

# INTERNATIONAL STANDARD

## NORME INTERNATIONALE



**Oil-filled electrical equipment – Sampling of free gases and analysis of free and dissolved gases in mineral oils and other insulating liquids – Guidance**

**Matériels électriques immergés – Échantillonnage de gaz libres et analyse des gaz libres et dissous dans les huiles minérales et d'autres liquides isolants – Recommandations**



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**Matériels électriques immergés – Échantillonnage de gaz libres et analyse des gaz libres et dissous dans les huiles minérales et d'autres liquides isolants – Recommandations**

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ELECTROTECHNICAL  
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## INTERNATIONAL ELECTROTECHNICAL COMMISSION

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**OIL-FILLED ELECTRICAL EQUIPMENT –  
SAMPLING OF FREE GASES AND ANALYSIS  
OF FREE AND DISSOLVED GASES IN MINERAL OILS  
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IEC 60567 has been prepared by IEC technical committee 10: Fluids for electrotechnical applications. It is an International Standard.

This fifth edition cancels and replaces the fourth edition published in 2011. This edition constitutes a technical revision.

This edition includes the following significant technical changes with respect to the previous edition:

- a) a new normative Annex F relating to DGA analysis of insulating liquids other than mineral oils (esters and silicones) has been added;
- b) Clause 4 to Clause 11 and informative Annex A to Annex E remain devoted to mineral oils;

- c) two new mercury-free gas extraction methods are described in Annex B (low pressure vacuum extraction and mechanical oscillation).

The text of this International Standard is based on the following documents:

|              |                  |
|--------------|------------------|
| Draft        | Report on voting |
| 10/1207/FDIS | 10/1211/RVD      |

Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this International Standard is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at [www.iec.ch/members\\_experts/refdocs](http://www.iec.ch/members_experts/refdocs). The main document types developed by IEC are described in greater detail at [www.iec.ch/publications](http://www.iec.ch/publications).

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## INTRODUCTION

Gases can be formed in oil-filled electrical equipment due to natural ageing but also, to a much greater extent, as a result of faults.

Operation with a fault can seriously damage the equipment, and it is valuable to be able to detect the fault at an early stage of development.

Where a fault is not severe, the gases formed will normally dissolve in the oil, with a small proportion eventually diffusing from the liquid into any gas phase above it. Extracting dissolved gas from a sample of the oil and determining the amount and composition of this gas is a means of detecting such faults, and the type and severity of any fault can often be inferred from the composition of the gas and the rate at which it is formed.

In the case of a sufficiently severe fault, free gas will pass through the oil and collect in the gas-collecting (Buchholz) relay if fitted; if necessary, this gas may be analysed to assist in determining the type of fault that has generated it. The composition of gases within the bubbles changes as they move through the oil towards the gas-collecting relay.

This can be put to good use, as information on the rate of gas production can often be inferred by comparing the composition of the free gases collected with the concentrations remaining dissolved in the liquid.

The interpretation of the gas analyses is the subject of IEC 60599.

These techniques are valuable at all stages in the life of oil-filled equipment. During acceptance tests on transformers in the factory, comparison of gas-in-oil analyses before, during and after a heat run test can show if any hot-spots are present, and similarly analysis after dielectric testing can add to information regarding the presence of partial discharges or sparking. During operation in the field, the periodic removal of an oil sample and analysis of the gas content serve to monitor the condition of transformers and other oil-filled equipment.

The importance of these techniques has led to the preparation of this document, to the procedures used for the sampling, from oil-filled electrical equipment, of gases and oils containing gases, and for subsequent analysis.

**NOTE** Methods described in this document apply to insulating oils, since experience to date has been almost entirely with such oils. The methods can also be applied to other insulating liquids, in some cases with modifications.

### **General caution, health, safety and environmental protection**

**WARNING** – This document does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this document to establish appropriate health and safety practices and determine the applicability of regulatory limitations prior to use.

The insulating oils which are the subject of this document should be handled with due regard to personal hygiene. Direct contact with the eyes can cause irritation. In the case of eye contact, irrigation with copious quantities of clean running water should be carried out and medical advice sought. Some of the tests specified in this document involve the use of processes that can lead to a hazardous situation. Attention is drawn to the relevant standard for guidance.

Mercury presents an environmental and health hazard. Any spillage should immediately be removed and be properly disposed of. Regulatory requirements for mercury use and handling can apply. Mercury-free methods may be requested in some countries.

**Environment**

**WARNING** – This document is applicable to insulating oils, chemicals and used sample containers.

Attention is drawn to the fact that, at the time of writing of this document, many insulating oils in service are known to be contaminated to some degree by polychlorinated biphenyls (PCBs). If this is the case, safety countermeasures should be taken to avoid risks to workers, the public and the environment during the life of the equipment, by strictly controlling spills and emissions. Disposal or decontamination of these oils can be subject to regulatory requirements. Every precaution should be taken to prevent the release of any type of insulating oil into the environment, including those partially biodegradable with time.

# **OIL-FILLED ELECTRICAL EQUIPMENT – SAMPLING OF FREE GASES AND ANALYSIS OF FREE AND DISSOLVED GASES IN MINERAL OILS AND OTHER INSULATING LIQUIDS – GUIDANCE**

## **1 Scope**

This document deals with the techniques for sampling free gases from gas-collecting relays from power transformers. Three methods of sampling free gases are described.

The techniques for sampling oil from oil-filled equipment such as power and instrument transformers, reactors, bushings, oil-filled cables and oil-filled tank-type capacitors are no longer covered by this document, but are instead described in IEC 60475:2022, 4.2.

Before analysing the gases dissolved in oil, they are first extracted from the oil. Three basic methods are described, one using extraction by vacuum (Toepler and partial degassing), another by displacement of the dissolved gases by bubbling the carrier gas through the oil sample (stripping) and the last one by partition of gases between the oil sample and a small volume of the carrier gas (headspace). The gases are analysed quantitatively after extraction by gas chromatography; a method of analysis is described. Free gases from gas-collecting relays are analysed without preliminary treatment.

The preferred method for ensuring the performance of the gas extraction and analysis equipment, considered together as a single system, is to degas samples of oil prepared in the laboratory and containing known concentrations of gases ("gas-in-oil standards") and quantitatively analyse the gases extracted. Two methods of preparing gas-in-oil standards are described.

For daily calibration checks of the chromatograph, it is convenient to use a standard gas mixture containing a suitable known amount of each of the gas components to be in a similar ratio to the common ratios of the gases extracted from transformer oils.

The techniques described take account, on the one hand, of the problems peculiar to analyses associated with acceptance testing in the factory, where gas contents of oil are generally very low and, on the other hand, of the problems imposed by monitoring equipment in the field, where transport of samples can be by un-pressurized air freight and where considerable differences in ambient temperature can exist between the plant and the examining laboratory.

## **2 Normative references**

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 60296, *Fluids for electrotechnical applications – Mineral insulating oils for electrical equipment*

IEC 60475:2022, *Method of sampling insulating liquids*

ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results – Part 1: General principles and definitions*

### 3 Terms, definitions, symbols and abbreviated terms

#### 3.1 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- IEC Electropedia: available at <https://www.electropedia.org/>
- ISO Online browsing platform: available at <https://www.iso.org/obp>

#### 3.2 Symbols and abbreviated terms

##### 3.2.1 Symbols

The symbols used in 8.5.2 are:

|            |                                                                                                                                   |
|------------|-----------------------------------------------------------------------------------------------------------------------------------|
| $V$        | total volume of the vial                                                                                                          |
| $V_G$      | volume of the gas phase in the vial                                                                                               |
| $V_L$      | volume of the oil phase in the vial                                                                                               |
| $C_G$      | concentration of gas (i) in the gas phase of vial, obtained by GC (gas chromatography)                                            |
| $C_L^{0*}$ | concentration of gas (i) in the oil sample, obtained directly from $C_G$ using calibration curves with gas-in-oil standards       |
| $P, t$     | atmospheric pressure and temperature when the oil sample was analysed ( $P$ in kPa; $t$ in °C)                                    |
| $P_s, t_s$ | atmospheric pressure and temperature when the gas-in-oil standard, or the gas standard, was analysed ( $P_s$ in kPa; $t_s$ in °C) |
| $K$        | partition coefficient of gas (i), for the calculation of $C_L^0$ using gas standards                                              |
| $C_L^0$    | concentration of gas (i) in the oil sample                                                                                        |

##### 3.2.2 Abbreviated terms

|      |                                                |
|------|------------------------------------------------|
| DGA  | dissolved gas analysis                         |
| FID  | flame ionization detector                      |
| GC   | gas chromatography                             |
| GILS | gas-in-liquid standards                        |
| GIOS | gas-in-oil standards                           |
| HID  | helium ionization detector                     |
| ID   | inner diameter                                 |
| NIST | National Institute of Standards and Technology |
| OD   | outer diameter                                 |
| OLTC | on-load tap-changer                            |
| PLOT | porous large open tubular                      |
| PTFE | polytetrafluoroethylene                        |
| TCD  | thermal conductivity detector                  |

## 4 Sampling of gases from gas-collecting relays

### 4.1 General remarks

It is important to bear in mind that receiving a qualitative and a representative sample is crucial for obtaining a reliable diagnosis of the electrical equipment. Even the most sophisticated extraction or diagnosis methods cannot overcome faulty samples.

Gas samples from relays should be taken from the equipment with the minimum delay after gas accumulation has been signalled. Changes in composition caused by the selective re-absorption of components can occur if free gases are left in contact with oil.

Certain precautions are necessary when taking gas samples. The connection between the sampling device and the sampling vessel shall avoid the ingress of air. Temporary connections should be as short as possible. Any rubber or plastic tubing used should have been proved to be impermeable to gases.

Gas samples shall be properly labelled (see Clause 5) and analysed without undue delay to minimize hydrogen loss from the syringe used for gas sampling (e.g. within a maximum period of one week).

Oxygen, if present in the gas, can react with any oil drawn out with the sample. Reaction is delayed by excluding light from the sample, for example, by wrapping the vessel in aluminium foil or suitable opaque material.

Of the three methods described in 4.2, 4.3 and 4.4, the syringe method is recommended. The other two methods are alternatives to be used exclusively in case of serious hindrance.

Sampling into a sampling tube by liquid displacement using transformer oil as a sealing liquid is simple, but require to take into account the different solubilities of the gas components if the gas quantity is such that some oil remains in the tube.

The vacuum method requires skill to avoid contaminating the sample by leakage of air into the system. It is particularly true where the gas to be sampled can be at less than atmospheric pressure (e.g. some sealed transformers).

