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Iron ores — Determination of combined water content — Karl Fischer titrimetric method

Minerais de fer — Dosage de l'eau de constitution — Méthode titrimétrique de Karl Fischer

Reference number
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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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Iron ores — Determination of combined water content — Karl Fischer titrimetric method

1 Scope and field of application

This International Standard specifies a titrimetric method for the determination of the combined water content of iron ores, using Karl Fischer solution.

This method is applicable to a concentration range of 0,05 to 10 % (m/m) of combined water in natural iron ores, and iron ore concentrates and agglomerates including sinter products.

NOTE — The term "combined water" means that part of the water content of an iron ore that can be removed only at temperatures substantially higher than 100 to 110 °C.

2 References

ISO 385, *Laboratory glassware — Burettes.*

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

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

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

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

3 Principle

Liberation of adventitious hygroscopic moisture by heating the predried test portion at 105 °C in a furnace in a stream of dry nitrogen. Successive heating up to 950 °C in another furnace and collection of the liberated combined water in ethylene glycol-methanol mixture.

Measurement of combined water content by titration with Karl Fischer solution using electrometric detection of the end point.

4 Reagents

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

4.1 Desiccant. Silica gel, self-indicating granules.

4.2 Desiccant. Anhydrous magnesium perchlorate [$Mg(ClO_4)_2$] of size 0,8 to 1,25 mm or other suitable desiccant.

NOTE — Magnesium perchlorate is a powerful oxidant and must not be allowed to come into contact with organic materials. When exhausted, it should be washed down the sink with a copious flow of water.

4.3 Nitrogen. A supply of filtered, predried, oil-free nitrogen containing less than 10 µl of oxygen per litre at a pressure of approximately 35 kPa above atmospheric pressure.

4.4 Ethylene glycol ($OHCH_2 \cdot CH_2OH$)-methanol (CH_3OH) mixture (1 + 1). This mixture should be tested each time before use for the amount of free moisture it contains. If it contains more than 0,05 % (m/m) of free moisture, it shall not be used.

NOTE — In place of this mixture, anhydrous ethylene glycol may be used. In this case, Karl Fischer solution must contain the appropriate amount of methanol.

4.5 Karl Fischer solution (2,5 to 3,0 mg H_2O/ml). This solution shall be standardized on the day of use by one of the following substances:

a) a standard water methanol solution; this solution shall previously be standardized by use of the following b), c) or d);

b) water added by means of a microsyringe;

c) citric acid monohydrate [$C(OH)(COOH)(CH_2COOH)_2 \cdot H_2O$];

d) disodium tartrate dihydrate [$(CHOH \cdot COONa)_2 \cdot 2H_2O$].

5 Apparatus

A suitable apparatus for the determination is illustrated in figure 1 (two-furnaces-in-series type) or in figure 2 (interchangeable furnace type).

5.1 Gas flowmeter, capable of measuring a flow rate up to 250 ml/min. If a pressure drop over a constriction is used as a means of measuring flow rate, the manometer liquid shall be a non-volatile oil.

5.2 Drying towers (t_1 and t_2), of 250 ml capacity, packed respectively with desiccant (4.1) and (4.2) to dry the stream of nitrogen entering the heating tube.

5.3 Heating furnaces (f_1 and f_2). Electric furnaces in series as in figure 1 or movable furnaces which can be located around, and removed from, the heating tube as in figure 2. The furnaces shall be capable of maintaining temperatures of 105 ± 2 °C and 950 ± 20 °C, respectively, over a minimum tube length of about 150 mm, by controlling the electric current. Furnace temperatures shall be measured at the upper surface of the heating tube by means of a pyrometer or thermometer.

5.4 Heating tube. A silica tube as shown in figure 1, of about 30 mm inside diameter, about 800 mm length, and provided with a long silica pushing rod. Another example (figure 2) is about 350 mm long, closed at one end and fitted with a thin inner tube of about 8 mm external diameter, through which gas flows towards the outlet.

5.5 Sample boats, of an inert and stable material such as quartz, platinum or porcelain. Approximate dimensions are 100 mm length, 20 mm width and 5 mm height, and sample loading shall not exceed 1 mg/mm^2 for 0,2 to 1 g test portions and 1,5 mg/mm^2 for 3 g test portions.

Before use, boats shall be heated at 950 °C, cooled and stored in a desiccator to maintain freedom from moisture.

