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ISO 9114

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Crude petroleum — Determination of water content by hydride reaction — Field method

Pétrole brut — Dosage de l'eau par la méthode à l'hydrure — Méthode de terrain

Reference number
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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.

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 9114 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 6*, Bulk cargo transfer, accountability, inspection and reconciliation*.

Annex A forms an integral part of this International Standard.

Crude petroleum — Determination of water content by hydride reaction — Field method

WARNING — The use of 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 responsiblity of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a field method for the determination of water in crude petroleum, at concentrations ranging from 0,05 %(*V/V*) to 2 %(*V/V*). It is applicable where due to circumstances the laboratory methods cannot be used. This method is not intended for custody transfer but could be so used if prior agreement from all parties is obtained.

NOTE — For the purposes of this International Standard, the expression "%(*V/V*)" is used to represent the volume fraction.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard 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 3170:1988, *Petroleum liquids — Manual sampling.*

ISO 3171:1988, *Petroleum liquids — Automatic pipeline sampling.*

ISO 3733:1976, *Petroleum products and bituminous materials — Determination of water — Distillation method.*

ISO 3734:1997, *Petroleum products — Determination of water and sediment in residual fuel oils — Centrifuge method.*

3 Principle

After homogenizing the crude petroleum with a mixer an aliquiot is transferred to the reaction flask where calcium hydride reacts with the water contained therein according to:

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2 \uparrow$$

The quantity of hydrogen released is proportional to the amount of water present, and is measured volumetrically enabling the percentage by volume of water in the sample to be calculated.

4 Reagents and materials

4.1 Capsules, each containing 0,6 g to 0,7 g calcium hydride in powder form.

4.2 Light aromatic-free mineral oil (medicinal type), used as balancing liquid surplus in the gas burette and reservoir [density at 15 °C: between 830 kg/m^3 and 850 kg/m^3; viscosity: between 14 mm^2/s and 30 mm^2/s (14 cSt and 30 cSt) at 20 °C].

4.3 Wetting agent (e.g. sodium dioctyl sulfosuccinate, technical).

4.4 Kerosine, clear and bright.

4.5 Acetone.

4.6 Heptane.

4.7 Water-free silicone grease.

5 Apparatus

The apparatus is illustrated in figure 1 and consists of the following parts:

5.1 Reaction flask: a 100 ml vessel graduated at volumes corresponding to 10 ml, 20 ml and 40 ml.

5.2 Tap R_1, consisting of a stopper impervious to hydrocarbons, fitting the flask and through which a PTFE device is fitted, consisting of two channels, one of which ends in a two-way tap, whilst the other links the flask with the gas burette (figure 2).

5.3 Gas burette, graduated from 0 % to 1,0 % H_2O in 0,01 % by volume scale units, the upper opening of which is fitted with a tap R_2 linked to tap R_1 by a flexible plastic tube, impervious to hydrocarbons.

The 1 % graduation mark corresponds to the volume of gas that under the reference conditions (20 °C and 101,325 kPa) would be released by the calcium hydride reaction on 20 ml of a sample containing 1,0 % water.

Tap R_2 has two positions (figure 3):

— position "A" in which the gases from reaction flask and burette can be released to the atmosphere;

— position "B" in which the contents are isolated from the surrounding atmosphere.

5.4 Reservoir, linked to the base of the gas burette by a flexible plastic tube, impervious to hydrocarbons and filled with a liquid (4.2) to balance the pressures inside the apparatus.