### 4.2 Sampling of free gases by syringe

#### 4.2.1 Sampling equipment

NOTE Numbers in brackets refer to those circled numbers in the relevant figure.

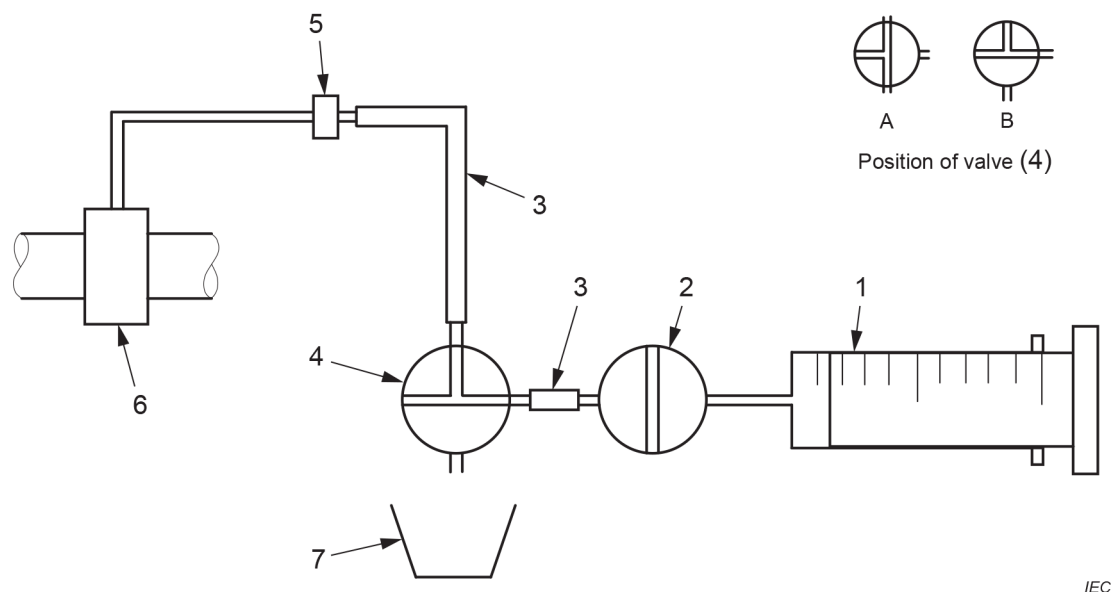
See Figure 1. The equipment shall be as follows:

- a) Impermeable oil-resistant plastic or rubber tubing (3) provided with a connector to fit onto a suitable sampling connection of the gas-collecting relay. To avoid cross-contamination, the tubing should be used only once.
- b) Gas-tight syringes of suitable volume (1) (25 ml to 250 ml). Medical or veterinary quality glass syringes with ground-in plungers may be suitable; alternatively, syringes with oil-proof seals may be used. The syringe should be fitted with a cock enabling it to be sealed. It is often convenient to use the same syringes for both gas sampling and for oil sampling (see IEC 60475:2022, 4.2.2).

The gas tightness of a glass syringe used for gas sampling may be tested by storing an oil sample containing a measurable quantity of hydrogen for at least two weeks and analysing aliquots for hydrogen at the beginning and end of the period. An acceptable syringe will permit losses of hydrogen of less than 2,5 % per week. General experience suggests that all-glass syringes leak less than those using plastic seals. Improvement of the gas tightness may be obtained by the use of a lubricant such as a light grease or transformer oil.

It is a good practice to test the integrity of syringes and valve system before the sampling. A recommended procedure is given in IEC 60475:2022, Annex B.

- c) Transport containers should be designed to hold the syringe firmly in place during transport, but allow the syringe plunger freedom to move, and prevent its tip from contacting the container, whatever its position during transportation.



#### Key

- 1 syringe
- 2 stopcock
- 3 rubber connecting tubing
- 4 three-way valve
- 5 equipment sampling valve
- 6 gas-collecting relay valve
- 7 waste vessel

**Figure 1 – Sampling of gas by syringe**

#### 4.2.2 Sampling procedure

The apparatus is connected as shown in Figure 1. The connections should be as short as possible and filled with oil at the start of sampling.

The sampling valve (5) is opened. If sampling from a gas-collecting relay on a transformer fitted with a conservator, a positive pressure will exist; the three-way valve (4) is carefully turned to position A and the oil in the connecting tubing (3) allowed to flow to waste (7). When gas reaches the three-way valve (4), the latter is turned to position B to connect the pre-lubricated syringe (1). The stopcock (2) is then opened and the syringe allowed to fill under the hydrostatic pressure, taking care that its plunger is not expelled. When a sufficient sample has been taken, the stopcock (2) and sampling valve (5) are closed and the apparatus is disconnected.

The oil in the syringe is expelled by inverting the syringe and applying gentle pressure to the plunger.

Label carefully the sample (see Clause 5).

### 4.3 Sampling of free gases by displacement of oil

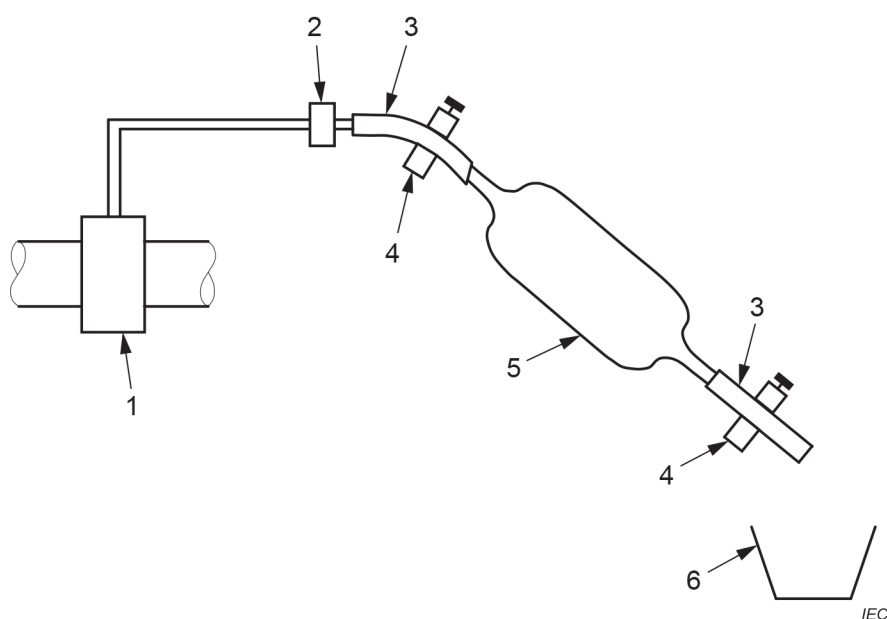
This method is reliable only where the gas sample is at or above atmospheric pressure. The apparatus is shown in Figure 2.

The sampling tube (5), typically of 100 ml capacity, is preferably of glass since the operator can then see how much oil remains in it during gas sampling. The sampling tube is filled with oil from the transformer on site. Before being used as described below, the connecting tube (3) should also be filled with oil.

The open end of the connecting tube (3) is fitted onto the gas-sampling valve (2). The sampling valve and inlet stopcock of the sampling tube are opened. The sampling tube is inclined so that its closed end is the lowest point. The outlet stopcock on the sampling tube is then opened, allowing oil to run out to waste (6), drawing first any oil from the connection between relay and sampling valve, and the gas from the relay, into the sampling tube.

Sampling is complete when the gas-collecting relay is completely filled with oil or when nearly all oil has gone from the sampling tube.

Both stopcocks (4) on the sampling tube and the sampling valve (2) are closed and then the connections removed.



#### Key

- 1 gas collecting relay valve
- 2 equipment sampling valve
- 3 oil-resistant connecting tubing
- 4 stopcock
- 5 sampling tube
- 6 waste vessel

**Figure 2 – Sampling of free gases by oil displacement**

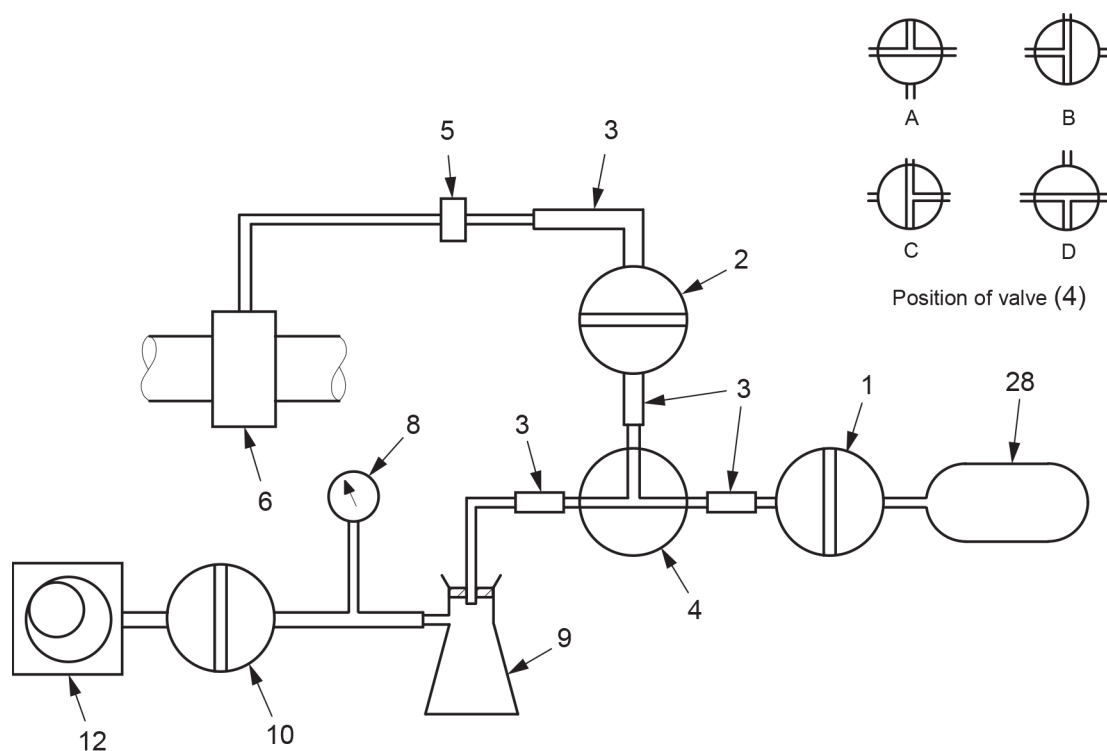
### 4.4 Sampling of free gases by vacuum

The apparatus is connected as shown in Figure 3. With the equipment sampling valve closed, stopcocks (1), (2) and (10) open, and the three-way valve (4) turned to position A, the vacuum pump (12) is allowed to evacuate the connecting tubing, the trap and the sampling vessel.

