

# International Standard



# 6712

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## Gas analysis — Sampling and transfer equipment for gases supplying an analytical unit

*Analyse des gaz — Organes de prélèvement et de transfert des gaz destinés à alimenter une unité analytique*

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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 6712 was developed by Technical Committee ISO/TC 158, *Analysis of gases*, and was circulated to the member bodies in December 1980.

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

Australia  
Belgium  
Cuba  
Czechoslovakia  
Egypt, Arab Rep. of  
France

Germany, F. R.  
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The member body of the following country expressed disapproval of the document on technical grounds :

South Africa, Rep. of

# Gas analysis — Sampling and transfer equipment for gases supplying an analytical unit

## 1 Scope and field of application

This International Standard specifies technical requirements for sampling and transfer equipment for gases supplying an analytical unit.

Analytical units supply data corresponding to representative quantities determined by analyses of gases (samples).

A sample may be either

- physically isolated as a discrete sample analysed *in situ* (for example analysis of oxygen by an electrochemical method), or
- transferred from a system to an analytical cell, either directly by means of a sampling system, or after storage in a bottle or vessel.

In the two cases under consideration, when there is transfer of gas, the equipment and sampling system shall ensure that the following functions are performed :

- a) Treatment of the sampled gases to eliminate certain chemical and physical factors which may have an effect on the analysis and certain factors likely to impair the functioning and maintenance of the analyser and its associated

equipment. This function is ensured along the **sampling line**. By convention, the bottle or vessel in which the gas sample is stored is considered as part of the sampling line.

- b) Storage of the samples thus obtained and, alternatively, of calibration gas mixtures until the analysis is carried out, avoiding changes likely to have an adverse effect on the results. This function is ensured along the **transfer line**.

The sample point is located between the two lines, and is the point from which the fluid conveyed may be considered as a representative sample. It is generally also the point at which calibration gases are injected into the analyser circuit.

It is, therefore, possible to represent a gas sampling system intended for analysis in diagrammatic form (see figure 1).

The actions appropriate to the treatment or storage of gases for analysis depend on a combination of the characteristics of the medium to be analysed, the analytical procedures and the instruments used. The choice as to which characteristics and properties have to be changed and those which have to be retained depends on a knowledge of these characteristics in relation to each application.

NOTE — The terms used in this International Standard and, in particular, those in figure 1 will be defined in ISO 7504, *Gas analysis — Vocabulary*.

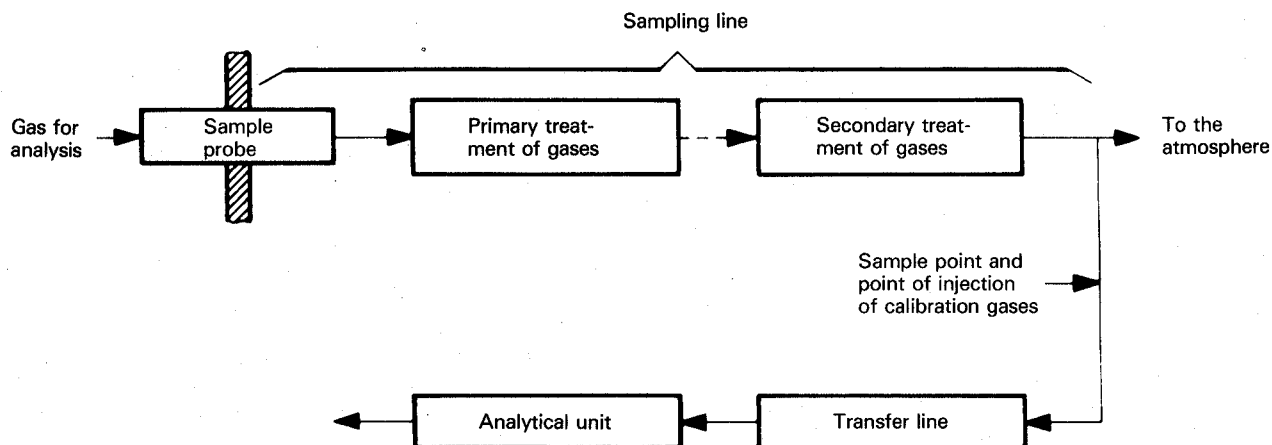


Figure 1 — Diagram of a gas sampling system

## 2 Sampling line

Owing to the extreme diversity of the problems to be resolved, it is not possible to standardize a single sampling line; these problems can only be resolved by grouping together numerous individual elements.

