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International Standard



2596

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Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric and Karl Fischer methods

Minerais de fer — Détermination de l'humidité hygroscopique dans les échantillons pour analyse — Méthodes gravimétrique et de Karl Fischer

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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.

International Standard ISO 2596 was prepared by Technical Committee ISO/TC 102, *Iron ores*.

The second edition of ISO 2596 was published in 1980. This third edition cancels and replaces the second edition, of which it constitutes a technical revision.

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Iron ores — Determination of hygroscopic moisture in analytical samples — Gravimetric and Karl Fischer methods

0 Introduction

In the analysis of iron ores, the reporting of the analytical value of each constituent on a dry sample basis can, in most cases, be achieved by using a predried sample. However, with certain types of ores, when the constituent being determined is above a certain concentration level, as specified below, this technique can produce erroneous results. In these cases a direct determination of the hygroscopic moisture content becomes necessary, for the purpose of the calculation of analytical values of the other constituents in the ore to a dry sample basis.

1 Scope and field of application

This International Standard specifies two methods for the determination of 0,05 % to 6 % of hygroscopic moisture content in test samples of natural or processed iron ores, namely

Method 1 — Gravimetric method

Method 2 — Karl Fischer method.

Either method 1 or method 2 shall be used when the analytical value of the constituent to be calculated to a dry sample basis is higher than 10 % (*m/m*) in the following types of ores:

- a) processed ores containing metallic iron (direct reduced iron);
- b) natural or processed ores in which the sulfur content is higher than 0,2 % (*m/m*);
- c) natural or processed ores in which the content of combined water is higher than 2,5 % (*m/m*).

The result from the determination of hygroscopic moisture using this International Standard shall not be reported as part of the analysis of an ore sample.

NOTES

1 When the reportable hygroscopic moisture content of a commercial consignment of ores is required, the procedure in ISO 3087, *Iron ores — Determination of moisture content of a consignment*, must be used.

2 With natural or processed ores outside the field of application specified in a) or b) or c), a determination of a constituent at any level of concentration can be conducted using a predried test sample prepared as specified in ISO 7764, *Iron ores — Preparation of predried test samples for chemical analysis*. (At present at the stage of draft).

2 References

ISO 3081, *Iron ores — Increment sampling — Manual method*.¹⁾

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method*.²⁾

ISO 3083, *Iron ores — Preparation of samples — Manual method*.³⁾

3 Principle

Method 1 — Gravimetric method

Equilibration of the test sample with the laboratory atmosphere. Heating of a test portion at 105 ± 2 °C in a heated tube in a stream of dry nitrogen and collection of the evolved moisture in an absorption tube containing a desiccant. Measurement of the corrected increase in mass of the absorption tube.

Method 2 — Karl Fischer method

Equilibration of the test sample with the laboratory atmosphere. Heating of a test portion at 105 ± 2 °C in a heated tube in a stream of dry nitrogen and collection of the evolved moisture in ethylene glycol. Measurement of the moisture content by titration with Karl Fischer solution using electrometric detection of the end-point.

1) At present at the stage of draft. (Revision of ISO 3081-1973.)

2) At present at the stage of draft.

3) At present at the stage of draft. (Revision of ISO 3083-1973.)

Section one: Method 1 – Gravimetric method

4 Reagents

4.1 Desiccant: Anhydrous magnesium perchlorate $[\text{Mg}(\text{ClO}_4)_2]$ of size 0,8 to 1,25 mm, or other suitable desiccant of equivalent drying efficiency. It is essential that the same desiccant be used in both the drying tower and the absorption tubes, since the incoming nitrogen and the gas leaving the system must be dried to exactly the same degree. A fresh condition of the desiccant in both the drying tower and the absorption tubes is important, and reliance should not be placed on self-indicating desiccants.

NOTE — Magnesium perchlorate is a powerful oxidant and must not be allowed to come into contact with organic materials. When exhausted, it should not be discarded into waste bins but should be washed down the sink.

4.2 Silica gel.

4.3 Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$): Free-flowing crystalline material, press-crushed if necessary under a pestle by hand, without grinding, to a size of approximately 1 mm.

4.4 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.

5 Apparatus

A suitable apparatus for the determination is shown diagrammatically in figure 1.

5.1 Balance, capable of reading to 0,1 mg at the mass load of the absorption vessel.

5.2 Oven, preferably aluminium metal block type, capable of accommodating one but preferably several glass drying tubes (5.3) and of maintaining a temperature within the range 105 ± 2 °C over a minimum tube length of 160 mm.

