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Iron ores — Determination of manganese content — Spectrophotometric method

Minerais de fer — Dosage du manganèse — Méthode spectrophotométrique

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FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up 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.

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

International Standard ISO 3886 was developed by Technical Committee ISO/TC 102, *Iron ores*, and was circulated to the member bodies in July 1975.

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

Australia	Italy	Sweden
Austria	Japan	Turkey
Belgium	Mexico	United Kingdom
Canada	Netherlands	U.S.A.
Czechoslovakia	New Zealand	U.S.S.R.
France	Poland	Yugoslavia
Germany	Romania	
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No member body expressed disapproval of the document.

Iron ores — Determination of manganese content — Spectrophotometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a spectrophotometric method using sodium periodate for the determination of manganese in iron ores.

This method is applicable to a concentration range of 0,02 to 8 % of manganese content in all natural iron ores, concentrates and agglomerates, including sinter products.

2 REFERENCES

ISO 2596, *Iron ores — Determination of hygroscopic moisture in analytical samples.*

ISO 3081, *Iron ores — Increment sampling — Manual method.*

ISO 3082, *Iron ores — Increment sampling — Mechanical method.*¹⁾

ISO 3083, *Iron ores — Preparation of samples.*

3 PRINCIPLE

Decomposition of a test portion, either

- a) by treatment with hydrochloric, nitric and perchloric acids, or
- b) by sintering with sodium peroxide, followed by treatment with hydrochloric and perchloric acids.

Filtration and ignition of the residue, followed by treatment with hydrofluoric and sulphuric acids and fusion with sodium carbonate. Dissolution of the cooled melt in the main solution. Oxidation of manganese in an aliquot to permanganate ion, using sodium periodate in sulphuric-phosphoric acid medium.

Spectrophotometric measurement of the optical absorbance due to the permanganate ion at a wavelength of about 535 nm.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity, except that water free from organic matter shall be used for the spectrophotometric measurement.

4.1 Water, free from organic matter.

Add 20 ml of sulphuric acid (1 + 1) (4.9) to 1 l of water, bring to the boil, add several crystals of sodium periodate, continue boiling for 10 min, then cool.

4.2 Sodium peroxide (Na_2O_2), powder.

NOTE — Sodium peroxide should be kept away from humidity and should not be used when once it begins to agglomerate.

4.3 Sodium carbonate (Na_2CO_3), anhydrous.

4.4 Hydrochloric acid, ρ 1,19 g/ml.

4.5 Hydrochloric acid, diluted 1 + 9.

4.6 Nitric acid, ρ 1,4 g/ml.

4.7 Perchloric acid, 60 % (m/m) (ρ 1,54 g/ml) or 70 % (m/m) (ρ 1,67 g/ml).

4.8 Hydrogen peroxide, 3 % (V/V).

4.9 Sulphuric acid, diluted 1 + 1.

4.10 Sulphuric acid, diluted 1 + 100.

4.11 Hydrofluoric acid, 40 % (m/m) (ρ 1,13 g/ml).

4.12 Sulphuric-phosphoric acid mixture.

Pour 100 ml of sulphuric acid, ρ 1,84 g/ml, into about 600 ml of water while stirring, cool, add 150 ml of phosphoric acid, ρ 1,70 g/ml, and dilute to 1 000 ml with water.

1) In preparation.

4.13 Sodium periodate (NaIO_4) solution, 50 g/l.

4.14 Sodium nitrite (NaNO_2) solution, 100 g/l.

4.15 Manganese, standard solution.

4.15.1 Stock solution

Dissolve 0,500 g of pure metallic manganese in 20 ml of the nitric acid (4.6), add 20 ml of the sulphuric acid (4.9) and heat to dense white fumes for about 10 min to expel all oxides of nitrogen. Cool, add about 100 ml of water to dissolve the salt, transfer into a 500 ml volumetric flask, dilute to the mark with water and mix.

1 ml of the stock solution contains 1,00 mg of manganese.

4.15.2 Standard solution A

Take 100 ml of the stock solution (4.15.1) and dilute to 1 000 ml in a volumetric flask.

1 ml of the standard solution A contains 0,100 mg of manganese.

4.15.3 Standard solution B

Take 250 ml of the standard solution A (4.15.2) and dilute to 1 000 ml in a volumetric flask.

1 ml of the standard solution B contains 0,025 mg of manganese.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Spectrophotometer.

