International Standard ISO 6830

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Iron ores — Determination of aluminium content — EDTA titrimetric method

Minerais de fer — Dosage de l'aluminium — Méthode titrimétrique à l'EDTA

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Foreword

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International Standard ISO 6830 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

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INTERNATIONAL STANDARD **ISO 6830-1986 (E)**

Iron ores — Determination of aluminium content — EDTA titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method using EDTA for the determination of the aluminium content of iron ores.

This method is applicable to a concentration range of 0,25 to 5,0 % (m/m) of aluminium in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

2 References

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

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

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method.*[1]

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

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

3 Principle

Fusion of a test portion, in a vitreous carbon or zirconium crucible, with a mixed flux of sodium carbonate and sodium peroxide. Dissolution of the cooled melt in hydrochloric acid, precipitation of R_2O_3 with ammonia solution, filtration and redissolution of the hydroxides in hydrochloric acid.

Treatment with cupferron and chloroform, extraction of elements such as iron and titanium and rejection of the organic phase. Treatment of the aqueous phase with nitric and perchloric acids, evaporation, treatment with hydrochloric acid, dilution and filtration.

Addition to the filtrate of an excess of disodium dihydrogen ethylenedinitrilotetraacetate (EDTA) and titration of the excess with zinc standard volumetric solution using xylenol orange indicator. Addition of ammonium fluoride to release the EDTA bound to aluminium, and titration with zinc solution as before.

4 Reagents

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

4.1 Sodium carbonate (Na_2CO_3), anhydrous.

4.2 Sodium peroxide (Na_2O_2), dry.

4.3 Nitric acid, ρ 1,40 g/ml.

4.4 Hydrochloric acid, ρ 1,16 to 1,19 g/ml.

4.5 Hydrochloric acid, ρ 1,16 to 1,19 g/ml diluted 1 + 5.

4.6 Hydrochloric acid, ρ 1,16 to 1,19 g/ml diluted 1 + 1.

4.7 Ammonia, solution.

Ammonia (ρ 0,880 to 0,890 g/ml) diluted 1 + 1.

4.8 Ammonium chloride (NH_4Cl), 10 g/l solution containing 2 drops (0,1 ml) of ammonia solution per 100 ml.

4.9 Cupferron (nitrosophenylhydroxylamine ammonium salt) [$C_6H_5N(NO)ONH_4$], 60 g/l solution.

Prepare this solution in cold (< 20 °C) water on the day of use. Filter through a rapid paper and cool to 10 °C.

4.10 Chloroform.

4.11 Perchloric acid, ρ 1,67 g/ml approx.

4.12 Sodium hydroxide, 100 g/l solution.

4.13 Sodium hydroxide, 10 g/l solution.

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[1] At present at the stage of draft.

4.14 **Acetate buffer.**

Dissolve 136 g of sodium acetate tri-hydrate ($CH_3COONa \cdot 3H_2O$) in about 600 ml water. Add 7 ml of glacial acetic acid and dilute to 1 litre.

Store this solution in a polyethylene bottle.

4.15 **Ammonium fluoride,** 100 g/l solution.

Dissolve 10 g of ammonium fluoride (NH_4F) in 100 ml water in a polyethylene beaker.

Prepare this solution on the day of use.

4.16 **Xylenol orange,** indicator.

Triturate 0,1 g of xylenol orange with a little water to make a paste. Dilute to 100 ml with water. Filter. Store in an amber-coloured glass-stoppered bottle.

The solution is stable for one week.

4.17 **Zinc,** standard volumetric solution, $c(Zn^{2+}) = 0{,}01$ mol/l.

