International Standard 4692

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Iron ores — Determination of calcium and/or magnesium contents — Flame atomic absorption spectrometric method

Minerais de fer — Dosage du calcium et du magnésium — Méthode par spectrométrie d'absorption atomique dans la flamme

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Foreword

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

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

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No member body expressed disapproval of the document.

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INTERNATIONAL STANDARD **ISO 4692-1980 (E)**

Iron ores — Determination of calcium and/or magnesium contents — Flame atomic absorption spectrometric method

1 Scope and field of application

This International Standard specifies a flame atomic absorption spectrometric method for the determination of the calcium and/or magnesium contents of iron ores.

This method is applicable to a concentration range of 0,01 to 10,0 % of calcium and/or to that of 0,01 to 3,0 % of magnesium in natural iron ores, and iron ore 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 3083, *Iron ores — Preparation of samples.*

3 Principle

Decomposition of the test portion by treatment with hydrochloric acid with the addition of a small amount of nitric acid.

Evaporation to dehydrate silica, followed by dilution and filtration. Ignition of the residue and removal of silica by evaporation with hydrofluoric and sulphuric acids. Fusion with sodium carbonate and dissolution of the cooled melt in the filtrate.

Aspiration of the solution into the flame of an atomic absorption spectrometer using a dinitrogen oxide-acetylene burner for calcium and an air-acetylene burner for magnesium.

Comparison of absorbance values obtained for calcium and/or magnesium with those obtained from the calibration solutions.

NOTE — If a dinitrogen oxide flame is used for the determination of magnesium, the sensitivity is decreased by a factor of about 3.

4 Reagents

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

4.1 **Sodium carbonate** (Na_2CO_3), anhydrous.

4.2 **Hydrochloric acid**, ϱ 1,19 g/ml.

4.3 **Hydrochloric acid**, (ϱ 1,19 g/ml) diluted 1 + 9.

4.4 **Nitric acid**, ϱ 1,4 g/ml.

4.5 **Hydrofluoric acid**, 40 % (*m/m*), ϱ 1,13 g/ml, or 48 % (*m/m*), ϱ 1,185 g/ml.

4.6 **Sulphuric acid**, (ϱ 1,84 g/ml) diluted 1 + 1.

4.7 Background solution.

Dissolve 10 g of iron wire (Fe > 99,9 %) free from calcium and magnesium in 50 ml of hydrochloric acid (4.2) and oxidize by dropwise addition of nitric acid (4.4). Evaporate to syrupy consistency. Add 20 ml of hydrochloric acid (4.2) and dilute to 200 ml with water. Dissolve 17 g of sodium carbonate (4.1) in water, add carefully to the iron solution and heat to remove carbon dioxide. Transfer the cooled solution to a 1 000 ml volumetric flask, dilute to volume with water and mix.

4.8 Lanthanum chloride solution.

Dissolve 50 g of lanthanum chloride ($LaCl_3.xH_2O$) in 50 ml of hydrochloric acid (4.2) and 300 ml of hot water. Cool and dilute to 1 litre.

4.9 **Calcium**, standard solution, 25 mg of Ca per litre.

Dissolve 1,248 7 g of dried calcium carbonate ($CaCO_3$) in 100 ml of hydrochloric acid (ϱ 1,19 g/ml), diluted 1 + 3. When dissolution is complete, cool, transfer to a 1 000 ml volumetric flask, dilute to volume with water and mix. Transfer 10 ml of this solution to a 200 ml volumetric flask. Dilute to volume with water and mix.

1 ml of this solution contains 25 µg of Ca.

4.10 **Magnesium**, standard solution, 15 mg of Mg per litre.

Dissolve 0,300 0 g of oxide-free magnesium metal by slowly adding 75 ml of hydrochloric acid (ϱ 1,19 g/ml), diluted 1 + 3. When dissolved, cool, transfer to a 1 000 ml volumetric flask, dilute to volume with water and mix. Transfer 10 ml of this solution to a 200 ml volumetric flask, dilute to volume with water and mix.

1 ml of this solution contains 15 µg of Mg.

4.11 Calcium and magnesium calibration solutions.

From the standard calcium solution (4.9) and the standard magnesium solution (4.10), prepare calibration solutions as follows : Using pipettes, transfer 2,0 — 5,0 — 10,0 — 20,0 — 40,0 and 50,0 ml portions of the calcium and magnesium standard solutions to 200 ml volumetric flasks (see note).