6 SAMPLING AND SAMPLES

For analysis, use a laboratory sample of minus 100 μm in size which has been taken in accordance with ISO 3081 or ISO 3082 and prepared in accordance with ISO 3082¹⁾ or ISO 3083. In the case of ores with high contents of combined water or oxidizable compounds, use a particle size of minus 160 μm .

7 PROCEDURE

The analysis shall be carried out generally in duplicate, independently on one ore sample.

NOTE — The expression "independently" implies the change of the person carrying out the analysis. If the same person must carry out the analysis, the procedure shall be carried out at a different time.

Simultaneously with the analysis, two 10 g test portions shall be taken to determine the hygroscopic moisture in accordance with ISO 2596.

7.1 Test portion

Weigh, to the nearest 0,000 2 g, approximately 1 g of the test sample obtained in accordance with clause 6.

7.2 Blank test and check test

In each run, one analysis of a standard sample of the same type of ore and one blank test shall be carried out in parallel with the analysis of one ore sample under the same conditions.

NOTE — The standard sample should be of the same type as the sample to be analysed. Notwithstanding, the standard sample cannot be considered as being of the same type if the properties of the sample to be analysed differ from those of the standard sample to such an extent that the analytical procedure must be changed greatly.

When 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 used are from the same reagent bottles.

When the analysis is carried out on several samples of the same type of ore at the same time, the analytical value of one standard sample may be used.

7.3 Determination

7.3.1 Decomposition of the test portion

If the decomposition is to be based on acid attack, proceed as instructed in 7.3.1.1. If the decomposition is to be based on alkali sintering, proceed as instructed in 7.3.1.2.

7.3.1.1 Place the test portion (7.1) in a 300 ml beaker, add 30 ml of the hydrochloric acid (4.4), cover the beaker with a watch glass and heat the solution gently without boiling; add 5 ml of the nitric acid (4.6), 20 ml of the perchloric acid (4.7), and 0,2 ml of the sulphuric acid (4.9), cover the beaker again with the watch glass, heat to dense white fumes of perchloric acid and maintain a steady refluxing of acid on the walls of the beaker for about 10 min.

NOTE — For decomposition of the test portion, place the beaker for about 1 h on the low-temperature zone (60 to 100 °C) of the hot-plate, then transfer to a higher-temperature zone and heat for about 10 min at just under boiling point.

Allow the beaker to cool, add about 50 ml of warm water and a few drops of the hydrogen peroxide (4.8), heat the mixture to dissolve the soluble salts, and boil to decompose the excess of hydrogen peroxide.

Filter the solution through a close-texture paper. Wash the beaker with water using a rubber-tipped glass rod. Wash the residue first with three or four portions of the sulphuric acid (4.10) and then with warm water. Collect the filtrate and washings in a 300 ml beaker and reserve as the main solution. Keep the filter paper with the residue and continue according to 7.3.2.

1) ISO 3082 will specify methods for mechanical preparation of the sample in addition to specifying the taking of samples.

7.3.1.2 Place the test portion (7.1) in a 40 ml nickel crucible free of manganese, add about 3 g of the sodium peroxide powder (4.2), mix well using a platinum or nickel spatula, and tamp the mixture. Place the crucible for 1 or 2 min at the entrance of a muffle furnace the temperature of which is regulated at $400 \pm 20^\circ\text{C}$, and then into the furnace for about 1 h to effect sintering. Take the crucible out of the furnace and cool.

NOTE — An alumina crucible free of manganese may be used in place of a nickel crucible.

Transfer the sintered mass to a 300 ml beaker, add about 30 ml of water and cover the beaker with a watch glass.

NOTE — If the volume of water added is insufficient, bumping may occur on subsequent heating. Therefore the volume, for safety, may be increased up to 100 ml.

Rinse the crucible first with water and then once with hydrochloric acid (4.5), and add the washings to the bulk solution. Acidify slowly with 30 ml of the hydrochloric acid (4.4) and heat the solution gently to decompose the sintered mass. Add 30 ml of the perchloric acid (4.7) and 0,2 ml of the sulphuric acid (4.9), cover the beaker again with the watch glass, heat to dense white fumes of perchloric acid and maintain a steady refluxing of acid on the walls of the beaker for about 10 min.

Allow the beaker to cool, add about 50 ml of warm water and a few drops of the hydrogen peroxide (4.8), heat the mixture to dissolve the soluble salts and boil to decompose the excess of hydrogen peroxide.