Weigh 0,653 8 g of high purity (99,99 % Zn) zinc metal (clippings or small pieces) into a 125 ml Erlenmeyer flask. Add 5 ml of water followed by 2,5 ml of nitric acid (4.1). Cover the flask and gently simmer. If the reaction subsides leaving undissolved metal, add 2 ml increments of water followed by simmering until complete solution is obtained. Add 50 ml of water and gently boil for 2 min. Cool. By dropwise addition of sodium hydroxide solution (4.13) adjust the pH to 4, measured by pH meter. Dilute to 1 000 ml with water in a volumetric flask.

4.18 **Disodium dihydrogen ethylenedinitrilotetraacetate dihydrate (EDTA),** solution, $c(C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O) = 0{,}01$ mol/l.

Dissolve 3,72 g of disodium EDTA dihydrate in water, and dilute to 1 litre with water.

Store this solution in a polyethylene bottle.

5 Apparatus

Ordinary laboratory apparatus and:

5.1 Vitreous carbon crucible, of 20 ml capacity; or **zirconium crucible** of 50 ml capacity.

5.2 Magnetic stirrer, with a polytetrafluorethylene-coated bar.

5.3 Spatula, of non-magnetic material or demagnetized stainless steel (for example austenitic stainless steel).

5.4 Burette, conforming to the specifications in ISO 385/1.

6 Sampling and samples

6.1 Laboratory sample

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

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

6.2 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 whole contents of the container. Dry the test sample at 105 ± 2 °C as specified in ISO 7764. (This is the predried test sample.)

7 Procedure

7.1 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 is not affected by the previous result(s). For this particular analytical method, this condition implies that the repetition of the procedure shall be carried out either by the same operator at a different time of by a different operator including, in either case, appropriate recalibration.

7.2 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 6.2.

NOTE — 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 would become necessary.

When the analysis is carried out on several test 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.

The blank test shall contain all reagents in the same amounts as added to the test portion during analysis.

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

7.3 Test portion

Taking several increments, weigh, to the nearest 0,000 2 g, the amount of predried test sample (6.2) specified in the table in accordance with the expected aluminium content.

NOTE — The test portion should be taken and weighed quickly in order to avoid reabsorption of moisture.

7.4 Determination

7.4.1 Dissolution of the test portion

Transfer 0,50 g of sodium carbonate (4.1) into a dry crucible (5.1). Add the test portion (7.3) to the crucible, followed by 2 g of sodium peroxide (4.2). Mix the contents with a dry spatula (5.3).

Fuse over a Meker burner (low heat) swirling the crucible until the melt is cherry red and clear. Remove from the heat and swirl until the melt solidifies on the inner wall of the crucible.

Place the crucible in a dry 250 ml beaker. Cool. Cover with a watch-glass and add about 10 ml of water to the crucible. After effervescence ceases, empty the contents of the crucible into the beaker and wash the crucible with about 10 ml of water. Add 20 ml of hydrochloric acid (4.6) via the crucible into the beaker. Rinse the crucible with water and add the rinsings to the beaker. Dilute to about 70 ml with water.

7.4.2 Removal of interfering elements

Bring the contents of the beaker to the boil. Add ammonia solution (4.7) dropwise until the precipitation of hydroxides is complete (pH 6,5). Boil for 1 min and immediately filter through a rapid paper. Retain this beaker. Wash the paper and precipitate five times with hot ammonium chloride solution (4.8). Then wash five times with hot water. Discard the filtrate. Place the unfolded filter paper, with the precipitated hydroxides, on the inner wall of the retained beaker and wash down the precipitate with a fine jet of hot water. Then wash down the filter paper with 25 ml of hot hydrochloric acid (4.6). Finally wash with a jet of hot water, and discard the filter paper. Cover the beaker with a watch-glass and bring the contents to the boil. Rinse. Cool to below 20 °C and adjust the volume to 50 ml using water.

NOTE — Prior to and during the extraction ensure that all reagents including water are cooled to below 20 °C.

Transfer the solution to a 250 ml separating funnel. Use 25 ml of water for rinsing the beaker and add to the separating funnel.

