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10697-1

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Steel — Determination of calcium content by flame atomic absorption spectrometry —

Part 1:
Determination of acid-soluble calcium content

Aciers — Dosage du calcium par spectrométrie d'absorption atomique dans la flamme —

Partie 1: Dosage du calcium soluble dans l'acide

Reference number
ISO 10697-1:1992(E)

Foreword

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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.

International Standard ISO 10697-1 was prepared by Technical Committee ISO/TC 17, *Steel*, Sub-Committee SC 1, *Methods of determination of chemical composition*.

ISO 10697 consists of the following parts, under the general title *Steel — Determination of calcium content by flame atomic absorption spectrometry*:

- *Part 1: Determination of acid-soluble calcium content*
- *Part 2: Determination of total calcium content*

Annex A forms an integral part of this part of ISO 10697. Annexes B and C are for information only.

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Steel — Determination of calcium content by flame atomic absorption spectrometry —

Part 1:
Determination of acid-soluble calcium content

1 Scope

This part of ISO 10697 specifies a flame atomic absorption spectrometric method for the determination of acid-soluble calcium content in steel.

The method is applicable to calcium contents between 0,000 5 % (m/m) and 0,003 % (m/m).

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 10697. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 10697 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 377-2:1989, *Selection and preparation of samples and test pieces of wrought steels — Part 2: Samples for the determination of the chemical composition.*

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

ISO 5725:1986, *Precision of test methods — Determination of repeatability and reproducibility for a standard test method by inter-laboratory tests.*

3 Definition

For the purposes of this part of ISO 10697, the following definition applies.

3.1 Acid-soluble calcium: Calcium dissolved in the acids specified in 8.3.1.

4 Principle

Dissolution of a test portion in hydrochloric and nitric acids.

Addition of potassium chloride/lanthanum nitrate solution as a spectrochemical buffer.

Spraying of the solution into a dinitrogen monoxide-acetylene flame.

Spectrometric measurement of the atomic absorption of the 422,7 nm spectral line emitted by a calcium hollow cathode lamp.

5 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade having very low calcium contents and only grade 2 water as specified in ISO 3696.

5.1 Pure iron, containing less than 0,000 1% (m/m) calcium.

5.2 Suitable solvent, for example acetone or dichloromethane.

5.3 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 1.

5.4 Hydrochloric acid, ρ about 1,19 g/ml, diluted 1 + 2.

5.5 Nitric acid, ρ about 1,40 g/ml.

5.6 Potassium chloride/lanthanum nitrate, solution.

Dissolve 95,34 g of potassium chloride (KCl) and 62,35 g of lanthanum nitrate hexahydrate [$La(NO_3)_3.6H_2O$] in water, dilute to 1 000 ml and mix.

5.7 Calcium, standard solutions.

5.7.1 Stock solution, corresponding to 100 mg of Ca per litre.

Dry several grams of calcium carbonate [purity $\geqslant$ 99,5 % (*m*/*m*)] in an air oven at 100 °C for at least 1 h and cool to room temperature in a desiccator. Weigh 0,249 7 g of the dried product into a 400 ml beaker, cover with a watch-glass and add 5 ml of hydrochloric acid (5.3) to dissolve. Cool and transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this stock solution contains 100 µg of Ca.

5.7.2 Standard solution, corresponding to 10 mg of Ca per litre.

Transfer 10,0 ml of the stock solution (5.7.1) into a 100 ml one-mark volumetric flask and add 5 ml of hydrochloric acid (ρ about 1,19 g/ml, diluted 1 + 10). Dilute to the mark with water and mix.

Prepare this standard solution immediately before use.

1 ml of this standard solution contains 10 µg of Ca.

6 Apparatus

All volumetric glassware shall be class A, in accordance with ISO 385-1, ISO 648 or ISO 1042, as appropriate.

Ordinary laboratory apparatus, and

6.1 Filter media, 0,22 µm pore size, 47 mm diameter cellulose-acetate filter.

6.2 Suction apparatus, i.e. a clean empty flask placed between the suction device and filtering flask to prevent any back suction and contamination.

6.3 Atomic absorption spectrometer, equipped with a calcium hollow cathode lamp and supplied with dinitrogen monoxide and acetylene sufficiently pure to give a steady clear fuel-lean flame, free from water and oil, and free from calcium.

The atomic absorption spectrometer used will be satisfactory if after optimization according to 8.3.5, the limit of detection and characteristic concentration are in reasonable agreement with the values given by the manufacturer and if it meets the precision criteria given in 6.3.1 to 6.3.3.