5.3 Glass drying tubes and connections, as shown diagrammatically in figure 2.

5.4 Drying towers, of 250 ml capacity, one filled with silica gel (4.2) and the second packed with desiccant (4.1), to dry the stream of nitrogen (4.4) entering the drying tubes.

5.5 Flowmeters, capable of measuring a flow rate within the range 100 to 200 cm^3/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.

5.6 Absorption tubes, of a suitable design and able to contain sufficient desiccant (4.1) to remove the moisture completely from the stream of nitrogen (4.4). The tubes should have sealable inlet and outlet connections and the direction of

gas flow should be unambiguously identified. (U-tubes are most suitable.) The desiccant shall be firmly packed to prevent "channelling" and be retained in position with glass-wool plugs.

5.7 Sample boats, of an inert and stable material such as glass, stainless steel or porcelain. Approximate dimensions are 100 mm \times 20 mm \times 10 mm, and the sample loading shall not exceed 1,5 mg/ mm^2 . Before use, boats should be dried at approximately 105 °C, then cooled and stored in a desiccator.

5.8 Sintered metal, sintered glass or similar filter discs, inserted in the flexible connections between the drying and absorption tubes.

5.9 Flexible connections: Neoprene elastomer tubing is suitable. Some types of silicone tubing have been found to be permeable. For the gas flow lines after the drying towers, the length of the flexible connections should be kept to a minimum with such tubing being used essentially only for the connection of butt-jointed glass sections.

5.10 Flow control needle-valves, placed on the outlet side of each flowmeter.

6 Sampling and samples

Use for the analysis, a laboratory sample of minus 160 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.

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.

The test sample is brought into approximate equilibrium with the laboratory atmosphere by exposure for at least 2 h on an inert tray at a layer density not greater than 1 mg/ mm^2 .

The sample shall be thoroughly mixed immediately before the determination.

7 Procedure

7.1 Apparatus conditioning

7.1.1 Conditioning of absorption tube

Bring the temperature of the drying tubes (5.3) to 105 ± 2 °C and maintain this temperature through steps 7.1 to 7.4. Adjust the rate of flow of the nitrogen (4.4) to provide a constant flow rate of 150 to 200 cm^3/min through the drying tube. Connect a closed absorption tube (5.6) to an empty drying tube and check for leaks in the system (zero flow). Open the taps of the absorption tube, re-adjust the flow rate if necessary, and pass the nitrogen through the drying tube for 15 min.

NOTE — The conditioning of the absorption tube is only necessary before the first determination of the day.

7.1.2 Weighing of absorption tube

Close the taps of the absorption tube, closing the outlet tap first, and stop the nitrogen flow. Disconnect the absorption tube and seal the outlet of the drying tube. Wipe the absorption tube with a clean dry cloth free from loose fibres and allow to stand for 20 min in the balance room. Open the taps of the absorption tube momentarily to equalize the pressure, and then weigh to the nearest 0,1 mg.

7.2 Blank test

Reconnect the weighed absorption tube, restore the nitrogen flow to the previous rate, check for leaks in the system and open the taps on the absorption tube.

Quickly remove the inlet connector, place an empty sample boat (5.7) in the drying tube at the entrance to the heated zone and insert the magnetic push rod. Immediately replace the inlet connector and move the boat to the centre of the oven using a magnet.

NOTES

1 During the placement of the boat in the drying tube in 7.2, 7.3 and 7.4, precautions should be taken, essentially involving careful technique, to prevent entry of moisture from extraneous sources into the drying tube.

2 Alternatively, a narrow-holed inlet connector and external push rod may be used, provided that the rod is withdrawn, and the inlet closed off, as quickly as possible.

After 2 h, follow the procedure exactly as described in 7.1.2.

The increase in mass of the absorption tube for the blank test should be as low as possible and not more than 2 mg. Repeat the determination of the blank test after the analysis of the test sample to ensure that the blank test value is essentially constant.

7.3 Check test

NOTE — The check test is required when first commissioning the complete apparatus and at other appropriate times, e.g. when changes in the equipment or operators have been made and when a regular interval check on the condition of the absorption tubes is required.

When a satisfactory value for the blank test has been obtained, weigh into the cooled sample boat used for the blank test, to the nearest 0,000 2 g, 0,1 to 0,2 g, of the copper(II) sulfate pentahydrate (4.3). The mass taken should relate to the approximate anticipated maximum moisture content of the ore type being analysed.

