TC 47

INTERNATIONAL STANDARD 5141

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Propylene for industrial use — Determination of traces of water — Karl Fischer method

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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.

International Standard ISO 5141 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in July 1976.

It has been approved by the member bodies of the following countries :

Austria	India	Portugal
Belgium	Israel	Romania
Brazil	Italy	South Africa, Rep. of
Chile	Korea, Rep. of	Switzerland
France	Mexico	Thailand
Germany	Netherlands	Turkey
Hungary	Poland	United Kingdom

No member body expressed disapproval of the document.

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

Printed in Switzerland

Propylene for industrial use — Determination of traces of water — Karl Fischer method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies the manner of application of the Karl Fischer method for the determination of traces of water in propylene for industrial use.

The method is applicable to products having water contents equal to or greater than 10 mg/kg.

2 REFERENCES

ISO 760, *Determination of water content — Karl Fischer method.*

ISO 3165, *Sampling of chemical products for industrial use — Safety in sampling.*

3 PRINCIPLE

Absorption of the traces of water in a test portion in methanol to which a sufficient quantity of the Karl Fischer reagent has been added so that there is neither an excess of water nor an excess of the Karl Fischer reagent. The methanol is said to be "at the equivalence point".

The principle and the chemical reaction of the Karl Fischer method are given in ISO 760.

4 REAGENTS

The prescriptions concerning the Karl Fischer reagent and the methanol (pure solvent) are given in ISO 760.

Use the Karl Fischer reagent in a more diluted form than that indicated in ISO 760; after having previously determined the water-equivalent of the available reagent, dilute the latter with methanol so that its water-equivalent is between 0,8 and 1,2 mg H_2O/ml.

5 APPARATUS

5.1 Composition

5.1.1 Three steel cylinders, suitable for the sampling of liquid propylene. Each shall have an available capacity of about 150 ml, account being taken of an ullage of about 50 ml, and shall, be fitted, *inter alia*, with two stopcocks which permit the total available capacity (for the liquid and the gas) to be swept by a current of gas after the contents have been discharged.

NOTE — It is recommended that the internal surfaces of the cylinders be highly polished.

5.1.2 Vacuum oven, capable of being controlled at 60 to 100 °C.

5.1.3 Cylinder containing compressed nitrogen, fitted with a perfectly clean pressure-reducing valve.

5.1.4 Drying device, capable of treating 60 litres of nitrogen per hour and of bringing it to a water content compatible with the requirements of 5.3.

NOTE — The drying agents recommended are phosphorus(V) oxide, "5A" molecular sieve or magnesium perchlorate of recognized analytical grade.

5.1.6 Reaction vessel, as shown in figure 1, also used to absorb the water contained in the test portion. The gas enters through the tube fitted with an S 13 spherical ground glass joint (e) connected to a dip-tube ending in a outlet with an opening diameter of between 0,5 and 1 mm. It escapes through the side tube fitted with an S 13 spherical ground glass joint (d). The electrode holder is fitted to a 14/23 conical ground glass joint. An opening, fitted with a 19/26 conical ground glass joint and stopper, is used to introduce the crystalline solids used, if necessary, as water content standards; it is closed with a ground glass stopper.

5.1.5 Karl Fischer apparatus, complying with the requirements of ISO 760 except with regard to the construction of the reaction vessel (see 5.1.6), and fitted with burettes of capacity 5 ml, graduated in 0,01 ml.

5.1.7 Vapour absorption device, for absorbing the vapours released from the Karl Fischer reagent but not the propylene.

5.1.8 Flow meter, calibrated for nitrogen and for propylene, allowing the measurement, at atmospheric pressure, of a flow rate of each of these two gases of between 10 and 60 l/h with a tolerance of not more than 20 %.

5.1.9 Extraction system, allowing the propylene to escape without danger and in conformity with safety regulations (see ISO 3165).

NOTE — Ensure that the extraction system is working safely before beginning the determination.

5.1.10 Tubes and stopcocks, used to connect the components of the apparatus in the following order, as shown in figure 2 :

- compressed nitrogen cylinder (5.1.3), fitted with its pressure-reducing valve;
- drying device (5.1.4);
- T-bore stopcock (a) upstream of the sampling cylinder (5.1.1) and T-bore stopcock (b) downstream;
- by-pass tube;
- sampling cylinder (the stopcocks built into the bottle are not shown; it shall be possible, by operating the built-in stopcocks and T-bore stopcocks (a) and (b) either to empty the contents into the apparatus, or for it to be swept by dry nitrogen, or for it to be short-circuited by the by-pass tube);
- double oblique T-bore stopcock (c), allowing the upstream tubing to be connected to the atmosphere but preventing the downstream tubing from being connected to the atmosphere;
- water absorption vessel (5.1.6) built into the Karl Fischer apparatus, with entry through the spherical ground glass joint (e);
- isolation stopcock (d);
- vapour absorption device (5.1.7);
- flow meter (5.1.8);
- extraction system (5.1.9).