A satisfactory vacuum will be below 100 Pa. The system should be checked for leaks by closing the pump suction stopcock (10) and observing that no appreciable change in vacuum occurs. Over a time equal to that which will be taken for sampling, the pressure should not increase by more than 100 Pa. Similarly, the stopcock (1) on the sampling tube should be vacuum tight to the same degree over several weeks.

If the connecting tubing between the equipment sampling valve (5) and the gas-collecting relay is filled with oil, the three-way valve (4) is turned to position B. The equipment sampling valve (5) is carefully opened and oil allowed to flow into the trap (9). When the end of the oil stream is observed to reach the three-way valve (4), it is turned to position D to evacuate the oil from it. Thereafter, valve (4) is turned to position C. When sampling is complete, stopcock (1) is closed first, then the equipment sampling valve (5) closed and the apparatus disconnected.

If the connecting tubing between the equipment and the sampling valve is empty of oil, the procedure for draining oil is omitted and the three-way valve (4) used in position C after evacuating and testing that the apparatus is leak tight.



IEC

#### Key

- 1 vacuum tight stopcock
- 2 vacuum tight stopcock
- 3 rubber connecting tubing
- 4 vacuum tight three-way valve
- 5 equipment sampling valve
- 6 gas collecting relay valve
- 8 vacuum gauge
- 9 trap
- 10 vacuum tight stopcock
- 12 vacuum pump
- 28 sampling tube

Figure 3 – Sampling of free gases by vacuum

#### 4.5 Sampling of oil from oil filled equipment

See IEC 60475:2022, 4.2.

### 5 Labelling of gas samples

Gas samples shall be properly labelled before dispatch to the laboratory.

The following information, as shown in Table 1, is necessary (whenever it is known).

**Table 1 – Information required for gas samples**

| Transformer                                    | Sampling                                                 |
|------------------------------------------------|----------------------------------------------------------|
| Customer                                       | Sampling date and time following a gas alarm             |
| Location                                       | Sampling point                                           |
| Identification number                          | Sampling person                                          |
| Manufacturer                                   | Reason for analysis                                      |
| General type (power, instrument or industrial) | Transformer non-energized, off-load energized or on-load |
| Rated MVA                                      |                                                          |
| Voltage ratio                                  |                                                          |
| Type and location of OLTC                      |                                                          |
| Date of commissioning                          |                                                          |
| <b>Oil</b>                                     |                                                          |
| Type of oil (mineral or non-mineral)           | Weight (or volume) of oil                                |
| Product name                                   | Date of last oil treatment                               |

The following additional information is desirable:

- ambient temperature, reading of MVA or load current or percentage load, operation of pumps, mode of communication of its tap-changer with the main tank, oil preservation system (conservator, nitrogen blanket, etc.), and any changes in operational conditions or any maintenance carried out since last sampling;
- time of sampling where more than one sample is taken.

### 6 Sampling, labelling and transferring of oil from oil-filled equipment

#### 6.1 Sampling and labelling of oil

Consult IEC 60475:2022, 4.2 to 4.4 for sampling equipment, sampling procedures and labelling to be used.

#### 6.2 Transfer of oil for DGA analysis

##### 6.2.1 General

For transferring oil from its sample container into the gas extraction vessels specified in Clause 8, the following procedures should be used.

##### 6.2.2 Transfer from oil syringes

Introduce a portion of the oil sample in the syringe into the gas extraction vessel by turning the three-way valve of the syringe to position B shown in IEC 60475:2022, Figure 5.

### 6.2.3 Transfer from ampoules

Attach the ampoule in the vertical position. Install a three-way plastic valve between the bottom plastic tubing of the ampoule and another piece of plastic tubing going to a waste oil container. Attach a glass syringe to the three-way plastic valve. Open the upper cock then the lower cock of the ampoule. Fill the syringe with oil following the procedures indicated in IEC 60475:2022, 4.2.2.2. Transfer a portion of the oil sample in the syringe into the gas extraction vessel as indicated in 6.2.2 above.

### 6.2.4 Transfer from flexible metal bottles

Open the screw cap of the bottle, introduce a long needle down to the bottom of the bottle, attach a glass syringe with a three-way valve to the needle and gently (to avoid creating gas bubbles due to negative pressure) draw a sample of oil into the syringe. Detach the three-way valve from the needle and invert the syringe to expel any gas bubble introduced in the oil. Then introduce a portion of the oil sample in the syringe into the gas extraction chamber as indicated in 6.2.2 above. Alternatively, a piece of tubing can be used to draw oil directly into the gas extraction vessel (Toepler or partial degassing) under vacuum.

The first sample taken from the bottle should always be used for DGA analysis. No other sample should be taken for DGA analysis, since significant gas loss can occur into the headspace of the bottle.

### 6.2.5 Transfer from glass and rigid metal bottles

The procedure used for flexible metal bottles in 6.2.4 is suitable for glass and rigid metal bottles.

## 7 Preparation of gas-in-oil standards

### 7.1 General remarks

As noted in Clause 1, the preferred method of ensuring the performance of the entire system for gas extraction and analysis is to analyse oils containing known concentrations of gases (gas-in-oil standards).

Two methods of preparing gas-in-oil standards are described in 7.2 and 7.3, a general method and a simpler method. The first method has the benefit of producing much larger quantities of oil.

If gas-in-oil standards are commercially available they can be used, provided they fulfil quality assurance requirements. If they are given under ASTM standard conditions (0 °C), they shall be converted to IEC conditions (20 °C).

### 7.2 First method: preparation of a large volume of gas-in-oil standard

#### 7.2.1 Equipment

A suitable apparatus design consists of (see Figure 4 a), Figure 4 b) and Figure 4 c)):

- a magnetic stirrer (12);
- a 5 l oil vessel (13) equipped with three side-arm outlets, two of which are fitted with high-vacuum stopcocks (1) and (2) and one with a rubber septum (16);
- a 6 l reservoir (14) equipped with a high-vacuum stopcock (3) connected with a 75 ml splash bulb (15) and a high-vacuum stopcock (4);
- a mercury displacement system (17) consisting of two 500 ml mercury glass bulbs connected with a high-vacuum oil-resistant flexible rubber tubing.

The gas-injection system (Figure 4 e), Figure 4 f) and Figure 4 g)) consists of

- a set of gas tight syringes of appropriate volumes (18);
- a plastic three-way valve of standard type (7), modified to minimize dead volume by inserting pieces of stainless steel tubing (approximately 0,4 mm inner diameter (ID) and 1,5 mm outer diameter (OD)) into the inner branches and connected to a gas-injecting needle (10) (approximately 10 cm long, 0,25 mm OD) to go through the rubber septum into the oil flask (16);
- gas cylinders equipped with a pressure reducer and a valve (20);

NOTE 1 Gas cylinders containing each of the individual gases to be injected can be used. Ready-made mixtures of these gases can also be obtained from some gas suppliers.

- a length of oil-resistant flexible tubing connecting the gas cylinder to the three-way valve (7) and incorporating a hypodermic needle (approximately 0,3 mm ID and 0,6 mm OD). The latter acts as a leak to a water bubbler (21) which is used to check the absence of back diffusion.

NOTE 2 The length of tubing connecting the gas cylinder to the three-way valve is replaced after each gas change.

The oil sampling system (Figure 4 h) to Figure 4 k)) consists of glass syringes (19) of suitable capacity equipped with two three-way plastic valves (8) and (9) and an oil-extracting needle (11) (approximately 0,6 mm ID, 1,0 mm OD and 120 mm long).

## 7.2.2 Procedure

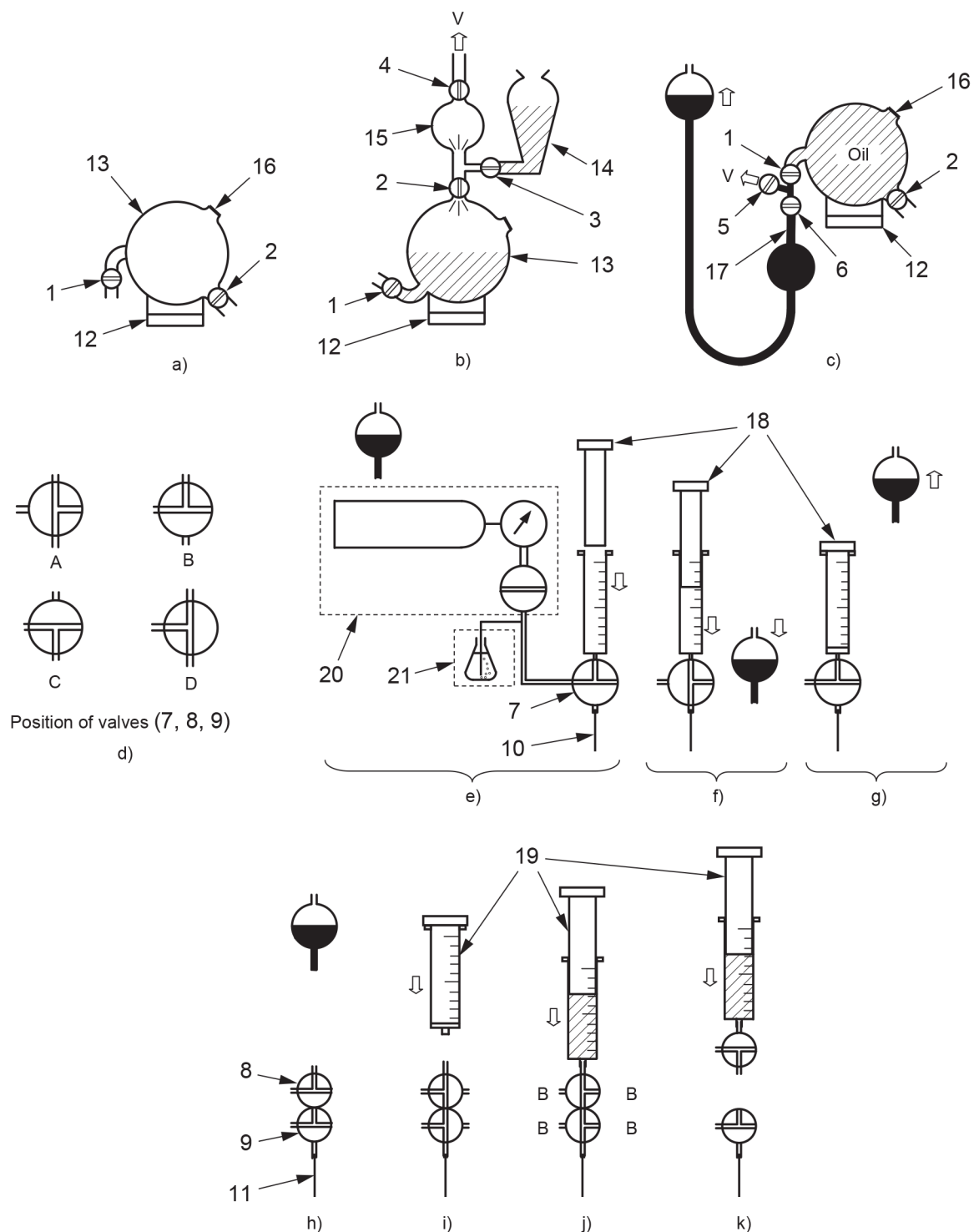
NOTE Numbers in brackets refer to those circled numbers in Figure 4. The positions A to D of the three-way valves (7, 8 and 9) are illustrated in Figure 4 d).

