International Standard 6191

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Light olefins for industrial use — Determination of traces of water — Karl Fischer method

Oléfines légères à usage industriel — Dosage des traces d'eau — Méthode de Karl Fischer

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Foreword

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Light olefins for industrial use — Determination of traces of water — Karl Fischer method

WARNING — Carry out the operations specified in this International Standard in a well-ventilated room (handling of inflammable gas and pyridine).

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 light olefins from C_2 to C_4 for industrial use.

The method is applicable to products having water contents between 10 and 100 mg/kg.

For higher contents use ISO 760 as sampling is not valid when there is a risk that condensation of water may occur.

2 References

ISO 760, *Determination of water — Karl Fischer method (General 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 a solvent to which a sufficient quantity of Karl Fischer reagent has been added so that there is neither an excess of water nor an excess of the Karl Fischer reagent, when the solvent 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

Karl Fischer reagent and the solvents are specified in ISO 760.

4.1 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 the solvent so that its water-equivalent is between 0,8 and 1,2 mgH_2O/ml.

4.2 Use methanol (containing less than 0,01 g of water per 100 ml) as the solvent for the lightest olefins (ethylene and propylene) and ethylene glycol (containing less than 0,01 g of water per 100 ml) for the heavier olefins such as butadiene which are more soluble in this solvent.

5 Apparatus

5.1 Composition

5.1.1 Three stainless and low-temperature resistant steel cylinders, suitable for the sampling of light olefins. 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 valves 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 — The sampling cylinders must satisfy the tests indicated in the actual legislation in each country and also for marking[1]. It is recommended that the internal surfaces of the cylinders be highly polished.

5.1.2 Vacuum oven, capable of being controlled at any desired temperature between 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 or "5A" molecular sieve of recognized analytical grade.

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, or, alternatively, burettes of the same capacity, with capillary end of 0,1 mm, supplied under pressure.

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[1] The marking of sampling cylinders will be specified in ISO 7382.

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 S13 (ISO 641) spherical ground glass joint (J_1) connected to a dip-tube ending in an outlet with an opening diameter of about 0,5 mm or having a sintered glass filter of grade P 100 (pore size index between 40 and 100 µm). It escapes through the side tube fitted with an S13 (ISO 641) spherical ground glass joint (J_2). The electrode holder is fitted to a 12/14 conical ground glass joint (ISO 383). An opening, fitted with a 19/26 conical ground glass joint and stopper (ISO 383), is used to introduce the crystalline solids used, if necessary, as water content standards; it is closed with a ground glass stopper.

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

5.1.8 Flow meter, calibrated for nitrogen and for the olefins concerned, 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 light olefins 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 3 :

- compressed nitrogen cylinder (5.1.3), fitted with its pressure-reducing valve;
- drying device (5.1.4);
- T-bore stopcock (T_1) upstream of the sampling cylinder (5.1.1) and T-bore stopcock (T_2) downstream;
- by-pass tube;
- sampling cylinder [the stopcocks built into the cylinder are not shown; it shall be possible, by operating the built-in valve and T-bore stopcocks (T_1) and (T_2) 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 (T_3), 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 (J_1);
- isolation stopcock (T_4);
- vapour-absorption device (5.1.7);
- flow meter (5.1.8);
- extraction system (5.1.9).

The tubes between the drying device and the water-absorption vessel shall be made from glass and shall 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 : an electrical thermo-controlled heating cord, one coil of which heats the stopcock (T_2).]

5.2 Preparation

Wash the interiors 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 interior 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, controlled at between 60 and 100 °C.

Assemble the apparatus as indicated in 5.1.10, ensuring that it is perfectly airtight when all 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 Control test

Place a magnetic bar and about 240 ml of the solvent (4.2) in the reaction vessel (5.1.6). While stirring at constant rate, neutralize exactly the residual water contained in the solvent with the Karl Fischer reagent (4.1). 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 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 solution having a water-equivalent of 1 mgH_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 — Atmospheric moisture may be introduced into the apparatus during exchange of the cylinders. Therefore, the volume of Karl Fischer reagent used during the control test may be greater than the 0,05 ml indicated above. In such cases, it is necessary to calculate the mean of the values found for the three cylinders (V_0) as the blank test and to deduct it from the volume found for the determination.

