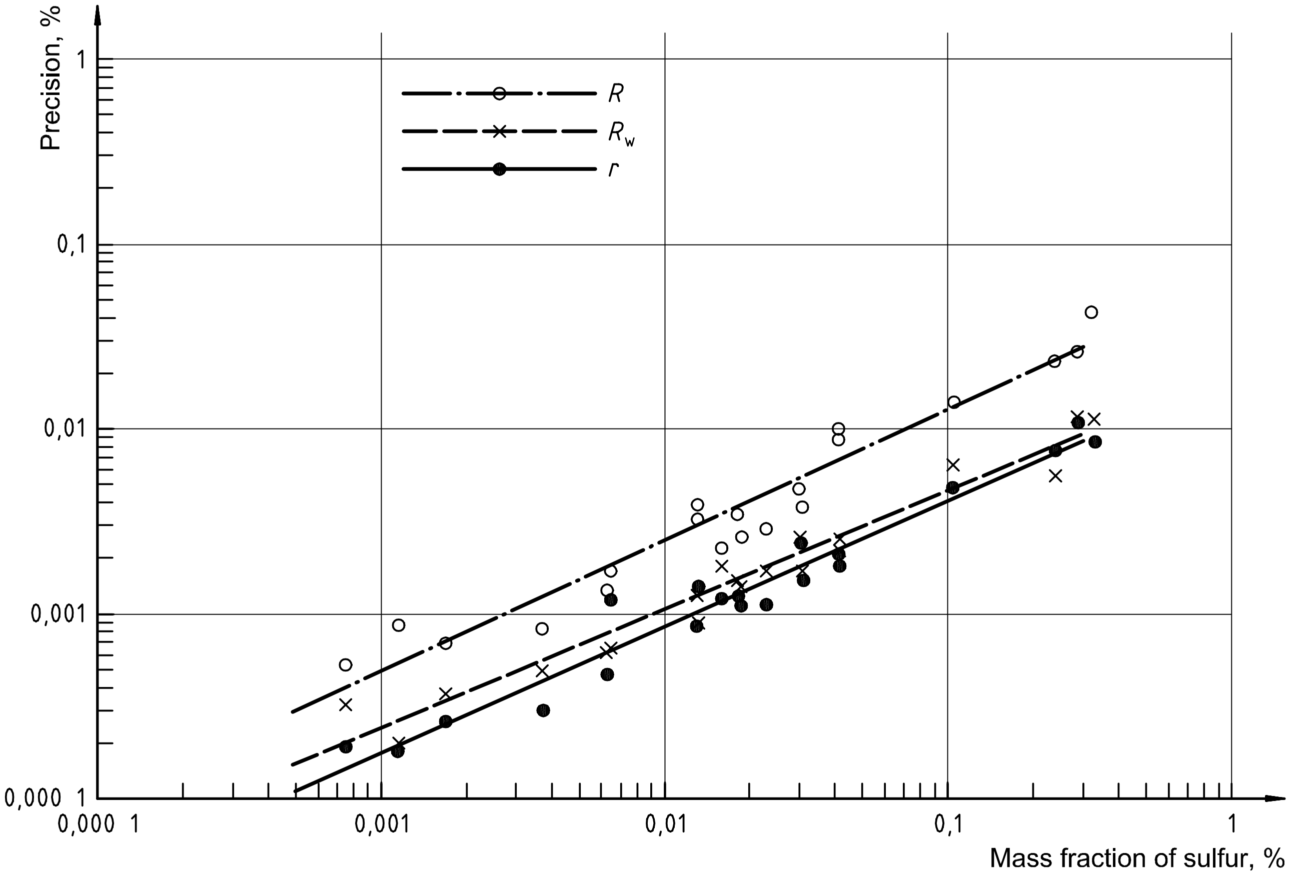
$$\lg r = 0{,}587 \lg \overline{w}_{C1} - 1{,}985$$
$$\lg R_W = 0{,}644 \lg \overline{w}_{C2} - 1{,}805$$
$$\lg R = 0{,}547 \lg \overline{w}_{C1} - 1{,}496$$

where

$\overline{w}_{C1}$ is the average carbon content, expressed as a percentage by mass, obtained within a day.

$\overline{w}_{C2}$ is the average carbon content, expressed as a percentage by mass, obtained between days.

**Figure D.1 — Logarithmic relationship between carbon content ($w_B$), and repeatability limit ($r$), and reproducibility limits ($R_W$ and $R$)**



$$\lg r = 0{,}682 \lg \overline{w}_{\mathrm{S1}} - 1{,}707$$

$$\lg R_{\mathrm{W}} = 0{,}649 \lg \overline{w}_{\mathrm{S2}} - 1{,}692$$

$$\lg R = 0{,}709 \lg \overline{w}_{\mathrm{S1}} - 1{,}198$$

where

$\overline{w}_{\mathrm{S1}}$ is the average sulfur content, expressed in percentage by mass, obtained within a day.

$\overline{w}_{\mathrm{S2}}$ is the average sulfur content, expressed in percentage by mass, obtained between days.

**Figure D.2 — Logarithmic relationship between sulfur content ($w_{\mathrm{B}}$), and repeatability limit ($r$), and reproducibility limits ($R_{\mathrm{W}}$ and $R$)**

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