### 7.2.2.1 Degassing the oil

- a) Thoroughly clean all the glassware before assembling.
- b) Secure the rubber septum and the flexible connections with pieces of twisted metal wire.
- c) Clean, if necessary, approximately 1 l of mercury with pentane and filter through a finely pierced filter paper.
- d) Adapt the oil reservoir (14), the splash bulb (15) and stopcocks (4) to the 5 l vessel (13). Connect the system to the vacuum pump (V) and evacuate the splash bulb (15) and the 5 l oil vessel (13) by opening stopcocks (2) and (4).
- e) Fill the oil reservoir (14) with mineral insulating oil complying with IEC 60296 and allow oil to flow slowly through stopcock (3) into the 5 l vessel (13) until it is full. Then close stopcock (2) and remove the oil reservoir (14) and the splash bulb.

NOTE If the procedure is followed carefully (filling time about 4 h) the oil in the vessel will be virtually gas-free.

- f) Turn the oil vessel to bring it into the position shown in Figure 4 c). Place a wet cloth over it to prevent its temperature rising and attach the mercury displacement system (17) to stopcock (1). Introduce 750 ml of mercury into the system with stopcock (6) closed.
- g) Connect the system to the vacuum (V), open stopcock (5) and evacuate the section between stopcocks (1) and (6). Open stopcock (6) to allow mercury to rise up to stopcocks (1) and (5), and then close stopcock (5). Raise the left bulb of the system (see Figure 7 c)) so that the mercury level is above the oil flask. Open stopcock (1). Remove the wet cloth and switch on the magnetic stirrer (12).



IEC

# Key

|                    |                         |                                                 |
|--------------------|-------------------------|-------------------------------------------------|
| 1 vacuum stopcocks | 9 three-way valves      | 17 mercury displacement system                  |
| 2 vacuum stopcocks | 10 gas-injecting needle | 18 precision gas-tight syringe                  |
| 3 vacuum stopcocks | 11 oil-sampling needle  | 19 glass syringe                                |
| 4 vacuum stopcocks | 12 magnetic stirrer     | 20 gas cylinder with pressure reducer and valve |
| 5 vacuum stopcocks | 13 5 l oil vessel       | 21 leak to water bubbler                        |
| 6 vacuum stopcocks | 14 6 l oil vessel       | V connection to vacuum pump                     |
| 7 three-way valves | 15 75 ml splash bubble  |                                                 |
| 8 three-way valves | 16 rubber septum        |                                                 |

Figure 4 – First method of preparing gas-in-oil standards

### 7.2.2.2 Preparation of gas-in-oil standards

See Figure 4 c) to Figure 4 g).

- a) To inject the gases, attach the modified three-way valve (7), in position B, to the gas-injecting needle (10). Then push the needle through the rubber septum (16) into the oil. Turn the three-way valve to position D to purge the needle and valve with oil, then turn it to position B. Attach to valve (7) the barrel of a precision calibrated gas-tight syringe (18) of appropriate volume (precision within 1 %) and the gas cylinder connecting tubing (see Figure 4 e). Allow a gentle flow of gas to flush the barrel, then slowly push the plunger several times into the barrel, finally down to the volume of gas to be injected, making sure there is continuous bubbling through the needle leak (21).
- b) Switch valve (7) to the injection position A, lower the mercury level below the needle tip, and push the plunger to inject the gas volume into the oil. Switch valve (7) to position B and raise the left mercury bulb above the oil vessel.
- c) Repeat the same procedure with each of the gases to be dissolved then remove the gas needle and valve (7).

When all the gases are dissolved, switch off the magnetic stirrer. Record the atmospheric pressure and temperature.

NOTE Instead of adding individual gases, it is more convenient to use a standard gas mixture, preferably containing all the gases listed in 9.1, in proportions representative of those found in the sampled oil.

### 7.2.2.3 Sampling of gas-in-oil standards

See Figure 4 h) to Figure 4 k).

- a) To remove oil samples from the 5 l vessel (13), attach two three-way valves (8) and (9) turned in position B, according to Figure 4 b), to the liquid-withdrawing needle (11) and push the needle through the rubber septum (16). With the mercury level up, switch valves (8) and (9) to the draw-off position D to purge them with oil (see Figure 4 i)).
- b) Attach a syringe (19) and turn both valves (8) and (9) to position A, and draw out a suitable volume of oil (see Figure 4 j)). Then turn valve (8) to position C and valve (9) to position B and remove the syringe together with valve (8) (see Figure 4 k)).

To remove more oil, additional mercury shall be added to the mercury displacement system.

### 7.2.3 Calculation

Calculate the concentration of each gas "i" dissolved as follows:

$$C_i = V_i / V \times 10^6$$

where

$C_i$  is the concentration of gas "i", in  $\mu\text{l/l}$ ;

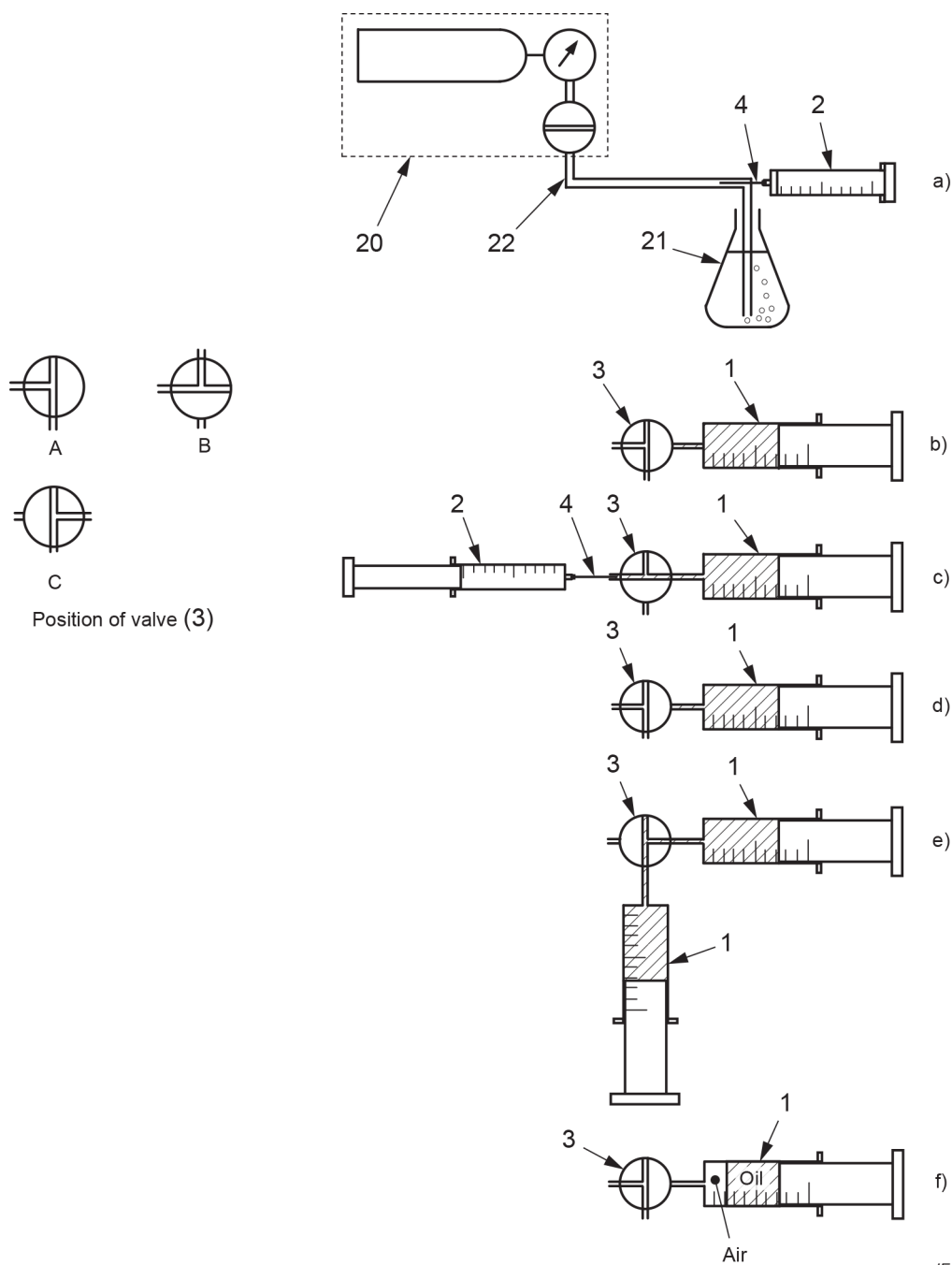
$V_i$  is the volume of gas "i" injected, corrected to 20 °C and 101,3 kPa in ml;

$V$  is the exact volume of oil in the 5 l oil flask, in ml.

## 7.3 Second method: preparation of gas-in-oil standards in a syringe or a vial

### 7.3.1 General

See Figure 5 a) to Figure 5 f).



IEC

# Key

- 1 glass syringe
- 2 precision gas-tight syringe
- 3 three-way valve
- 4 gas-injecting needle
- 20 gas bottle fitted with a pressure reducer and a valve
- 21 leak to water bubbler
- 22 silicone rubber tubing

**Figure 5 – Second method for preparing gas-in-oil standards**

### 7.3.2 Equipment

The equipment consists of

- a set of gas-tight syringes of appropriate volume (2),
- a set of glass syringes of appropriate volume (1),
- a set of gas-injecting needles (4),
- three-way plastic valves (3),
- gas cylinders equipped with a pressure reducer and a valve (20).