Repeat the procedure in 7.2, using the boat containing the weighed copper(II) sulfate. The increase in mass of the absorption tube, corrected with the blank test value, should indicate a value of water evolution from the copper(II) sulfate within the range of 28,5 to 29,2 % (*m/m*). If not, the cause should be located.

7.4 Determination

When a satisfactory value for the blank test has been obtained (and similarly for the check test if appropriate), weigh from the equilibrated test sample (clause 6), the required test portion for the determination of the constituent to be reported on a dry basis. Reserve this test portion in the vessel specified. Immediately weigh to the nearest 0,1 mg, in accordance with table 1, the test portion for the determination of hygroscopic moisture.

Table 1 — Mass of test portion —
Method 1 (Gravimetric method)

Hygroscopic moisture content	Mass of test portion
% (<i>m/m</i>)	g
0,05 to 2	2,0
2 to 6	1,0

Transfer to a dried boat (5.7), distributing the material evenly. Without delay, repeat the procedure in 7.2 using the boat containing the test portion instead of an empty boat and record the total increase in mass of the absorption tube.

Repeat the determination of hygroscopic moisture whenever the determination of the constituent to be reported on a dry basis is repeated, preferably with a change of operator but otherwise at a different time. The hygroscopic moisture values shall not be averaged but shall be used individually to correct the corresponding constituent value.

8 Expression of results

8.1 Calculation of hygroscopic moisture

The content of hygroscopic moisture *A*, expressed as a percentage by mass, is calculated from the following formula:

$$A = \frac{m_1 - m_2}{m_3} \times 100$$

where

*m*₁ is the increase in mass, in grams, of the absorption tube during the test;

*m*₂ is the increase in mass, in grams, of the absorption tube during the blank test;

*m*₃ is the mass, in grams, of the test portion.

8.2 Calculation of the final result

The result calculated in 8.1 to the third decimal place, shall be 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 greater than 5, it is discarded and the figure in the second decimal place is increased by one;

c) when the figure in the third decimal place is 5, it is discarded and the figure in the second decimal place is kept unchanged if it is 0, 2, 4, 6 or 8, and increased by one if it is 1, 3, 5, 7 or 9.

For internal reporting purposes, the percent hygroscopic moisture shall be reported to the nearest 0,05 % (*m/m*). For this calculation, double the final result which has been rounded off to two decimal places, round it off to the first decimal place using the procedure described above and divide the result by 2.

9 Test report (For internal laboratory use only)

The test report shall include the following information:

- a) identification of the sample;
- b) reference to this International Standard;
- c) results of the analysis;
- d) reference number of the results;
- e) any characteristics noticed during the determination and any operations not specified in this section which may have had an influence on the results.

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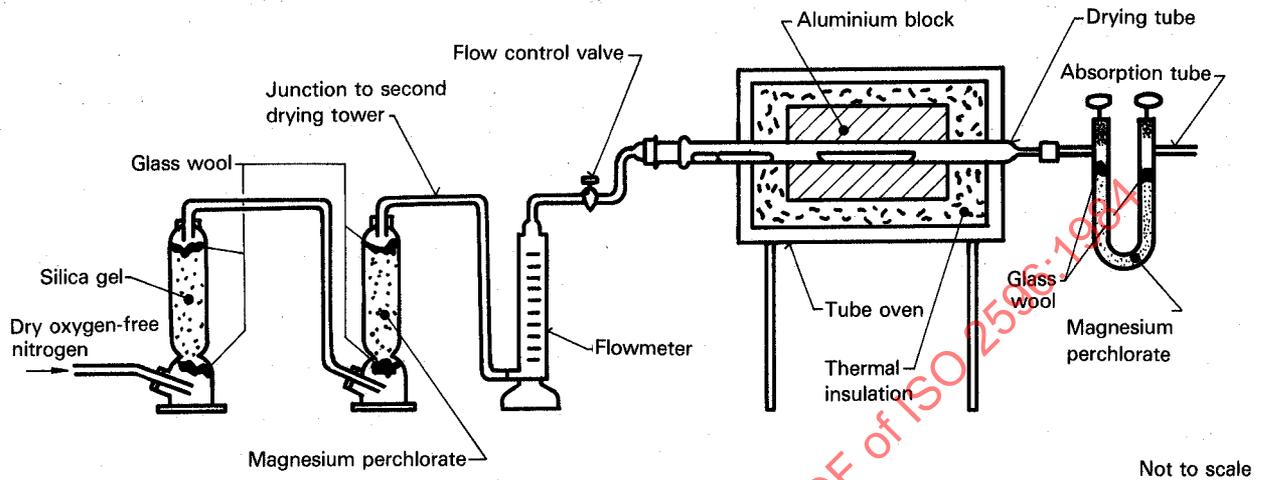