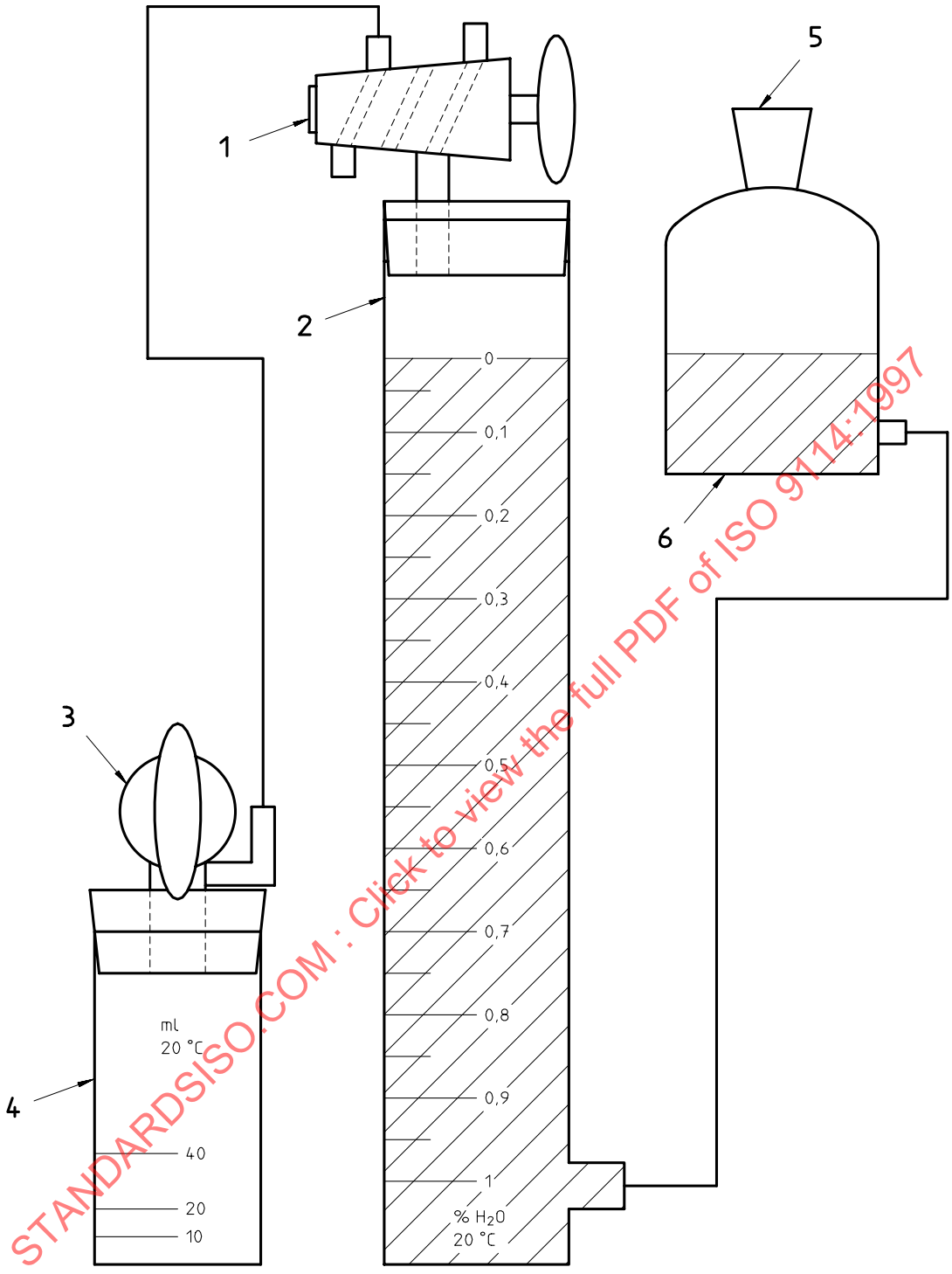
The height of the reservoir shall be adjustable in order to obtain the required balance of liquid.

The stopper of the reservoir has two positions (figure 4):

— position "α" (open): the "working" position in which the stopper is open to the surrounding atmosphere,

— position "β" (closed): in which the flask is isolated from the atmosphere (storage and carrying position).