Add 6 ml of hydrochloric acid (4.2), 60 ml of background solution (4.7) and 40 ml of lanthanum chloride solution (4.8). Dilute all solutions to volume with water and mix.

NOTE — The range of calcium or magnesium which can be covered may vary from instrument to instrument. Attention should be paid to the minimum criteria given in 5.2. For instruments with high sensitivity, smaller portions of standard solution or a more diluted standard solution can be used.

4.12 Zero calibration solution

Transfer 60 ml of the background solution (4.7) to a 200 ml volumetric flask, add 6 ml of hydrochloric acid (4.2) and 40 ml of lanthanum chloride solution (4.8), dilute to volume with water and mix.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Platinum crucible.

5.2 Atomic absorption spectrometer, equipped with an *air-acetylene and a dinitrogen oxide-acetylene burner.*

The atomic absorption spectrometer used in this method will be satisfactory if it meets the following criteria :

a) Minimum sensitivity — The absorbance of the highest calibration solution (see 4.11) shall be at least 0,3.

b) *Curve linearity* — The slope of the calibration curve covering the top 20 % of the concentration range (expressed as a change in absorbance) shall not be less than 0,7 of the value of the slope for the bottom 20 % of the concentration range determined in the same way.

c) Minimum stability — The standard deviation of the absorbance of the most concentrated calibration solution and the standard deviation of the absorbance of the zero calibration solution, each being calculated from a sufficient number of repetitive measurements, shall be less than 1,5 % and 0,5 % respectively of the mean value of the absorbance of the most concentrated solution.

NOTES

1 A strip chart recorder and/or digital readout device is advisable to measure the above criteria and for all subsequent measurements.

2 Instrument parameters may vary with each instrument. The following parameters were successfully used in several laboratories and they can be used as guidelines. In the case of calcium, solutions were aspirated into a dinitrogen oxide-acetylene flame of a premix burner. For magnesium, an air-acetylene flame was used.

	Ca	Mg
Hollow cathode lamp, mA	15	15
Wavelength, nm	422,7	285,2
Dinitrogen oxide flow rate, l/min	13,8	—
Air flow rate, l/min	—	22
Acetylene flow rate, l/min	6,6	4,2

In systems where the values shown above for gas flow rates do not apply, the ratio of the gas flow rates may still be a useful guideline.

6 Sampling and samples

For analysis, a laboratory sample of minus 100 µm particle size which has been taken in accordance with ISO 3081[1] and prepared in accordance with ISO 3083[1] shall be used. In the case of ores with high contents of combined water and/or oxidizable compounds, the particle size shall be minus 160 µm.

7 Procedure

Carry out the analysis 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 different times.

Simultaneously with the analysis, determine the hygroscopic moisture in accordance with ISO 2596.

7.1 Safety precaution

Follow the manufacturer's instructions for igniting and extinguishing the dinitrogen oxide-acetylene flame to avoid possible explosion hazards. Wear tinted safety glasses whenever the flame is burning.

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[1] A further International Standard now in preparation (ISO 3082) will specify mechanical methods of increment sampling and will also specify methods for preparation of samples.

7.2 Test portion

Weigh, to the nearest 0,000 2 g, approximately 1 g of the test sample.

7.3 Blank test and check test

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

NOTE — The certified reference material should be of the same type as the sample to be analysed. Such certified reference material cannot, however, be considered as being of the same type if the properties of the sample to be analysed differ from those of the certified reference material to such an extent that the analytical procedure must be changed substantially.

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 that 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 certified reference material may be used.

7.4 Determination

7.4.1 Decomposition of the test portion

Transfer the test portion (7.2) to a 250 ml beaker. Moisten with a few millilitres of water, add 25 ml of hydrochloric acid (4.2), cover with a watch-glass, and heat gently. Increase the heat and digest just below boiling, until no further attack is apparent. Add 2 ml of nitric acid (4.4) and digest for several minutes. Remove the watch-glass and evaporate the solution to dryness. Heat the salts on a hot-plate at 105 to 110 °C for 30 min. Add 5 ml of hydrochloric acid (4.2), cover the beaker with a watch-glass, and warm for several minutes. Add 50 ml of water, stirring to avoid the hydrolysis of titanium and heat to boiling. Wash the watch-glass and the walls of the beaker and filter the solution through a medium-texture paper containing some filter pulp into a 250 ml beaker. Carefully remove all adhering particles with a rubber-tipped glass rod or moistened filter paper and transfer to the filter, washing three times with dilute hydrochloric acid (4.3), then with hot water until the paper is free of iron. Transfer the paper and residue to a platinum crucible (5.1). Evaporate the filtrate to about 100 ml and reserve.