Between the drying device and the water absorption vessel, the tubes shall be made from glass and be as short as possible, and the connection shall be made by means of spherical ground glass joints.

5.1.11 Device, capable of maintaining the temperature of the liquid in the reaction vessel (5.1.6) at between 15 and 25 °C throughout the determination (for example : water bath).

5.2 Preparation

Wash the inside of the three sampling cylinders (5.1.1) with acetone of recognized analytical grade and dry them, first with compressed air and then, open, for 1 h in the vacuum oven (5.1.2), controlled at between 60 and 100 °C. Allow the cylinders to cool in a dry atmosphere and finally close them.

Using the same grade of acetone, wash the inside of the reaction vessel (5.1.6) and the connection tubes between the drying device (5.1.4) and the vessel and dry them for 1 h in the vacuum oven (5.1.2), controlled at between 60 and 100 °C.

Assemble the apparatus as indicated in 5.1.10, ensuring that it is perfectly airtight when all the stopcocks are closed. Place the first empty sampling cylinder in position.

Pass a current of dry nitrogen, for about 15 min, at a flow rate of about 60 l/h, through the by-pass tube, the empty reaction vessel and the remainder of the apparatus. Then pass a current of dry nitrogen at the same rate for about 1 h through the sampling cylinder. Close all the stopcocks, beginning upstream. Replace the first sampling cylinder by the second sampling cylinder and sweep it with dry nitrogen in the same way. Finally, proceed in the same way for the third sampling cylinder.

5.3 Checking

Place about 430 ml of the methanol in the reaction vessel (5.1.6). Neutralize exactly the residual water contained in the methanol with the Karl Fischer reagent. Ensure that the equivalence point is stable for at least 1 min.

Circulate dry nitrogen through the by-pass tube, the reaction vessel and the rest of the apparatus for about 30 min at a flow rate of about 60 l/h. Close all the stopcocks, beginning upstream. Re-establish, using the Karl Fischer reagent, an equivalence point stable for at least 1 min. The volume of Karl Fischer reagent necessary shall be about the same as that which corresponds to the experimental error of the titration and shall be less than 0,05 ml for a water-equivalent of 1 mg H_2O/ml.

Carry out the same procedure, circulating the nitrogen through the first sampling cylinder instead of the by-pass tube. Finally proceed in the same way for the other two sampling cylinders.

NOTE — During exchange of the cylinders, atmospheric moisture may be introduced into the apparatus. Thereby, the volume of Karl Fischer reagent used for the checking may be greater than the 0,05 ml indicated above. In this case, it is necessary to calculate the mean of the values found for the three cylinders and to deduct it from the volume found for the determination.

6 PROCEDURE

6.1 Test portion

Following the checking of the apparatus (5.3), weigh, to the nearest 0,1 g, each of the three sampling cylinders (5.1.1).

Then take three samples of liquid propylene using these three cylinders, filling them partially in order to respect the safety rules specified in ISO 3165. Allow the cylinders to reach ambient temperature and then weigh each to the nearest 0,5 g. The mass of propylene collected in each cylinders shall be about 75 g.

6.2 Determination

Place the first sampling cylinder in position. Open stopcocks (b) and (c) to connect the sampling cylinder to the reaction vessel, and also open stopcock (d). Gradually open the outlet valve of the cylinder until the propylene flow rate approaches 60 l/h. Maintain the flow rate between 40 and 60 l/h until all the propylene has evaporated.

When the propylene flow has ceased spontaneously, open the valve of the sample cylinder to allow the sweeping gas to enter and maintain a current of dry nitrogen at a flow rate of about 60 l/h for about 30 min through the cylinder, the water absorption vessel and the remainder of the apparatus.

Close all the stopcocks, wait for 5 min and re-establish, with the Karl Fischer reagent, an equivalence point stable for at least 1 min. Let V_1 be the volume of Karl Fischer reagent used.

Repeat the measurement with the second sampling cylinder. Let V_2 be the volume of Karl Fischer reagent used.

NOTES

1 It is also possible to proceed by means of back-titration, by adding an excess of Karl Fischer reagent and by titrating the excess with a standard solution of water in methanol.

2 A surface active agent (such as *N*-ethylpiperidine) may be added to the titration vessel so as to increase the speed with which the water reacts with the pyridine.

7 CALCULATION AND EXPRESSION OF RESULTS

From V_1 and V_2, deduct the value of the blank test, if any (see note in 5.3), and calculate, as specified in ISO 760, the corresponding masses of water, m_1 and m_2, in milligrams.

