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Iron ores — Determination of water-soluble chloride — Ion-selective electrode method

Minerais de fer — Dosage des chlorures solubles dans l'eau — Méthode par électrode sélective des ions

Reference number
ISO 9517:2007(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 9517 was prepared by Technical Committee ISO/TC 102, *Iron ore and direct reduced iron*, Subcommittee SC 2, *Chemical analysis*.

This second edition cancels and replaces the first edition (ISO 9517:1989), which has been technically revised. It has been updated to alter the manner in which precision data are presented.

INTERNATIONAL STANDARD **ISO 9517:2007(E)**

Iron ores — Determination of water-soluble chloride — Ion-selective electrode method

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

1 Scope

This International Standard specifies an ion-selective electrode method for the determination of the mass fraction of water-soluble chloride in iron ores. This method is applicable to a mass-fraction range of 0,007 % to 0,1 % of water-soluble chloride in natural iron ores, concentrates and agglomerates, including sinter products.

NOTE Water-soluble chloride is the part of the mass fraction of chloride in an iron ore that is extractable by leaching with aqueous solution under substantially neutral conditions.

2 Normative references

The following referenced documents are indispensable for the application 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 — One-mark pipettes*

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

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

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

3 Principle

The test portion is digested in water containing potassium sulfate; the suspension is transferred to a volumetric flask and diluted to volume. The solution is dry filtered, an aliquot is treated with potassium persulfate solution, and neutral buffer is added. Ionic-strength adjuster solution is added and the chloride concentration is determined potentiometrically using a chloride-ion electrode and a double-junction reference electrode.

4 Reagents

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

The preparation of reagent and calibration solutions, and all operations specified in Clauses 5, 6 and 7, shall be conducted in an area adequately isolated from any areas in which hydrochloric acid is used.

4.1 Potassium sulfate (K_2SO_4) solution, 2 g/l.

4.2 Potassium sulfate (K_2SO_4) solution, 4 g/l.

4.3 Potassium persulfate ($K_2S_2O_8$) solution, 1,5 g/100 ml.

Prepare freshly for each series of tests.

4.4 Sodium nitrate solution, $c(NaNO_3)$ = 5 mol/l.

Dissolve 42,5 g of sodium nitrate in about 60 ml of water, transfer to a 100 ml volumetric flask, dilute to volume and mix.

4.5 Phosphate buffer solution.

Dissolve 2,72 g of potassium dihydrogen phosphate (KH_2PO_4) and 2,84 g of disodium hydrogen phosphate (Na_2HPO_4) in 40 ml of water. Transfer to a 100 ml volumetric flask, dilute to volume and mix.

4.6 Stirring-bar cleaning solution.

Add carefully to about 700 ml of water, 150 ml of sulfuric acid (ρ 1,84 g/ml) and 150 ml of phosphoric acid (ρ 1,7 g/ml) and mix.

4.7 Chloride standard solution A, 1 000 µg of chloride per ml.

Dry about 2 g of sodium chloride at 105 °C for 1 h and cool in a desiccator. Weigh 0,824 g of the dried material, dissolve in about 50 ml of water and transfer to a 500 ml volumetric flask. Dilute to volume and mix.

1 ml of chloride standard solution A contains 1 000 µg of chloride.

4.8 Chloride standard solution B, 50 µg of chloride per ml.

Measure 25,0 ml of standard chloride solution A into a 500 ml volumetric flask, dilute to volume and mix.

1 ml of chloride standard solution B contains 50 µg of chloride.

4.9 Chloride standard solution C, 20 µg of chloride per ml**.**

Measure 10,0 ml of chloride standard solution A into a 500 ml volumetric flask, dilute to volume and mix.

1 ml of chloride standard solution C contains 20 µg of chloride.

Standard solutions B (4.8) and C (4.9) should be prepared freshly.

4.10 Calibration solutions.

Prepare the calibration solutions specified in Table 1 for the expected range of mass fractions of chloride.

If the mass fraction of chloride is unknown, prepare calibration solutions containing 5,0 µg, 10,0 g and 50,0 g of chloride per ml. If the mass fraction of chloride is then found to be less than 0,012 %, prepare additional calibration solutions containing 2,0 µg and 3,0 µg of chloride per ml. For higher mass fractions of chlorides, prepare any additional solutions required in accordance with Table 1.

Table 1 — Calibration solutions required for each range of mass fraction of chloride

Mass fraction of chloride in test sample %	Concentration in calibration solution µg/ml
0,005 to 0,025	2,0; 3,0; 5,0; 10,0
0,012 to 0,025	5,0; 10,0
0,025 to 0,10	10,0; 25,0; 50,0

For the preparation of the required calibration solutions, measure into a series of 100 ml volumetric flasks the aliquots of chloride standard solutions specified in Table 2.

