INTERNATIONAL STANDARD

ISO 4689-3

Third edition
2017-03

Iron ores — Determination of sulfur content —

Part 3:
Combustion/infrared method

Minerais de fer — Dosage du soufre —

Partie 3: Méthode par combustion et infrarouge

Reference number
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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This third edition cancels and replaces the second edition (ISO 4689-3:2015), of which it constitutes a minor revision, with the following changes:

- "0,001 %" has been inserted before "sulfur" in 5.1;
- in 6.7:
  - under "Combustion crucible", "Length" has been changed to "Height";
  - under "Combustion crucible", outer diameter has been changed from "10 mm" to "26 mm";
  - under "Combustion crucible", inner diameter has been changed from "26 mm" to "10 mm";
- "0,2 g" has been added after "sulfur" in 8.2;
- Formula (7) and the relevant descriptions in 9.2.4 have been modified to harmonize this clause across all standards for which ISO/TC 102/SC 2 is responsible.

A list of all parts in the ISO 4689 series can be found on the ISO website.

Introduction

ISO 4689-2 was originally published as ISO 4690:1986. Under a policy of rationalization of the numbering system used in ISO/TC 102, it has been decided to re-designate ISO 4690:1986 as ISO 4689-2. It was further decided to introduce a combustion/infrared method, numbered ISO 4689-3, i.e. this document.

When next revised, ISO 4689:1986 will be re-designated as ISO 4689-1.

Iron ores — Determination of sulfur content —

Part 3:
Combustion/infrared method

WARNING — This document may involve hazardous materials, operations, and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This document specifies a combustion/infrared method, using a high-frequency induction furnace, for the determination of the sulfur content of iron ores.

This method is applicable to sulfur contents between 0,002 % (mass fraction) and 0,25 % (mass fraction) in natural iron ores, iron ore concentrates and agglomerates, including sinter products. The method is not applicable to iron ores containing more than 1,0 % (mass fraction) of combined water. The apparatus, of which the metal filter is equipped with a heating device, can be applied to iron ores containing less than 3,0 % (mass fraction) of combined water.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements 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 648, *Laboratory glassware — Single-volume pipettes*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks*

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric, Karl Fischer and mass-loss methods*

ISO 3082, *Iron ores — Sampling and sample preparation procedures*

ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis*

ISO Guide 35, *Reference materials — General and statistical principles for certification*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at http://www.iso.org/obp

4 Principle

The sample is mixed with a flux containing iron, tin and tungsten and heated in a high-frequency induction furnace, using oxygen as a supporting fuel and carrier gas.

The evolved sulfur dioxide is carried by oxygen into the cell of an infrared detector, where the absorption scale is read.

5 Reagents

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

5.1 Metallic iron, particle size 0,2 mm to 1,2 mm containing less than 0,001 % sulfur.

5.2 Magnesium perchlorate, $Mg(ClO_4)_2$, anhydrous, free flowing, particle size 0,5 mm to 2 mm.

5.3 Iron(III) oxide, containing less than 0,003 % sulfur.

5.4 Metallic tin, particle size 0,2 mm to 1,2 mm, containing less than 0,001 % sulfur.

5.5 Metallic tungsten, particle size 0,2 mm to 1,2 mm containing less than 0,001 % sulfur.

5.6 Sodium hydroxide coated silica, particle size 0,5 mm to 2 mm.

5.7 Sodium hydroxide, particle size 0,5 mm to 2 mm.

5.8 Standard sulfur solution, prepared as follows.

Dry 8 g of potassium sulfate [purity > 99,99 % (mass fraction)] to constant mass at 105 °C to 110 °C and cool in a desiccator. Weigh the dried masses of potassium sulfate specified in Table 1 and dissolve each portion in water. Cool, transfer each portion to separate volumetric flasks and dilute to volume with water.

