INTERNATIONAL STANDARD

ISO 4934

Second edition
2003-12-15

Steel and iron — Determination of sulfur content — Gravimetric method

Aciers et fontes — Dosage du soufre — Méthode gravimétrique

Reference number
ISO 4934:2003(E)

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Contents

Foreword

ISO (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 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 4934 was prepared by Technical Committee ISO/TC 17, *Steel*, Subcommittee SC 1, *Methods of determination of chemical composition*.

This second edition cancels and replaces the first edition (ISO 4934:1980), which has been technically revised.

INTERNATIONAL STANDARD **ISO 4934:2003(E)**

Steel and iron — Determination of sulfur content — Gravimetric method

1 Scope

This International Standard specifies a gravimetric method for the determination of the sulfur content in steels and iron, excluding steels containing selenium. The method is particularly suitable as a reference method for the standardization of samples on which certified standard values are to be established.

The method is applicable to a sulfur content between 0,003 % (mass fraction) and 0,35 % (mass fraction).

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 565, *Test sieves — Metal wire cloth, perforated metal plate and electroformed sheet — Nominal sizes of openings*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

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

ISO 5725-2, *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, *Accuracy (trueness and precision) of measurement methods and results — Part 3: Intermediate measures of the precision of a standard measurement method*

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

3 Principle

Dissolution of a test portion in dilute nitric acid in the presence of bromine, or in the mixed acid of nitric acid and hydrochloric acid in the presence of bromine (with the aid of an appropriate device to prevent sulfur losses).

Addition of perchloric acid and evaporation of the solution until white fumes of perchloric acid are evolved.

Filtration of the solution and removal of the dehydrates of silicon, tungsten, niobium,etc.

Addition of a determined quantity of sulfate ions to aid precipitation.

Chromatographic separation of the sulfate ions from the test solution by adsorption on an alumina column, and elution using an ammonium hydroxide solution.

Precipitation of the sulfate ions as barium sulfate under controlled conditions and filtering, washing, heating and weighing.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and only grade 2 water as specified in ISO 3696.

4.1 Aluminium oxide (alumina, Al_2O_3), prepared for chromatography, of particle size corresponding to a sieve mesh size of 75 µm to 150 µm (supplementary series R 40/3 of ISO 565)

Alumina designated alkaline, neutral or acid may be used.

Place approximately 200 g of the dry alumina in a 400 ml beaker containing 300 ml of water and place the beaker in a sink. Insert a glass tube having a bore of 5 mm, such that it extends to the bottom of the beaker and connect the tube to a water supply. Adjust the water flow so that the suspended fine material overflows the rim of the beaker. Continue this treatment until all the fine material, which does not settle within 1 min of stopping the water flow, is removed.

Pour off the supernatant liquid from the coarser material, add the hydrochloric acid (4.5) in an amount sufficient to cover the alumina; stir and allow to stand for not less than 12 h. Pour off the hydrochloric acid and wash the alumina with water as described in the second paragraph.

For preparation of the column, make a slurry of the washed alumina and the hydrochloric acid solution (4.8).

4.2 Bromine (Br_2), min 99 % (mass fraction)

4.3 Nitric acid (HNO_3), $\rho =$ approximately 1,40 g/ml

4.4 Nitric acid (HNO_3), $\rho =$ approximately 1,40 g/ml, diluted $1 + 1$

4.5 Hydrochloric acid (HCl), $\rho =$ approximately 1,19 g/ml

4.6 Hydrochloric acid (HCl), $\rho =$ approximately 1,19 g/ml, diluted $1 + 1$

4.7 Hydrochloric acid (HCl), $\rho =$ approximately 1,19 g/ml, diluted $1 + 9$

4.8 Hydrochloric acid (HCl), $\rho =$ approximately 1,19 g/ml, diluted $1 + 19$

4.9 Perchloric acid ($HClO_4$), $\rho =$ approximately 1,54 g/ml

NOTE If this reagent is shown to have a high sulfate content, this may be removed by passing the reagent through the adsorption column (5.4).