5.6 Filter. Sintered metal, sintered glass or similar filter disc inserted in the flexible connection between the heating tube and the inlet to the absorption cell.

5.7 Flexible connections. Neoprene elastometer tubing is suitable. Some types of silicone tubing have been found to be permeable. For the gas flow lines after the drying towers, glass tubing should be used to the maximum extent possible, with the flexible tubing being used only for the connection of butt-jointed glass sections.

5.8 Flow control valve. A needle valve is placed on the outlet side of the flowmeter.

5.9 Absorption cell. A glass vessel is illustrated in figure 3. The entries for the platinum electodes, burettes and gas inlet shall all be gas-tight to prevent moisture from entering the cell.

5.10 Platinum electrodes, either as a pair or as a dual platinum electrode.

5.11 Magnetic stirrer.

5.12 Electrometric titrator, suitable for Karl Fischer titration and equipped with a microammeter (0 to 50 µA) or an equivalent means for the electrometric indication of the end point.

5.13 Burette, of about 25 ml capacity, conforming to the specifications of ISO 385.

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

7.2 Test portion

Taking several increments, weigh, to the nearest 0,1 mg, approximately the amount of the predried test sample (6.2) specified in table 1.

Table 1 — Mass of test portion

Combined water content of test sample %	Mass of test portion g
0,05 to 0,5	3
0,5 to 2	1
2 to 5	0,5
5 to 10	0,2

NOTE — The test portion should be taken and weighed quickly on the day of predrying to avoid reabsorption of moisture.

7.3 Blank test and check test

In each run, one blank test and one analysis of a certified reference material[1] 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 become necessary.

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 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.

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[1] The certified reference material should have been previously certified using this method.

7.4 Determination

7.4.1 Apparatus conditioning

Bring the heating tube in the furnace (f_1) to a temperature of 105 ± 2 °C and maintain at this temperature through steps 7.4.1 to 7.4.3.

Adjust the flow rate of nitrogen (4.3) to about 200 ml/min through the system. Momentarily close the outlet from the heating tube to check for leaks in the system. Reconnect the outlet from the heating tube to the inlet of the absorption cell, and readjust the flow rate if necessary. Allow 10 min for the system to be purged and maintain this flow through steps 7.4.1 to 7.4.5.

Remove the stopper from the absorption cell and transfer 40 ml of ethylene glycol-methanol mixture (4.4) through the absorbent inlet into the absorption cell by pipette. Replace the stopper of the inlet tightly.

Switch on the titrator and magnetic stirrer, adjusting the speed of the latter to ensure adequate mixing. Maintain a constant stirring speed during the titration.

7.4.2 Titration

Add Karl Fischer solution (4.5) slowly to the absorption cell by burette. The approaching end point will be indicated by a rapid increase in current due to the presence of free iodine from the excess Karl Fischer solution. At this point of rapid change, select a current (30 to 40 µA) for the end point. Continue the titration until this current can be maintained for a period of 30 s. Make further additions of Karl Fischer solution at intervals of 10 min until the increment required to restore the current to the predetermined value for a period of 30 s is less than 0,05 ml.

The absorbent solution shall be titrated to this end point immediately prior to the commencement of all tests and calibration.

7.4.3 Liberation of adventitious hygroscopic moisture

Remove the inlet connector to the heating tube, place the sample boat containing the predried test portion (7.2) in the heating tube at the entrance to the heated zone and insert the magnetic push rod.

Immediately replace the inlet connector and, using a magnet, move the boat to the centre of the heated zone of the heating tube in the low temperature furnace (f_1). Expel any adventitious hygroscopic moisture in the predried test portion together with any environmental moisture which may have been introduced during insertion of the boat.

After 30 min, carry out and repeat the titration at 10 min intervals as described in 7.4.2.

NOTE — It should be confirmed that any adventitious hygroscopic moisture is completely liberated before heating the sample at 950 °C even though a predried test sample prepared in accordance with ISO 7764 has been used.

7.4.4 Evolution and collection of combined water

Move the boat to the centre of the heated zone of the heating tube in the furnace (f_2) operating at 950 ± 20 °C, or replace the furnace (f_1) at 105 °C with the furnace (f_2) at 950 ± 20 °C, and heat the sample boat for 15 min. Heat also the cold parts of the heating tube up to about 100 °C using a small flame or an electric dryer, to collect condensed water completely.

Titrate with Karl Fischer solution (4.5) until the end point is attained as described in 7.4.2.