6 Sampling[1]

After the control test (5.3) on the apparatus, weigh, to the nearest 0,1 g, each of the three sampling cylinders (5.1.1).

Then sample the olefin in triplicate by means of these three cylinders, filling them only partially in accordance with the safety rules specified in ISO 3165, as follows.

6.1 Connect the sampling line from the plant or from the storage vessel to one of the three cylinders as indicated in figure 4.

6.2 Check that the connectors are tight enough to ensure hermetic sealing and that all the stopcocks are closed.

6.3 Purge and fill the cylinder in the following sequence :

- open the valves from the unit to be sampled in the order (A), and then (B);
- open valves (C) and (F) for about 1 min in order to purge the coils (a) and (b);
- shut valves (F) and (C) and purge the cylinder by opening first valve (D) and then valve (E) for about 1 min and then shut valve (E);
- allow the cylinder to fill until the pressure is equalized (about 1 min);
- close the cylinder by means of valve (D);
- close valves (A) and then (B);
- purge coils (a) and (b) by opening valves (C) and (F);
- disconnect all the connections.

6.4 Carry out the same procedure with the other two cylinders.

6.5 Allow the cylinders to reach ambient temperature and weigh them to the nearest 0,1 g. The mass of olefin in each bottle should be at maximum :

51 g of ethylene;

64 g of propylene;

82 g of butadiene.

7 Procedure

Place the first sampling cylinder in position. Open stopcocks (T_2) and (T_3) to connect the sampling cylinder to the reaction vessel, and also open stopcock (T_4). Gradually open the outlet valve of the cylinder until the olefin flow rate approaches 60 l/h. Maintain the flow rate between 40 and 60 l/h until all the olefin has evaporated.

When the olefin 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, while stirring at constant rate, 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 the solvent.

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

8 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, in milligrams, of water m_1 and m_2.

Calculate the water contents C_1 and C_2, in milligrams of water per kilogram, of the olefin 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 olefin in the first sampling cylinder (6.1);

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

8.1 First case

If the difference $|C_1 - C_2|$ is lower than 3 mgH_2O/kg or 15 % of the arithmetic mean of these two values, the determination is complete.

Take this mean as the result.

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[1] The sampling of light olefins for industrial use will form the subject of ISO 7382.

8.2 Second case

If the first case (8.1) does not apply, carry out a determination using the third sampling cylinder and calculate the corresponding water content C_3.

8.2.1 If only one of the differences $|C_1 - C_3|$ and $|C_2 - C_3|$ meets the condition specified in 8.1, take the corresponding mean as the result.

8.2.2 If both differences meet the condition specified in 8.1, take the mean of the three results C_1, C_2, C_3 as the result.

8.2.3 If none of the differences meets the condition specified in 8.1 and it is not possible to repeat all the operations, beginning with the sampling, give the three results C_1, C_2, C_3.

9 Notes on the procedure

Carry out the following steps of the procedure without interruption :

- preparation of the apparatus (5.2), starting from the fourth paragraph : "Pass a current of dry nitrogen...";
- control test (5.3);
- sampling (clause 6);
- determination carried out on one sampling cylinder (clause 7).

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.