This clause gives general information on the various elements.

### 2.1 General characteristics required for a sampling line

#### 2.1.1 Representativeness of the sample taken

One of the difficulties encountered is generally the disproportion between the flow rate at which sampling is performed (for example several hundreds of litres per hour) and the flow rates currently encountered in industry (several tens of thousands of cubic metres per hour), the ratio lying most commonly between  $10^{-3}$  and  $10^{-6}$ .

#### 2.1.2 Storage of the sample

It is essential that the composition of the sample is not changed, especially in any unpredictable way, between the sample point and the analytical cell.

The phenomena which contribute to changes in composition of the sample are mainly :

- a) Pollution of the gas caused by leakage in the flow system (for example by diffusion or by differences in pressure).
- b) Dissolution of certain constituents in liquids likely to be encountered, such as water (this may be only condensation water), oil from pumps, etc.
- c) Selective sorption and retention of certain constituents (for example sulphur dioxide) on the surfaces of pipes, particularly if these are not perfectly clean.
- d) Selective action, in general detrimental and mostly irreproducible, of chemical compounds (particularly if present in small traces) intentionally added as an absorbant for a specified constituent (desiccants in particular).
- e) Corrosion.
- f) Condensation.

Precautions to minimize or eliminate the effects of such phenomena are described in 2.1.3 and 2.1.4.

#### 2.1.3 Preparation of the sample for analysis

Analysers generally require the gas supplied to be carefully prepared. The sampling line shall therefore supply a gas

- from which the dust has been removed;
- if necessary, dried (if required by the conditions of the analysis and the analyser);

- at a pressure, flow rate and temperature lying between fixed and usually very narrow limits.

#### 2.1.4 Transport of the gas

The analyser and its accessories cannot always be located in the place where the user wishes to carry out the analysis. It is therefore important that the sampling line permits transport of the gas in good conditions. In the case of a sampling system, the response time to a change of sample composition shall be as small as possible. In cases where vessels are used to transport the gas, these vessels shall have all the qualities required for satisfactory storage of the gas.

### 2.2 Sample probe

Whereas the analytical unit receives a gas in the optimum condition, the sample probe is the first element in the sampling line which is subjected to all the industrial conditions in force at the place where the user wishes to conduct the test.

Consequently, the type of sample probe shall be carefully selected on the basis of the following three parameters :

- physical (pressure, temperature) and chemical conditions of the ambient environment, taking account, in particular, of precautions to be taken with respect to safety;
- response time;
- representativeness of the gas sample.

Therefore :

- a) the sample probe should usually contribute to the treatment of the sample and should comprise, for example
  - one or more carefully positioned sampling orifices,
  - one or more means of filtration,
  - a device for collecting condensates,
  - a washing device or device for trapping dust and various agglomerates : injection of water, air or steam,
  - sometimes, a motor-powered unit : steam or water pump, Mariotte bottle, Sprengel pump, other pumps of various kinds,
  - a pressure reducer (the response time of the line is roughly proportional to the pressure prevailing therein),
  - a vaporizer (intended to convert a liquid phase completely into a gaseous phase) with temperature control and mixer, and, in this case, an isokinetic gas sampling device,
  - a heating or cooling device,
  - a mechanical support,

— a device for diluting the sample with an inert gas, if the constituents of the mixture are particularly reactive;

b) the materials should be chosen on the basis of

- their behaviour under local conditions at the sample point (metals, plastics, ceramics),
- their lack of retention and, generally, their passivity towards the constituent under consideration (porosity, chemical reaction, adsorption),
- the ease of maintenance or replacement (cost),
- the ease with which they can be machined and connected without leaks to other elements;

c) the design selected depends on

- the mechanical strength (temperature, vibration or impact),
- ensuring adequate flow of the sample,
- manufacturing possibilities and ease of replacement,
- conformity with accepted standards for probe supports (flanges, joints).

Some examples of sample probes are described in annex A.