NOTE Gas cylinders containing each of the individual gases to be injected can be used. Ready-made mixtures of these gases can also be obtained from some gas suppliers.

### 7.3.3 Procedure

- a) Bubble argon through 1 l of oil for 1 h under agitation, adjusting the gas flow to maintain agitation of the oil in order to purge all the other dissolved gases. Degas this argon-saturated oil under a vacuum down to 1 Pa over an 8 µm filter, in a 2 l vessel (residual contents of 500 µl/l O<sub>2</sub> and 2 000 µl/l N<sub>2</sub> are acceptable). When the oil is completely degassed, break the vacuum with argon up to 20 kPa.
- b) Weigh a 100 ml glass syringe containing 10 ml of glass beads. Connect the syringe to the bottom of the 2 l vessel and purge the syringe twice with 20 ml of oil. Make sure the cylinder and plunger are completely wetted with oil. Fill the syringe with 90 ml of degassed oil.
- c) Connect a gas-tight syringe of the required volume with a needle long enough to introduce a gas mixture in the syringe cylinder part, for instance of 115 mm length, to a cylinder containing a standard gas mixture, and purge four times with the standard gas. Fill the syringe with a known volume of standard gas. Insert the needle through the tip of the oil syringe and transfer the volume of standard gas into the oil syringe. Reweigh to determine the actual oil volume. Wrap the oil syringe with aluminium foil to avoid degradation with daylight and attach it to a laboratory 3-D shaker. Shake for 1 h or until all gasses are dissolved.

NOTE 1 Any other procedure that assists dissolution of gases in oil (e.g. mixing with magnetic stirrer or other) is suitable and can be used.

- d) Record the atmospheric pressure and temperature: also refer to the note in 7.2.2.2. Calculate the dissolved gas concentration from the oil volume, injected calibration gas volume, temperature and atmospheric pressure, as in 7.2.3. Express the quantities of gases injected in µmol, or in µl converted to normal conditions (20 °C; 101,3 kPa).
- e) Repeat the procedure in order to obtain at least three gas-in-oil samples (in the case of headspace only) having concentrations that allow a calibration curve to be drawn covering the values expected in the unknown samples.

NOTE 2 If a total gas-saturated mixture is desired, draw dry CO<sub>2</sub>-free air or nitrogen into the syringe to make, with the gases already injected, a total gas volume of 10 % to 8 % of the oil volume, according to the gas chosen (see Figure 5 f)).

Turn the three-way valve (3) to position A and shake the syringe again until the air or nitrogen is dissolved. Cooling the syringe in a refrigerator accelerates the dissolution of the gas in the oil.

NOTE 3 A vial can be used instead of a syringe. The vial is filled with the same amount of degassed oil as when the ordinary analysis is performed, with the exact volume of oil measured by weight. Into this vial are introduced known quantities of a calibrated gas mixture, so that the concentrations in the oil are in the same range as in the unknown field sample.

## 8 Extraction of gases from oil

### 8.1 General remarks

Removal of dissolved gases from oil for analysis may be accomplished either by vacuum, stripping or headspace extraction.

The multi-cycle vacuum extraction (Toepler) method is described in 8.2.

The single-cycle vacuum extraction (partial degassing) method is described in 8.3.

The stripping method is described in 8.4.

The headspace method is described in 8.5.

## **8.2 Multi-cycle vacuum extraction using Toepler pump apparatus**

### **8.2.1 General**

In this method, an operating procedure which attempts to remove as much as possible of the dissolved gas from the oil is used. It is normally possible to remove about 97 % of the more soluble gases and even higher percentages of the less soluble gases. Such a small imperfection is rarely significant when considering overall accuracies, but, in any case, the preferred method of calibration using gas-in-oil standards takes account of incomplete extraction.

**NOTE** To calibrate this method with gas-in-oil standards, the procedure described in 7.2 for preparation of argon-free standards is used, since the calculation will be affected by the amount of dissolved argon that will be extracted but not detected by the gas chromatograph.

### **8.2.2 Toepler pump extraction apparatus**

An example of a suitable design is shown in Figure 6 a). Note that Figure 6 b) includes recommended volumes. In this design, oil containing gas in solution is injected through a septum (9). Alternatively, after the equipment has been evacuated, oil may be withdrawn from an oil sample bottle via a tube attached to valve (V8) that has previously been filled with oil (see Figure 6 c)).

The Toepler pump extraction apparatus shall

- a) be capable of subjecting the liquid to a vacuum less than 10 Pa,
- b) be vacuum-tight. The vacuum tightness of the whole system may be verified by carrying out the extraction procedure but without introducing oil, as follows:  
carry out steps b), c) and d) of 8.2.3. Omit step e). Continue with steps f), g) and h) as if oil were present. After compression of gas to atmospheric pressure in step h), the amount of gas should be less than 0,1 ml,
- c) permit the measurement of extracted gas to be made to the nearest 0,05 ml or better, at normal temperature and pressure.

In addition:

- d) all tubing connecting the degassing flask (3) to the gas collection flask (2) (in Figure 6 a)) shall be of large bore, at least 5 mm internal diameter and as short as practicable;
- e) the vacuum gauge used cannot be of a type that operates at high temperature or uses ionizing radiation (thermocouple, ionization or Penning gauges) since these can produce gases of the types being measured by cracking the oil vapours present in the system. Since it can react with extracted gases, a Pirani gauge is not suitable either. A sensor based on capacitance changes between two chambers is suitable. It is recommended that two sensors be used, one in the vacuum chamber, the second for measuring gas volumes at atmospheric pressure.

Further requirements are noted in 8.3 in which the partial degassing method is described.

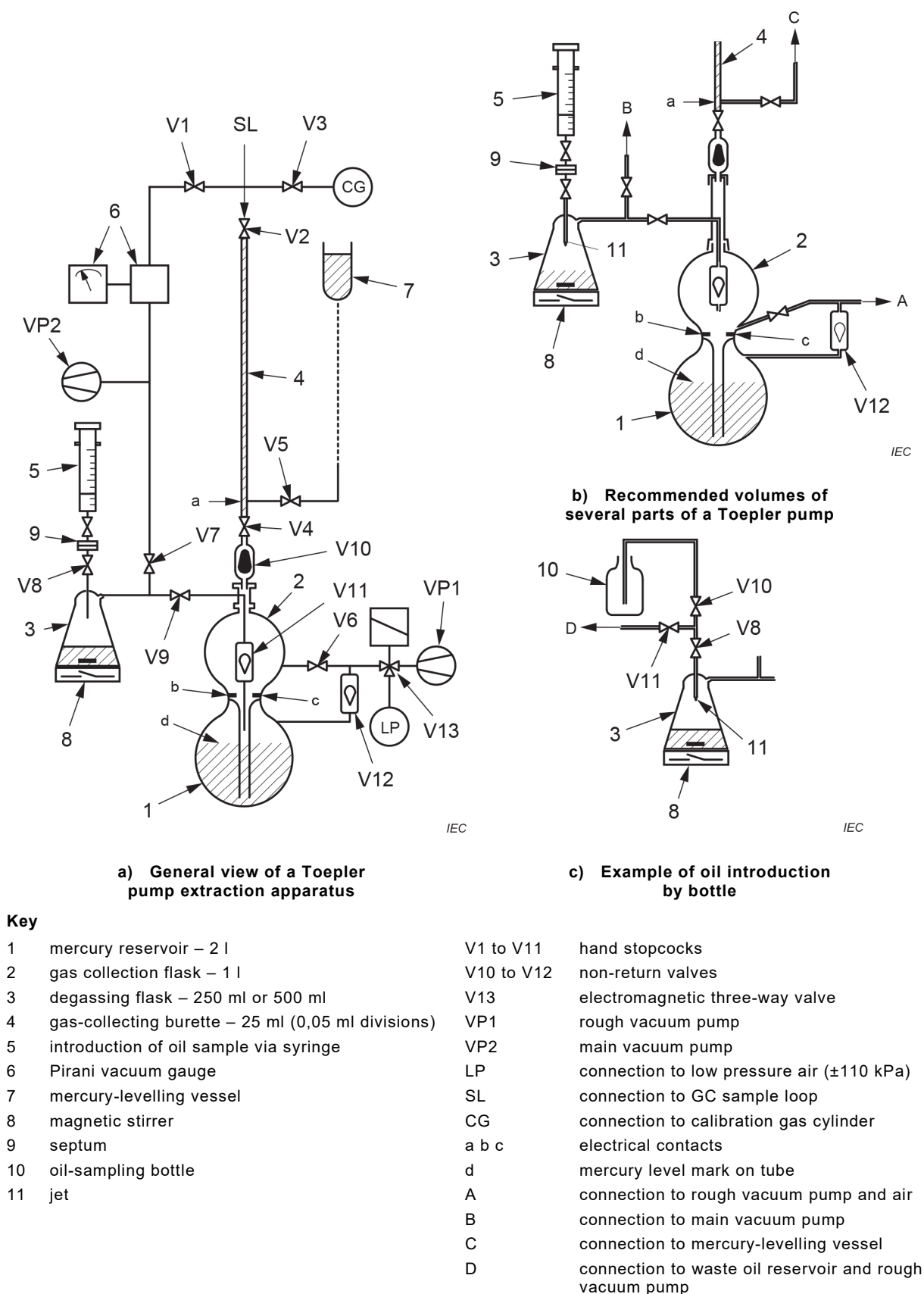
Since the detailed design of this apparatus is not standardized, it is necessary to establish an operation that will ensure adequate extraction of all components of the dissolved gas. The main parameters to be established are the number of degassing cycles (strokes) of the Toepler pump that should be used and the time for which each degassing cycle should last. This operation is preferably established by degassing a gas-in-oil standard as follows.

Use the extraction procedure as detailed in 8.2.3 but, instead of degassing an unknown oil sample, substitute a gas-in-oil standard of the volume normally used containing all the gases listed in 9.1.

Degas successive standards until a number of cycles of the Toepler pump, together with a degassing time on each stroke, has been established so that the area or height of each peak on the chromatogram of the extracted gases is within 95 % of the area or height of that peak on the chromatogram of the same quantities of gases injected directly into the chromatograph by means of a standard gas mixture (see 9.6).

A degassing time on each cycle of 1 min to 3 min for mineral oils is frequently used; the shorter the time the more degassing cycles are likely to be required. Similar degassing times can be used for non-mineral oils of similar viscosity, and longer ones for more viscous oils (e.g. 5 min to 10 min for silicone oils, see Annex F).