Figure 1 — Apparatus for the determination of hygroscopic moisture — Method 1 (Gravimetric method)

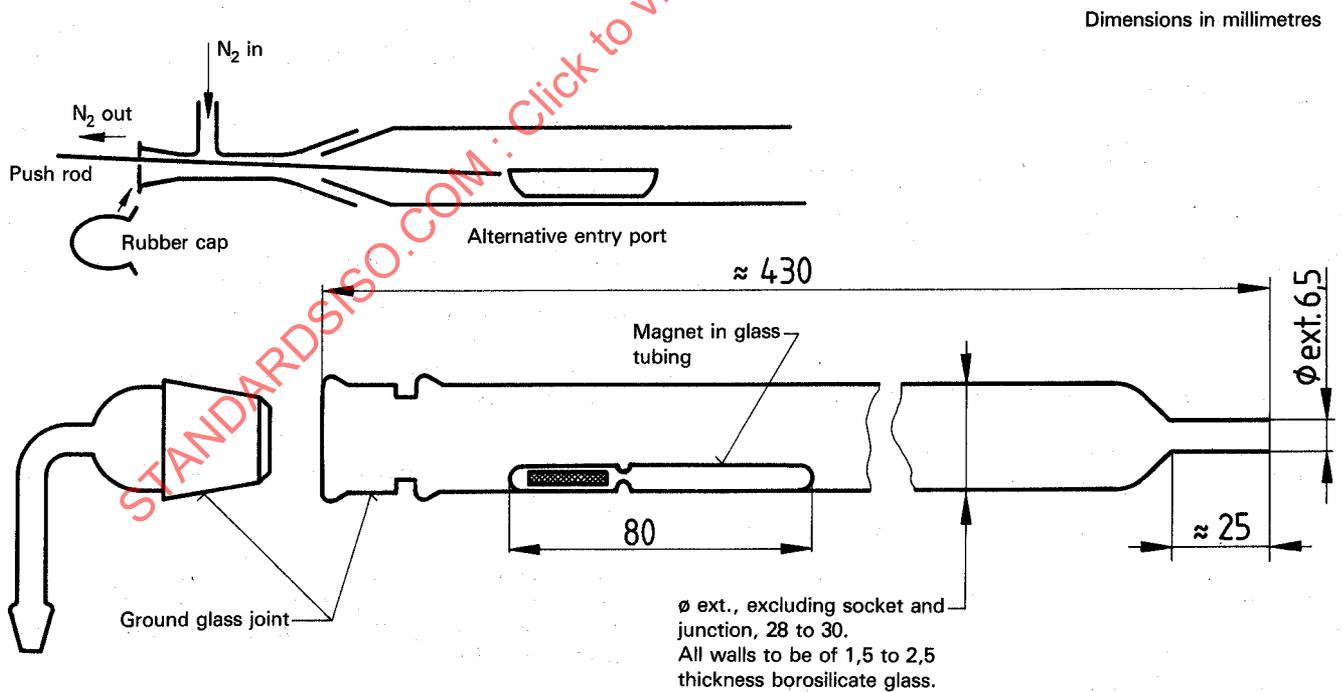


Figure 2 — Drying tube (5.3)

Section two: Method 2 – Karl Fischer method

10 Reagents

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

10.1 Desiccant: Anhydrous magnesium perchlorate [$\text{Mg}(\text{ClO}_4)_2$] of size 0,8 to 1,25 mm, or other suitable desiccant of equivalent drying efficiency.

NOTE — Magnesium perchlorate is a powerful oxidant and must not be allowed to come into contact with organic materials. When exhausted, it should not be discarded into waste bins but should be washed down the sink.

10.2 Silica gel.

10.3 Copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$): Free-flowing crystalline material, press-crushed if necessary under a pestle by hand, without grinding, to a size of approximately 1 mm.

10.4 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.

10.5 Ethylene glycol, anhydrous, ($\text{CH}_2\text{OH CH}_2\text{OH}$).

10.6 Karl Fischer solution, 2,5 to 3,0 $\text{mgH}_2\text{O}/\text{ml}$.

This reagent is commercially available or can be prepared as specified in ISO 760, *Determination of water — Karl Fischer method (General method)*.