7.4.2 Treatment of the residue

Ignite the paper and residue in a platinum crucible at a low temperature (500 to 800 °C). Cool, moisten with a few drops of water, add 3 or 4 drops of sulphuric acid (4.6) and 10 ml of hydrofluoric acid (4.5). Evaporate slowly to expel silica and then fume to remove the excess sulphuric acid. Ignite at about 700 °C. Add 1,0 g of sodium carbonate (4.1) to the residue (see note 1), cover the crucible, and fuse over a burner or in a muffle furnace until a clear melt is obtained (at about 1 100 °C for 15 min).

Dissolve the cool melt in the reserved filtrate from 7.4.1, then remove and wash the crucible and the cover (see note 2).

Transfer the solution to a 200 ml volumetric flask, and dilute to volume with water and mix. Transfer an appropriate aliquot of this solution (see table 1) to a 200 ml volumetric flask and add 40 ml of lanthanum chloride solution (4.8). Add the amount of background solution (4.7) and hydrochloric acid (4.2) indicated in table 1, dilute to volume with water and mix (see note 3). (This solution is the final test solution.)

Transfer corresponding amounts of blank test solution to a 200 ml one-mark volumetric flask, add the same volumes of lanthanum chloride solution (4.8), background solution (4.7) and hydrochloric acid (4.2) as used for the test solution. Dilute to volume with water and mix. (This solution is the diluted blank test solution.)

NOTES

1 If difficulties are experienced with the fusion, 2 g of sodium carbonate (4.1) may be used, in which case it is advisable to double the amount of sodium carbonate (4.1) and the volume of hydrochloric acid (4.2) in the background solution (4.7).

2 If the solution is cloudy at this stage, indicating the presence of substantial amounts of hydrolysed titanium, it should be filtered prior to the transfer to the 200 ml volumetric flask.

Table 1 — Dilution guide for test solution

Element	Expected percentage of element in sample	Aliquot	Equivalent mass of sample	Background solution (4.7) to be added	Hydrochloric acid (4.2) to be added
	%	ml	g	ml	ml
Calcium	0,01 up to 0,1	100	0,50	30	3
	0,1 up to 0,5	50	0,25	45	4
	0,5 up to 2,5	10	0,05	60	6
	2,5 up to 10,0	2	0,01	60	6
Magnesium	0,01 up to 0,1	60	0,30	40	4
	0,1 up to 0,25	40	0,20	50	4
	0,25 up to 1,25	10	0,05	60	6
	1,25 up to 3,00	2	0,01	60	6

3 Dilutions shown in table 1 will provide concentrations of calcium and magnesium falling within the range of the calibration solutions. For instruments with high sensitivity, smaller portions of the test solution may be preferable. Avoid aliquot portions of less than 2 ml by making a preliminary dilution. Treat the blank test solution similarly. In this case the amounts of background solution (4.7) and hydrochloric acid (4.2) should be adjusted.

7.4.3 Adjustment of atomic absorption spectrometer

Set the wavelength for calcium (422,7 nm) or magnesium (285,2 nm) to obtain minimum absorbance. Fit the correct burner and, in accordance with manufacturer's instructions, light the appropriate flame. After 10 min preheating of the burner, adjust fuel and burner to obtain maximum absorbance while aspirating the highest calibration solution (see 4.11), and evaluate the criteria in 5.2.

Aspirate water and the calibration solution to establish that the absorbance reading is not drifting and then set the initial reading for water to zero absorbance.

7.4.4 Atomic absorption measurements

Aspirate the calibration solutions and the final test solution in order of increasing absorption starting with diluted blank test solution and the zero calibration solution, with the final test solution being aspirated at the proper point in the series. Aspirate water between each solution and record the readings when stable responses are obtained.

Repeat the measurements at least twice more. If necessary, convert the average of the readings for each solution to absorbance. Obtain the net absorbance of each calibration solution by subtracting the absorbance of the zero calibration solution. Similarly, obtain the net absorbance of the final test solution by subtracting the absorbance of the diluted blank test solution. Prepare a calibration curve by plotting the net absorbance values of the calibration solutions against the mass of calcium or magnesium, in micrograms per millilitre.