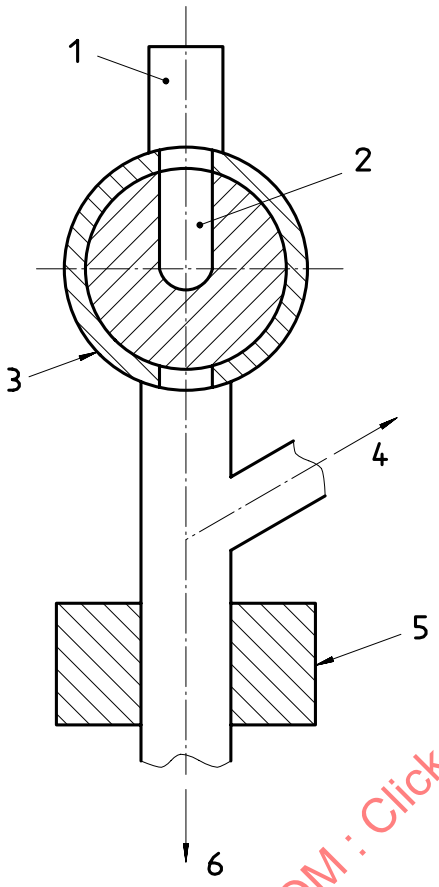
For convenience, the apparatus should be designed to fit compactly into a portable case or box.



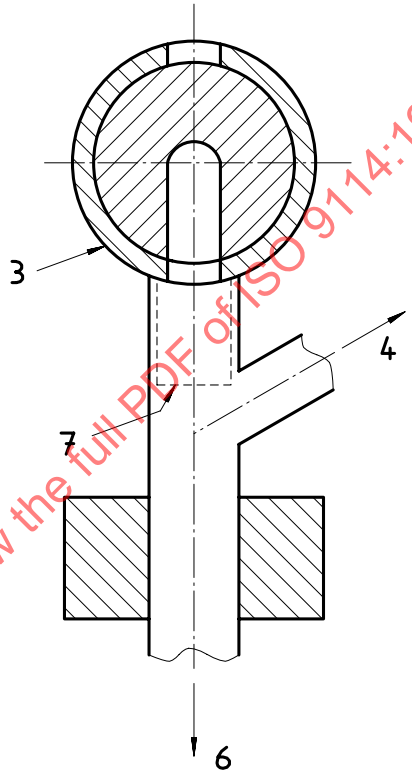
Key

1 Tap R_2
2 Gas burette
3 Tap R_1
4 Reaction flask
5 Plug with two positions
6 Reservoir

Figure 1 — Diagram of the apparatus



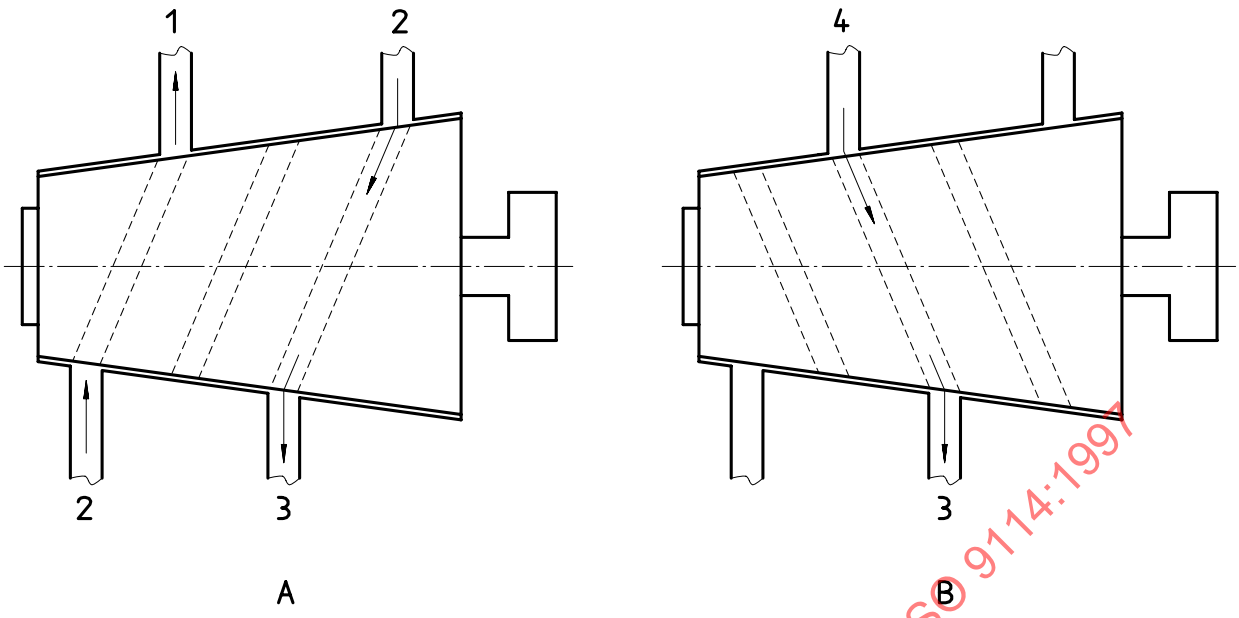
Position a for the lever
Introducing capsules
in the tap