It is also desirable that the instrument should conform to the additional performance requirements given in 6.3.4.

6.3.1 Minimum precision (see A.1)

Calculate the standard deviation of 10 measurements of the absorbance of the most concentrated calibration solution. The standard deviation shall not exceed 1,5 % of the mean absorbance.

Calculate the standard deviation of 10 measurements of the absorbance of the least concentrated calibration solution (excluding the zero member). The standard deviation shall not exceed 0,5 % of the mean absorbance of the most concentrated calibration solution.

6.3.2 Limit of detection (see A.2)

This is defined as twice the standard deviation of 10 measurements of the absorbance of a solution containing the appropriate element at a concentration level selected to give an absorbance just above that of the zero member.

The limit of detection of calcium in a matrix similar to the final test portion solution shall be better than 0,02 µg of Ca per millilitre.

6.3.3 Graph linearity (see A.3)

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

For instruments with automatic calibration using two or more standards, it shall be established prior to the analysis, by obtaining absorbance readings, that the above requirements for graph linearity are fulfilled.

6.3.4 Characteristic concentration (see A.4)

The characteristic concentration of calcium in a matrix similar to the final test portion solution shall be better than 0,05 µg of Ca per millilitre.

6.4 Ancillary equipment

A strip chart recorder and/or digital readout device is recommended to evaluate the criteria of 6.3 and for all subsequent measurements.

Scale expansion can be used until the noise observed is greater than the read-out error and is always recommended for absorbances below 0,1. If scale expansion has to be used and the instrument does not have the means to read the value of the scale expansion factor, the value can be calculated by measuring the absorbances of a suitable solution with and without scale expansion, and simply dividing the signal obtained.

7 Sampling

Carry out sampling in accordance with ISO 377-2 or appropriate national standards for steel.

8 Procedure

All glassware shall first be washed in hydrochloric acid (5.3), then in water. The quantity of calcium present in the glassware can be checked by measuring the absorption of water introduced into the glassware after washing with acid.

For each series of blank, calibration and samples, all reagents, including water, shall be from the same batch.

8.1 Test portion

Wash the test sample in a suitable solvent (5.2) and dry.

Weigh, to the nearest 0,001 g, approximately 2,0 g of the test sample.

8.2 Blank test

Parallel with the determination and following the same procedure, carry out a blank test using the same quantities of all the reagents used for the test portion.

8.3 Determination

8.3.1 Preparation of the test solution

Place the test portion (8.1) in a 250 ml beaker. Add 20 ml of hydrochloric acid (5.3), cover the beaker with a watch-glass and heat gently until solvent action ceases. Add 2 ml of nitric acid (5.5). Simmer the solution for 5 min to remove oxides of nitrogen.

8.3.2 Filtration of the test solution

After placing a filter (6.1) in the suction apparatus (6.2) and flask, wash several times with warm hydrochloric acid (5.4) and then warm water. Discard the washings from the flask prior to filtration.

Filter the warm solution (below about 75 °C) through the filter (6.1) using the suction apparatus (6.2) and collect the filtrate in a clean flask. Rinse the beaker with a small volume of water. Remove adherent particles with a clean rubber-tipped rod and transfer through the filter by rinsing with small volumes of water. Wash the beaker and filter several times with a small volume of water.

Cool and transfer the filtrate at room temperature into a 100 ml one-mark volumetric flask. Add 10,0 ml of potassium chloride/lanthanum nitrate solution (5.6). Dilute to the mark with water and mix.

8.3.3 Preparation of the calibration solutions

Place 2,00 g ± 0,01 g of the pure iron (5.1) in a series of seven 250 ml beakers. Add 20 ml of hydrochloric acid (5.3) to each beaker, cover each with a watch-glass and heat until solvent action ceases. Add 2 ml of nitric acid (5.5). Simmer the solution for 5 min to remove oxides of nitrogen.

Using the burette, add the volumes of calcium standard solution (5.7.2) as indicated in table 1.

Proceed as specified in 8.3.2.

8.3.4 Adjustment of atomic absorption spectrometer

See table 2.