Calculate the values C_1 and C_2, in milligrams per kilogram, of the water content of the propylene using the formulae

$$C_1 = \frac{m_1}{m_3}$$

and

$$C_2 = \frac{m_2}{m_4}$$

where

m_3 is the mass, in kilograms, of propylene in the first sampling cylinder (6.1);

m_4 is the mass, in kilograms, of propylene in the second sampling cylinder (6.1).

7.1 First case

If the difference $|C_1 - C_2|$ is less than 3 mg/kg or 15 % of the arithmetic mean of these two values, the determination is complete.

Take this mean as the result.

7.2 Second case

If the first case (7.1) does not apply, carry out a determination using the third sampling cylinder and calculate the corresponding value C_3.

7.2.1 If only one of the differences $|C_1 - C_3|$ and $|C_2 - C_3|$ meets the condition specified in 7.1, take the corresponding mean as the result.

7.2.2 If both differences meet the condition specified in 7.1, take the mean of the three results C_1, C_2, C_3 as the result.

7.2.3 If none of the differences meets the condition specified in 7.1 and it is not possible to repeat all the operations, beginning with the sampling, give the three results C_1, C_2, C_3.

8 NOTES ON THE PROCEDURE

Each of the following steps of the procedure shall take place without interruption :

- preparation of the apparatus, from : "Pass a current of dry nitrogen for about 15 min . . .";
- checking of the apparatus;
- taking of the test portion;
- determination carried out on one sampling cylinder.

During the intervals between these steps, and during sampling of the test portion, maintain a current of dry nitrogen at a flow rate of about 10 l/h in the by-pass tube and the remainder of the apparatus.

For operations where requirements are not given, proceed according to normal laboratory practice, but note carefully the procedures carried out. Attach an account of these to the test report.

9 TEST REPORT

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference to the method used;

c) the results, as well as the method of expression used;

d) any unusual features noted during the determination;

e) a detailed diagram of the apparatus used;

f) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

Dimensions in millimetres

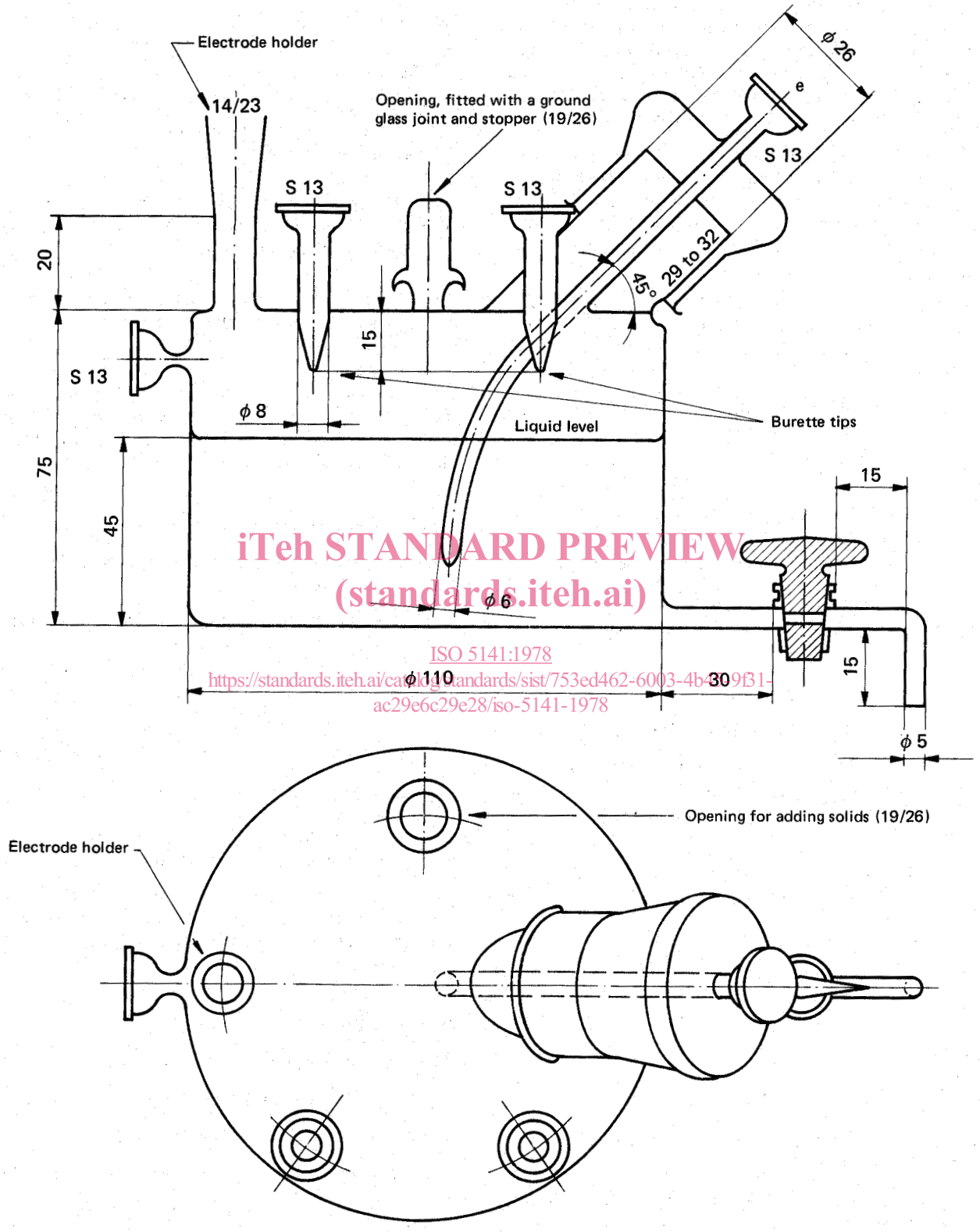

FIGURE 1 — **Reaction vessel**

(14/23 and 19/26 designate conical ground glass joints complying with the requirements of ISO 383. S 13 designates spherical ground glass joints complying with the requirements of ISO 641.)

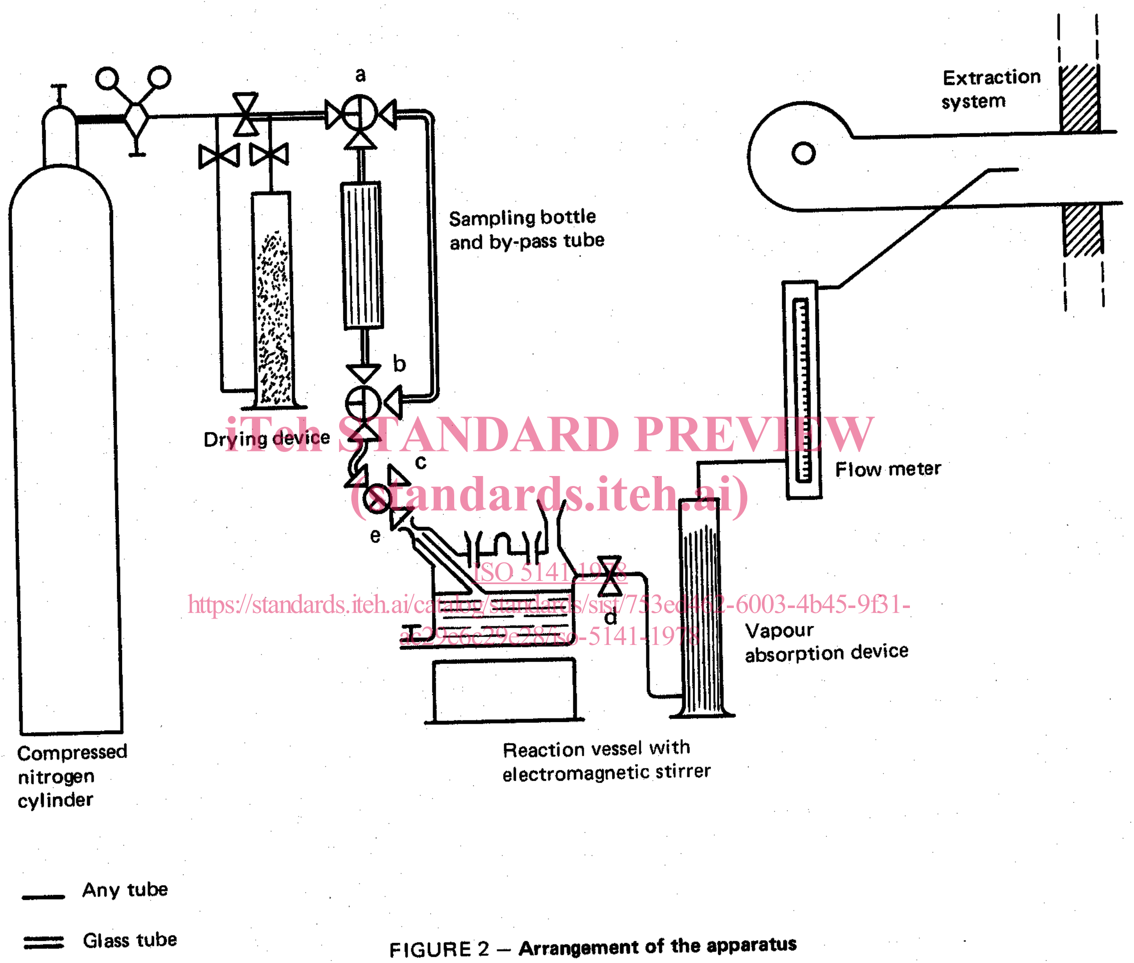

FIGURE 2 — **Arrangement of the apparatus**