Filter the solution through a close-texture paper. Wash the beaker with water using a rubber-tipped glass rod. Wash the residue first with three or four portions of the sulphuric acid (4.10) and then with warm water. Collect the filtrate and washings in a 300 ml beaker and reserve as the main solution. Keep the filter paper with the residue and continue according to 7.3.2.

7.3.2 Treatment of residue

Place the residue from 7.3.1 with the filter in a platinum crucible, dry, ash the paper, and finally ignite at 950 to $1\,050^\circ\text{C}$. Allow the crucible to cool, then moisten the residue with sulphuric acid (4.9). Add 5 to 15 ml of the hydrofluoric acid (4.11), depending on the silica content, heat gently to expel silica, and fume off sulphuric acid. Allow the crucible to cool, add 2 g of the sodium carbonate (4.3), and heat, gently at first, then finally to dull red, to fuse the residue.

Allow the melt to cool, place the crucible in the beaker containing the main solution from 7.3.1, and heat gently to dissolve the melt. Take out the crucible and rinse it with water. Evaporate the solution to approximately 50 ml. Cool to room temperature, transfer directly, or filter if necessary, into a 100 ml volumetric flask for manganese contents less than 4,0 %, or to a 500 ml volumetric flask for manganese contents between 4,0 and 8,0 %, and dilute with water to the mark, shaking at intervals.

7.3.3 Determination

Transfer to a 300 ml beaker an aliquot of the solution from 7.3.2, chosen in accordance with table 1, and add 30 ml of the sulphuric-phosphoric acid mixture (4.12). Dilute to about 60 ml with water.

TABLE 1 — Aliquots

Manganese content % Mn	Aliquots
0,02 up to 0,1	take a 25 ml aliquot out of 100 ml
0,1 up to 1,0	take a 20 ml aliquot out of 100 ml
1,0 up to 2,0	take a 10 ml aliquot out of 100 ml
2,0 up to 4,0	take a 5 ml aliquot out of 100 ml
4,0 up to 8,0	take a 10 ml aliquot out of 500 ml

Add 10 ml of the sodium periodate solution (4.13), cover the beaker with a watch glass, heat to boiling, and maintain just below boiling point for 10 min after colour development of the permanganate ion. Cool the solution, transfer to a 100 ml volumetric flask, and make up to volume with water (4.1).

NOTE — For manganese contents below 0,1 %, the heating time should be approximately 30 min and, if necessary, water (4.1) should be added to maintain the volume.

Transfer a part of this solution into a photometric cell with a suitable optical path length, and measure the absorbance (a_1) with the spectrophotometer (5.1), at a wavelength of the maximum absorption located near 535 nm, after having adjusted the instrument to zero absorbance against water.

Add sodium nitrite solution (4.14), drop by drop, to the solution in the volumetric flask, while mixing, until 1 drop in excess decolorizes the pink colour of the permanganate ion; transfer a part of this solution to the same photometric cell, and measure the absorbance (a_2) as described above.

NOTES

1 Increase in the volume of the solution by addition of sodium nitrite solution is disregarded.

2 The measurement of absorbance should not be postponed unduly after decoloration of the pink colour of the permanganate ion by sodium nitrite solution, because reoxidation of the manganese ion occurs on standing.

Determine the amount of manganese from the difference between these absorbances ($a_1 - a_2$) by using the calibration curve prepared as instructed in 7.4. Calculate the percentage of manganese from formula (1) in 8.1.

7.4 Calibration curve

7.4.1 For samples containing more than 0,1 % manganese

Place 0 — 2,0 — 5,0 — 10,0 — 15,0 and 20,0 ml of standard manganese solution A (4.15.2) into six 300 ml beakers, add 30 ml of the sulphuric-phosphoric acid mixture (4.12), and dilute to about 60 ml with water. Add 10 ml of the sodium periodate solution (4.13), and continue as indicated in

7.3.3, second paragraph, with the exception of the spectrophotometric measurement which shall be made after having adjusted the spectrophotometer to zero absorbance against the solution containing no added manganese (compensation solution). Plot the calibration curve showing the differences between the absorbances ($a_1 - a_2$) of the standard matching solutions as a function of the quantities of manganese contained in these solutions.