Table 1

Volume of calcium standard solution (5.7.2) ml	Corresponding concentration of calcium in final test solution µg/ml	Corresponding content of calcium in test sample % (*m*/*m*)
0[1]	0	0
1,0	0,1	0,000 5
2,0	0,2	0,001 0
4,0	0,4	0,002 0
6,0	0,6	0,003 0
8,0	0,8	0,004 0
10,0	1,0	0,005 0

1) Zero member

Table 2

Element	Characteristic
Type of lamp	Calcium hollow cathode
Wavelength	422,7 nm
Flame	Dinitrogen monoxide-acetylene red-feather flame The height of the red-feather flame shall be 10 mm to 20 mm adjusted for maximum calcium response
Lamp current	Follow manufacturer's recommendations
Bandwidth	Follow manufacturer's recommendations. If no recommendation is given, a bandwidth between 0,3 nm and 1,0 nm is suggested
Background correction	If the zero member gives an absorbance comparable with the precision of the least concentrated calibration solution, background correction may be required

WARNING — The manufacturer's recommendations should be closely followed and particular attention is drawn to the following safety points:

a) the explosive nature of acetylene, and regulations concerning its use;

b) the need to shield the eyes of the operator from ultraviolet radiation by means of tinted glass;

c) the need to keep the burner head clear of deposits because a badly clogged burner may cause a flashback;

d) the need to ensure that the liquid trap is filled with water;

e) always spray water between the test solutions, blank solution and/or calibration solutions.

8.3.5 Optimizing the atomic absorption spectrometer settings

Follow the manufacturer's instructions for preparing the instrument for use.

When the current to the lamp, the wavelength and the flow of gas have been adjusted and the burner lit, spray water until the indication has stabilized.

Set the absorbance value to zero using water.

Choose a damping setting or integration time to give a signal steady enough to fulfil the precision criteria of 6.3.1 to 6.3.3 .

Adjust the flame to be non-luminous and oxidizing with an approximate 10 mm to 20 mm of red feather. Spraying alternately the calibration solution of highest concentration and the zero member (see table 1), adjust the gas flow and burner position (horizontally, vertically and rotationally) until the difference in absorbance between the calibration solution is at a maximum. Check that the spectrometer is set accurately on the required wavelength.

Evaluate the criteria of 6.3.1 to 6.3.3 and the additional performance requirement of 6.3.4, to ensure that the instrument is suitable for the determination.

8.3.6 Spectrometric measurements

Set the scale expansion so that the calibration solution of highest concentration gives nearly full scale deflection. Spray the calibration solutions in ascending order repeatedly until each gives the specified precision, thus showing that the instrument has achieved stability. Select two calibration solutions, one having an absorbance just lower than the test portion solution and one just higher. Spray these first in ascending order, then in descending order, with the test solution as the middle solution, in each case measuring the absorption in relation to water.

Spray the complete range of calibration solutions, including the zero member again in ascending and descending order. The means of the last ascending and descending series of calibration solutions are used for the calibration graph.

It is recognized that these procedures cannot be followed with automatic instruments which accept two calibration solutions only. In this case, it is suggested that the two "sandwiching" solutions should not be used for the primary calibration but should be analysed alternately with the test solution.

Spray calibration solutions at frequent intervals during the measurement of a batch of determinations. Clean the burner if the results show loss of precision caused by clogging.

Obtain the mean absorbance of each calibration solution.

Obtain the mean absorbance of the test solution and the mean absorbance of the blank solution.

8.4 Plotting the calibration graph

It is necessary to prepare a new calibration graph for each series of determinations.

If pure metals and reagents have been used, the blank test and zero member should give very small absorbance readings with a negligibly small difference. In this case, prepare a calibration graph by plotting the mean absorbance values of the calibration solutions against micrograms of calcium per millilitre.

If, however, the zero member has a significant absorbance, a more complicated procedure is required. In this case, the concentration of calcium $\rho_{\mathrm{Ca,z}}$ in the zero member can be calculated using the formula

$$\rho_{\mathrm{Ca,z}} = \rho_{\mathrm{Ca,c1}} \times \frac{A_{\mathrm{z}}}{A_{\mathrm{Ca,c1}} - A_{\mathrm{z}}}$$

where

$\rho_{\mathrm{Ca,c1}}$ is the concentration of calcium, expressed in micrograms per millilitre, added to the first calibration solution;

A_{z} is the absorbance of the zero member;

$A_{\mathrm{Ca,c1}}$ is the absorbance of the first calibration solution.

The derived value $\rho_{\mathrm{Ca,z}}$ is then added to each of the nominal calibration concentrations in order to obtain a mean calibration graph passing through the origin.

Refer the absorbances of two adjacent calibration solutions to the graph. If these two calibration readings do not deviate from the graph by more than the permitted precision criteria, then the test solution reading is also acceptable.