Position b for the lever
Capsule drops into
the reaction flask

Key
1 Lever to turn tap R_1 by 180°
2 Opening for capsules
3 Tap
4 To gas burette
5 Plug to close the reaction flask
6 To reaction flask
7 Tap lever

Figure 2 — Tap R_1 (plug and device with two channels)

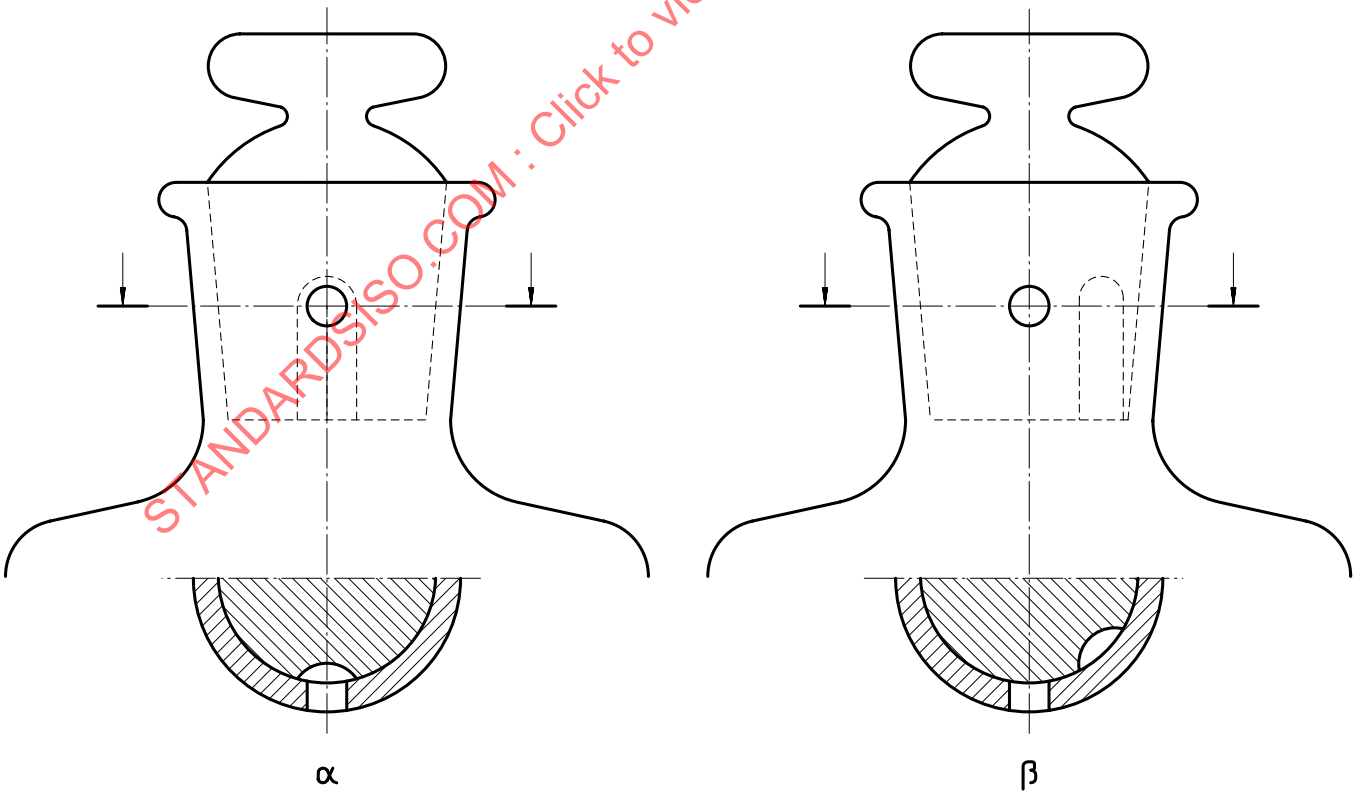


Position open to air **Position closed to air**

Key

1 Towards tap R_1 and reaction flask
2 Air
3 Towards gas burette
4 From tap R_1 and reaction flask

Figure 3 — Diagram of tap R_2 in its two positions



Position open to air **Position closed to air**

Figure 4 — Diagram of reservoir plug in its two positions

6 Sampling (see annex A)

The water content of a crude petroleum sample depends on the water present when the sample is taken. The water content obtained by this method depends largely upon the representativity of the sample and great care shall be taken to ensure that any sample taken is representative of the bulk.

Sample handling, homogenization and transfer are given in annex A.

6.1 General

Sampling is defined as all steps necessary to obtain a representative sample of the contents of any pipe, tank, or other system and to place the sample into the laboratory test container.

6.2 Laboratory sample

Only representative samples obtained as specified in ISO 3170 or ISO 3171 shall be tested using this International Standard. Before taking the test portion from the sample received by the laboratory, homogenize the sample using the procedure described in annex A.

6.3 Test portion

The aliquot taken from the laboratory sample for analysis. The entire volume of the test portion shall be used for analysis.

7 Procedure

7.1 Preparation of apparatus