Table 2 — Preparation of calibration solutions

Chloride concentration in calibration solution µg/ml	Standard-solution aliquot volume ml	Standard solution
2,0	10,0	C (4.9)
3,0	15,0	C (4.9)
5,0	10,0	B (4.8)
10,0	20,0	B (4.8)
25,0	50,0	B (4.8)
50,0	5,0	A (4.7)

Add to the aliquots of standard solution in the 100 ml volumetric flasks, 6 ml of potassium persulfate solution (4.3), 35 ml of potassium sulfate solution (4.2), 2 ml of phosphate buffer solution (4.5) and 2 ml of sodium nitrate solution (4.4) (ionic strength adjuster). Dilute to volume and mix.

Calibration solutions containing from 2,0 µg to 10,0 µg of chloride per ml should be prepared on the day of use.

5 Apparatus

Any one-mark pipettes and volumetric flasks required shall comply with the specifications of ISO 648 and ISO 1042, respectively.

Ordinary laboratory equipment and the following.

5.1 Magnetic stirrer (optional, see fourth paragraph of 7.6.4).

5.2 Magnetic stirrer/hotplate.

5.3 PTFE or polyethylene-covered stirring bars, 25 mm to 30 mm long.

Before use, stirring bars shall be cleaned to remove adhering iron ore and chloride contamination by leaching in the cleaning solution (4.6) for 30 min, and then in water for 30 min. Only clean tweezers should be used for handling the cleaned stirring bars.

5.4 Filtration apparatus, glass or polycarbonate plastic, with 25 mm to 50 mm diameter cellulose membrane microfilters of less than 1 µm pore size[1].

The microfilters should at all times be handled only with clean tweezers.

5.5 Ion-selective electrode meter, or high-sensitivity pH meter, or high-impedance millivoltmeter, capable of reading with a sensitivity of 0,1 mV.

5.6 Chloride ion-selective electrode and separate double-junction, free-flowing, reference electrode.

Both of the electrodes shall be maintained and used in accordance with the manufacturers' specifications, and the outer chamber solution in the reference electrode should be changed as specified and replenished as necessary. The flow rate across the nitrate/test solution junction should be such that the level of the outer chamber solution falls at a rate of approximately 4 mm to 5 mm per day.

As some chloride ion-selective electrodes are light sensitive, they should not be used in direct sunlight or in very bright daylight.

NOTE "Combined" electrodes, which normally are not provided with a reference electrode incorporating a double junction, are not suitable.

6 Sampling and samples

6.1 Laboratory sample

For analysis, use a laboratory sample of minus 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 less than 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 °C ± 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.

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 or by a different operator including, in either case, appropriate recalibration.

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[1] Millipore (XX10 apparatus with HAWP filters), Sartorius, Gelman are examples of suitable apparatus available commercially. This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of these types of apparatus.

7.2 Blank test and check test

NOTE For technical reasons, a blank test, as usually understood, cannot be conducted for methods using ion-selective electrodes. For this method, the procedure in 7.4.2 is substituted.

In each run, one analysis of a certified reference material of the same type of ore shall be carried out in parallel with the analyses 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.

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 samples of the same type of ore at the same time, the analytical value of one certified reference material may be used.

7.3 Temperature setting

7.3.1 Magnetic stirrer/hotplate

Determine the temperature setting required to maintain a temperature of 90 °C to 95 °C in a 35 ml volume of water.

7.3.2 Laboratory hotplate

Preheat the hotplate and determine the temperature setting required to produce, in a 50 ml volume of water, a temperature of at least 90 °C (but without boiling) after heating for 25 min.

7.4 Preliminary tests

7.4.1 Electrode-system check test

Before use of the electrodes for each series of tests, carry out the following check test of the electrode function.

Add to a 150 ml or 250 ml beaker, 100 ml of water, a stirring bar (5.3) and 2 ml of sodium nitrate solution (4.4). Place the electrodes in the solution, stir for 5 min and record the electrode potential in millivolts (E_1).

Stir at a rate that will displace any air bubbles from the electrode surface, but without causing a vortex.

Add 1 ml of chloride standard solution A (4.7), stir for 5 min to allow a stable reading to be obtained and record the electrode potential (E_2). Add 10 ml of chloride standard solution A (4.7), stir for 5 min and again record the electrode potential (E_3). The electrodes can be regarded as operating satisfactorily when the difference between E_2 and E_3 is 57 mV ± 2 mV, for a temperature of the test solutions within the range 20 °C to 25 °C.