Table 1 — Sulfur standard solution (calibration series)

Solution no.	Mass of potassium sulfate g	Concentration of sulfur mg/ml
1	0,543 5	1,00
2	1,087 0	2,00
3	1,902 2	3,50
4	2,717 4	5,00

6 Apparatus

Ordinary laboratory apparatus, including one-mark pipettes and one-mark volumetric flasks complying with the specifications of ISO 648 and ISO 1042, respectively, as well as the following. See Figure 1.

6.1 Oxygen supply.

6.2 Absorption tower, containing soda-asbestos (5.6) or sodium hydroxide (5.7).

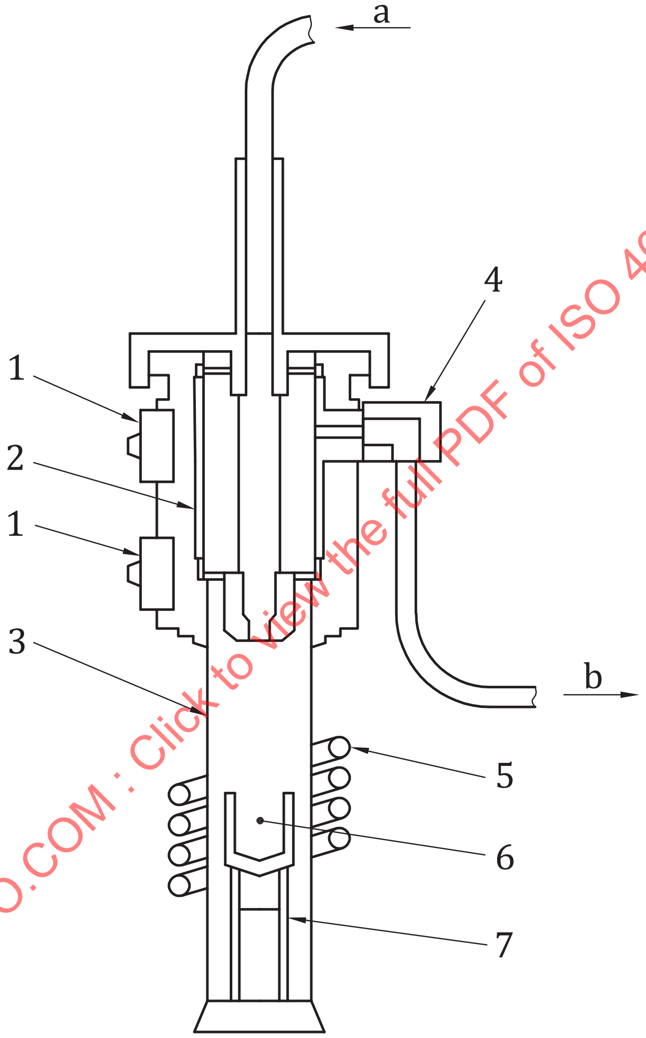
6.3 Drying tower, containing magnesium perchlorate (5.2).

6.4 High-frequency induction furnace, having a heating induction coil (height 30 mm to 55 mm, 4 to 5 rolls), capable of heating to a temperature of 1 200 °C.

An example of a combustion furnace, with combustion gas-refining section, is given in Figure 1.

6.5 Combustion tube, quartz.

6.6 Refractory combustion crucible.



Key

1	metal filter
2	heating device
3	quartz combustion tube
4	dust trap
5	high-frequency induction coil
6	crucible
7	holder
a	Oxygen.
b	Combustion gas.

Figure 1 — Example of combustion furnace with combustion gas-refining section

6.7 Tin capsule.

The following dimensions may be used as guidelines.