The above procedure serves to establish a routine of operation, which will apply until any major changes are made to the equipment and will also apply to other equipment of the same design. It is recommended that the overall calibration of the complete equipment (degassing equipment plus chromatograph) is checked periodically (e.g. every six months) using gas-in-oil standards to provide correction factors to be applied to areas or heights of chromatogram peaks.



<sup>a</sup> Item 6 of Figure 6 a) is a "capacitance measurement device".

**Figure 6 – Example of a Toepler pump extraction apparatus**

### 8.2.3 Extraction procedure

The following is a typical extraction procedure used when a sample is in a syringe. It is described by reference to the apparatus shown in Figure 6 a) and Figure 6 b). Modifications in the procedure can be used for apparatus of other designs.

- a) Weigh the syringe (5) containing the oil sample and connect it to the degassing flask (3). When a bottle is used as a container (Figure 9 c)), the mass of oil degassed is determined by weighing the degassing flask before and after introducing the oil.
- b) Open valves V1, V2, V4, V6, V7 and V9. Close valves V3, V5 and V8. The valve V13 is a solenoid-operated three-way valve, which at this stage is not energized and connects the vacuum pump VP1 to the system.
- c) Switch on the vacuum pumps VP1 and VP2 and the magnetic stirrer (8).
- d) When the pressure has fallen to 10 Pa, close valves V2, V6 and V7.
- e) Open valve V8 and inject a sufficient oil sample through the septum (9) into the degassing flask (3). This is the start of the degassing part of the Toepler pump cycle.

NOTE 1 A gas bubble in the syringe suggests that the plunger has stuck and indicates the desirability of a new sample. If this cannot be provided, the bubble is introduced together with all of the oil or is re-dissolved in the oil by shaking the syringe.

NOTE 2 The minimum oil volume used is the volume necessary to produce enough gas volume for injection in the gas chromatograph. When this is possible, larger oil volumes can be used to increase the precision of the analysis. For oil from a factory test, a modification is made; see Note 3 of step j) below.

- f) After the established degassing time (e.g. 1 min to 3 min) continue the first Toepler pump cycle by switching valve V13 so as to admit low-pressure compressed air above the mercury which rises to the level of contact (a), compressing gas from the collection flask into the burette. Reversal of valve V13 to connect the vacuum pump to the mercury reservoir (1) allows the mercury to return (the gas collected in the burette being trapped by the non-return float valve V10) and further gas to be extracted from the oil. The contacts allow this cycle to be automated. Inductive level switches may be used instead.

An electric counter is helpful in counting the number of cycles and for stopping the procedure after the required number of cycles, as established as standard for the apparatus. Alternatively, the equipment may be run automatically for a standard time (e.g. 10 min for a cycle time of 1 min).

The number of strokes should be such that the vacuum at the end of extraction approaches the initial value before extraction. The number of strokes necessary depends on the ratio between the total volume of the equipment and the volume of the pump. Typically, 4 to 20 strokes have been found suitable to reach 97 % extraction for the more soluble gases, depending on the equipment used.

- g) Switch off the automatic cycling control (if used) and set valve V13 to admit air. Allow mercury to rise into the burette to above the level of valve V5. Close valve V4.
- h) Open valve V6 and adjust the mercury levelling vessel (7) to bring the mercury surfaces to the same level. Read the total volume of gas collected in the burette. Note the ambient temperature and pressure.
- i) Remove and reweigh the oil syringe to obtain the mass of oil that has been degassed. Determine the density of the oil at ambient temperature.
- j) Close valve V1, open valve V2 to admit the extracted gas into the sample loop. Again adjust the mercury levelling vessel to bring both the mercury surfaces to the new level and close the valve.

NOTE 3 Another arrangement frequently used is to fit a septum on the top of the burette in place of valve V2 and to transfer an aliquot of gas to the chromatograph by means of a precision gas-tight syringe. In such a case, it is good practice to fit a new septum each time the equipment is used.

NOTE 4 If an inadequate quantity of gas has resulted from degassing the first oil sample, the degassing flask is disconnected and emptied, and the method repeated with a new oil sample. The first quantity of extracted gas is retained in the burette by keeping valve V4 closed until the remainder of the system is re-evacuated (step d) above).

Alternatively, where concentrations of gas are expected to be low, a larger degassing flask, up to 2 l, may be fitted, with sample volumes up to 500 ml. Introduce the oil sample slowly to facilitate gas extraction.

- k) Calculate the total gas content extracted  $C_T$  of the oil sample in  $\mu\text{l/l}$  at 20 °C and 101,3 kPa from the expression:

$$C_T = (P / 101,3) \times (293 / 273 + t) \times (Vd / m) \times 10^6$$

where

$P$  is the ambient air pressure, in kPa;

$t$  is the ambient air temperature, in °C;

$V$  is the total volume of gas extracted, at ambient temperature and pressure, in ml;

$d$  is the density of oil corrected to 20 °C, in g/ml;

$m$  is the mass of oil degassed, in g.

- l) Carry out the analysis as in Clause 9.

NOTE 5 Because the gas is not totally extracted from the oil, a rinse step can be required after a high concentration has been run (e.g. after analysis of the oil sample from the tap changer). The extractor can be rinsed with oil containing non-detectable quantities of gases, except for those present in the air.

### 8.3 Vacuum extraction by partial degassing method

#### 8.3.1 General remarks

In this method, gas extraction is accomplished by only one exposure to vacuum (between 3 min for mineral oils and 10 min for the more viscous silicone oils, see Annex F). Extraction efficiency depends on component gas solubility. Correction of this incomplete gas extraction can be obtained by calculation from the Ostwald solubility coefficients of the gases in transformer oil, either mineral or non-mineral (see Annex A).

#### 8.3.2 Partial degassing apparatus

Equipment such as that shown in Figure 6 a) and Figure 6 b) is equally suitable for this method with the following changes:

- The automatic control arrangements used in the Toepler pump mode (valves V10 and electric contacts a, b and c) are not required. A simple hand pump (blow-ball) can be fitted in place of the low-pressure compressed air supply.
- The total expansion volume (degassing flask (3) plus collection flask (2) and connecting tubing, less the oil volume) should be at least 20 times the oil volume. In the apparatus shown in Figure 6 b), a collection flask of 500 ml and a degassing flask of 150 ml are suitable for an oil volume of 25 ml to 30 ml.
- The mercury reservoir volume should not greatly exceed that of the collection flask; in the apparatus shown in Figure 6 b), a reservoir volume of approximately 600 ml to 700 ml is recommended. The reservoir should be filled with mercury to leave an air space of not more than 100 ml to 150 ml.
- A mark should be made on the dip tube in the mercury reservoir, (mark d in Figure 6 a) and Figure 6 b)) so that when the equipment is used for partial degassing, the mercury can be brought to this mark and the expansion volume thus accurately defined.
- The apparatus shall be leak-free and capable of evacuation to 0,1 Pa. The burette, typically 3,5 ml, shall be calibrated in 0,01 ml divisions, and the connecting tubing and vacuum gauge as in points d) and f) of 8.2.2.
- Alternatively to the syringe, the needle and the septum, a flexible polytetrafluoroethylene (PTFE) tubing connected to the valve can be used to introduce oil samples.

### 8.3.3 Extraction procedure

- a) Weigh the syringe (5) containing the oil sample and connect it to the degassing flask (3).
- b) Proceed as in steps b) to e) of 8.2.3, evacuating down to 0,1 Pa.
- c) Allow degassing to continue for 5 min to 10 min, depending on the oil viscosity, with the stirrer operating vigorously. Then close valve V9.
- d) Proceed as in steps g) and h) of 8.2.3.
- e) Calculate the total gas volume extracted by dividing the volume of gas collected in the burette by the volumetric collection ratio  $V_c/V_t$ , where
  - $V_c$  (collection volume) is the volume of the burette and collection flask (2), from mark "d" to valves V9, V6, V5 and V2;
  - $V_t$  (total expansion volume) is  $V_c$  plus the volume of the degassing flask (3) and connecting tubing to V9, V8 and V7, less the volume of oil.
- f) Remove and reweigh the syringe to obtain the mass of oil that has been degassed. Determine the density of the oil at ambient temperature.
- g) Correct the calculated total volume of gas extracted to 20 °C and 101,3 kPa as in step k) of 8.2.3.
- h) Inject an aliquot of the gas extracted into the chromatograph as in step j) of 8.2.3.
- i) Carry out the analysis as in Clause 9.
- j) Calculate the actual concentration of each gas component originally present in the oil sample, by dividing its chromatographically measured concentration by its extraction efficiency  $E_i$  (see Annex A).

NOTE Because the gas is not totally extracted from the oil, a rinse step can be required after a high concentration has been run (e.g. after analysis of the oil sample from the tap changer). The extractor can be rinsed with oil containing non-detectable quantities of gases, except for those present in the air.

Mercury-free versions of the Toepler and partial degassing methods are described in Annex B.

## 8.4 Stripping extraction method

### 8.4.1 General

The extraction of dissolved gases is carried out by the carrier gas itself bubbling through a small volume of the oil. Typically an oil volume between 0,25 ml and 5 ml is used.

The time required to extract larger volumes would give unacceptable gas chromatograms except when used with cold traps or for hydrogen analysis only.

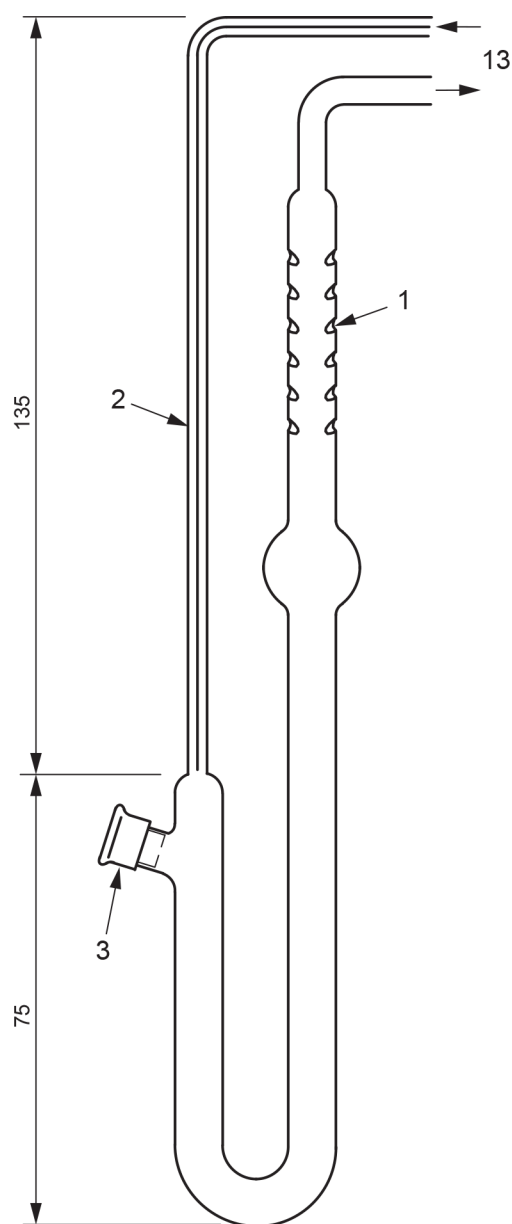
### 8.4.2 Stripping apparatus

Various designs of strippers are used. Figure 7 shows borosilicate glass strippers. Oil is injected into the stripper from a syringe via a rubber septum. This septum can be used several times (3 to 10 depending on the size of the needles) before leakage occurs.