9 Expression of results

9.1 Method of calculation

Convert the absorbances of the test solution and the blank solution to micrograms of calcium per millilitre by reference to the calibration graph (8.4).

The calcium content w_{Ca}, expressed as a percentage by mass, is given by the equation

$$w_{\mathrm{Ca}} = \frac{(\rho_{\mathrm{Ca,1}} - \rho_{\mathrm{Ca,0}}) \times 100}{10^6} \times \frac{100}{m}$$

$$= \frac{\rho_{\mathrm{Ca,1}} - \rho_{\mathrm{Ca,0}}}{100m}$$

where

$\rho_{\mathrm{Ca,0}}$ is the concentration, expressed in micrograms per millilitre, of calcium in the blank test (8.2);

$\rho_{\mathrm{Ca,1}}$ is the concentration, expressed in micrograms per millilitre, of calcium in the test solution (see 8.3.2);

m is the mass, in grams, of the test portion (8.1).

9.2 Precision

A planned trial of this method was carried out by 12 laboratories. All laboratories made three determinations for acid-soluble calcium on each of the test samples (see notes 1 and 2).

The test samples used are listed in table B.1.

The results obtained were treated statistically in accordance with ISO 5725.

The data obtained showed a logarithmic relationship between calcium content and repeatability (r) and reproducibility (R and R_{w}) of the test results (see note 3), as summarized in table 3. The graphical representation of the data is shown in figure C.1.

Table 3

Calcium content % (m/m)	Repeatability r	Reproducibility R	R_w
0,000 5	0,000 18	0,000 23	0,000 20
0,001 0	0,000 21	0,000 31	0,000 30
0,002 0	0,000 25	0,000 43	0,000 45
0,003 0	0,000 28	0,000 52	0,000 55

NOTES

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

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

3 From the results obtained on day 1, the repeatability (r) and reproducibility (R) were calculated using the procedure specified in ISO 5725. From the first result obtained on day 1 and the result obtained on day 2, the within-laboratory reproducibility (R_w) was calculated.

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 analysis;

b) the method used by reference to this part of ISO 10697;

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 part of ISO 10697, or any optional operation which may have influenced the results.

Annex A
(normative)

Procedures for the determination of instrumental criteria

For the preparation of standard methods of analysis using flame atomic absorption spectrometry, the values for the instrumental criteria should be decided from inter-laboratory test results, by the working group in charge.

A.1 Determination of minimum precision

Spray the most concentrated calibration solution 10 times to obtain 10 individual absorbance readings $A_{\mathrm{A}i}$ and calculate the mean value $\bar{A}_{\mathrm{A}}$.

Spray the least concentrated calibration solution (excluding the zero member) 10 times to obtain 10 individual absorbance readings $A_{\mathrm{B}i}$ and calculate the mean value $\bar{A}_{\mathrm{B}}$.

The standard deviations s_{A} and s_{B} of the most and least concentrated calibration solutions respectively are obtained from the equations

$$s_{\mathrm{A}} = \sqrt{\frac{\Sigma(A_{\mathrm{A}i} - \bar{A}_{\mathrm{A}})^2}{9}}$$

$$s_{\mathrm{B}} = \sqrt{\frac{\Sigma(A_{\mathrm{B}i} - \bar{A}_{\mathrm{B}})^2}{9}}$$

The minimum precisions of the most and least concentrated calibration solutions are obtained from $s_{\mathrm{A}} \times 100/\bar{A}_{\mathrm{A}}$ and $s_{\mathrm{B}} \times 100/\bar{A}_{\mathrm{A}}$.

A.2 Determination of limit of detection, $\rho_{\mathrm{Ca,min}}$

Prepare two solutions each containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentrations:

— ρ'_{Ca} µg/ml to give an absorbance A' of approximately 0,01;

— matrix blank to give an absorbance A_0.

Spray the ρ'_{Ca} solution and blank solution 10 times each, recording each reading for about 10 s, and using sufficient scale expansion to make the fluctuations in signal clearly visible.

Obtain the mean absorbance readings $\bar{A}'$ and $\bar{A}_0$.

The standard deviation $s_{A'}$ is given by the equation

$$s_{A'} = \sqrt{\frac{\Sigma(A'_i - \bar{A}')^2}{9}}$$

where

A'_i is the individual measured absorbance reading;

$\bar{A}'$ is the mean value of A'_i.