7.4.2 For samples containing less than 0,1 % manganese

Place 0 – 2,0 – 5,0 – 10,0 – 15,0 and 20,0 ml of standard manganese solution B (4.15.3) into six 300 ml beakers, add 30 ml of the sulphuric-phosphoric acid mixture (4.12), and dilute to about 60 ml with water. Add 10 ml of the sodium periodate solution (4.13), and continue as indicated in 7.3.3, second paragraph and note, with the exception of the spectrophotometric measurement which shall be made after having adjusted the spectrophotometer to zero absorbance against the solution containing no added manganese (compensation solution). Plot the calibration curve showing the differences between the absorbances ($a_1 - a_2$) of the standard matching solutions as a function of the quantities of manganese contained in these solutions.

8 EXPRESSION OF RESULTS

8.1 Calculation of manganese content

The manganese (Mn) content, as a percentage by mass, is calculated from the formula

$$\frac{m_1 \times V}{m_2 \times V_1} \times 100 \times K \quad \dots (1)$$

where

m_1 is the mass, in grams, of manganese found in the aliquot of sample solution in table 1 (7.3.3), after correction for the blank value (7.2);

m_2 is the mass, in grams, of the test portion (7.1);

V is the total volume, in millilitres, depending on the manganese content (7.3.2);

V_1 is the volume, in millilitres, taken as an aliquot in table 1 (7.3.3);

K is the conversion factor found from the formula

$$K = \frac{100}{100 - A}$$

where A is the hygroscopic moisture content, as a percentage by mass, determined in accordance with ISO 2596.

8.2 General treatment of results

8.2.1 Adoption of analytical values

Analytical results (manganese content) shall be calculated as a percentage by mass and recorded to the fourth decimal place, figures beyond the fourth decimal place being unconditionally discarded.

The analytical value of the sample shall be accepted when the analytical value of the corresponding standard sample agrees with the standard value within the limit of permissible tolerance of a standard sample, and the difference between the two values of the test sample does not exceed the permissible tolerance for the test sample specified in table 2.

When the analytical value of the standard sample is outside the limit of the permissible tolerance (table 2, second column), a simultaneous analysis shall be carried out on one test sample and one standard sample of the same type of ore, with one blank test. The analytical value of the standard sample shall be examined for adoption as above. This procedure shall be repeated until two acceptable values are obtained.

When the range (absolute difference) of the two values of test sample is outside the limit of permissible tolerance (table 2, third column), a simultaneous analysis shall be carried out on one test sample and one standard sample of the same type of ore, with one blank test, in accordance with the flow sheet presented in annex A.

8.2.2 Calculation of final results

The arithmetical mean of the acceptable values of the test sample is the final result.

The arithmetical mean of the acceptable analytical values, calculated to the fourth decimal place, shall be rounded off to the second decimal place as follows :

- when the figure in the third decimal place is less than 5, it is discarded and the figure in the second decimal place is kept unchanged;
- when the figure in the third decimal place is 5 and there are figures other than 0 in subsequent decimal places, or when the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;
- when the figure in the third decimal place is 5 and there are no figures other than 0 in subsequent decimal places, the 5 is discarded and the figure in the second 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.

8.3 Permissible tolerances

The permissible tolerances described in 8.2.1 are shown in table 2.1)

TABLE 2 — Permissible tolerances within laboratories

Manganese content % Mn	Standard sample % Mn	Test sample % Mn
0,02 up to 0,1	± 0,009	± 0,013
0,1 up to 0,5	± 0,016	± 0,023
0,5 up to 1,0	± 0,025	± 0,035
1,0 up to 2,0	± 0,043	± 0,060
2,0 up to 4,0	± 0,079	± 0,110
4,0 up to 8,0	± 0,151	± 0,210