7.4.2 Contamination check test

To ensure that the apparatus and reagents are free from chloride contamination, carry out the complete procedure specified in 7.6 without the addition of a test portion. The electrode potential reading obtained should be within 20 mV of the reading E_1 obtained in 7.4.1. If not, the cleaning procedures should be repeated. If the potential reading is again not within 20 mV of E_1, use a different source of potassium sulfate and then, if necessary, potassium persulfate or buffer reagents.

7.5 Test portion

Weigh, to the nearest 0,001 g, approximately 2 g of the predried test sample (6.2).

7.6 Determination

7.6.1 Leaching of water-soluble chloride

Transfer the test portion (7.5) to a 150 ml beaker and, using tweezers, add a cleaned plastics-covered stirring bar (5.3). Add 35 ml of potassium sulfate solution (4.1), place on a preheated magnetic stirrer/hotplate (7.3.1) set at the required temperature, cover and stir for 1 h. Remove from the hotplate and cool in a water bath, transfer the solution and suspended solids to a 50 ml volumetric flask, and dilute to volume. Allow to settle for 10 min.

7.6.2 Filtration

Assemble the microfilter filtration apparatus (5.4) on a dry 250 ml filter flask and, using tweezers, fit the specified microfilter membrane (5.4). Without washing, transfer as much as possible of the solution and suspended solids to the filter, and complete the filtration without washing.

7.6.3 Treatment of the test solution

Measure an aliquot of 45,0 ml (20,0 ml + 25,0 ml) of the filtrate into a 100 ml tall-form beaker, add 3 ml of potassium persulfate solution (4.3) and 1,0 ml of phosphate buffer solution (4.5). Place the solution on a preheated hotplate (7.3.2) and heat for 30 min. Cool in a water bath and transfer to a 50 ml volumetric flask that has not been used in 7.6.1 in the current series of tests. Add 1 ml of sodium nitrate solution (4.4) to the beaker, and transfer to the volumetric flask while rinsing. Dilute to volume and mix, retaining the beaker.

7.6.4 Measurement of electrode potential

Prepare the appropriate calibration solutions (4.10) and stand these solutions, together with the test solution, in an ambient-temperature water bath. When equilibrium has been obtained, remove all solutions from the bath.

Transfer the test solution back to the retained 100 ml beaker and, using tweezers, add a clean plastics-coated stirring bar (5.3). Allow to stand for 15 min to allow the temperature to reach equilibrium with ambient temperature.

Place the electrode system in the beaker and, after stirring magnetically on a non-hotplate stirrer (5.1) at ambient temperature for 5 min to allow a stable reading to be obtained, record the electrode potential.

If a separate non-hotplate stirrer is not available, ensure that the stirrer-hotplate is at ambient temperature. In either case, place a piece of cardboard between the stirrer and the beaker to avoid heating effects from the stirrer.

Stir at a rate that will displace air bubbles from the electrode surface, but without causing a vortex.

7.6.5 Preparation of calibration graph

Select the calibration solutions (4.10) appropriate to the chloride concentration, using the guideline values for potential versus chloride concentration given in Table 3.

Table 3 — Electrode potentials related to chloride concentration

Chloride concentration µg/ml	**Electrode potential** mV
1 to 10	260 to 190
10 to 50	195 to 155

7.6.6 Measurement of chloride concentration

Process the calibration solutions, as specified in 7.6.4, and measure the electrode potentials in ascending order of concentration, in the same manner as for the test solutions.

Between measurements, rinse the electrodes and blot dry with tissue.

If the electrode response becomes slow (> 5 min), follow the manufacturer's recommendations for removing possible deposits from the electrode-sensing membrane.

The electrode assembly should not be subjected to large variations in temperature. If this occurs, sufficient time should be allowed for temperature equilibration between the test and calibration solutions to be achieved.

Regard the first series of readings as guidelines, so that readings of calibration and test solutions may then be grouped in ascending order with completion of sets of readings within the same decade of chloride concentration, before proceeding to the next series of readings. Accept the readings from this second set as definitive.

Using single-cycle semilogarithmic graph paper, prepare separate calibration graphs for each decade of chloride concentration as necessary, plotting chloride concentration on the logarithmic axis and decreasing electrode potential on the linear axis.

NOTE At concentrations below 3 µg of chloride per ml, a certain amount of curvature will be observed.

Read the chloride concentration of the test solution from the calibration graph.