Standardize this solution by use of one of the following standard reagents:

- a) a standard water/methanol solution;
- b) water added by means of a microsyringe;
- c) citric acid monohydrate $\text{C}(\text{OH})(\text{COOH})(\text{CH}_2\text{COOH})_2 \cdot \text{H}_2\text{O}$;
- d) disodium tartrate dihydrate $(\text{CHOH} \cdot \text{COONa})_2 \cdot 2\text{H}_2\text{O}$.

Transfer an appropriate quantity of one of the reagents a), b), c) or d), listed above into the absorption cell containing ethylene glycol which has been titrated to the end-point, then follow the titration procedure described in 13.1.1. The factor (F), in milligrams of water per millilitre of Karl Fischer solution, is calculated from this titration.

Add water by means of a microsyringe through the rubber septum. For the addition of citric acid or disodium tartrate dihydrate, remove the rubber septum, and with nitrogen flowing through the apparatus, add the reagent, then immediately replace the septum. Add standard water/methanol solution by means of a burette.

11 Apparatus

A suitable apparatus for the determination is shown diagrammatically in figure 3.

11.1 Oven, preferably aluminium metal block type, capable of accommodating one but preferably several drying tubes (11.2) and of maintaining a temperature within the range $105 \pm 2 \text{ }^\circ\text{C}$ over a minimum tube length of 160 mm.

11.2 Glass drying tubes and connections, as shown diagrammatically in figure 4.

11.3 Drying towers, of 250 ml capacity, one filled with silica gel (10.2) and the second packed with desiccant (10.1), to dry the stream of nitrogen entering the drying tube.

11.4 Flowmeters, capable of measuring a flow rate within the range 100 to 200 cm^3/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.

11.5 Sample boats, of an inert and stable material such as glass, stainless steel or porcelain. Approximate dimensions are 100 mm \times 20 mm \times 10 mm, and the sample loading shall not exceed 1,5 mg/mm^2 . Before use, boats should be dried at approximately 110 $^\circ\text{C}$, then cooled and stored in a desiccator.

11.6 Sintered metal, sintered glass or similar filter discs, inserted in the flexible connections between the drying tubes and the inlets to the absorption cells.

11.7 Flexible connections: Neoprene elastomer tubing is suitable. Some types of silicone tubing have been found to be permeable. For the gas flow lines after the drying towers, the length of the flexible connections should be kept to a minimum, with such tubing being used essentially only for the connection of butt-jointed glass sections.

11.8 Flow control needle-valves, placed on the outlet side of each flowmeter.

11.9 Absorption cells: Glass vessels as shown diagrammatically in figure 5. The entries for the platinum electrodes, burettes and gas inlet shall be gastight to prevent moisture entering the cells.

NOTE — If standard water/methanol solution is not to be used for the calibration, only one burette entry to the absorption cell will be required.

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

11.11 Magnetic stirrers and rotators.

11.12 Electrometric titrators, suitable for Karl Fischer titration and equipped with an ammeter (0,50 μ A) or an equivalent means for the electrometric indication of the end-point.

11.13 Burettes, conforming to the specifications of ISO 385/2 (Class A) or equivalent, 25 ml capacity.

12 Sampling and samples

Use for the analysis, a laboratory sample of minus 160 μ m particle size which has been taken in accordance with ISO 3081 or ISO 3082, and prepared in accordance with ISO 3082 or ISO 3083.

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.

The test sample is brought into approximate equilibrium with the laboratory atmosphere by exposure for at least 2 h on an inert tray at a layer density not greater than 1 mg/mm².

The sample shall be thoroughly mixed immediately before the determination.

13 Procedure

13.1 Apparatus conditioning

Bring the drying tubes (11.2) to a temperature of $105 \pm 2^\circ\text{C}$ and maintain at this temperature through steps 13.1 to 13.5.

Adjust the rate of flow of nitrogen (10.4) to provide a constant flow rate of 150 to 200 cm³/min through the drying tubes. Close the outlet from each drying tower and check for leaks in the system (zero flow). Reconnect the outlet from each drying tube to the inlet of each absorption cell, readjust the flow rate if necessary. Allow 10 min for the system to be purged and maintain this flow through steps 13.3 to 13.5.

Remove the rubber septum from the absorption cell and transfer 40 ml of the ethylene glycol (10.5) into the cell by pipette. Replace the rubber septum.

Switch on the electrometric titrator (11.12) and magnetic stirrer (11.11), adjusting the speed of the latter to ensure adequate mixing. Maintain a constant stirring speed during the titration and between the successive titrations of the blank test, standard and test sample.