It is essential that all glass and rubber joints are tight, and that the reaction flask is clean and dry before each analysis.

To achieve this use the following routine prior to each determination:

7.1.1 Wash the reaction flask with heptane, followed by acetone. Dry in a stream of dry air or wipe carefully with a paper tissue.

7.1.2 Clean tap R_1 with heptane, wipe dry and lubricate carefully with the water-free silicone grease (4.7) (it is essential that this step is carried out as tap R_1 can easily become contaminated with particles of hydride allowing gas to escape).

7.1.3 Examine the plastic tubing for deterioration. If necessary, replace with a new tube of similar material and dimensions.

7.1.4 Examine the mineral oil in the reservoir and gas burette. If contaminated, replace it with the same volume of fresh mineral oil (4.2).

7.1.5 Check that the apparatus is gas tight. Open the tap and lower the reservoir. Close and raise the reservoir whilst observing the mineral oil level. If this level changes, the apparatus has a leak. Repeat steps 7.1.1 to 7.1.4 until the apparatus is gas tight.

7.2 Test procedure

7.2.1 Immediately after homogenization, carefully transfer to the reaction flask either a specified volume (see table 1) of the sample, or an accurately weighed mass of the sample equivalent to that volume. If a pipette is used to transfer the sample, wash it through with a small volume of dry kerosine (4.4).

If a viscous crude oil is being tested it may be diluted with a quantity of dry kerosine. However, if the test portion is diluted with kerosine, first carry out a blank analysis with the kerosine alone, using the same procedure as described in 7.2.2 to 7.2.12.