8.4 Oxide factor

$$\text{MnO (\%)} = 1,291 \text{ 2 Mn (\%)}$$

9 TEST REPORT

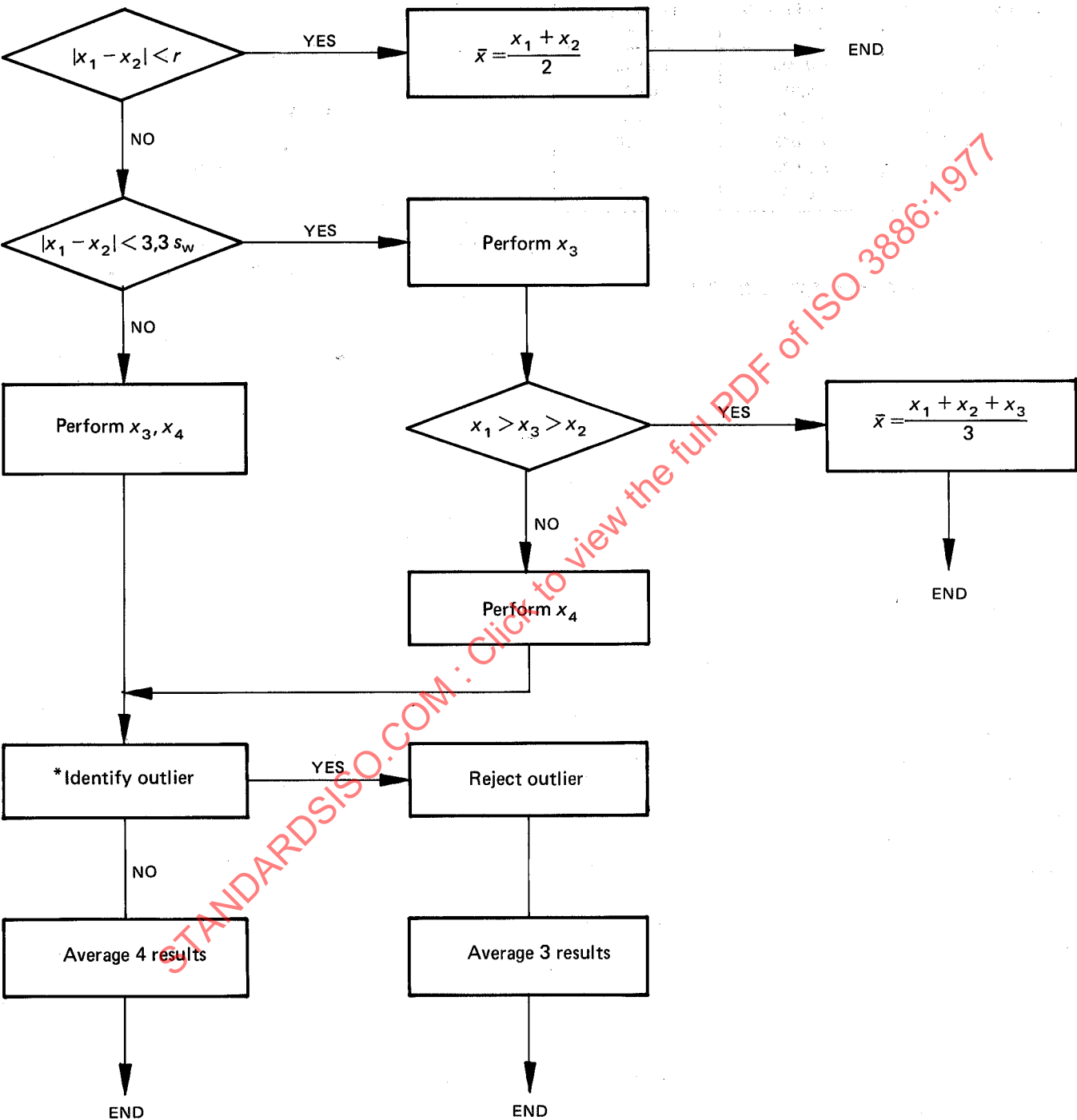
The test report shall include the following particulars :

- a) indications necessary for the identification of the sample;
- b) reference to this International Standard;
- c) results of the analysis;
- d) reference number of the results;
- e) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have had an influence on the results.

1) The derivation of the figures in the table is given in annex B.

ANNEX A

FLWSHEET ON THE PROCEDURE FOR THE ADOPTION OF ANALYTICAL VALUES FOR TEST SAMPLES



r = repeatability
= 2,77 sw
x̄ = average
• use Dixon's criteria for outlier.

ANNEX B

DERIVATION OF PERMISSIBLE TOLERANCES

The standard deviation within laboratories (s_{LAB}) was obtained by a comparison of the results of international analytical trials carried out in 1969 to 1971 on five iron ores samples : Australian iron ore (0,019 % Mn), Canadian iron ore (0,20 % Mn), Philippine iron sand (0,61 % Mn), CSR ore (Krivoj-Rog) (2,64 % Mn) and German Rostspat (8,42 % Mn).

The permissible tolerance for the standard sample (see table 2, second column) is equal to twice the standard deviation ($\pm 2 s_{LAB}$) and relates to the upper limit of the range of contents respectively.

The permissible tolerance for the test sample (see table 2, third column) is calculated by multiplying the standard deviation with the statistical factor 2,77 ($n = 2$ with 95 % confidence) and relates to the upper limit of the range of contents respectively.

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