4.10 Perchloric acid ($HClO_4$), $\rho =$ approximately 1,54 g/ml, diluted $1 + 49$

4.11 Acid mixture

Mix hydrochloric acid (4.5) and nitric acid (4.3) in proportions liable to ensure total solubility of the samples. This mixture should be freshly prepared as required.

NOTE Generally, aqua regia can be used. For some samples, the proportion of hydrochloric acid and nitric acid can be adjusted.

4.12 Ammonium hydroxide (NH_4OH), $\rho =$ approximately 0,90 g/ml

4.13 Ammonium hydroxide (NH_4OH), $\rho =$ approximately 0,90 g/ml, diluted $1 + 19$

4.14 Ammonium hydroxide (NH_4OH), $\rho =$ approximately 0,90 g/ml, diluted $1 + 99$

4.15 Sulfuric acid (H_2SO_4), solution corresponding to approximately 48 mg/l of sulfur

Add 2,8 ml of sulfuric acid, $\rho =$ approximately 1,84 g/ml, to about 500 ml of water. Dilute to 1 000 ml and mix. Take 30 ml of this solution, dilute to 1 000 ml and mix.

4.16 Barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$), 1,22 g/l solution

Dissolve 1,22 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in water, dilute to 1 000 ml and mix. Filter the solution through close texture filter paper just before use.

1 ml of this solution is equivalent to approximately 0,16 mg of sulfur.

4.17 Methyl orange ($C_{14}H_{14}N_3NaO_3S$), 0,50 g/l solution

4.18 Glacial acetic acid (CH_3COOH), $\rho =$ approximately 1,05 g/ml

4.19 Hydrogen peroxide (H_2O_2), $\rho =$ approximately 1,10 g/ml

5 Apparatus

Use normal laboratory apparatus.

5.1 Analytical balance, calibrated with nationally or internationally traceable mass, to provide measurement traceability

5.2 Conical flask, of capacity 1 000 ml, having a ground-glass neck

5.3 Allihn condenser, four- or six-bulb type

5.4 Chromatographic adsorption column (see Figure 1)

Prepare the adsorption column as follows.

Fit the column tube into a one-hole rubber bung just below the valve to act as a gasket for fixing the tube in a suction filtration flask. Fit the tube into the suction flask and place a well-packed plug of quartz wool, about 20 mm thick, in the narrow end of the tube. Turn on the valve. Transfer sufficient alumina slurry (4.1) into the tube to make a column 100 mm to 120 mm long. Using the hydrochloric acid solution (4.8), rinse all the alumina particles from the sides of the reservoir into the tube. Insert a plug of quartz wool and press down with a glass rod so that the quartz wool makes contact with the alumina. Compact the plug again if contact is not maintained with the alumina column. Ensure that all alumina particles are removed from the column sides above the top plug.

Pass 20 ml hydrochloric acid (4.8) and then 20 ml of water through the column and follow with 20 ml of the ammonium hydroxide solution (4.13) and then 20 ml of water. Combine the last two eluates and test for absence of aluminium salts by adjusting the pH of solution until faintly ammoniacal. If aluminium hydroxide precipitates on standing, pass 20 ml of the hydrochloric acid solution (4.7) and then 20 ml of water through the column. Repeat the treatment with 20 ml of the ammonium hydroxide solution (4.13) and 20 ml of water, testing the ammoniacal eluates for absence of aluminium salts as before.

If aluminium hydroxide still precipitates, pass some of the hydrochloric acid solution (4.6) through the column for 1 h without suction and then wash with 50 ml of water. Pass 20 ml of the ammonium hydroxide solution (4.13) and 20 ml of water through the column and test the eluates for absence of aluminium salts.

Repeat this sequence of washing until there is no evidence of aluminium salts being eluted from the column. Finally, wash with 30 ml of the hydrochloric acid solution (4.8).

When the tube is not in use, turn the valve off, fill the tube with hydrochloric acid (4.8) and fit a rubber bung to the reservoir.