8 Expression of results

8.1 Calculation of mass fraction of water-soluble chloride

The mass fraction of water-soluble chloride in the test sample, expressed as a percentage by mass, is calculated to five decimal places using the equation

$$w_{\mathrm{Cl}}(\%) = \frac{1{,}11 \rho_{\mathrm{Cl}}}{200 m} \tag{1}$$

where

ρ_{Cl} is the concentration, in micrograms per millilitre, of chloride in the test solution obtained from the calibration graph;

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

1,11 is the ratio 50,0/45,0.

8.2 General treatment of results

8.2.1 Repeatability and permissible tolerance

The precision of this analytical method is expressed by the following regression equations[2]:

$$R_\mathrm{d} = 0{,}0381\,X^{0{,}6045} \tag{2}$$

$$P = 0{,}1298\,X^{0{,}7267} \tag{3}$$

$$\sigma_\mathrm{d} = 0{,}0135\,X^{0{,}6045} \tag{4}$$

$$\sigma_\mathrm{L} = 0{,}0456\,X^{0{,}7410} \tag{5}$$

where

X is the mass fraction of water-soluble chloride, expressed as a percentage by mass, of the predried test sample calculated as follows:

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

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.

8.2.2 Determination of analytical result

Having computed the independent duplicate results in accordance with Equation (1), compare them with the independent duplicate limit (R_d), using the procedure given in Annex A, and obtain the final laboratory result μ (see 8.2.5).

8.2.3 Between-laboratories precision

The 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 procedure described in 8.2.2.

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.

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[2] Additional information is given in Annexes B and C.

Substitute $\mu_{1,2}$ for X in Equation (3) and calculate P.

If $|\mu_1 - \mu_2| \leqslant P$, the final results are in agreement.

8.2.4 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) (see the third paragraph of 7.2). Calculate the analytical result (µ) for the CRM/RM using the procedures in 8.1 and 8.2.1 to 8.2.3, and compare it with the reference or certified value A_c. There are two possibilities:

a) $|\mu_1 - \mu_2| \leqslant C$ in which case, the difference between the reported result and the certified/reference value is statistically insignificant.

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

where

μ_c is the final result for the CRM/RM;

A_c is the certified/reference 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 35:2006, *Reference materials — General and statistical principles for certification*.

For a CRM/RM certified by an interlaboratory test programme

$$C = 2\sqrt{\sigma_L^2 + \frac{\sigma_d^2}{n} + V(A_c)}$$

where

$V(A_c)$ is the variance of the certified/reference value A_c (= 0 for a CRM/RM certified by only one laboratory);

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

CRMs certified by only one laboratory should be avoided, unless they are known to have an unbiased certified value.

8.2.5 Calculation of final result

The final result is the arithmetic mean of the acceptable analytical values for the test sample calculated to five decimal places, and rounded off to the third decimal place as follows:

a) when the figure in the fourth decimal place is less than 5, it is discarded and the figure in the third decimal place is kept unchanged;

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

c) when the figure in the fourth decimal place is 5 and there is the figure 0 in the fifth decimal place, the 5 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.

9 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) a reference to this International Standard, i.e. ISO 9517;

d) details necessary for the identification of the sample;