Convert the net absorbance values of the final test solution to micrograms of calcium and/or magnesium per millilitre by means of the calibration curve.

8 Expression of results

8.1 Calculation of calcium or magnesium content

The calcium or magnesium content, as a percentage by mass, is calculated from the following formula :

$$\frac{c \times 200}{m \times 10\,000} \times K$$

$$= \frac{c}{m \times 50} \times K$$

where

c is the concentration, in micrograms per millilitre, of calcium or magnesium in the final test solution;

m is the mass, in grams, of sample represented in 200 ml volume of the final test solution, taking into account any preliminary dilution which may have been made;

K is the conversion factor found from the following 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 Acceptance of analytical values

The analytical values for the test sample shall be accepted when the respective analytical values obtained for the corresponding certified reference material agree with the certified value within the limit of permissible tolerance for certified reference materials, and when the difference between the two values for the test sample does not exceed the permissible tolerance for test samples (table 2).

When the analytical value obtained for the certified reference material is outside the limit of the permissible tolerance (table 2, second column), an analysis shall be carried out simultaneously on one test sample and one certified reference material, with one blank test. The analytical value obtained for the certified reference material shall be examined for the acceptance of the value for the test sample, as above. If the value obtained for the certified reference material is again outside the limit, the procedure shall be repeated with a different reference material of the same type of ore, until two acceptable values for the test sample are obtained.

When the range (absolute difference) of the two values for the test sample is outside the limit of the permissible tolerance (table 2, third column), additional analyses shall be carried out on one test sample with one blank test, as required by the procedure in annex A, simultaneously with an analysis of a certified reference material of the same type of ore. Acceptance of such additional values for the test sample shall be subject, in each case, to the acceptability of the value obtained for the certified reference material.

8.2.2 Calculation of final result

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

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

a) 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;

b) when the figure in the third decimal place is 5 and there is a figure other than 0 in the fourth decimal place, or when the figure in the third decimal place is greater than 5, the figure in the second decimal place is increased by one;

c) when the figure in the third decimal place is 5 and there is no figure other than 0 in the fourth decimal place, 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 tolerance

The permissible tolerances described in 8.2.1 are shown in table 2.[1]

8.4 Oxide factors :

CaO (%) = 1,399 2 × Ca (%)

MgO (%) = 1,658 2 × Mg (%)

9 Test report

The test report shall include the following information :

a) reference to this International Standard;

b) details necessary for the identification of the sample;

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.

Table 2 — Permissible tolerances within laboratories

Ca content Ca (%)	**C.R.M.** Ca (%)	**Test sample** Ca (%)	
	$1,96\ s_w$	$2,77\ s_w$	$3,31\ s_w$
0,01 to 0,3	± 0,028	0,038	0,045
0,3 to 1,0	± 0,052	0,072	0,086
1,0 to 5,0	± 0,140	0,194	0,232
5,0 to 10,0	± 0,295	0,408	0,488

Mg content Mg (%)	**C.R.M.** Mg (%)	**Test sample** Mg (%)	
	$1,96\ s_w$	$2,77\ s_w$	$3,31\ s_w$
0,01 to 0,3	± 0,020	0,027	0,032
0,3 to 1,0	± 0,034	0,047	0,056
1,0 to 3,0	± 0,054	0,074	0,089