7.4.5 Blank test value

Determine the blank test value by carrying out exactly the same procedure as described in 7.4.1 to 7.4.4 without the test portion. The indicated value of water for the blank test should not be more than 1,0 mg/h (0,25 mg per 15 min).

8 Expression of results

8.1 Calculation of combined water content

Calculate the combined water content, as a percentage by mass, to four decimal places using the formula

$$\frac{(V - V_0) \times F}{m \times 1\,000} \times 100$$

$$= \frac{(V - V_0) \times F}{m \times 10} \qquad \ldots (1)$$

where

V is the volume, in millilitres, of Karl Fischer solution (4.5) consumed in 7.4.4 for the test portion;

V_0 is the volume, in millilitres, of Karl Fischer solution (4.5) consumed in 7.4.5 for the blank test;

F is the factor, in milligrams per millilitre, of Karl Fischer solution (4.5);

m is the mass, in grams, of the test portion (7.2).

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[1]:

$$r = 0{,}043\,1\,X + 0{,}017\,7 \qquad \ldots (2)$$

$$P = 0{,}093\,9\,X + 0{,}028\,7 \qquad \ldots (3)$$

$$\sigma_r = 0{,}015\,2\,X + 0{,}006\,3 \qquad \ldots (4)$$

$$\sigma_L = 0{,}031\,3\,X + 0{,}008\,8 \qquad \ldots (5)$$

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

where

X is the combined water content, expressed as a percentage by mass, of the test sample:

— within-laboratory equations (2 and 4): the arithmetic mean of the duplicate values;

— between-laboratories equations (3 and 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 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 15 laboratories using method(s) that are comparable both in accuracy and precision with this method, the following formula may be used to test the significance of the difference:

$$|A_c - A| \leqslant 2\sqrt{\frac{s_{Lc}^2 + \frac{s_{Wc}^2}{n_{Wc}}}{N_c} + \sigma_L^2 + \frac{\sigma_r^2}{n}} \qquad \ldots (6)$$

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

σ_L and σ_r are as defined in 8.2.1.

If condition (6) is satisfied, i.e. if the left-hand side of the formula is less than or equal to the right-hand side, then the difference, $|A_c - A|$ 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), one or more additional tests shall be carried out in accordance with the flowsheet presented in annex A, simultaneously with a corresponding blank test and 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.

NOTE — The following procedure shall 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_{Wc}^2/n_{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, it is advisable not to use this material for this purpose. In case its use is unavoidable, use the formula

$$|A_c - A| \leqslant 2\sqrt{2\sigma_L^2 + \frac{\sigma_r^2}{n}}$$

8.2.3 Calculation of final result

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

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;

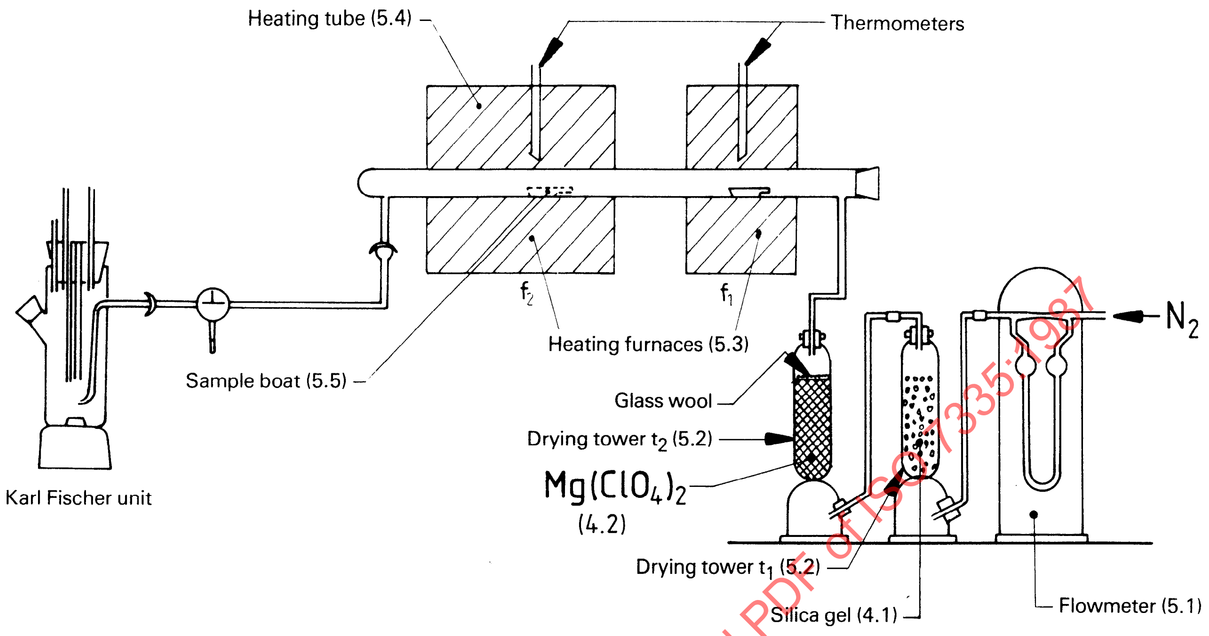
c) reference to this International Standard;