Add 20 ml of cupferron solution (4.9). Mix slightly. Add 20 ml of chloroform (4.10). Shake vigorously for 1 min. Allow the layers to separate. Drain off the lower organic layer. Add 5 ml of chloroform (4.10) to the separating funnel to displace the cupferrates on the surface of the aqueous layer. Drain off the organic layer. Carry out additional treatment with cupferron (4.9) and chloroform (4.10) as shown in table 1 (commensurate with the mass of test portion).

Finally add two successive 20 ml portions of chloroform (4.10) to the aqueous phase, shaking vigorously for 1 min. Allow to settle and separate. Drain off and reject the organic layer. Wipe the stem of the separating funnel with a filter paper wick.

Drain the aqueous phase into a 250 ml beaker, rinsing with 5 ml of hydrochloric acid (4.5). Boil for a few minutes. Remove from the heat.

Add 5 ml of nitric acid (4.3) and 10 ml of perchloric acid (4.11). Cover with a ribbed cover glass. Evaporate nearly to dryness. Remove from the heat.

Add 10 ml of hydrochloric acid (4.6). Heat to dissolve the salts and then add 50 ml of water and bring to the boil. Filter through a rapid paper washing with hot water several times. Cool the filtrate.

7.4.3 Titration

Add, by means of a pipette, an excess of EDTA (4.18) (25 ml is sufficient) to the filtrate. Adjust the pH to 2,5 measured by pH meter, by the dropwise addition of sodium hydroxide (4.12), then adjust the pH to 4 by the dropwise addition of sodium hydroxide (4.13). Dilute the contents to 100 ml with water. Cover the beaker and bring the contents to the boil. Keep boiling gently for 10 min. Cool.

Add 15 ml of acetate buffer (4.14), and 7 drops (about 0,3 ml) of xylenol orange indicator (4.16). Stir the solution using the magnetic stirrer (5.2). Titrate with zinc standard volumetric solution (4.17). The colour changes to a persistent (30 s) pink at the end-point.

Add 10 ml of ammonium fluoride solution (4.15), heat the contents to boiling and boil gently for 10 min. Cool and add 2 to 3 drops of xylenol orange indicator (4.16). Stir the solution and titrate the liberated EDTA with zinc standard volumetric solution (4.17).

The colour changes to a persistent (30 s) pink at the end-point. Record the titre, V ml.

Table — Mass of test portion and extraction volume

Expected aluminium content	Mass of test portion	Second extraction		Third extraction	
		Cupferron	Chloroform	Cupferron	Chloroform
% (m/m)	g	ml	ml	ml	ml
0,25 to 1,0	0,3	20	20	15	20
1,0 to 2,5	0,2	15	20	—	—
2,5 to 5,0	0,1	10	20	—	—

8 Expression of results

8.1 Calculation of aluminium content

The aluminium content, as a percentage by mass, is calculated to four decimal places using the equation

$$W_{\mathrm{Al}}(\%) = \frac{0{,}026\,98 \times V}{m} \qquad \ldots (1)$$

where

V is the volume, in millilitres, of zinc standard volumetric solution (4.17) used in 7.4.3;

m is the mass, in grams, of the test portion (7.3);

0,026 98 is the relative atomic mass of aluminium times 10^{-3}.

8.2 General treatment of results[1]

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations[1]:

$$r = 0{,}028\,9\,X + 0{,}016\,7 \qquad \ldots (2)$$

$$P = 0{,}042\,2\,X + 0{,}032\,3 \qquad \ldots (3)$$

$$\sigma_r = 0{,}010\,4\,X + 0{,}006\,0 \qquad \ldots (4)$$

$$\sigma_{\mathrm{L}} = 0{,}013\,4\,X + 0{,}010\,2 \qquad \ldots (5)$$

where

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

- within-laboratory equations (2, 4); the arithmetic mean of the duplicate values,
- between-laboratory equations (3, 5); the arithmetic mean of the final results (8.2.3) of the two laboratories;

r is the permissible tolerance within a laboratory (repeatability);

P is the permissible tolerance between laboratories;

σ_r is the within-laboratory standard deviation;

σ_{L} is the between-laboratories standard deviation.