10 Test report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

c) the results, and 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

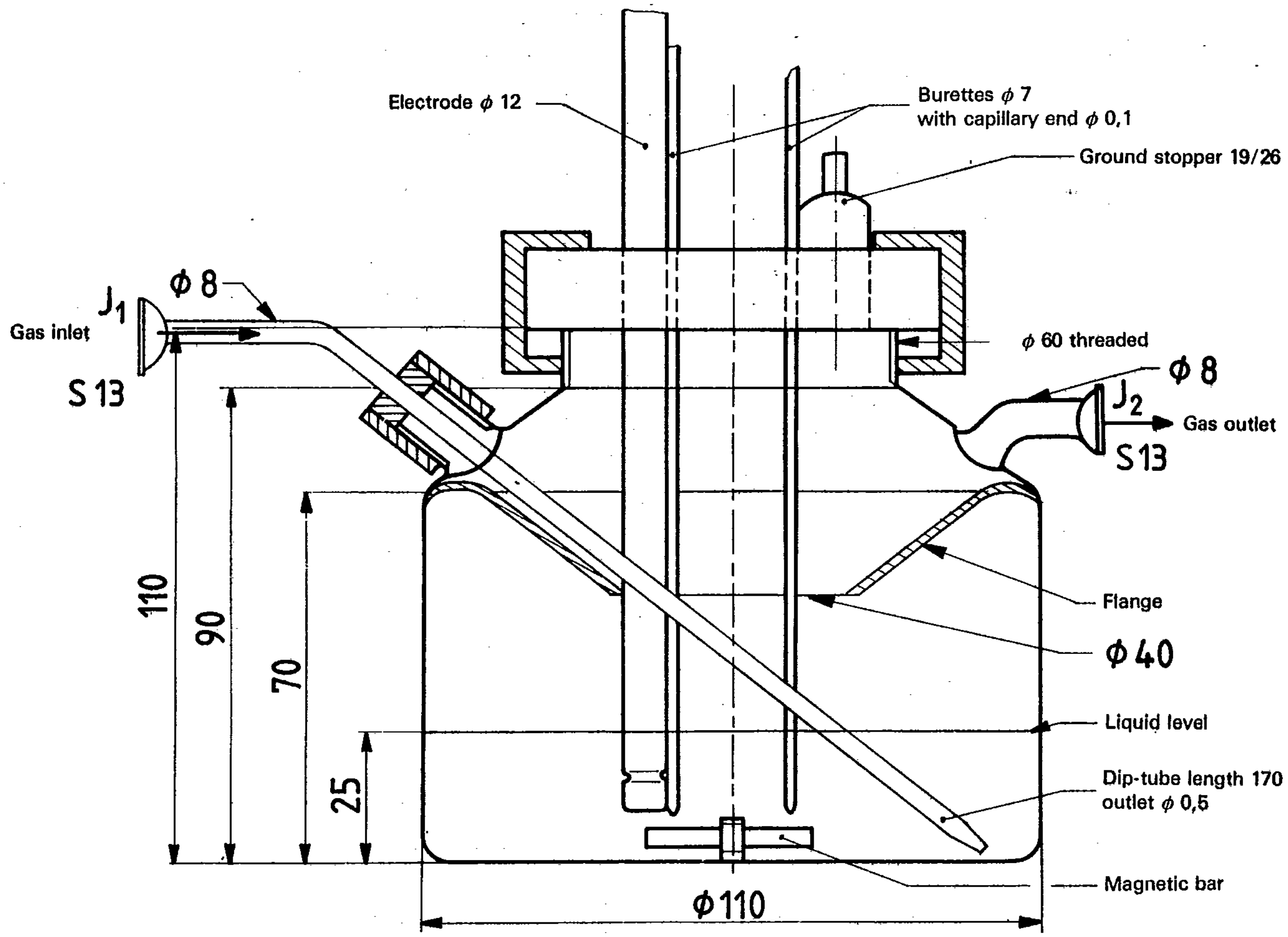


Figure 1 — Reaction vessel

Dimensions in millimetres

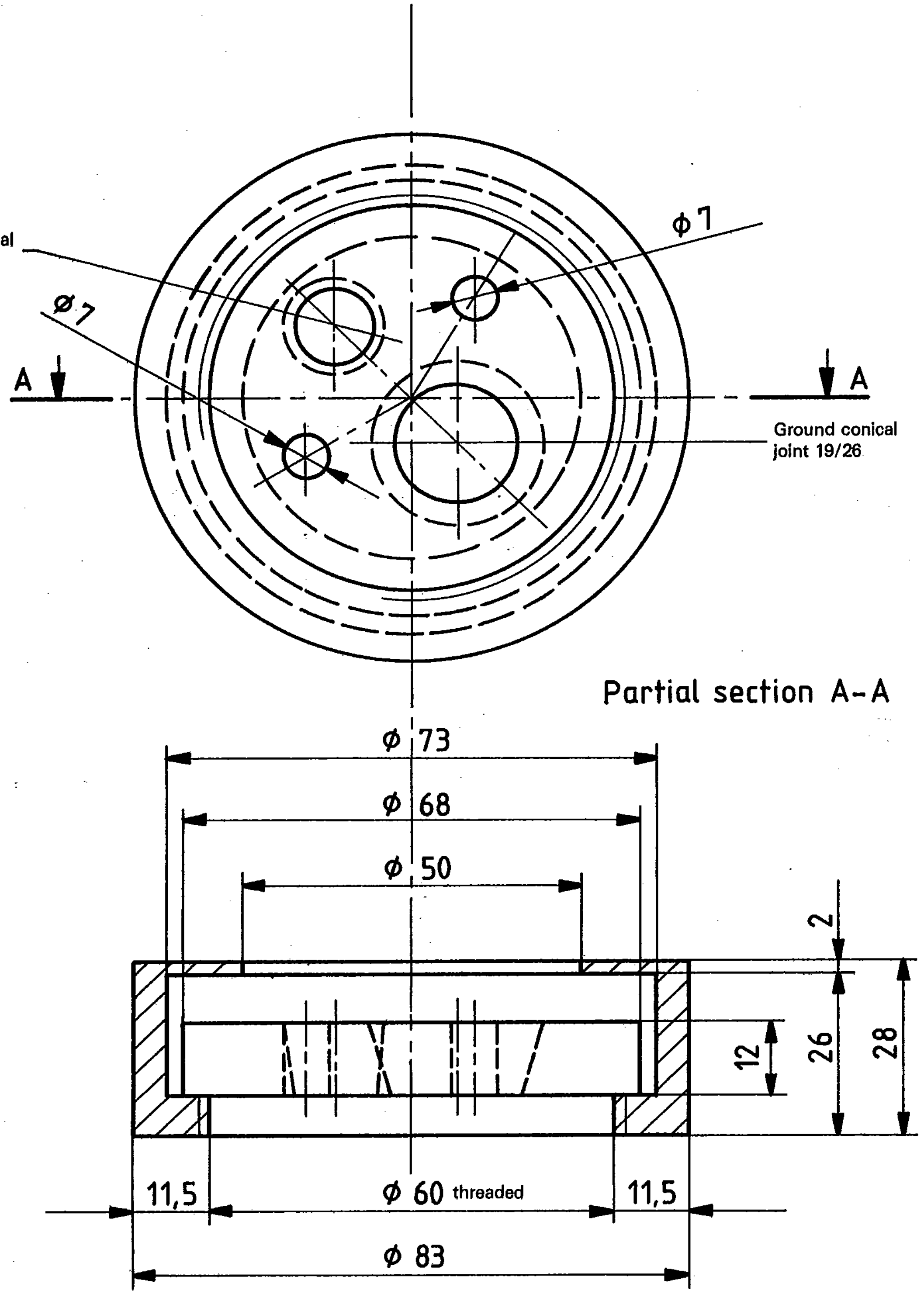