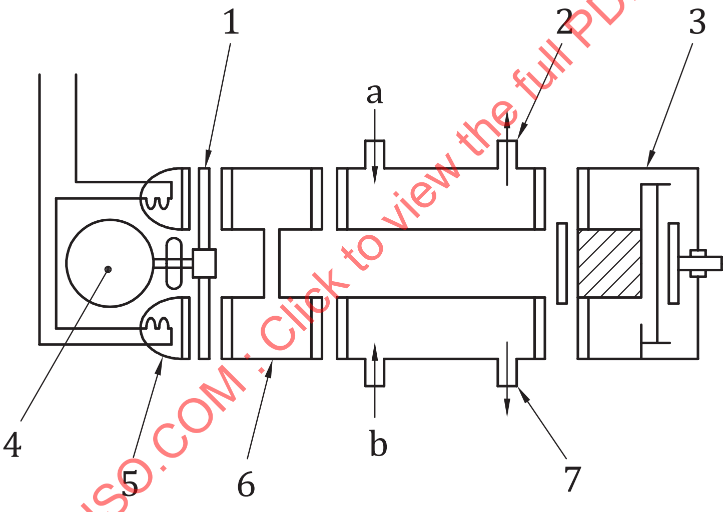
Combustion tube		Combustion crucible		Tin capsule	
Length	140 m to 220 m	Height	26 mm	Diameter	6 mm
Outer diameter	30 mm to 44 mm	Outer diameter	26 mm	Height	18 mm
Inner diameter	26 mm to 37 mm	Inner diameter	10 mm	Mass	0,3 g
				Volume	0,4 ml

6.8 Metal filter.

6.9 Dust trap, containing glass wool.

6.10 Detector for infrared absorption, an example of which is shown in Figure 2.

6.11 Micro-pipette, capacity 100 µl, accurate to 1 µl.



Key

1 chopper
2 measuring cell
3 infrared detector
4 motor
5 infrared source
6 filter cell
7 reference cell
a Combustion gas.
b Oxygen.

Figure 2 — Example of an infrared detection system

7 Sampling and samples

7.1 Laboratory sample

For analysis, use a laboratory sample of −100 µm particle size which has been taken and prepared in accordance with ISO 3082. In the case of ores having significant contents of combined water or oxidizable compounds, use a particle size of −160 µm.

NOTE A guideline on significant contents of combined water and oxidizable compounds is incorporated in ISO 7764.

7.2 Preparation of predried test samples

Thoroughly mix the laboratory sample and, taking multiple increments, extract a test sample in such a manner that it is representative of the entire contents of the container. Dry the test sample at 105 °C ± 2 °C as specified in ISO 7764. This is the predried test sample.

For ores having significant content of combined water or oxidizable compounds, an air-equilibrated test sample shall be prepared in accordance with ISO 2596.

8 Procedure

8.1 Number of determinations

Carry out the analysis at least in duplicate in accordance with Annex A, independently, on one predried test sample.

NOTE The expression "independently" means that the second and any subsequent result are not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure is carried out either by the same operator at a different time or by a different operator, including in either case, appropriate recalibration.

8.2 Test portion

Taking several increments, weigh to the nearest 0,000 2 g, approximately 0,5 g of the predried test sample obtained in accordance with 7.2. For samples containing in excess of 0,1 % (mass fraction), sulfur 0,2 g should be taken.

The test portion should be taken and weighed quickly to avoid re-absorption of moisture.

8.3 Blank test and check test

In each run, one blank test and one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analysis of the ore sample(s) under the same conditions. A predried test sample of the certified reference material shall be prepared as specified in 7.2.

The certified reference material should be of the same type as the sample to be analysed, and the properties of the two materials should be sufficiently similar to ensure that in either case, no significant changes in the analytical procedure will become necessary.

Where the analysis is carried out on several samples at the same time, the blank value may be represented by one test, provided that the procedure is the same and the reagents are from the same reagent bottles.

Where the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

8.4 Determination

Connect the furnace (6.4) with components (6.1, 6.2, 6.3, 6.5, 6.8, 6.9, and 6.10) and switch on the power. Set the condition for heating in accordance with the manufacturer's instructions after stabilization of the apparatus.