d) details necessary for the identification of the sample;

e) result of the analysis;

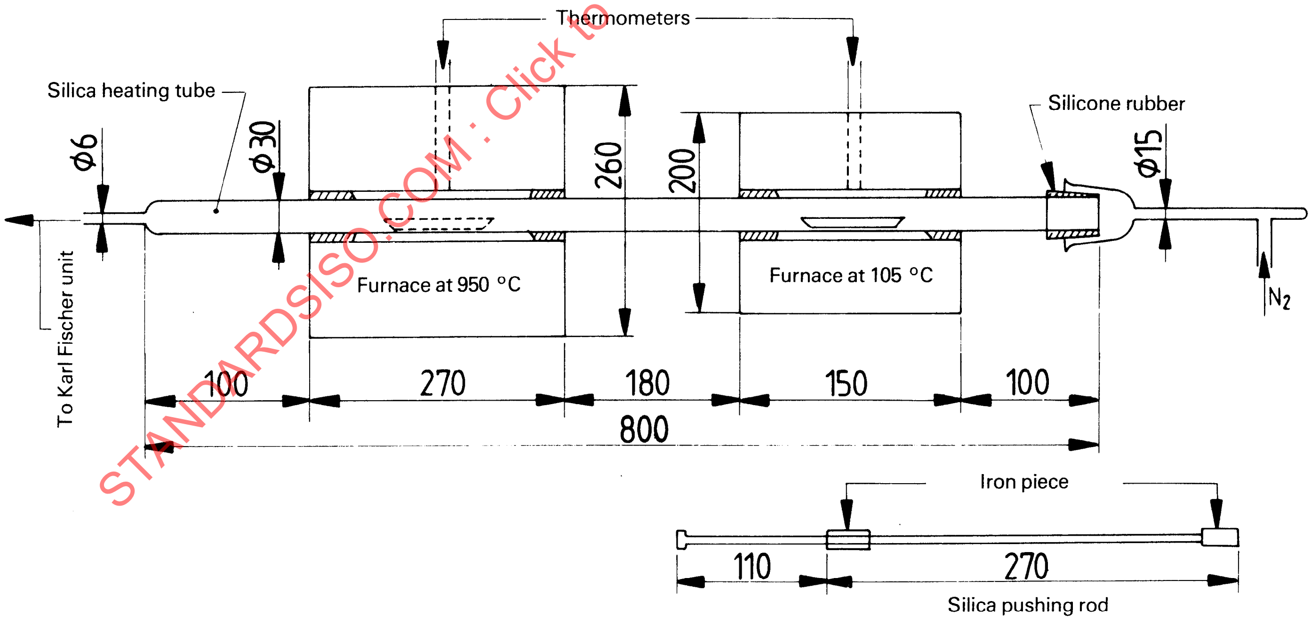
f) reference number of the result;