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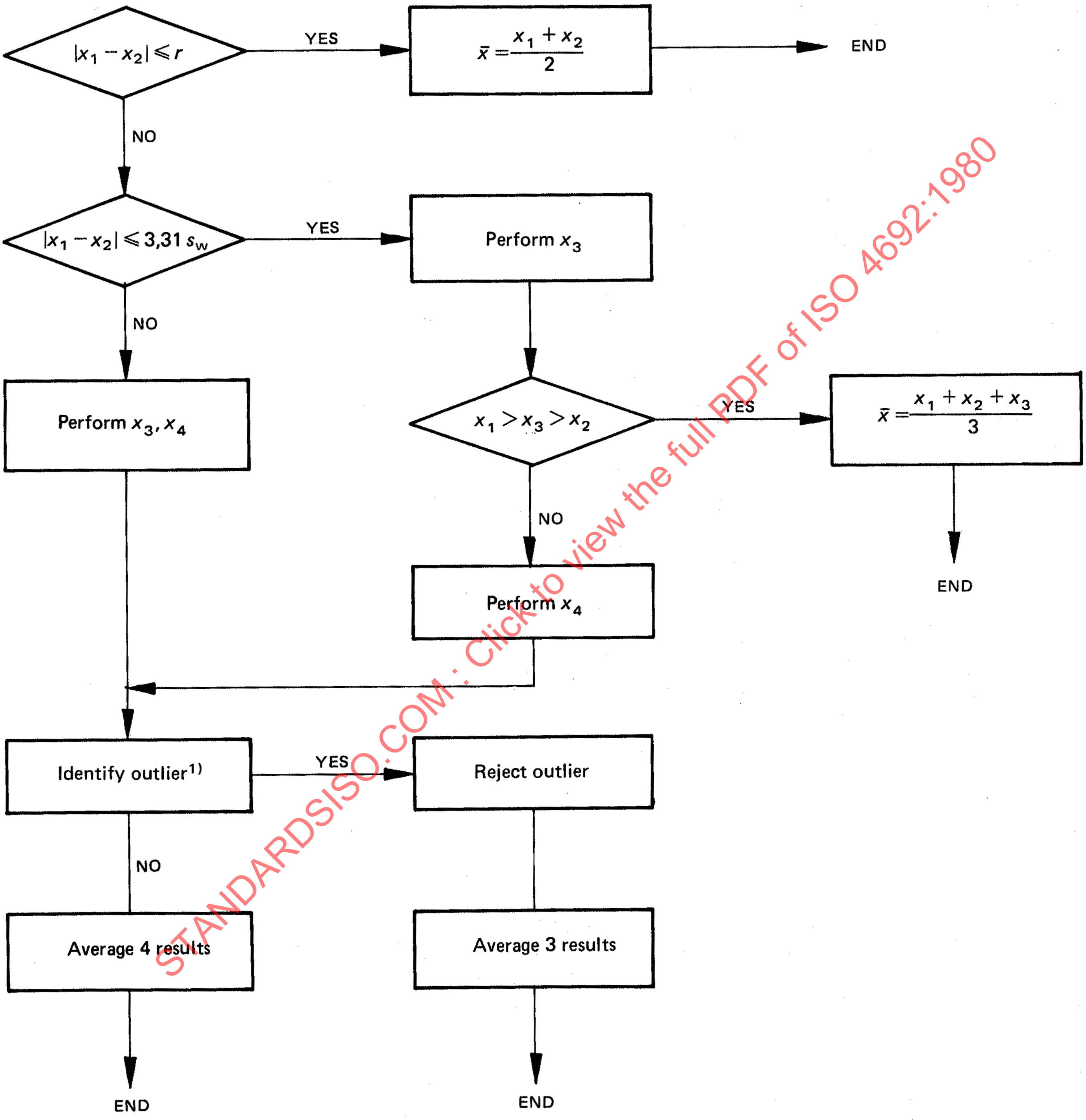
[1] The derivation of the figures in the table is given in annex B.

Annex A

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



r = repeatability

= $2{,}77\, s_w$ 2)

$\bar{x}$ = average

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[1] Use Dixon's criteria for outlier.

[2] For definition of s_w, see annex B.

Annex B

Derivation of permissible tolerances

The standard deviation within laboratories (s_w) was obtained by a comparison of the results of international analytical trials carried out in 1971/1972 and 1972/1973 on seven iron ore samples for calcium :

- Bomi Hill (0,074 % Ca), Canadian Ore (0,342 % Ca), Philippine Iron Sand (0,483 % Ca), Sweden No. 7 Ore (3,59 % Ca), Minette Ore (4,04 % Ca), ASTM No. 4 Ore (4,52 % Ca), 72-10 Ore (9,98 % Ca),

and six samples for magnesium :

- Bomi hill (0,298 % Mg), Canadian Ore (0,316 % Mg), Philippine Iron Sand (1,28 % Mg), Sweden No. 7 Ore (0,589 % Mg), Minette Ore (0,99 % Mg), ASTM No. 4 Ore (3,14 % Mg).

The permissible tolerances for the certified reference material (second column in table 2) are calculated by multiplying the standard deviations by the statistical factor 1,96, and relate to the upper limit of each range of contents respectively.

The permissible tolerances for the test sample (third column in table 2) are calculated by multiplying the standard deviations by the statistical factors 2,77 and 3,31 (n = 2 with 95 % confidence), and relate to the upper limit of each range of contents respectively.