Analyse a standardization sample as follows.

a) Adjust the reading of the detector to the sulfur content of the standardization sample. Place the test portion in a refractory combustion crucible (6.6) and cover the test portion with 0,50 g of iron (5.1), 0,3 g to 0,5 g of tin (5.4), and 1,0 g of tungsten (5.5) in that order. For 0,2 g of sample, cover the test portion with 0,8 g of iron, 0,3 g to 0,5 g of tin, and 1,0 g of tungsten in that order.

b) Insert the crucible into a quartz combustion tube (6.5) of the furnace at the centre position of the heating induction coil. Substitute oxygen for air in the combustion tube, adjust the inner pressure to the specified pressure and load the power to the heating induction coil. Continue combustion of the test portion until the reading of the detector does not vary. Read out and record the indicated value. Switch off the power and take out the crucible.

c) After combustion, the used crucible shall be checked to determine whether the combustion is complete or not.

d) If incomplete, the test shall be carried out again.

A standardization sample means a sample used for adjusting the sensitivity of a detector. It should not easily degenerate and should be homogeneous.

NOTE An apparatus equipped with a timer stops automatically.

8.5 Preparation of calibration graph

Decant water and sulfur standard solution (5.8), in accordance with Table 2, into five tin capsules (6.7). Heat each capsule gently at 90 °C, to dryness, and cool in a desiccator.

Place the dried capsule in a refractory combustion crucible (6.6) and press the capsule against the bottom of the crucible. Cover the capsule with 0,5 g of iron oxide (5.3), 0,5 g of iron (5.1), and 1,0 g of tungsten (5.5) in that order.

Treat each crucible as described in 8.4. Plot the relationship between the quantity of sulfur, in micrograms, and the net reading.

Several CRMs may be used instead of sulfur standard solutions. In this case, the sulfur contents of the CRMs should cover the applicable range of this method. CRMs should be treated as indicated in 8.3 and 8.4.

Table 2 — Aliquot of sulfur standard solution

No. of sulfur standard solution	Volume of aliquot µl	Mass of sulfur in aliquot mg
(Water)	100	0
1	100	0,100
2	100	0,200
3	100	0,350
4	100	0,500

9 Expression of results

9.1 Calculation of sulfur content

The sulfur content, w_s, is calculated as a percentage by mass, to five decimal places for contents higher than 0,01 % and to six decimal places for contents lower than 0,01 %, using Formula 1.

$$w_s\ (\%) = \frac{m_1 - m_2}{m \times 10^4} \tag{1}$$

where

m_1 is the mass, in micrograms, of sulfur in the test portion;

m_2 is the mass, in micrograms, of sulfur in the blank test;

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

9.2 General treatment of results

9.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following formulae:

NOTE Additional information is given in Annexes B and C.

$$R_d = 0{,}030\ 6\ X + 0{,}000\ 66 \tag{2}$$

$$P = 0{,}137\ 977\ X^{0{,}781\ 21} \tag{3}$$

$$\sigma_d = 0{,}010\ 8\ X + 0{,}000\ 23 \tag{4}$$

$$\sigma_L = 0{,}048\ 827\ X^{0{,}791\ 96} \tag{5}$$

where

R_d is the independent duplicate limit;

P is the permissible tolerance between laboratories;

σ_d is the independent duplicate standard deviation;

σ_L is the between-laboratories standard deviation;

X is the sulfur content, expressed as a percentage by mass, of the predried test sample calculated as follows:

- within-laboratory [Formulae (2) and (4)]: the arithmetic mean of the duplicate values;
- between-laboratories [Formulae (3) and (5)]: the arithmetic mean of the final results (9.2.5) of the two laboratories.

9.2.2 Determination of analytical result

Having computed the independent duplicate results according to Formula (1), compare them with the independent duplicate limit, R_d, using the procedure given in Annex A.