6 Sampling

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

7 Procedure

7.1 Test portion

Take a test portion according to the anticipated sulfur content as follows:

a) for sulfur contents up to 0,005 % (mass fraction), weigh, to the nearest 0,001 g, two test portions of approximately 10 g;

b) for sulfur contents of 0,005 % (mass fraction) up to 0,05 % (mass fraction), weigh, to the nearest 0,001 g, a test portion of approximately 10 g;

c) for sulfur contents greater than 0,05 % (mass fraction), select an amount of test portion such that the sulfur content to be determined lies in the range 0,001 g to 0,005 g, and weigh to the nearest 0,001 g.

NOTE Ideal conditions for the implementation of this method require a knowledge of the approximate sulfur content of the test portion. If this is not known, a determination by the combustion technique should be made in order to establish the optimum mass of the test portion and the correct amount of barium chloride required for precipitation.

7.2 Blank test

With each set of determinations, carry out a blank test under identical conditions, using the specified amounts of reagents used in the determination, but omitting the test portion.

In the determination of sulfur contents below 0,005 % (mass fraction), for which two 10 g test portions are used, two blank tests under identical conditions shall be carried out (see 7.3.4).

7.3 Determination

7.3.1 Dissolution of the test portion

7.3.1.1 Samples soluble in dilute nitric acid

Place the test portion (7.1) in a dry conical flask (5.2) then add 1 ml of the bromine (4.2) and connect the condenser (5.3). Add slowly 50 ml of the nitric acid solution (4.4) in order to control the reaction as far as possible.

Add slowly a further 50 ml of the nitric acid solution (4.4) and when the emission of fumes has ceased, rinse down the inner walls of the condenser with a small volume of water, collecting the washings in the conical flask.

When dissolution is complete, heat the solution to boiling until the condensing vapours just reach the first bulbs of the condenser. Allow to cool.

After 5 min to 6 min, pour 50 ml of water through the condenser (5.3) into the conical flask (5.2). Disconnect the conical flask from the condenser, transfer quantitatively the contents to a 500 ml beaker and wash the flask walls with water.

7.3.1.2 Samples insoluble in dilute nitric acid

Place the test portion (7.1) in a dry conical flask (5.2) then add 1 ml of the bromine (4.2) and connect the condenser (5.3). In order to control the speed of reaction, add slowly the acid mixture (4.11). For samples from which it is difficult to make a solution, heat slightly until the condensing vapours just reach the first bulbs of the condenser. Allow to cool, and then heat slightly again till dissolution is complete. During dissolution, replenish some bromine if it is consumed too fast.

When dissolution is complete, heat the solution to boiling until the condensing vapours just reach the first bulbs of the condenser. Allow to cool.

After 5 min to 6 min, pour 50 ml of water through the condenser (5.3) into the conical flask (5.2). Disconnect the conical flask from the condenser, transfer quantitatively the contents to a 500 ml beaker and wash the flask walls with water.

7.3.2 Addition of sulphate

Add from a burette 10,0 ml of the sulfuric acid solution (4.15) to each sample solution (7.3.1.1 and 7.3.1.2) and also to the solution for the blank test (7.2).

7.3.3 Treatment with perchloric acid and filtration

Add 120 ml of the perchloric acid (4.9).

Heat until the emission of abundant white fumes. Cover with a dry watch glass and continue heating until carbonaceous matter is completely decomposed and all the chromium is oxidized. Allow to cool. After 5 min or 6 min, add 200 ml of hot water to dissolve the salts. Filter through 12,5 cm close texture filter paper into an 800 ml beaker. Carefully wash the beaker and the filter with warm perchloric acid solution (4.10). Discard the filter.

The volume of solution should be 500 ml to 600 ml; if the volume is greater, concentrate the solution.

7.3.4 Chromatographic separation of sulphate

Place the chromatographic adsorption column (5.4) into the neck of the suction filtration flask. Wash the column with 30 ml of water to remove any ammonium hydroxide solution remaining from the previous elution. Acidify the column with 10 ml of the hydrochloric acid solution (4.8). Discard the eluate.

Quantitatively transfer the test solution to the column, drawing it through the column at a flow rate not exceeding 10 ml/min by adjusting the valve. Always maintain some solution above the alumina.