8.2.2 Acceptance of analytical values

The result obtained for the certified reference material (7.2) shall be such that the difference between this result and the certified value of the reference material is statistically insignificant. For a certified reference material that has been analysed by at least 10 laboratories using method(s) that are comparable both in accuracy and precision with this method, the following condition may be used to test the significance of the difference:

$$|A_{\mathrm{c}} - A| \leqslant 2\sqrt{\frac{s_{\mathrm{Lc}}^2 + \dfrac{s_{\mathrm{Wc}}^2}{n_{\mathrm{Wc}}}}{N_{\mathrm{c}}} + \sigma_{\mathrm{L}}^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (6)$$

where

A_{c} is the certified value;

A is the result or the mean of results obtained for the certified reference material;

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 on the certified reference material (in most cases $n = 1$);

σ_{L} and σ_r are as defined in 8.2.1.

If condition (b) is satisfied, i.e. if the left-hand side of condition (6) is less than or equal to the right-hand side, then the difference $|A_{\mathrm{c}} - A|$ is statistically insignificant; otherwise, it is statistically significant.

When the difference is significant, the analysis shall be repeated, simultaneously with an analysis of the test sample. If the difference is again significant, the procedure shall be repeated using a different certified reference material of the same type of ore.

When the range of the two values for the test sample is outside the limit for r calculated according to equation (2) of 8.2.1, one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with an analysis of a certified reference material of the same type of ore.

Acceptability of the results for the test sample shall in each case be subject to the acceptability of the results for the certified reference material.

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[1] Additionnal information is given in annex B and annex C.

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

a) if there are sufficient data to enable the between-laboratories standard deviation to be estimated, delete the expression $s_{\mathrm{Wc}}^2/n_{\mathrm{Wc}}$ and regard s_{Lc} as the standard deviation of the laboratory means;

b) if the certification has been made by only one laboratory or if the interlaboratory results are missing, use the following condition:

$$|A_{\mathrm{c}} - A| \leqslant 2\sqrt{2\sigma_{\mathrm{L}}^2 + \frac{\sigma_r^2}{n}} \qquad \dots \quad (7)$$

8.2.3 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 four decimal places and 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 the figure 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 Oxide factor

$$w_{\mathrm{Al_2O_3}}\ (\%) = 1{,}889\,5 \times w_{\mathrm{Al}}\ (\%)$$

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) result of the analysis;