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## 2.3 Containers for storage of the sample

If the sample cannot be transferred directly by the sampling system to the analyser, containers, which shall permit transport of the sample to the laboratory, shall be used to store the sample.

The containers shall be easy to handle and shall be hermetically sealed to avoid gas leaks and pollution. The valves shall be made of a material which is as inert as possible to the gases to be stored (for example valves made entirely of metal, valves with PTFE seat).

The design and shape of the containers can vary according to their purpose, i.e. bottles, tubes, etc.

Some examples of such containers are shown in annex B.

The method of sampling depends on the quantity of gas available, its pressure and other characteristics which may affect the constituents under consideration.

If there is an abundant quantity of gas at a considerable pressure, it is recommended to sweep the container with the gas to be sampled until the original gas is displaced. A gas flow equivalent to 10 times the volume of the sampling container is sufficient for this purpose. It is also possible to carry out a series of 10 operations of filling the container with the gas to be sampled, and emptying after each filling.

If the quantity of gas is limited, it is possible to use one of the following techniques :

a) Method of displacement by liquid. The displacing liquid used in the sampling container shall not react either with the container or the sample; water, acidulated water, saline solution or mercury may be used, as appropriate.

b) Use of a container in which a vacuum has been created.

If the gas to be sampled is at low pressure, it is possible to use one of the various types of aspirators or pumps available.

Account shall be taken of the following considerations relating to the nature of the sample :

a) Toxicity.

b) Condensable material

1) if the concentration can be affected by condensation due to a high sampling level or temperature variation;

2) if the concentration of certain constituents does not form the object of the analysis but can affect the constituent under consideration, for example humidity with sulphur dioxide.

c) Exclusion of oxygen from the atmosphere or steam, if very low levels can affect the constituent under consideration, for example mercaptans, silane.

d) Isokinetic sampling of heterogeneous systems, for example aerosols.

## 2.4 Treatment of the gas

A distinction is usually made between

a) the primary treatment, which has to impart to the gas the properties which enable it to be transported in conditions suitable for its use, and

b) the secondary treatment or finishing, the aim of which is to ensure that the gas conforms to the requirements of the analysers.

Treatment comprises the functions of filtration and dehydration.

### 2.4.1 Filtration

Filtration of gases for analysis is intended to remove solid particles and, where necessary, bubbles of liquid, the transfer of which into the analyser could present difficulties, for example :

— deposits likely to obstruct ducts, openings, capillary tubes, permeable membranes etc.,

— deposits which could hinder the physical functioning of the analyser : opacity in an optical system, changes in conductivity or field in an electrochemical system, etc.,

— chemical reactions in a liquid (or other) medium occurring in the analytical cell : electrolyte, colorimetric reagent, etc.,

— chemical, physical and mechanical action on the materials and the functioning of the equipment.

In view of the fact that gases for analysis very often contain aerosols, devices for stopping these aerosols are widely used.

Stopping devices for particles mainly comprise :

— grilles, sieves or strainers, which mechanically stop relatively large particles ( $> 25 \mu\text{m}$ ). These devices are made of a metal fabric, perforated sheets, layers of pieces of material, agglomerated or sintered materials (see figures 2 and 3);

— filters made of various kinds of porous materials produced from metals, ceramics, or natural, artificial or synthetic fibres, etc. (see figure 4);

— various more specialized devices : magnetic or electrostatic devices, impactors, bubblers, washers, condensers, cyclones, etc.

Even if their use is essential, these devices present inconveniences :

— from the technical point of view, the devices may become clogged or obstructed, which necessitates inspection (checking the flow or testing for loss of load) and maintenance. These phenomena may indirectly influence the results of the analysis;

— from the analytical point of view, filtration devices and, in particular, deposits of particles and condensates may react with the constituents of the gases for analysis and falsify the analysis. The precautions to be taken shall be considered for each case.

## 2.4.2 Dehydration

Dehydration is intended to reduce the amount of water vapour contained in a gas; the amount of permissible residual water depends on the analyser.

The various methods of dehydration may be grouped into four types :

- chemical desiccants;
- adsorbants;
- cold trapping;
- permeation.