13.2 Titration

Add Karl Fischer solution (10.6) slowly to the absorption cell by burette (11.13). 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, a current is selected for the end-point (30 to 40 μ A). The titration is continued until this current can be maintained for a period of 20 s. The absorbent solution shall be titrated to this end-point immediately prior to the commencement of all tests and calibrations.

13.3 Blank test

Quickly remove the inlet connector to the drying tube (11.2), place an empty sample boat (11.5) in the drying tube at the entrance to the heated zone and insert the magnetic push rod. Immediately replace the inlet connector and move the boat to the centre of the oven using a magnet.

NOTES

1 During the placement of the boat in the drying tube in 13.3, 13.4 and 13.5, precautions should be taken, essentially involving careful technique, to prevent entry of moisture from extraneous sources into the drying tube.

2 Alternatively, a narrow-holed inlet connector and external push rod may be used, provided that the rod is withdrawn, and the inlet closed off, as quickly as possible.

After 2 h, carry out the titration as described in 13.2. The indicated value of water for the blank test should be as low as possible and not more than 2 mg. Repeat the determination of the blank test after the analysis of the test sample to ensure that the blank test value is essentially constant.

13.4 Check test

NOTE — The check test is required when first commissioning the complete apparatus and at other appropriate times, e.g. when changes in the equipment or operators have been made and when a regular interval check on the performance of the equipment is required.

When a satisfactory value for the blank test has been obtained, weigh into the cooled sample boat used for the blank test, to the nearest 0,000 2 g, 0,05 to 0,1 g of the copper(II) sulfate pentahydrate (10.3). The mass taken should relate to the approximate anticipated maximum moisture content of the ore type being analysed.

Repeat the procedure in 13.3 using the boat containing the weighed copper(II) sulfate. The indicated water content, corrected with the blank test value should fall within the range 28,5 to 29,2 % (m/m). If not, the cause should be located.

13.5 Determination

When a satisfactory value for the blank test has been obtained (and similarly for the check test if appropriate), weigh from the equilibrated test sample (clause 12), the required test portion for the determination of the constituent to be reported on a dry basis. Reserve this test portion in the vessel specified. Immediately weigh to the nearest 0,1 mg, in accordance with table 2, the test portion for the determination of hygroscopic moisture.

Table 2 — Mass of test portion — Method 2
(Karl Fischer method)

Hygroscopic moisture content	Mass of test portion
% (m/m)	g
0,05 to 0,5	2,0
0,5 to 2	1,0
2 to 6	0,5

Transfer to a dried boat (11.5), distributing the material evenly. Without delay, repeat the procedure in 13.3 using the boat containing the test portion instead of an empty boat and record the final volume of Karl Fischer solution consumed.

Repeat the determination of hygroscopic moisture whenever the determination of the constituent to be reported to a dry basis is repeated, preferably with a change of operator but otherwise at a different time. The values shall not be averaged but shall be used individually to correct the corresponding constituent value.

14 Expression of results

14.1 Calculation of hygroscopic moisture content

The content of hygroscopic moisture A , as a percentage by mass, is calculated from the following formula:

$$A = \frac{(V_1 - V_2) \times F}{m \times 1000} \times 100$$

$$= \frac{(V_1 - V_2) \times F}{10 m}$$

where

V_1 is the volume, in millilitres, of the Karl Fischer solution (10.6) consumed in the titration of the test portion (13.5);

V_2 is the volume, in millilitres, of the Karl Fischer solution (10.6) consumed in the titration of the blank test (13.5);

F is the factor, in milligrams of water per millilitre of Karl Fischer solution, as determined in 10.6;

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

14.2 Calculation of final result

The result, calculated in 14.1 to the third decimal place, shall be rounded off to the second place as follows:

- 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;
- when the figure in the third decimal place is greater than 5, it is discarded and the figure in the second decimal place is increased by one;
- when the figure in the third decimal place is 5, it 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.

For internal reporting purposes, the percent hygroscopic moisture shall be reported to the nearest 0,05 % (m/m). For this calculation, double the final result which has been rounded off to two decimal places, round it off to the first decimal place using the procedure described above and divide the result by 2.

15 Test report (For internal laboratory use only)

The test report shall include the following information:

- identification of the sample;
- reference to this International Standard;
- results of the analysis;
- reference number of the results;
- any characteristics noticed during the determination and any operations not specified in this section which may have had an influence on the results.