9.2.3 Between-laboratories precision

Between-laboratories precision is used to determine the agreement between the final results reported by two laboratories. The assumption is that both laboratories followed the same procedure described in 9.2.2.

Compute the following quantity:

$$\mu_{1,2} = \frac{\mu_1 + \mu_2}{2} \tag{6}$$

where

μ_1 is the final result reported by laboratory 1;

μ_2 is the final result reported by laboratory 2;

$\mu_{1,2}$ is the mean of the final results.

If $\left|\mu_1 - \mu_2\right| \leq P$, the results are in agreement.

9.2.4 Check for trueness

The trueness of the analytical method shall be checked by applying it to a certified reference material (CRM) or a reference material (RM). The procedure is the same as that described above. After confirmation of the precision, the final laboratory result is compared with the reference or certified value, A_c. There are two possibilities:

a) $\left|\mu_c - A_c\right| \leq C$, in which case, the difference between the reported result and the reference/certified value is statistically insignificant.

b) $\left|\mu_c - A_c\right| > C$, in which case, the difference between the reported result and the reference/certified value is statistically significant.

where

μ_c is the final result for the certified reference material;

A_c is the reference/certified value for the CRM/RM;

C is a value dependent on the type of CRM/RM used.

Certified reference materials used for this purpose should be prepared and certified in accordance with ISO Guide 35.

C should be calculated as follows:

$$C = 2\sqrt{\frac{s_{\mathrm{Lc}}^2 + \dfrac{s_{\mathrm{Wc}}^2}{n_{\mathrm{Wc}}}}{N_c} + \sigma_{\mathrm{L}}^2 + \frac{\sigma_{\mathrm{d}}^2}{n}} \tag{7}$$

where

s_{Lc} is the between-laboratories standard deviation of the certifying laboratories;

s_{Wc} is the within-laboratory standard deviation of the certifying laboratories;

n_{Wc} is the average number of replicate determinations in the certifying laboratories;

N_c is the number of certifying laboratories;

n is the number of replicate determinations carried out on the CRM/RM;

σ_L and σ_d are as defined in 9.2.1.

The following procedure should be used when the information on the reference material certificate is incomplete:

- if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression s_{Wc}^2 / n_{Wc} and regard s_{Lc} as the standard deviation of the laboratory means;
- if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the following condition:

$$C = 2\sqrt{2\,\sigma_L^2 + \frac{\sigma_d^2}{n}} \qquad (8)$$

A CRM certified by only one laboratory should be avoided unless it is known to have an unbiased certified value.

9.2.5 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample, or as otherwise determined by the operations specified in Annex A, calculated to five decimal places for contents of sulfur higher than 0,01 % (mass fraction) and to six decimal places for contents lower than 0,01 % (mass fraction). For contents higher than 0,01 % (mass fraction), the value is rounded off to the third decimal place as specified in a), b), and c). In a similar manner, with the ordinal numbers increased by one, the value for sulfur contents lower than 0,01 % (mass fraction) is rounded off to the fourth decimal place.

a) Where the figure in the fourth decimal place is less than five, it is discarded and the figure in the third decimal place is kept unchanged.

b) Where the figure in the fourth decimal place is five and there is a figure other than 0 in the fifth decimal place, or if the figure in the fourth decimal place is greater than five, the figure in the third decimal place is increased by one.

c) Where the figure in the fourth decimal place is five and the figure 0 is in the fifth decimal place, the five is discarded and the figure in the third decimal place is kept unchanged if it is 0, 2, 4, 6, or 8, and is increased by one if it is 1, 3, 5, 7, or 9.