The limit of detection $\rho_{\mathrm{Ca,min}}$ is given by the equation

$$\rho_{\mathrm{Ca,min}} = \frac{\rho'_{\mathrm{Ca}} \times s_{A'} \times k}{\bar{A}' - \bar{A}_0}$$

(k is normally taken as 2)

A.3 Criterion for graph linearity

Having established the calibration graph (see figure A.1), before the application of any curve-straightening device, obtain the net absorbance value A_{A} corresponding to the top 20 % of the concentration range and the net absorbance A_{B} corresponding to the bottom 20 % of the concentration range. Calculate $A_{\mathrm{A}}/A_{\mathrm{B}}$. This must not be less than 0,7.

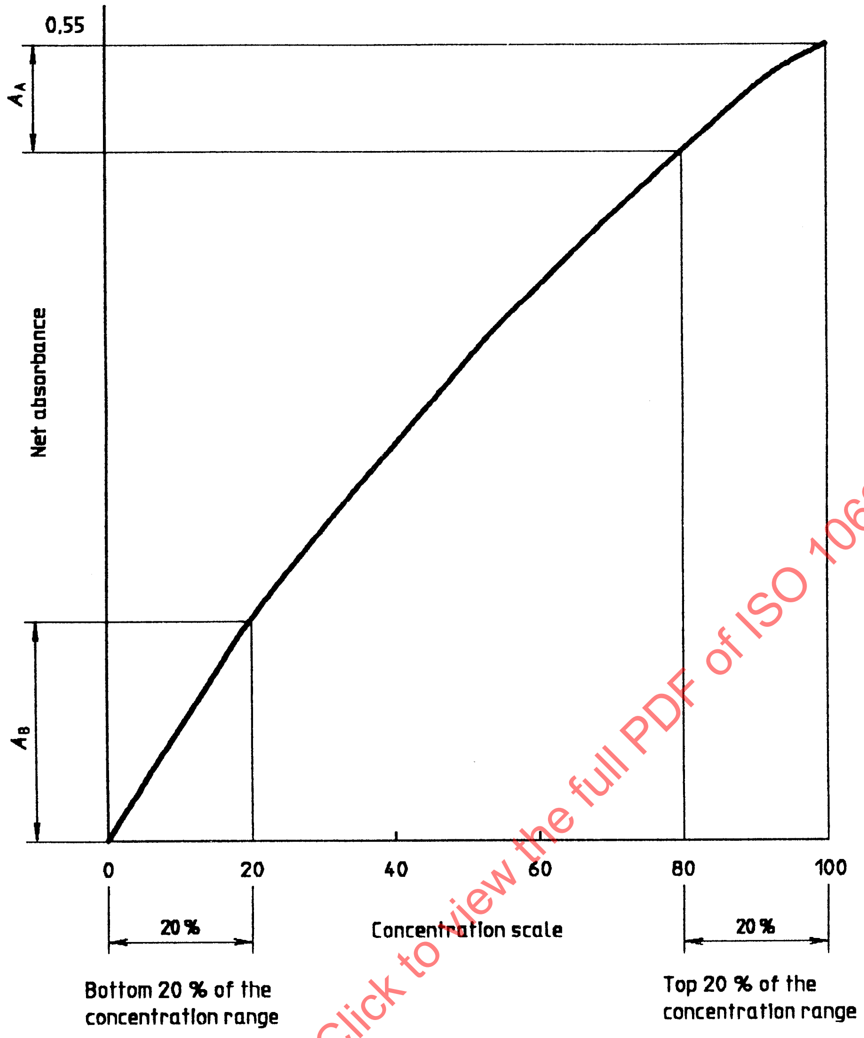


Figure A.1 — Calibration graph

A.4 Determination of characteristic concentration, $\rho_{\mathrm{Ca,k}}$

Prepare a solution containing the same matrix concentration as the sample solution, but with the element of interest at the following known concentration:

> ρ_{Ca} µg/ml to give an absorbance A of approximately 0,1.

Spray the ρ_{Ca} and the blank solutions without scale expansion and measure the absorbances A and A_0. The characteristic concentration $\rho_{\mathrm{Ca,k}}$ is given by the equation

$$\rho_{\mathrm{Ca,k}} = \frac{\rho_{\mathrm{Ca}} \times 0{,}004\,4}{A - A_0}$$

Annex B
(informative)

Additional information on the international co-operative tests

Table 3 was derived from the results of international analytical trials carried out in 1989 on five steel samples in nine countries involving 12 laboratories.