### 2.4.2.1 Chemical desiccants

Water reacts chemically with a compound to form a new product with very variable vapour tensions. The most commonly used products are calcium chloride, sulphuric acid,

phosphoric anhydride, magnesium perchlorate, anhydrous potash and anhydrous calcium sulphate.

The residual water concentrations under optimum conditions for some compounds are given in table 1.

Table 1

| Compound                                     | Residual water concentration, in milligrams per cubic metre of dry air under normal conditions (0 °C, 1 013 mbar) |
|----------------------------------------------|-------------------------------------------------------------------------------------------------------------------|
| P <sub>2</sub> O <sub>5</sub>                | < 0,02                                                                                                            |
| Fused KOH                                    | 2                                                                                                                 |
| Anhydrous Mg(ClO <sub>4</sub> ) <sub>2</sub> | 2                                                                                                                 |
| Anhydrous CaSO <sub>4</sub>                  | 5                                                                                                                 |
| Fused CaCl <sub>2</sub>                      | 340                                                                                                               |
| Granulated CaCl <sub>2</sub>                 | 1 500                                                                                                             |

The efficiency of these products is very variable and diminishes more or less quickly during saturation; unwanted by-products may be formed; finally, their chemical reactivity makes it essential to exercise care in choosing the products, taking into account the nature of the sample under consideration.

As an example, the combustion gases of a hydrocarbon contain approximately 10 % (V/V) of water vapour, which corresponds to about 25 ml of water per hour for a flow rate of gas for analysis of 300 l/h. Since the potential capacity of calcium sulphate to absorb water is 3 to 4 % (m/m), approximately 1 000 g of product is required per hour of operation.

### 2.4.2.2 Adsorbants

Adsorbants fix water non-selectively by physical adsorption.

These products have in common the characteristics that they can be regenerated by heating in a stream of gas, that they have a large specific surface area and that they are generally suitably chemically inert.

The most commonly used adsorbants are silica gel, which can be dyed with a cobalt salt (the transition from blue to pink indicates that the silica gel has become saturated), activated alumina, and molecular sieves, the most selective of which has an average pore dimension of 0,3 nm.

In general, the efficiency of an adsorbant depends ultimately on its degree of dryness before use, the conditions in which the gas is passed, the pressure at which it is used and the temperature at which the system operates.

Adsorbants may retain other constituents of a gas flow; such constituents may be desorbed or displaced at a later stage by other constituents of the gas flow and can affect the composition of the gas sample.

Using the example given in 2.4.2.1, and given that the adsorbing capacity of silica gel is 20 to 25 %, about 130 g of product is required per hour of operation.

### 2.4.2.3 Cold trapping

If the sample is difficult to condense, it may be circulated in a cooled condenser at a few degrees above 0 °C. The effectiveness of the process depends entirely on the geometry of the condenser and the working conditions, i.e. gas flow rate and temperature. Some examples of condensers as used in the laboratory are shown in figure 5. One disadvantage may arise from dissolution of constituents in the condensate thus formed.

Using the example given in 2.4.2.1, 25 g of water per hour, formed in this way, may be continuously removed, and the gas will contain about 1 % of water vapour provided it is at atmospheric pressure and the temperature of the trap is between 0 and 7 °C.

### 2.4.2.4 Permeation

Certain semi-permeable membranes allow water to migrate from an area of high partial pressure to an area of very low partial pressure (sweeping with a dry gas).

These membranes are in the form of a cluster of tubes in which the gas circulates for drying. The dry sweeping gas circulates in the outer jacket.

Under normal operating conditions, selectivity is good; however, it is necessary to check in each individual case that the permeation of gases other than water vapour is low.

As an example of the efficiency of this device, a gas entering a system with  $2 \times 10^{-2}$  (V/V) of water (which corresponds to saturation at 14 °C) leaves the system with  $40 \times 10^{-6}$  (V/V). This concentration corresponds to a frost point of -51 °C.

In conclusion, the choice of drying process is generally specific to a given sample.

There is no universal solution, and it is often necessary to make a satisfactory compromise, based on a certain number of selection criteria (see table 2).

## 2.5 Transport line — Pump

The most important requirement is that the gas is not polluted; the line shall therefore be airtight, particularly if it is under low pressure, and the pump shall also be airtight and shall not introduce any pollutants such as oil vapours. For these reasons, membrane pumps are usually chosen.