NOTE In the determination of sulfur contents below 0,005 % (mass fraction), for which two test portions of 10 g each are used, pass both solutions through the same column using the same procedure as for a single test portion. This combines the sulfur from the two separate portions, to produce one test portion equivalent to one of 20 g.

Wash each beaker with 25 ml of the hydrochloric acid solution (4.8). Repeat this procedure. Transfer the washing fractions to the column whilst maintaining the same flow rate. Repeat the washing twice, using 20 ml of water each time, and transfer the washing to the column.

Carry out the blank test (7.2) and if necessary pass both solutions through the same column.

Wash each beaker with 25 ml of the hydrochloric acid solution (4.8). Repeat this procedure. Transfer the washing fractions to the column whilst maintaining the same flow rate. Repeat the washing twice, using 20 ml of water each time, and transfer the washing to the column.

Remove the adsorption column from the suction flask and rinse the outer walls of the lower part of the column with water.

7.3.5 Elution with ammonium hydroxide

Place a 250 ml beaker under the column, so that the inner wall of the beaker is in contact with the lower end of the column. Add to the column 15 ml of the ammonium hydroxide solution (4.13) allowing it to flow through by gravity. Then add 40 ml of the ammonium hydroxide solution (4.14), allowing it to flow completely into the beaker.

Finally, run 30 ml to 40 ml of water through the column, collecting this in the beaker.

7.3.6 Precipitation of sulphates and weighing

Neutralize the combined eluates with some of the hydrochloric acid solution (4.7) in the presence of a few drops of the methyl orange solution (4.17), add 2 ml excess of the acid and evaporate the solution to approximately 50 ml. Filter through a 9 cm diameter filter paper of close texture, collecting the filtrate in a 250 ml beaker and wash the original beaker and the filter paper four times with small volumes of water.

Add 1 ml of glacial acetic acid (4.18) and 5 drops of hydrogen peroxide (4.19) to reduce the small amount of chromium ion in the solution. After the blue colour is invisible, add, dropwise from a burette, an amount of barium chloride solution (4.16) while constantly stirring the filtrate. The amount of barium chloride is in stoichiometric relationship with the expected sulfur content of the test portion together with that of the added sulphate solution. Allow to stand for 1 h, and then add, from the same burette, 20,0 ml excess of the barium chloride solution (4.16). Stir the solution, cover with a watch-glass and allow to stand for about 12 h.

Filter through a 9 cm diameter non-hardened, close texture filter paper or alternatively through a small, tightly packed, ashless paper pulp pad. Wash six times with 5 ml to 10 ml portions of cold water.

Put the filter and precipitate in a platinum crucible that has been previously calcined to 800 °C, cooled in a desiccator and weighed until a constant weight, to within 0,1 mg, has been obtained. Dry and oxidize at as low a temperature as possible (not above 550 °C) until carbonaceous matter is removed, and finally heat to 800 °C. Cool in a desiccator and weigh with an analytical balance (5.1) until a constant weight, to within 0,1 mg, is obtained.

8 Expression of results

8.1 Method of calculation

The sulfur content, W_S, expressed as a percentage by mass, is given by the equation

$$W_\mathrm{S} = \frac{(m_1 - m_2)}{m_0} \times 0{,}137\,4 \times 100$$

where

m_1	is the mass of barium sulphate obtained from the test portion, in grams;
m_2	is the mass of barium sulphate obtained from the blank test, in grams;
m_0	is the mass of the test portion, in grams;
0,137 4	is the conversion factor from barium sulphate ($BaSO_4$) to sulfur (S).

8.2 Precision

A planned trial of this method was carried out by 8 laboratories, at 8 levels of sulfur, each laboratory making four determinations of sulfur content at each level.

The first and second determinations were carried out under repeatability conditions as defined in ISO 5725-1; i.e. one operator, same apparatus, identical operating conditions, same calibration, and a minimum period of time.

The third and fourth determinations were carried out at a different time (on a different day), by the same operator as for the first and second, using the same apparatus.

The samples used and mean results obtained are listed in Table A.1 of Annex A.

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

The data obtained are used to define a logarithmic relationship between sulfur content and repeatability limit, r, and reproducibility limits, R_w and R, of the test results as summarized in Table 1. The graphical representation of the figures is given in Annex B.