The results of the trials were reported in document ISO/TC 17/SC 1 N 825, March 1990. The graphical representation of the precision data is given in annex C.

The test samples used are listed in table B.1.

Table B.1

Sample	Acid-soluble calcium content % (m/m)		
	Certified	Found	
		$\overline{w}_{Ca,1}$	$\overline{w}_{Ca,2}$
JSS 168-4 (mild steel)	0,000 6	0,000 48	0,000 49
JSS 169-5 (mild steel)	0,001 2	0,001 06	0,001 09
JSS 171-5 (mild steel)	0,002 8	0,002 64	0,002 70
ECRM 096-1 (mild steel)	0,002 1	0,002 34	0,002 37
Sandvik (stainless steel)	0,001[1]	0,001 43	0,001 47

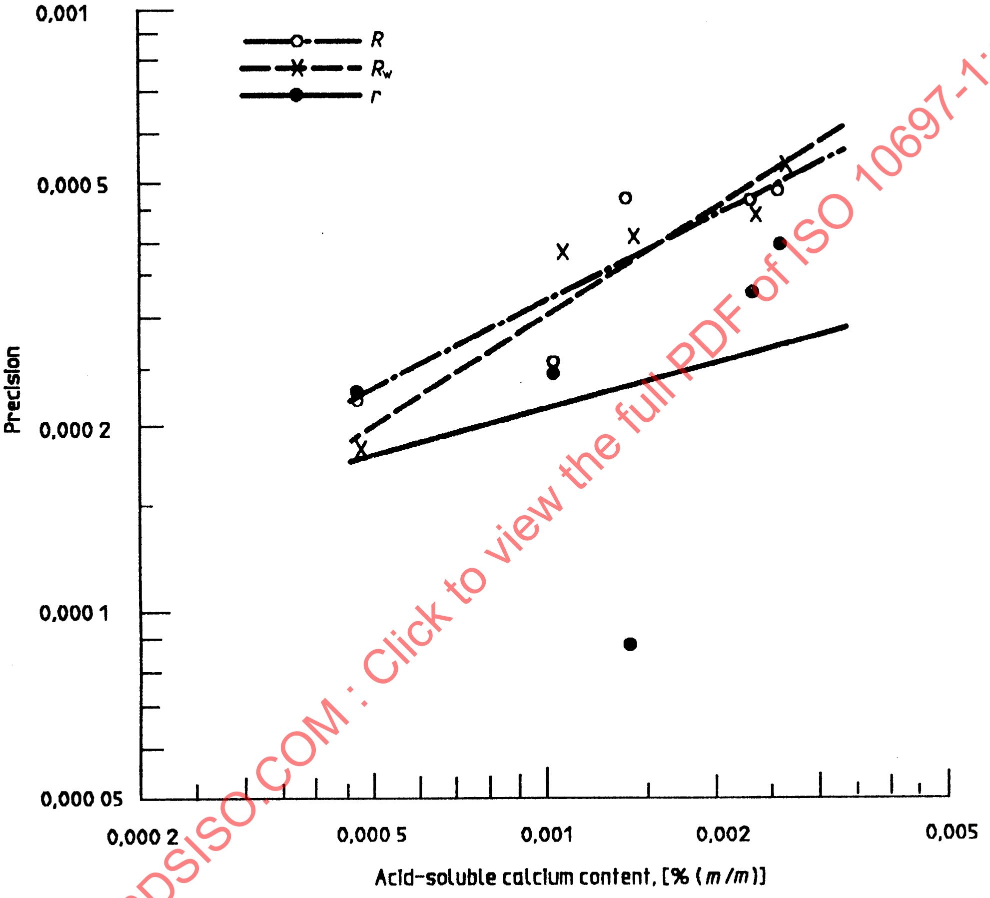
$\overline{w}_{Ca,1}$: general mean within a day

$\overline{w}_{Ca,2}$: general mean between days

[1] Non-certified value.

Annex C
(informative)

Graphical representation of precision data



$$\lg r = 0{,}297\,2 \lg \bar{w}_{\mathrm{Ca},1} - 2{,}806\,0$$
$$\lg R_w = 0{,}646\,1 \lg \bar{w}_{\mathrm{Ca},2} - 1{,}573\,4$$
$$\lg R = 0{,}258\,3 \lg \bar{w}_{\mathrm{Ca},1} - 2{,}665\,8$$

Figure C.1 — Logarithmic relationship between acid-soluble calcium content (w_{Ca}) and repeatability (r) or reproducibility (R and R_w)