Figure 2 — Stopper of reaction vessel

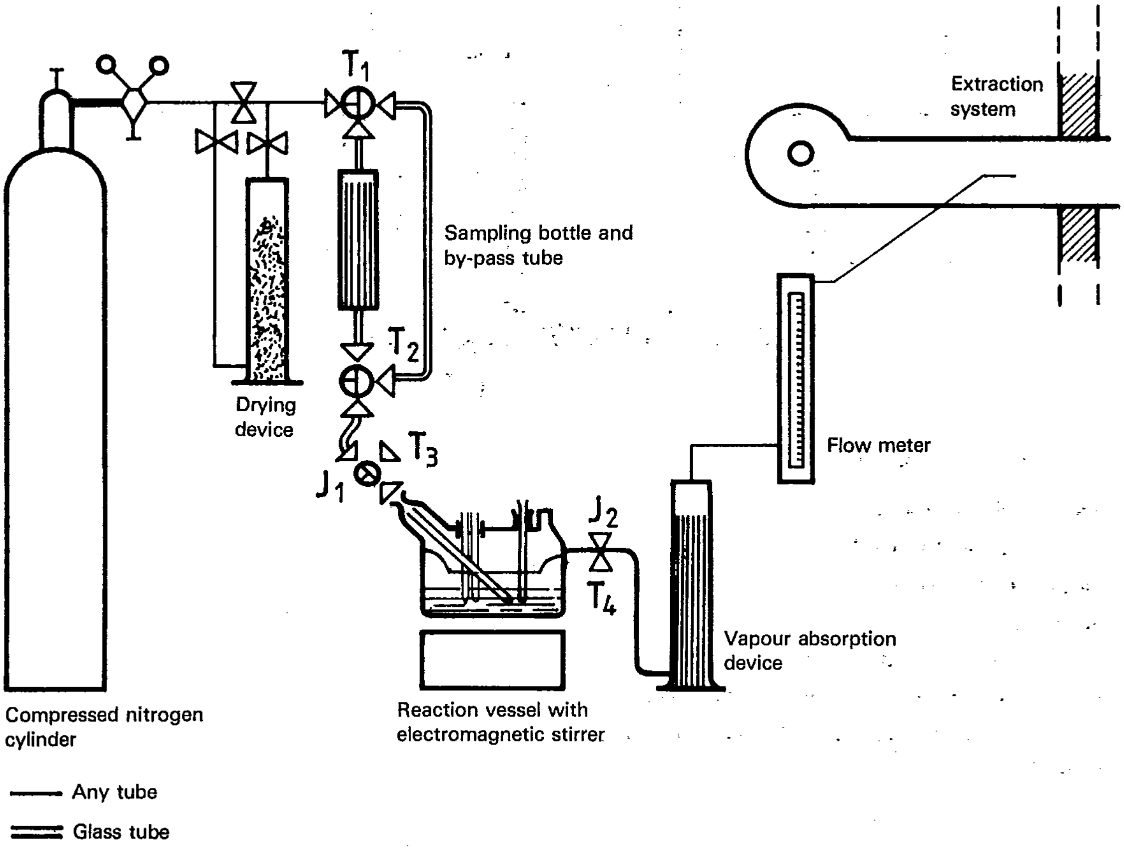
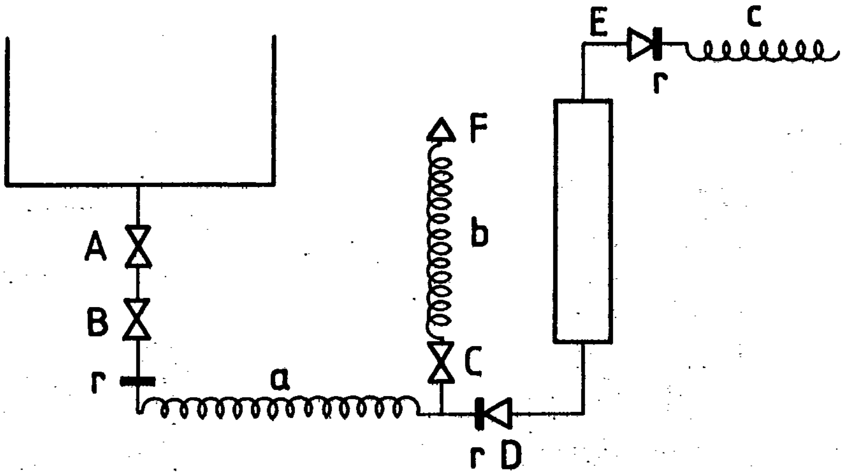


Figure 3 — Arrangement of the apparatus



Key (Dimensions given for information)

A and B — Analysis unit sampling line valves

C — Connecting valve for coils (a) and (b)

D and E — Sampling cylinder valves

F — Purge valve

a — Stainless steel coil; length : 2 m; internal diameter : 4 mm

b — Stainless steel coil; length : 1 m; internal diameter : 2 mm

c — Stainless steel coil; length : 3,5 m; internal diameter : 2 mm

r — Connector

Figure 4 — Sampling device