If the characteristics of the pump and the dimensions of the transport line are carefully co-ordinated, it is possible to achieve a minimum dead time. For a given pump and a fixed length of line, there is an optimum tube diameter for obtaining the best possible dead time (see annex C). Any variation in diameter has a very great effect on the gas flow velocity.

## 3 Transfer line

A transfer line may comprise

- devices for regulating pressure or flow;
- ducts;
- valves and, where appropriate, circulation pumps.

The sample or the calibration gas shall not, especially during transfer,

- be polluted or denatured by other gases (for example constituents of the air or atmospheric pollutants);
- be changed in its composition (for example by absorption, adsorption or permeation);
- be subject to chemical changes, such as decomposition, changes in proportion, oxidation-reduction.

In view of the diversity of cases which may be encountered, all possibilities cannot be considered here and special precautions shall be taken as necessary, depending on the nature of the sample or calibration gases, their concentration, their pressure and the volumes available.

Table 2

| Dehydration method  | Selection criteria |                           |                        |
|---------------------|--------------------|---------------------------|------------------------|
|                     | Inspection         | Necessity of action       | Necessity of filtering |
| Chemical            | YES                | YES change of load        | YES after              |
| Adsorbant           | YES                | YES regeneration          | YES after              |
| Condensation > 0 °C | NO                 | NO                        | NO                     |
| < 0 °C              | YES                | YES removal of ice formed | NO                     |
| Permeation          | NO                 | NO                        | YES before             |

3.1 Characteristics of the materials

The materials coming into contact with the sample or the calibration gas during transfer shall fulfil the following requirements :

- a) impermeability to all gases;
- b) minimum sorption;
- c) chemical inertness to the constituents being transferred.

A list indicating the suitability for use of certain materials as a function of the composition of the sample or the calibration gas being transferred is given in table 3 for guidance only. In addition, all the precautions mentioned in 3.1 and 3.2 shall be taken.

NOTES

- 1 Polymers are generally permeable. Their use depends on the nature of the sample or the calibration gas and its concentration.
- 2 For a particular application, it is preferable to test the suitability of a material before use.

3.2 Characteristics of the elements constituting the transfer line

Airtightness and cleanliness of the various valves (including the valve on the cylinder), the ducts and the connections to the sampling system shall be ensured. In general, the permissible rate of leakage shall be adapted to the measurement problem under consideration. As a guide, the following value might be given for the rate of leakage of the various parts of the system :  $10^{-6}$  bar $\cdot$ cm $^3$ .s $^{-1}$ .

The concentration by volume *C* of polluting air introduced into the sample or calibration gas as the result of a lack of air-

tightness in the sampling system, is proportional to the rate of leakage *P* of this system and inversely proportional to the volumetric flow rate *q<sub>V</sub>* of the sample or calibration gas :

$$C = 4 \frac{P}{q_V}$$

where

- C* is the concentration, expressed as a volume ratio;
- P* is the rate of leakage, expressed in bar cubic centimetres per second;
- q<sub>V</sub>* is the volumetric flow rate of the sample or the calibration gas, expressed in litres per hour.

*Example :* For a sample or calibration gas flow rate of 40 l/h, sampled from a system with a rate of leakage of  $10^{-6}$  bar $\cdot$ cm $^3$ .s $^{-1}$ , the air pollution in the sample or calibration gas will have a concentration equal to  $10^{-6}$  (V/V), and, therefore, an oxygen concentration from the air of  $2 \times 10^{-7}$  (V/V).

Valves and joints with small dead spaces should be used for preference. In particular, dead spaces retain moisture and air, and are difficult to evacuate and sweep (see figure 6). Ducts shall be as short as possible and it shall be possible to dry them.

The pressure reducing valve shall be airtight and, if possible, capable of being dried to eliminate previously sorbed gases. With regard to humidity, a temperature of 100 °C is recommended if the line components can tolerate this temperature (regulators, nature of material, etc.).

For safety reasons, it is recommended that a throttling or stop valve should be placed at the outlet of the pressure reducer. This valve can prevent dangerous back-diffusion.