From the two values obtained on day 1, the repeatability limit, r, and reproducibility limit, R, were calculated using the procedure specified in ISO 5725-2. From the first value obtained on day 1 and the value obtained day 2, the within laboratory reproducibility limit, R_w, was calculated using the procedure given in ISO 5725-3.

Table 1 — Results for repeatability limit and reproducibility limits

Sulfur	**Repeatability limit**	**Reproducibility limits**	
% (mass fraction)	r	R_w	R
0,003	0,000 65	0,000 60	0,000 68
0,005	0,000 83	0,000 84	0,001 06
0,01	0,001 16	0,001 34	0,001 93
0,02	0,001 62	0,002 14	0,003 51
0,05	0,002 52	0,003 98	0,007 74
0,1	0,003 52	0,006 36	0,014 07
0,2	0,004 92	0,010 15	0,025 59
0,35	0,006 44	0,014 82	0,041 47

9 Test report

The test report shall contain the following information:

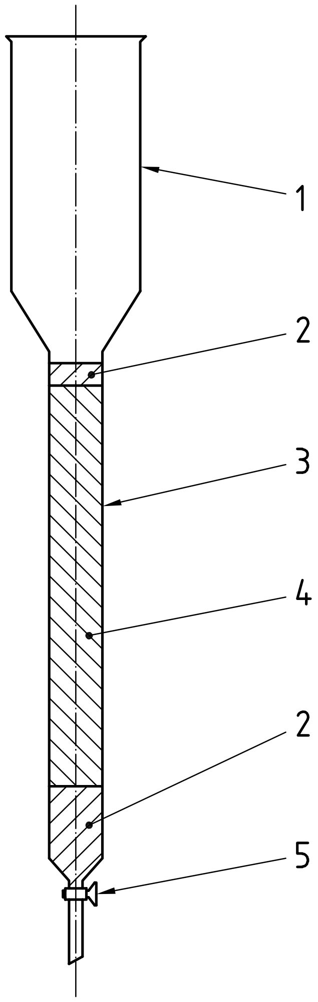
a) all information necessary for the identification of the sample, the laboratory and the date of analysis;

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.



Key

1	reservoir (volume approximately 50 ml)
2	quartz wool plug
3	column section (length 120 mm to 150 mm, internal diameter 10 mm to 11 mm)
4	alumina column (length approximately 100 mm)
5	valve

Figure 1 — Chromatographic adsorption column

Annex A
(informative)

Additional information on international cooperative tests

The results of the trials were reported in document ISO/TC 17/SC 1 N 1267 in 2000. The precision data are presented in graphical form in Annex B.

The test samples used are listed in Table A.1. Results obtained in international cooperative tests are shown in Table A.2.

Table A.2 was derived from the results of international analytical trials carried out in 1999 on steel and iron samples in 3 countries involving 8 laboratories.

Table A.1 — Test samples used

No.	Sample	S	C	Si	Mn	Cr	Ni	Others
1	YSB C 11417b-95	0,003	0,72	0,34	0,18	—	0,013	Cu 0,024
2	JSS 651-14	0,005 8	0,046	0,005 8	1,19	18,26	9,03	Cu 0,12, Mo 0,11, Co 0,17
3	GBW01122	0,010	1,89	1,27	1,29	24,58	2,18	Mo 0,61, V 0,26, Ti 0,038
4	JSS 519-1	0,022	0,39	0,25	0,70	0,120	0,056	Cu 0,105, Pb 0,097
5	GSB H40123	0,056	0,741	0,821	1,39	0,016	0,016	Cu 0,015 4, V 0,157
6	NIST SRM368	0,132	0,089	0,007	0,82	0,030	0,008	Mo 0,003, V 0,001
7	ECRM484-1	0,230	3,20	0,717	0,395	0,155	—	
8	ECRM085-1	0,336	0,067	0,008	0,977	—	—	Cu 0,291, Co 0,019, Pb 0,001 0, Sb 0,007 3, V 0,002 1