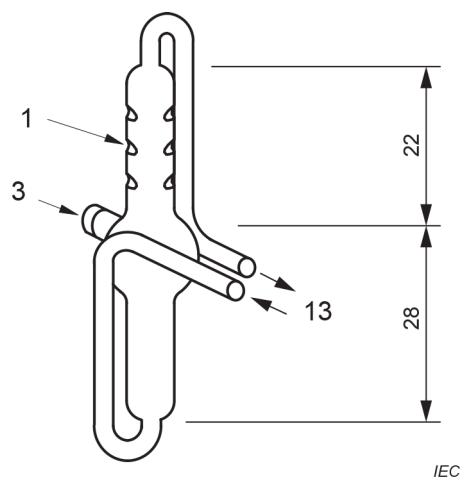
A design of a stripper made of stainless steel is shown in Figure 8. A needle with a cock and interchangeable syringe connection is permanently fixed into the base of the stripper and a syringe containing oil is attached to the fixed needle. The oil is injected by the movement of a pneumatic actuator on the syringe plunger.

The volume of oil injected shall be measured with an accuracy better than 1,0 %. Injection from a precision syringe has been found to achieve this requirement but the difference of syringe mass before and after injection is to be preferred if better accuracy is required.

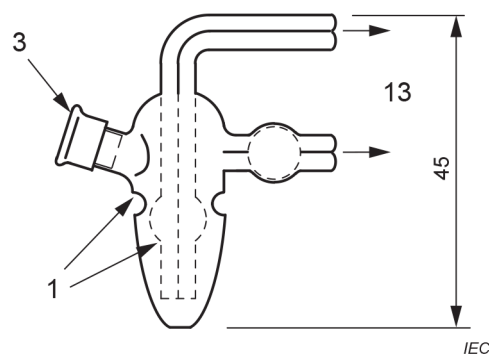
Dimensions in millimetres



a) Stripper for hydrogen analysis



b) Example 1 of stripper for general analysis



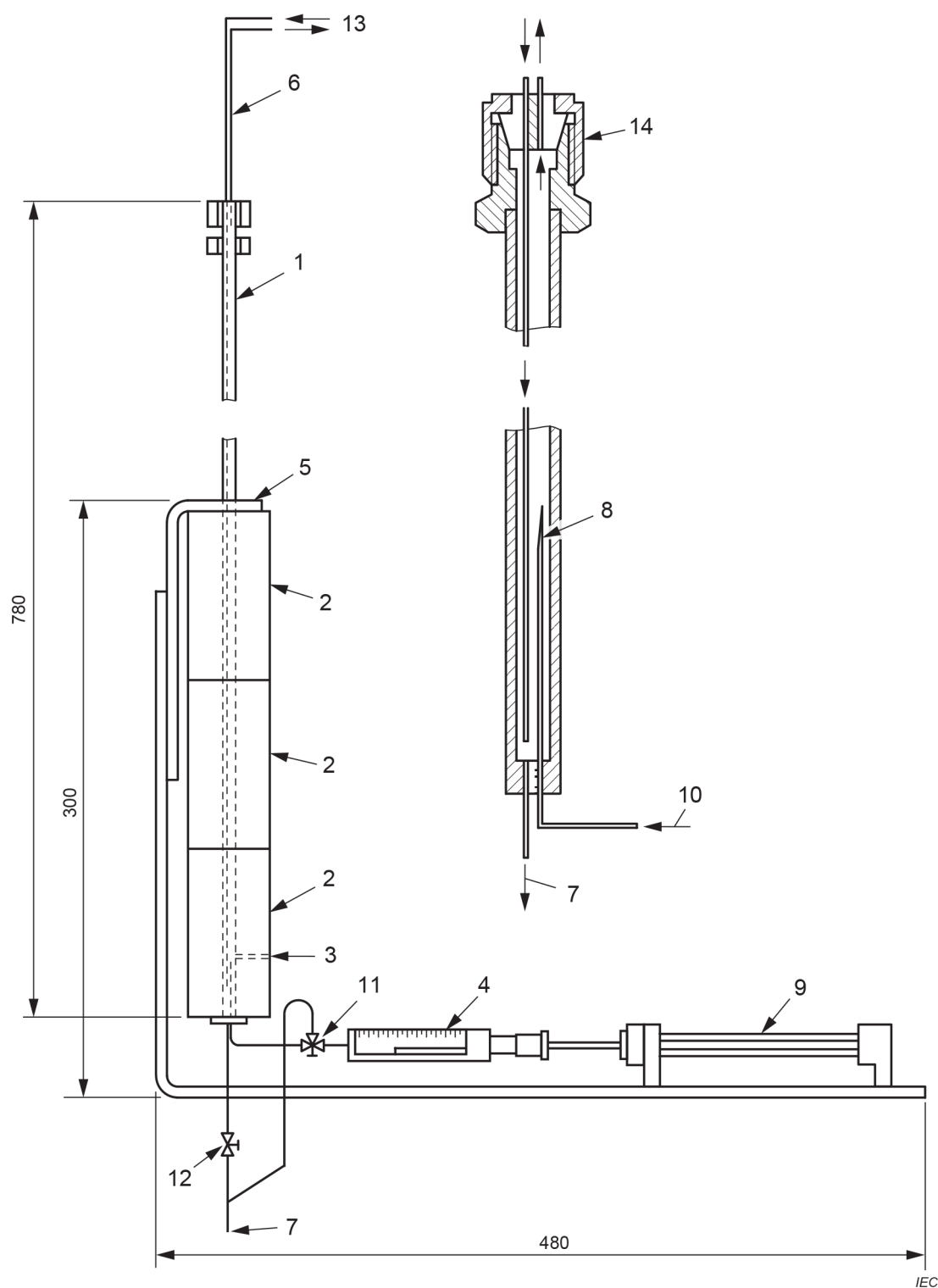
c) Example 2 of stripper for general analysis

#### Key

- 1 glass indentations
- 2 capillary tube
- 3 oil injection septum
- 13 connection to six-port gas-sampling valve (see Figure 12 a))

**Figure 7 – Types of glass strippers**

Dimensions in millimetres



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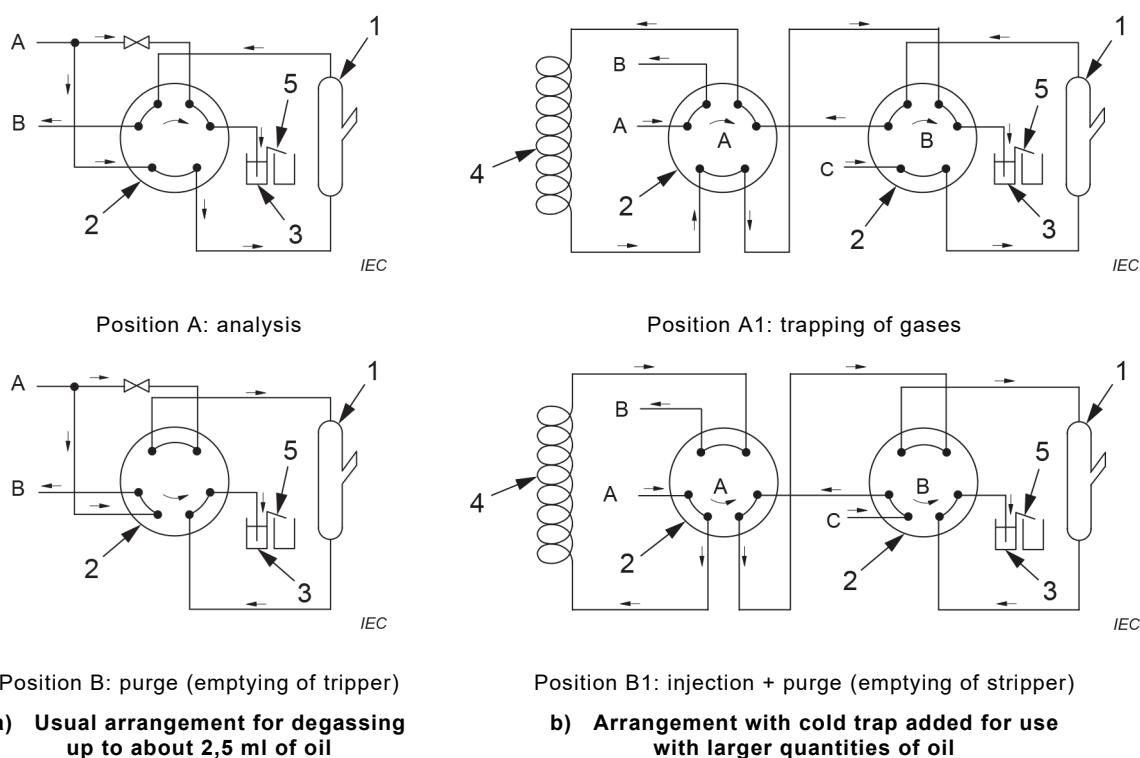
**Key**

- |   |                                                               |    |                                                              |
|---|---------------------------------------------------------------|----|--------------------------------------------------------------|
| 1 | stainless steel tube (OD 6 mm – ID 4 mm)                      | 8  | end of oil injection needle                                  |
| 2 | heating blocks                                                | 9  | air cylinder                                                 |
| 3 | temperature sensor                                            | 10 | oil injection                                                |
| 4 | 5 ml syringe                                                  | 11 | three-way valve                                              |
| 5 | aluminium bracket                                             | 12 | stopcock                                                     |
| 6 | stainless steel capillary tubing inlet and outlet (OD 1,6 mm) | 13 | connection to six-port gas-sampling valve (see Figure 12 a)) |
| 7 | waste oil                                                     | 14 | biconical union                                              |

**Figure 8 – Stainless steel stripper**

### 8.4.3 Outline of procedure

- As shown in Figure 9 a) connect the stripper in place of the sample loop of the gas chromatograph gas-sampling valve preferably using compression fittings. Vacuum rubber tubing may alternatively be used for the connections then verify that there is no leakage due to overpressure of the carrier gas; if such is the case, reduce the overpressure.
- Maintain the stripper at a controlled temperature between 20 °C and 80 °C. Indeed, elevated temperatures reduce oil viscosity and facilitate gas stripping.
- Allow the carrier gas to flow through the stripper.
- Before injection of the oil, check that the operating conditions of the equipment are satisfactory and particularly that the baseline on the recorder is stable.
- Inject the oil to be analysed into the stripper. The volume of oil to be injected will depend upon the type of stripper used and the expected gas content. During this operation, the carrier gas flow through the stripper shall be maintained.
- After the analysis has been completed, some stripper designs permit a back flush of the injected oil to waste without disconnecting the stripper. If the stripper is to be disconnected for cleaning, the gas outlet tube should be disconnected first to avoid the possibility of the oil sample entering the gas-sampling valve. Carry out the analysis as in Clause 9.