Table 3

| Material        | Suitability for use with |                |                 |               |                       |                        |                       |                  |
|-----------------|--------------------------|----------------|-----------------|---------------|-----------------------|------------------------|-----------------------|------------------|
|                 | Rare gases               | O <sub>2</sub> | SO <sub>2</sub> | Hydro-carbons | CO<br>CO <sub>2</sub> | Cl <sub>2</sub><br>dry | NO<br>NO <sub>2</sub> | H <sub>2</sub> S |
| Copper/brass    | a                        | a              | c               | b             | a                     | c                      | c                     | c                |
| Stainless steel | a                        | a              | a               | a             | a                     | b                      | b                     | a                |
| Glass           | a                        | a              | a               | a             | a                     | a                      | a                     | a                |
| Rubber, natural | c                        | c              | c               | c             | c                     | c                      | c                     | c                |
| Rubber, butyl   | a                        | b              | c               | c             | b                     | b                      | c                     | c                |
| PTFE            | a                        | b              | a               | b             | b                     | b                      | b                     | b                |
| Aluminium       | a                        | a              | b               | a             | a                     | b                      | b                     | b                |

- a = Suitable
- b = With reservations
- c = Not recommended

\* 1 bar = 10<sup>5</sup> Pa

### 3.3 Preparation for gas transfer

The surfaces in contact with the gas shall be free from grease, oil and other polluting products.

Cleaning may be carried out by chemical methods (acid scouring, passivation or other appropriate chemical surface treatments) or by mechanical methods (for example ultra-sonic methods).

In certain cases, passivation may improve the corrosion properties of the material, but there is a danger that it may encourage sorption phenomena.

It may sometimes be necessary to treat the line in a different manner, for example using phosphoric acid on PTFE (traces of SO<sub>2</sub> or volatile acid).

NOTE — If the calibration gas is taken from a cylinder, check that the temperature of the cylinder is not lower than 5 °C.

If it is suspected that the cylinder and its contents have been exposed to low temperatures during an intermediate period (for example during transport), it is recommended that the cylinder be placed in the horizontal position for at least 2 days at ambient temperature.

#### 3.3.1 Monitoring of airtightness

A careful inspection for airtightness (see annex D) shall be carried out in ducts, threaded joints and other welded joints. Very small leaks occurring in porous welded joints cause a molecular discharge of the gases in both directions. This outward flow increases as the difference in the partial pressures of the gases under consideration, inside and outside the line, increases.

#### 3.3.2 Evacuation and heating

In view of the possibility of desorption phenomena, it is preferable to evacuate the system by heating the devices to be

evacuated to a temperature of up to 70 °C. However, the small cross-sections of the valves and pressure reducers make this operation lengthy and delicate.

Back diffusion of oil vapours outside the evacuating pump shall be eliminated using a filter.

#### 3.3.3 Periodic purging

A simple purging operation with penetration of the sample or calibration gas into the pressure reducer, valves and ducts is not very effective. Indeed, residual gases and traces of moisture may persist for very long periods in the dead spaces and subsequently diffuse into the gas being conveyed.

A more efficient method is to carry out a periodic purging procedure with repeated increases and reductions in pressure. In this way, the gas penetrates into the dead spaces, mixes with the residual gases trapped in these areas, absorbs the moisture and is expelled from them when the pressure is reduced (see figures 7, 8 and 9).

Care should be taken, however, that the increase in pressure in the line does not reach the pressure of the gas in the cylinder, in order to prevent any mixing of the residual gases and the moisture contained in the valve of the cylinder and in the pressurized section of the pressure reducing valve with the calibration gas.

In order to prevent chemical reactions, it may prove necessary to introduce a purging gas (dry inert gas or complementary gas for the calibration gas) into the ducts lying between the valve of the cylinder and the pressure reducing valve (see figure 10).

The purging gas thus penetrates into both the dead spaces of the valve of the cylinder and into the pressurized sections of the pressure reducing valve, and expels the residual gases from these areas.