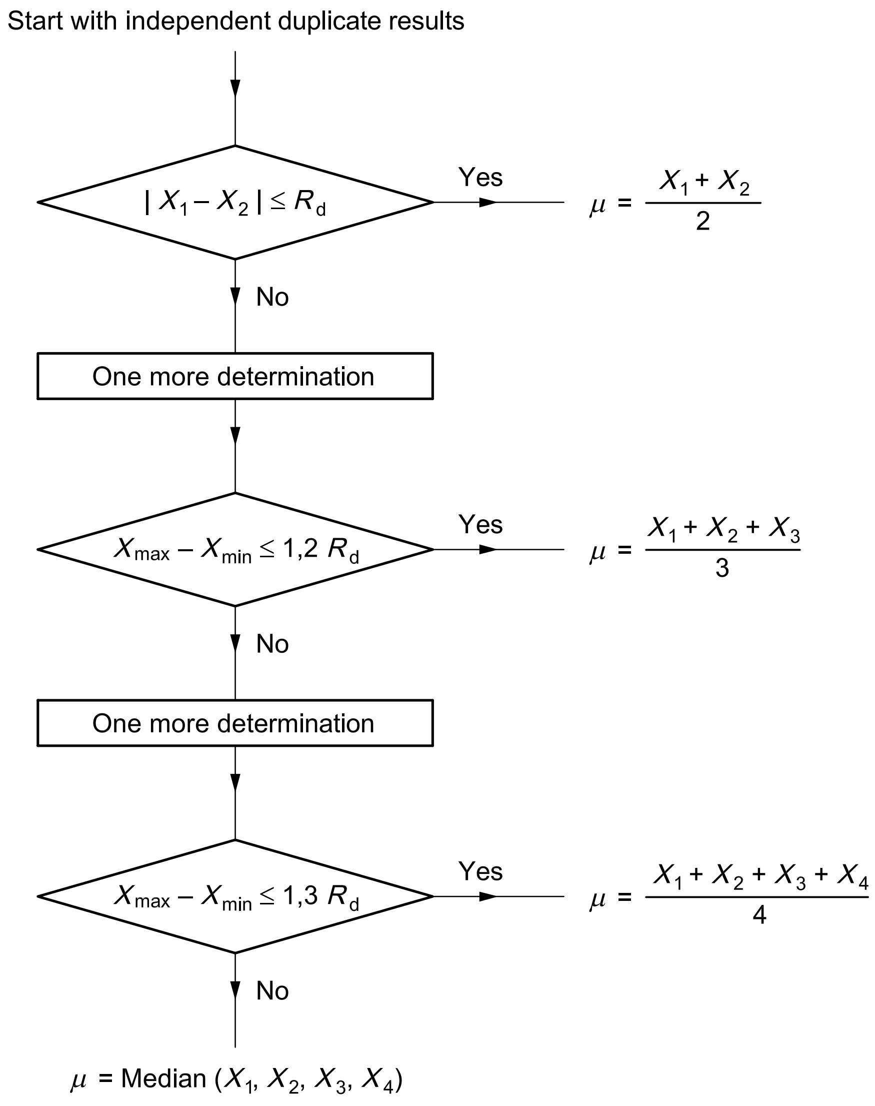
e) result of the analysis;

f) reference number of the result;

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

Annex A
(normative)

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



R_d is as defined in 8.2.1.

Annex B
(informative)

Derivation of repeatability and permissible tolerance equations

The regression equations in 8.2.1 were obtained by statistical evaluation of the results of international analytical trials carried out in 1983 and 1984 on three iron samples (see Table B.1), involving 18 laboratories in 6 countries.

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

Table B.1 — Mass fractions of water-soluble chloride in test samples

Sample	Mass fractions of water-soluble chloride %
Mt Newman, fines	0,007 3
Usinor KDF	0,017 2
Malmberget (synthetic)	0,096 1

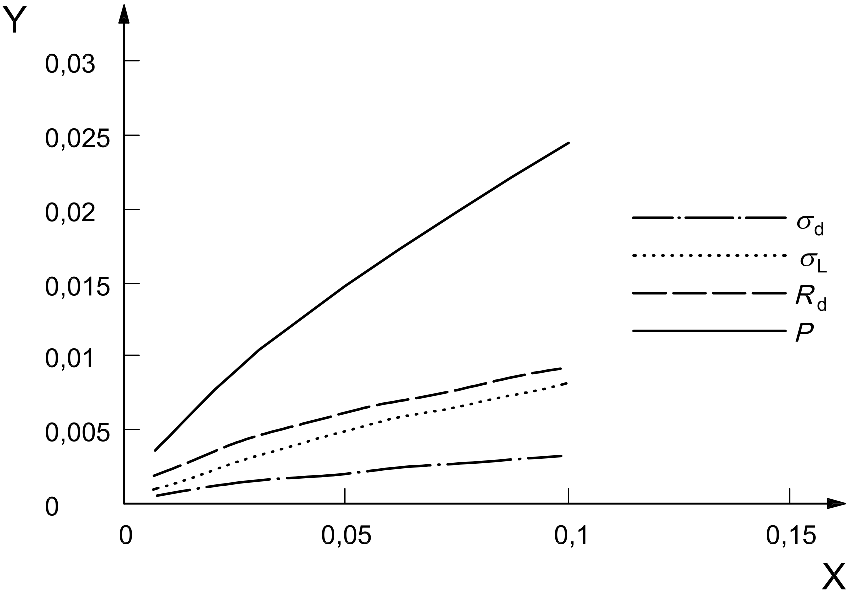
NOTE 1 A report of the international trials and a statistical analysis of the results (document ISO/TC 102/SC 2 N756E, July 1984) is available from the secretariat of ISO/TC 102/SC 2.

NOTE 2 The statistical analysis has been performed in accordance with the principles established in ISO 5725-2:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.*

Annex C
(informative)

Graphical presentation of precision data obtained by international analytical trials

NOTE This figure is a graphical presentation of the equations in 8.2.1.



X mass fraction of water-soluble chloride, %

Y precision, %

Figure C.1 — Least-squares fit of precision against X for water-soluble chloride

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