The total volume within the flask shall not exceed 40 ml.

Table 1 — Test portion based on expected water content

Expected water content % by volume	Volume of test portion ml
$< 0,5$	40
$0,5 \leqslant$ water % < 1	20
$1 \leqslant$ water % $\leqslant 2$	10

7.2.2 Add three drops of wetting agent (4.3). Connect to the gas burette and reservoir by closing the vessel with tap R_1.

7.2.3 Check that the reservoir stopper is in position "α" (figure 4) and that the tap R_2 is turned to position "B" (figure 3). Check that the tap R_1 is in position "b" (figure 2).

7.2.4 Note the position of the meniscus of the mineral oil in the gas burette. Shake the reaction flask and contents manually in order to remove volatile components from the test portion. When gases cease to evolve (i.e. when the level of the meniscus remains constant) place tap R_2 in position "A" (figure 3) in order to release to the atmosphere all the volatile material. Repeat the actions above until the level of the liquid remains constant.

7.2.5 Adjust the height of the liquid in the gas burette to zero by adjusting the reservoir height.

7.2.6 Turn tap R_2 through 180° to position "B" (figure 3).

7.2.7 Open a calcium hydride capsule (4.1) and place the opened capsule upwards in tap R_1, whilst in position "a" (figure 2). Slowly rotate tap R_1 through 180° (position "b" - figure 2) to introduce the capsule and contents into the reaction flask. Initially agitate the flask gently by hand to ensure that there is only a small formation of foam (copious quantities of foam may result with high water content and vigorous shaking).

7.2.8 Intermittently shake the flask vigorously in order to ensure good contact between reagent and sample.

7.2.9 If large quantities of foam are produced, rapidly turn tap R_2 to position "A" (figure 3). This prevents contamination of the apparatus by "carry over" of the sample. If this occurs repeat the test using a smaller test portion.

7.2.10 When the capsule has dropped to the bottom of the vessel, tighten tap R_1 to prevent any leakage.

7.2.11 When all evolution of hydrogen has ceased and the liquid level in the gas burette is once again stationary, stop shaking, then lower the reservoir until the two liquid levels are equal.

7.2.12 Record the liquid level in the burette as *V*.

NOTE — Unreacted hydride should be destroyed by reaction with 10 ml of alcohol before discarding the contents of the reaction flask.

8 Calculation

8.1 Calculate the water content of the sample using the factors given in table 2.

Table 2 — Calculation factors based on sample size

Volume of sample admitted ml	Water content of sample % (*V*/*V*)
40	*V*/2
20	*V*
10	2*V*
V = Reading on burette	

8.2 If the test portion was weighed (see 7.2.1), calculate the water content, *w,* as a percentage by volume by converting the burette reading as follows:

$$w = \frac{20 \times V \times \rho}{m}$$

where

V is the burette reading, in millilitres;

ρ is the sample density at 20 °C, in grams per millilitre;

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

8.3 If the test is carried out under different temperature and pressure conditions to the reference conditions, the following correction shall be applied:

$$w = \frac{p \times 293{,}2}{101\,325 \times [293{,}2 + (t - 20)]}$$

where

p is the observed barometric pressure, in pascals;

t is the observed temperature, in degrees Celsius.

9 Precision

The precision of the method as determined by the statistical examination of interlaboratory test results is as follows and is shown graphically in figure 5:

9.1 Repeatability, *r*

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value below only in one case in twenty.

$$r = 0{,}117X^{2/3}$$

where

X is the average of the results being compared, as a percentage by volume.

9.2 Reproducibility, *R*

The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the long run, in the normal and correct operation of the test method, exceed the value below only in one case in twenty.

$$R = 0{,}467X^{2/3}$$

where

X is the average of the results being compared, as a percentage by volume.