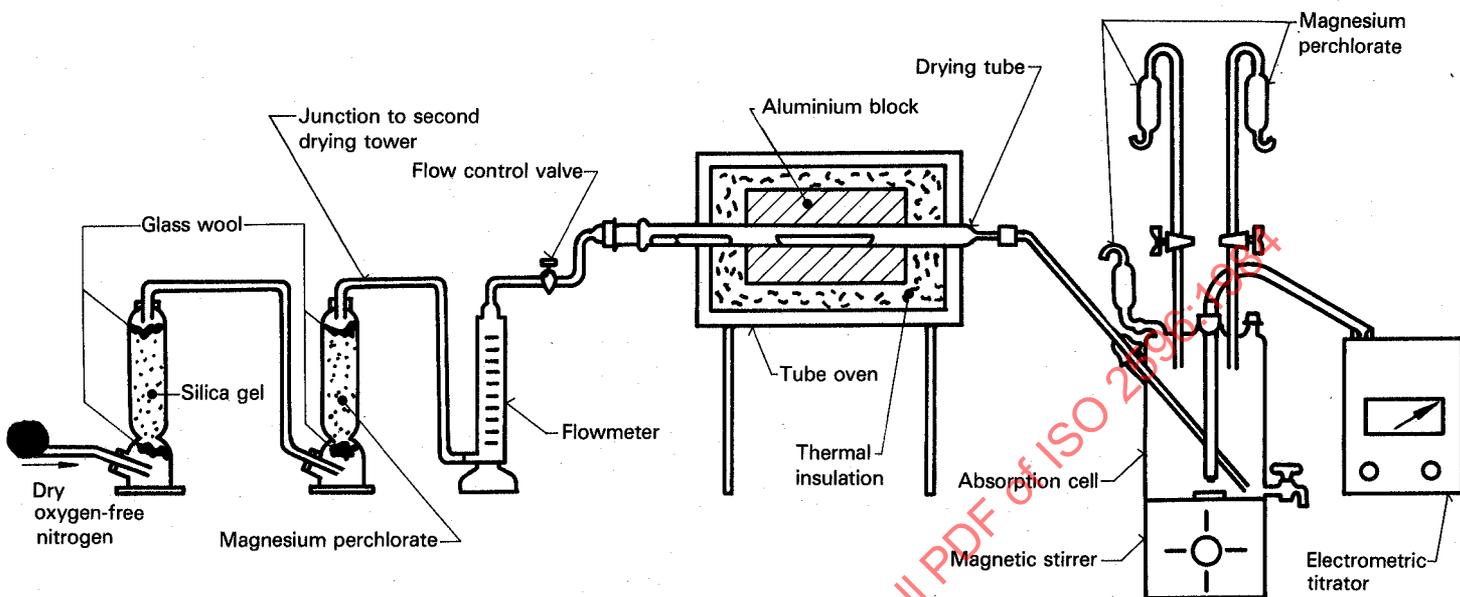


Figure 3 — Apparatus for the determination of hygroscopic moisture — Method 2 (Karl Fischer method)