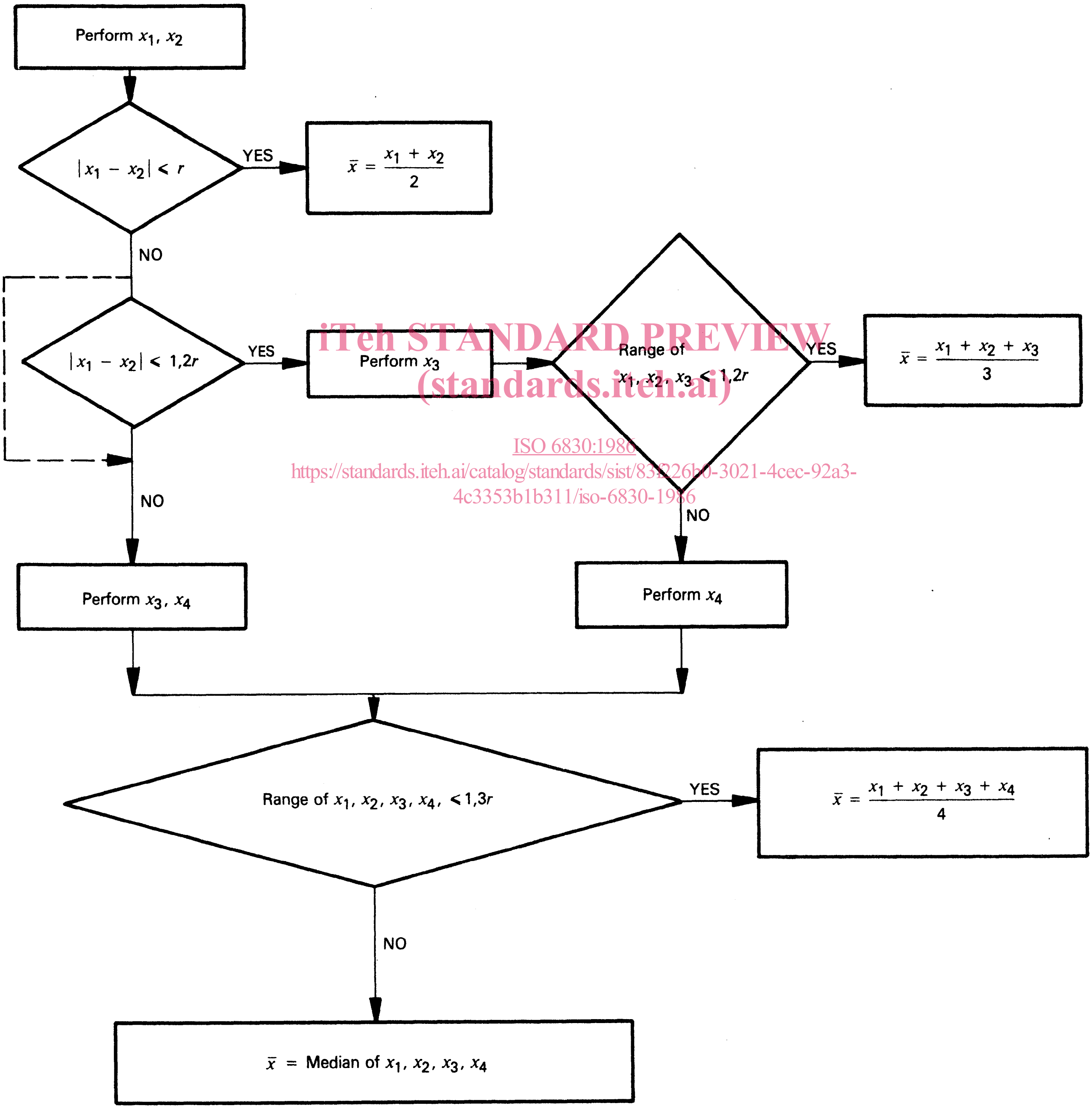
d) reference number of the result;

e) any characteristics noticed during the determination, and any operations not specified in this International Standard which may have influenced the result, either for the test sample or the certified reference material(s).

Annex A

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

(An integral part of this International Standard.)



r: as defined in 8.2.1.

Annex B

Derivation of repeatability and permissible tolerance

(This annex is for information only, and is not an integral part of this International Standard.)

The regression equations in 8.2.1 have been obtained by statistical evaluation of the results of international analytical trials carried out from 1976 to 1978 on six iron ore samples, involving 23 laboratories in nine countries.

Graphical treatment of the precision data is given in annex C.

The test samples used were:

Sample	**Aluminium content % (*m*/*m*)**
Marcona	0,36
Krivoj Rog	0,66
Philippine Iron Sand	1,44
British sinter (Scunthorpe)	1,76
Minette	2,34
British sinter (Rotherham)	3,50

NOTES

1 A report of the international trial and a statistical analysis of the results (Document ISO/TC 102/SC 2 N 490E, May 1978) is available either from the Secretariat of ISO/TC 102/SC 2 or the Secretariat of ISO/TC 102.

2 The statistical analysis has been performed in accordance with the principles embodied in ISO 5725.