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



General arrangement

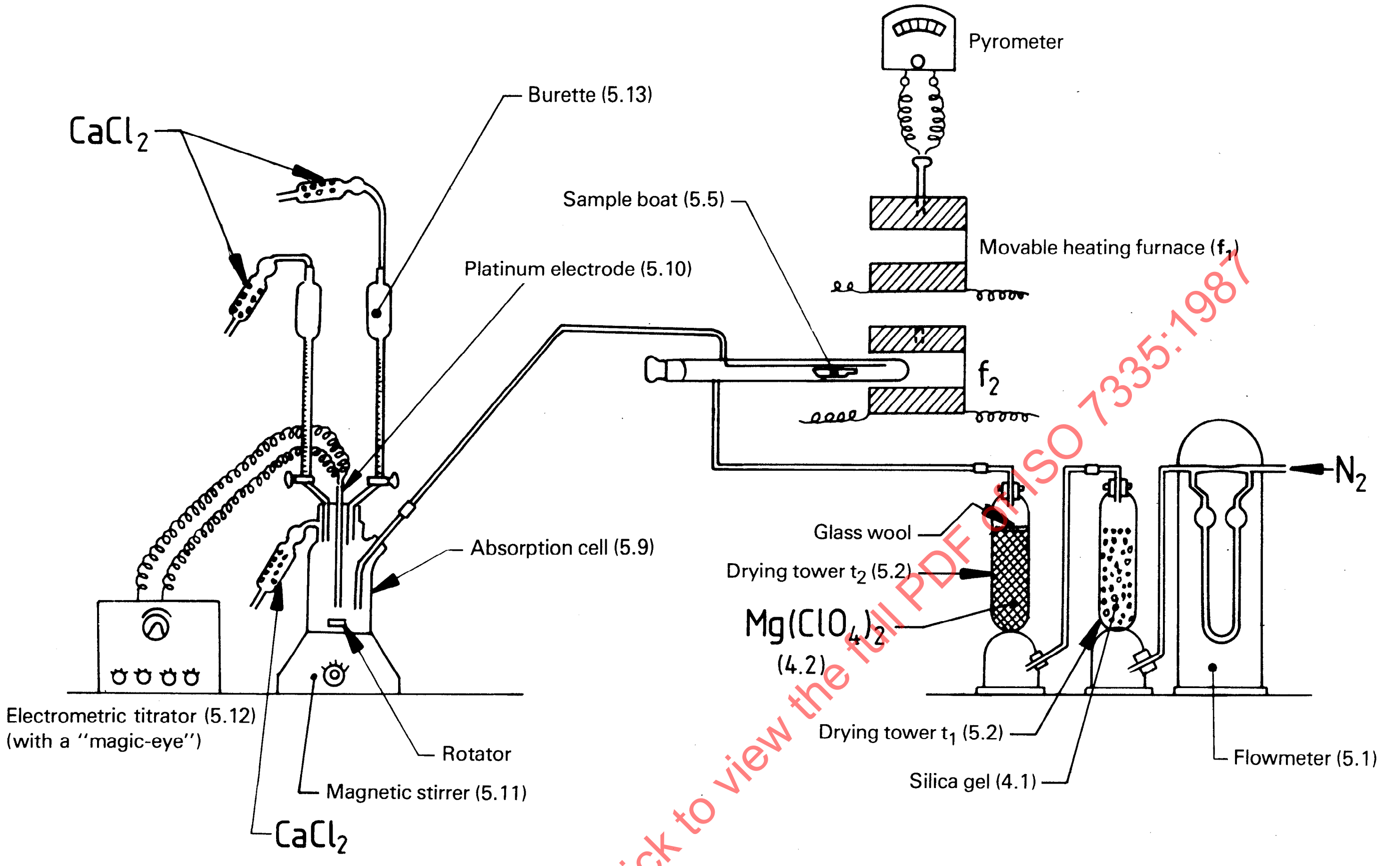
Dimensions in millimetres



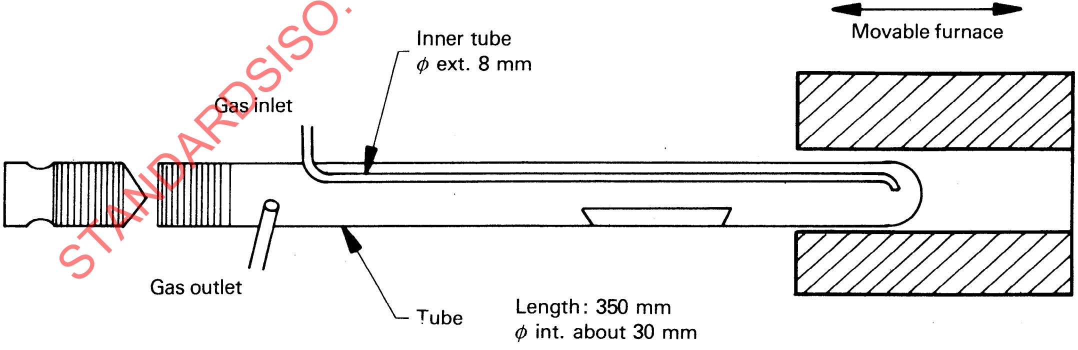
Details for heating tube (5.4)

NOTE — Dimensions not specified in clause 5 are shown for information.