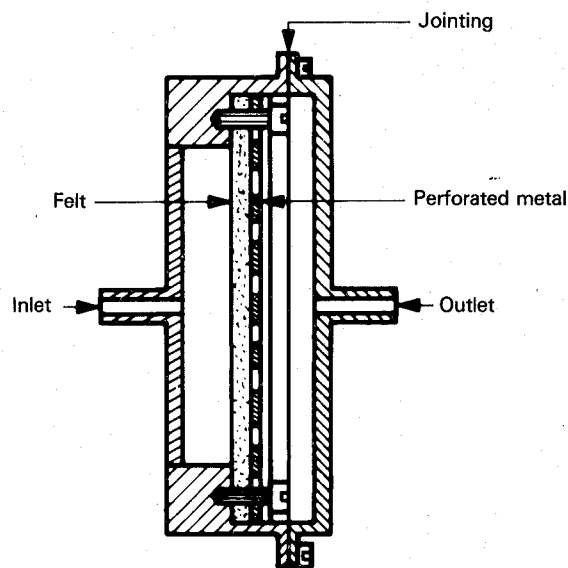


Figure 2 — Dust filter (felt pad type of external filter)

Dimensions in millimetres

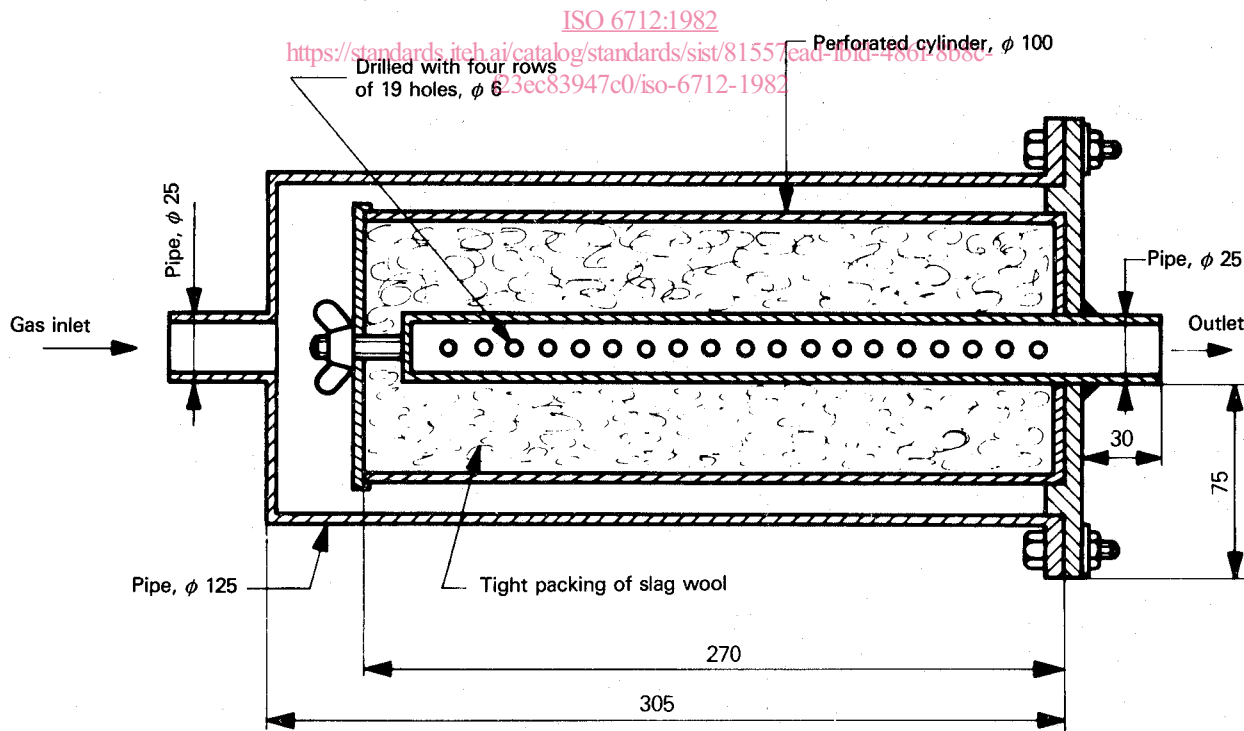