Table A.2 — Results obtained in international cooperative test

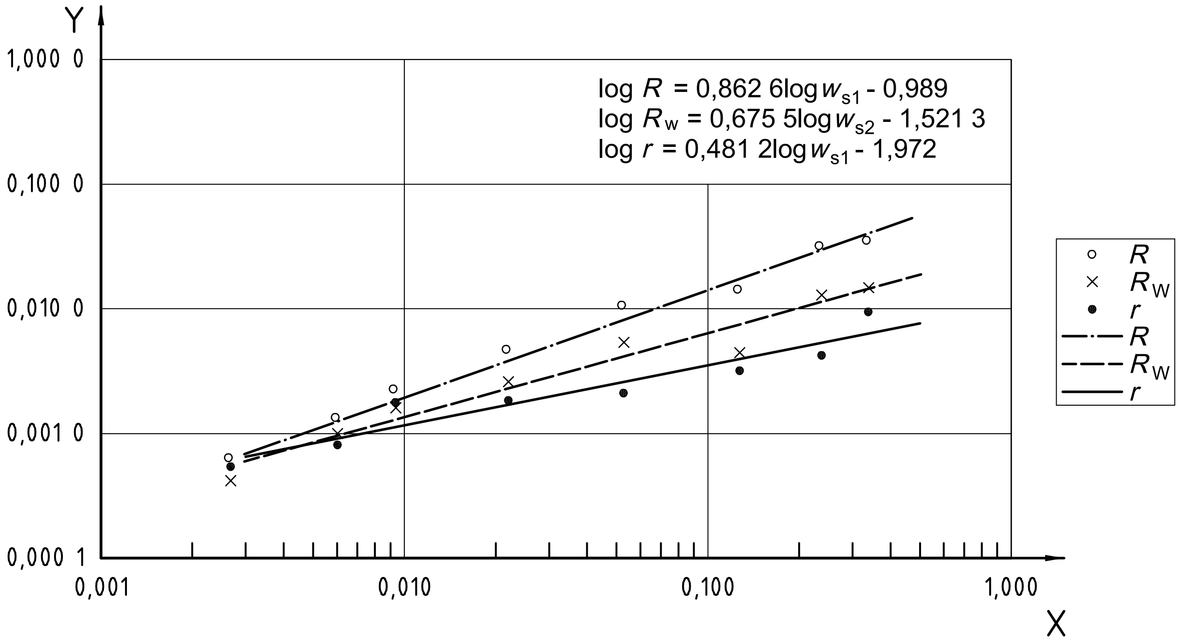
No.	Sample	Certified	Found		Precision data		
			$\overline{W}_{S1}$	$\overline{W}_{S2}$	Repeatability limit	Reproducibility limits	
					r	R_w	R
1	YSB C 11417b-95	0,003	0,002 683	0,002 679	0,000 539	0,000 416	0,000 638
2	JSS 651-14	0,005 8	0,006 036	0,006 018	0,000 808	0,001 000	0,001 334
3	GBW01122	0,010	0,009 521	0,009 357	0,001 771	0,001 601	0,002 279
4	JSS 519-1	0,022	0,021 69	0,022 017	0,001 833	0,002 592	0,004 769
5	GSB H40123	0,056	0,053 62	0,052 938	0,002 100	0,005 377	0,010 715
6	NIST SRM368	0,132	0,128 2	0,127 346	0,003 182	0,004 464	0,014 285
7	ECRM484-1	0,230	0,235 5	0,237 517	0,004 200	0,012 886	0,031 861
8	ECRM085-1	0,336	0,340	0,338 906	0,009 431	0,014 758	0,035 301

$\overline{W}_{S1}$ is the general mean within a day.

$\overline{W}_{S2}$ is the general mean between days.

Annex B
(informative)

Graphical representation of precision data



Key

X	sulfur content, % (mass fraction)
Y	precision, % (mass fraction)

where

$\overline{W}_{S1}$ is the general mean within a day;

$\overline{W}_{S2}$ is the general mean between days.

Figure B.1 — Logarithmic relationship between sulfur content ($\overline{W}_{S1}$ or $\overline{W}_{S2}$), and repeatability limit (r), and reproducibility limits (R_w and R)

ICS 77.080.01

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