10 Test report

The test report shall include the following information:

a) name and address of the testing laboratory;

b) date of issue of the test report;

c) reference to this document, i.e. ISO 4689-3;

d) details necessary for the identification of the sample;

e) result of the analysis;

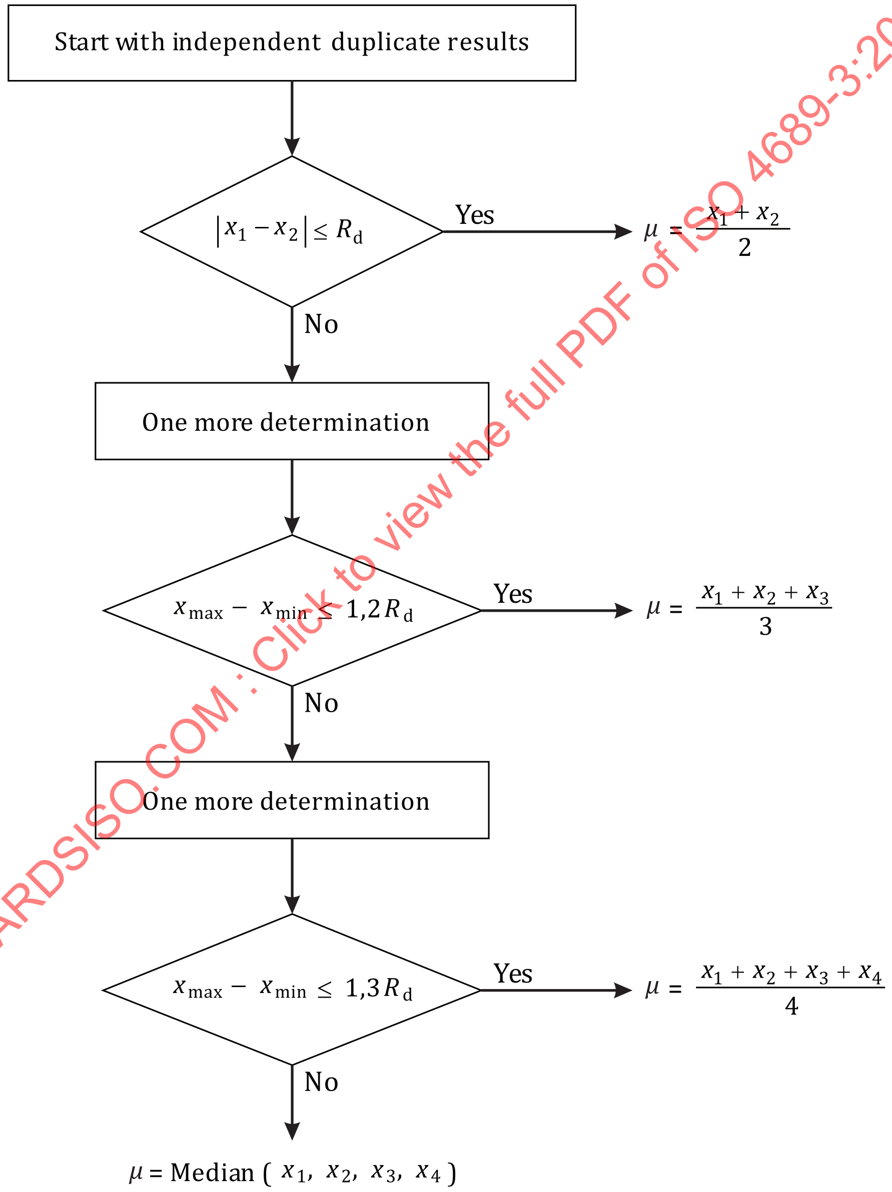
f) reference number of the result;

g) any characteristics noticed during the determination and any operations not specified in this document, which may have had an influence on the result, either for the test sample or for the certified reference material(s).

Annex A
(normative)

Flowsheet of the procedure for the acceptance of analytical values for test samples

Figure A.1 shows the procedure for the acceptance of analytical values for test samples.



NOTE R_d is as defined in 9.2.1.

Figure A.1 — Flowsheet of the procedure for the acceptance of analytical values for test samples