Figure 3 — Cartridge filter

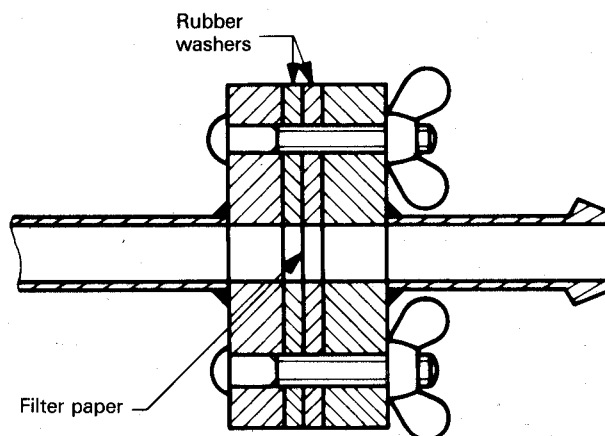


Figure 4 — Paper filter holder

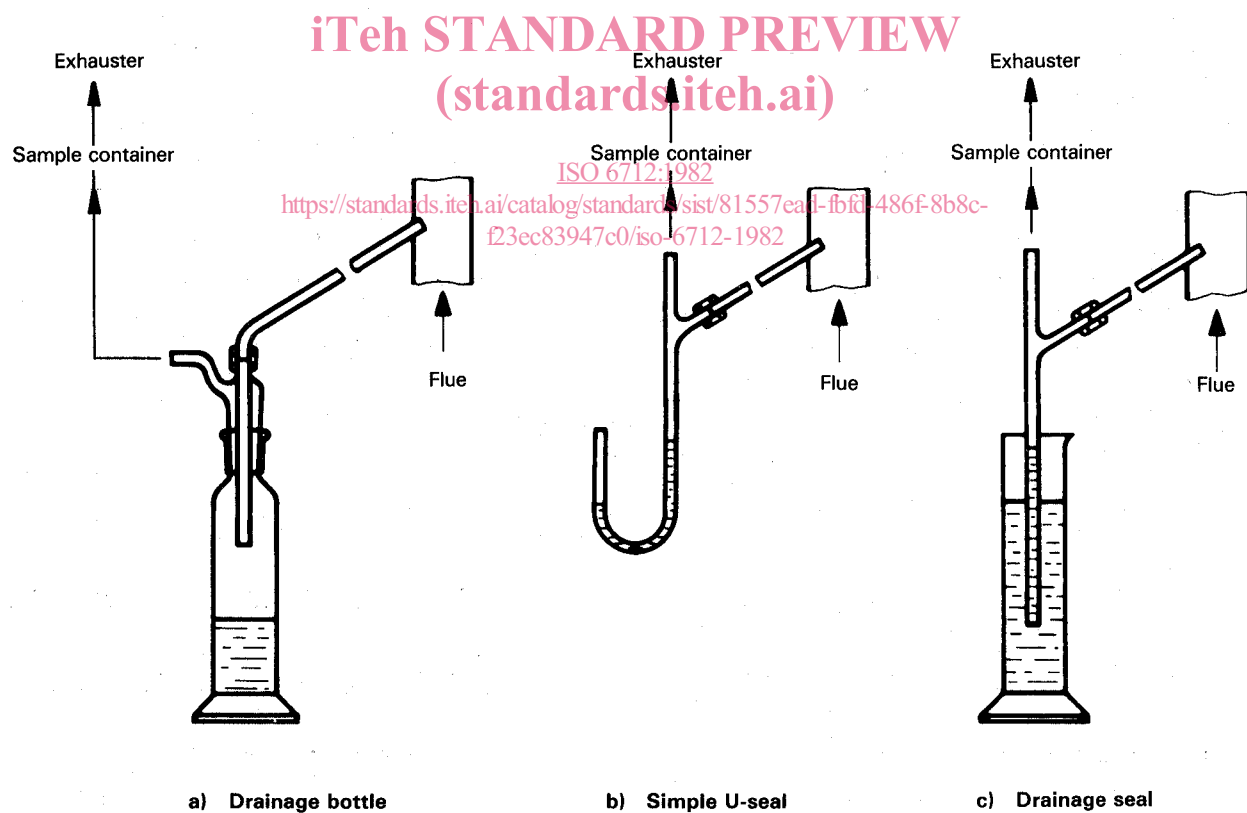


Figure 5 — Types of condensate trap