Figure 1 — Apparatus for the Karl Fischer measurement (two-furnaces-in-series type) (Example)



General arrangement

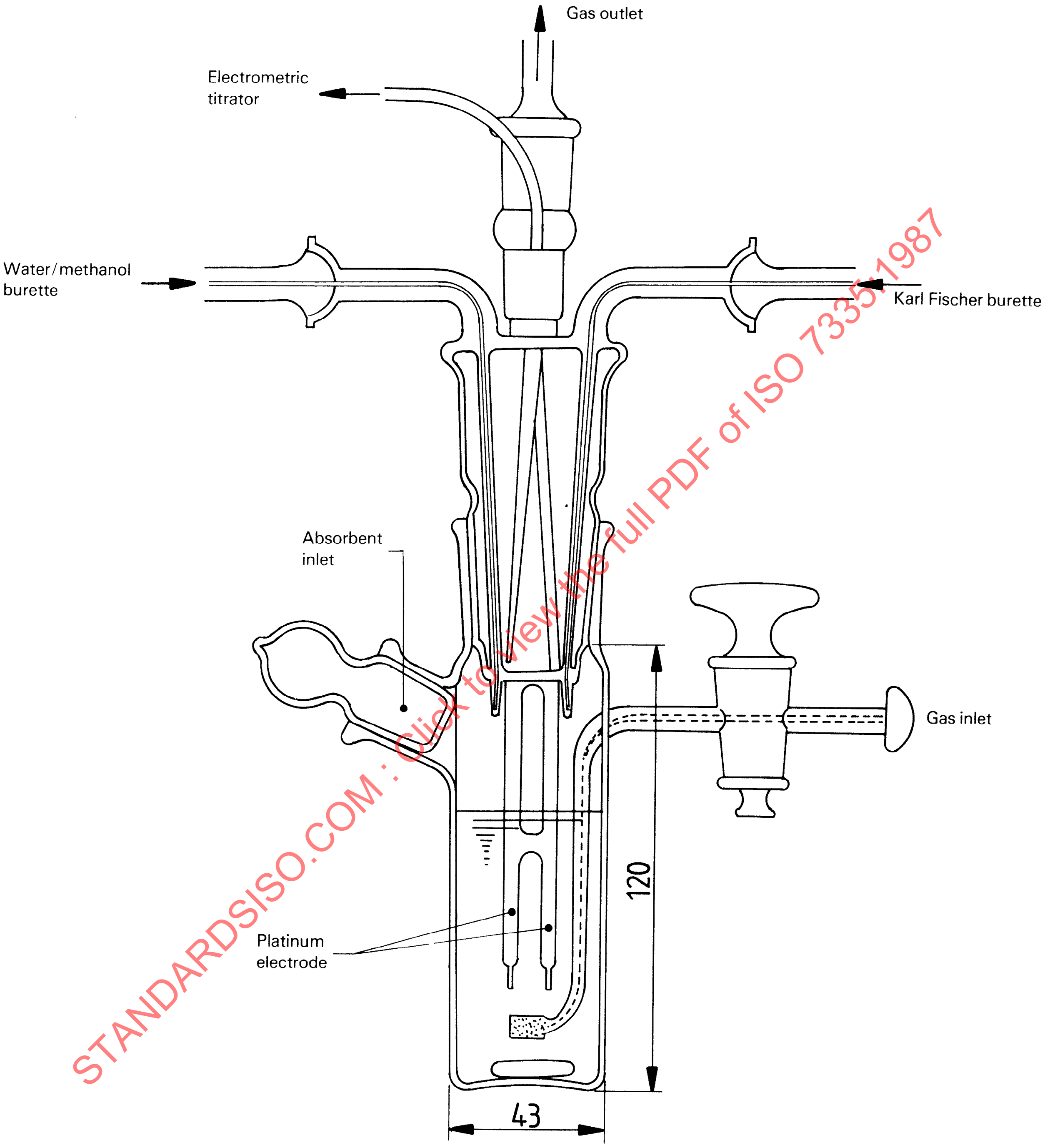


Details for heating tube (5.4)

NOTE — Dimensions not specified in clause 5 are shown for information.

Figure 2 — Apparatus for the Karl Fischer measurement (interchangeable furnace type) (Example)

Dimensions in millimetres



NOTE — Dimensions are shown for information.

Figure 3 — Karl Fischer absorption cell (Example)