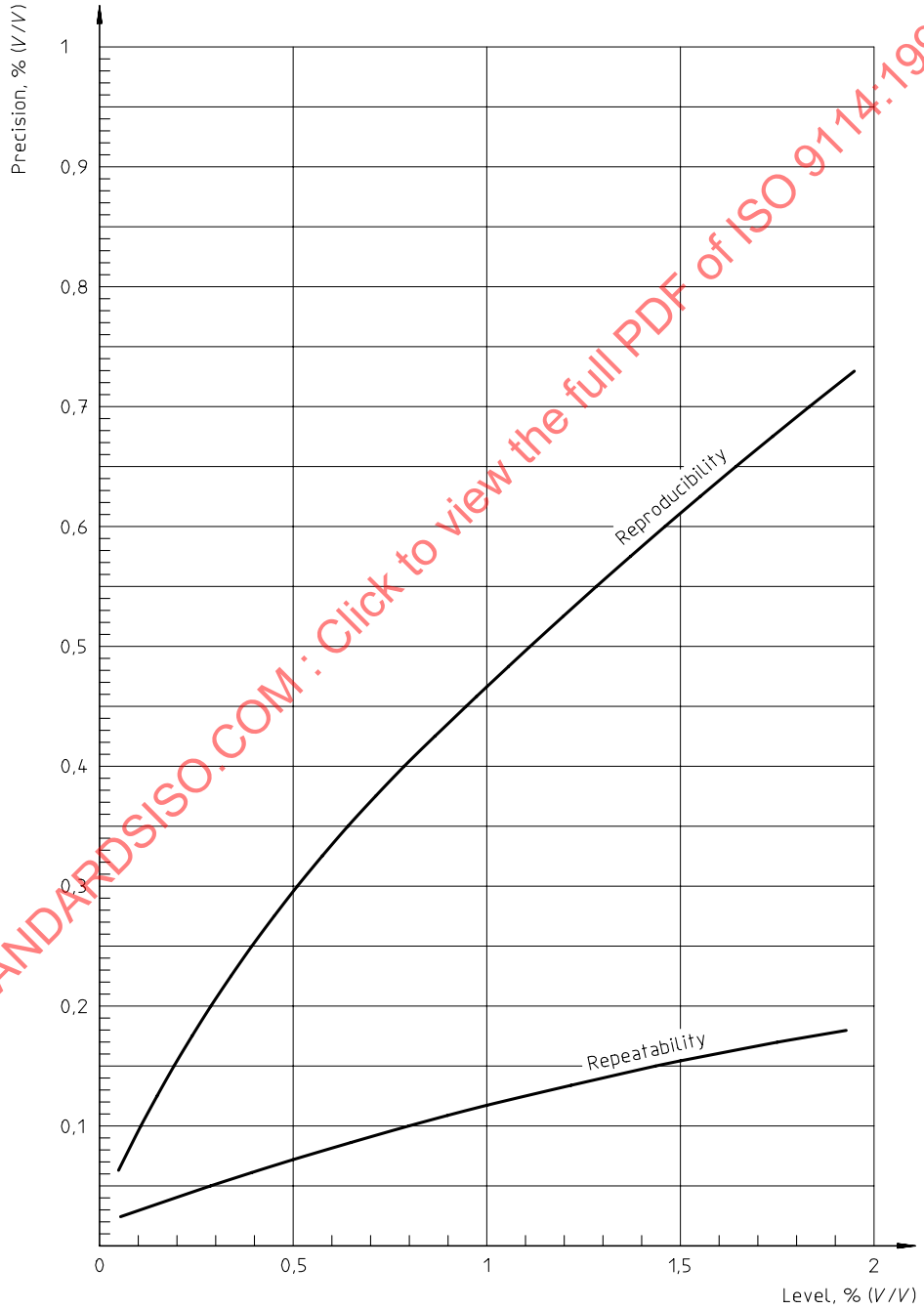


Figure 5 — Precision

10 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 8);

d) any deviation, by agreement or otherwise, from the procedure specified;

e) the date of the test.