Dimensions in millimetres

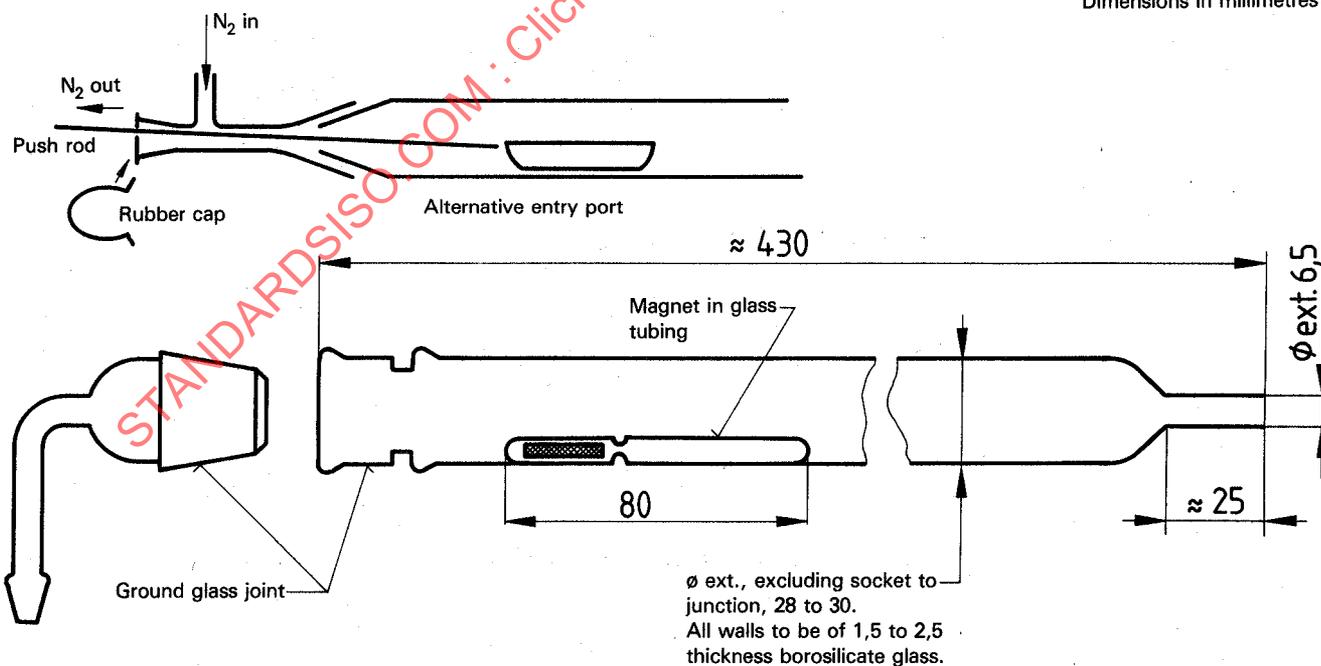


Figure 4 — Drying tube (11.2)

Dimensions in millimetres

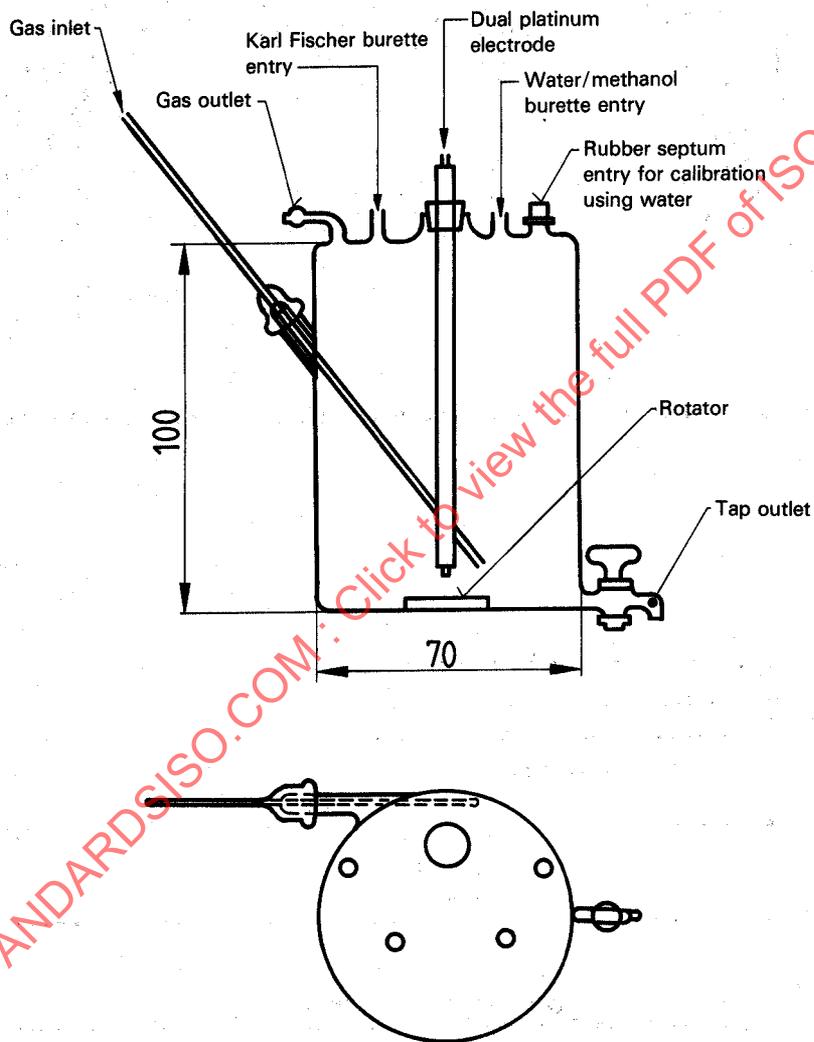


Figure 5 — Absorption cell (11.9)