#### Key

- A inlet carrier gas  
B outlet carrier gas (to chromatograph)  
C carrier gas for extraction

- 1 stripper  
2 six-port gas-sampling valve  
3 mercury valve  
4 cold trap  
5 waste vessel

**Figure 9 – Schematic arrangement for connecting an oil stripper to a gas chromatograph**

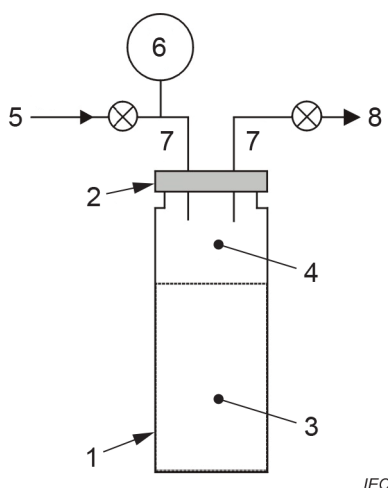
## 8.5 Headspace method

### 8.5.1 Principle of the method

In this method a volume of oil  $V_L$  is introduced in a glass vial in contact with a gas phase ("headspace") of volume  $V_G$ . A portion of the gases dissolved in the oil ( $H_2$ ,  $O_2$ ,  $N_2$ ,  $CH_4$ ,  $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ,  $CO$  and  $CO_2$ ) transfers to the headspace, under equilibrium conditions of temperature, pressure and agitation. The headspace is transferred to an injection loop or directly in the column of the gas chromatograph depending on the apparatus used. Calibration curves are used to establish the concentration of each gas in the headspace. The concentrations of the gases in oil are then calculated by using Henry's law and experimentally determining the partition coefficients of the oil or by direct calibration with gas-in-oil standards. A schematic representation of this method is shown in Figure 10.

**WARNING** – This method will provide reproducible results only if all the operation and calibration parameters are precisely controlled, otherwise significant errors can occur. The following parameters are of particular importance: total volume of vials, volume of oil, tightness of septa, temperature, dilution with argon and actual pressure in the vials after each step of the procedure. The same exact parameters should always be used for field samples, gas standards and oil standards.

**NOTE** Symbols and abbreviated terms used in 8.5 are listed in 3.2.1 and 3.2.2.



#### Key

- 1 vial
- 2 septum
- 3 oil sample
- 4 gas phase
- 5 carrier gas
- 6 pressurization gauge
- 7 headspace sampler needles
- 8 to GC injection loop and detectors

**Figure 10 – Schematic representation of headspace sampler**

## 8.5.2 Headspace extraction apparatus

### 8.5.2.1 General remark

An example of a suitable design includes the following components.

### 8.5.2.2 Headspace sampler

This sampler is equipped with a transfer line connected directly or through a T union to the first column of the gas chromatograph. Samplers equipped with a syringe injection have not been evaluated.

**NOTE** The size of injection loops is adapted to the type of columns in order to avoid broadening of peaks. If injection loops larger than 1 ml are used, an overpressure high enough to adequately flush the sample loop is used and filled to atmospheric pressure prior to the injection step (this will depend on the volume of the circuit between the vial and the vent in some systems).

A second injection loop can be necessary for injecting gas mixtures directly into the chromatograph, to check the response of the GC detectors daily with calibrated gas, and to perform the gas collecting relay analysis. These operations are also possible using the headspace sampler, after transferring the calibrated gas mixture or the gas sample from the gas collecting relay into pre-purged vials.

### 8.5.2.3 Headspace glass vials

#### 8.5.2.3.1 General

Use headspace vials suitable for use with the equipment. The actual volume of commercial vials can differ from the nominal value.

**NOTE** 20 ml vials have shown good performance. Their actual volume is closer to 22,3 ml.

The total volume of the vial  $V$  has a great influence on the value of the  $V_G/V_L$  ratio, and on the final results. Since significant variations of volume can occur between different batches of vials and between different vials of the same batch, the average value for each batch of vials purchased by the laboratory should be determined when they have different batch numbers. This can be done by measurement of the mass of pure water that can be contained in a vial according to the procedure described below in 8.5.2.3.2.

Condition 10 to 20 vials from the same batch and 100 ml of distilled water for 1 h at room temperature and note the temperature.

#### 8.5.2.3.2 Headspace glass vials calibration procedure

Determine the weight of the empty vials to the nearest 0,01 g. Fill the vials completely with distilled water as shown in Figure 11 and reweigh to the nearest 0,01 g. Calculate the volume of each vial by using the following equation:

$$V = (W - W_0) / D$$

where

$V$  is the total volume of the vial, in ml;

$W_0$  is the weight of the empty vial, in g;

$W$  is the weight of the vial filled with water, in g;

$D$  is the density of water at measurement temperature, in g/ml.

Calculate the mean volume and the relative standard deviation,  $s$  % for the vials tested. If the value of  $s$  % is higher than 1 %, the controlled batch of vials is rejected and a new batch of vials shall be tested.

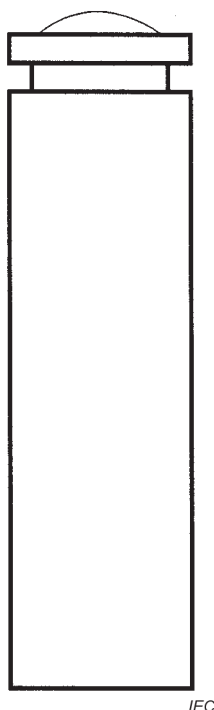


**Figure 11 – Vial filled with water**

#### **8.5.2.4 Septa**

The brands of septa used should not introduce contamination of the vials during analysis and should not leak after having been punctured by needles, especially by the large diameter needles in 8.5.3.1.3.

The suitability of septa is checked by analysis on blank vials containing argon only at atmospheric pressure, having been punctured the same number of times as the vials containing the oil samples or gas standards and left for 24 h at room temperature. Very low quantities of oxygen and nitrogen should be found (not more than 150  $\mu\text{l/l}$   $\text{O}_2$  and 350  $\mu\text{l/l}$   $\text{N}_2$ ).

Another means of checking septa is by immersing the closed vial with its pierced septum in a water bath heated at 90 °C and checking for bubbles. This test is useful also for checking the crimping method.

Porosity of septa can also be tested by filling a number of crimped vials (at least 10) with a gas mixture containing approximately 100  $\mu\text{l/l}$  hydrogen using one of the methods within 8.5.3.1. Using the method in 8.5.4.3, analyse duplicate vials for hydrogen content at intervals over a period of about one week, the first analyses being made as soon as possible after filling the vials. Normal calibration procedures should be carried out. The septum and seal are acceptable if the rate of decrease in hydrogen concentration is less than 2,5 % per day.

NOTE 1 Only polytetrafluoroethylene-lined septa are used, preferably of the chlorobutyl rubber, high-temperature type. Silicone rubber septa have been found to leak and are best avoided.

In any case, new types of septa are checked before use. The quality of the crimping equipment (crimping head and perforated aluminium caps) and the skill of the operator have been reported as critical.

NOTE 2 When the reliability of septa cannot be assessed with certainty, a subprocedure 8.5.3.1.2 (preparation of vials in an inert box) is used.

NOTE 3 These tests are typically performed on each batch of 3 000 vials.

### 8.5.2.5 Oil syringes

Appropriate oil volumes, measured as precisely as possible, are introduced in the vials, so that the  $V_G/V_L$  ratio is the same for all field samples and gas-in-oil standards analysed. Volumes of 10 ml to 15 ml have been found suitable, but lower or larger oil volumes may be used, depending on the gas content of the oil sample. Glass syringes of 20 ml, 30 ml or 50 ml can be used. New batches of syringes should be calibrated with the following procedure.

Fill a syringe with 20 ml of oil of known density. Weigh the filled syringe to the nearest 0,01 g. Draw 15 ml of oil from the syringe then reweigh the syringe. Subtract the two weights to obtain the weight of oil drawn. Calculate the volume of oil by dividing the weight of oil by the density of the oil. Perform this test on 20 syringes of each new batch. Calculate the standard deviation(s) and  $s$  % for the 20 syringes. If  $s$  % is higher than 1,3 %, the controlled batch of syringes is rejected and a new batch of syringes shall be tested.

Glass syringes are not intended for precise volumetric work. The index mark on the piston is about 0,5 ml in width, allowing considerable variations with operators. Therefore, the exact amount of oil introduced in a vial should be measured by weighing the vial or the syringe before and after introduction of the oil (see 8.5.3.1).

Two different types of needles are needed (A and B). For type A, 0,84 mm ID (gauge 18) (for the transfer of oil) and for type B, 0,25 mm ID (gauge 26) (for the transfer of gases and pressure equilibration) have been found suitable. Needle size should be adapted to the type of septa to ensure that they will not induce leaks (see 8.5.2.4).

For the procedure of 8.5.3.1.3, a maximum size of 0,84 mm ID and 1,27 mm OD (gauge 18) is recommended to avoid leaks through the septa.

For the procedure of 8.5.3.1.2, larger size needles may be used as they will not be used to pierce septa, and a larger size needle will facilitate oil introduction.

### 8.5.2.6 Inert boxes

#### 8.5.2.6.1 General

An inert box (either a glove box, a glove bag or a "revolving table") is required for the procedure of 8.5.3.1.2.

#### 8.5.2.6.2 Glove box

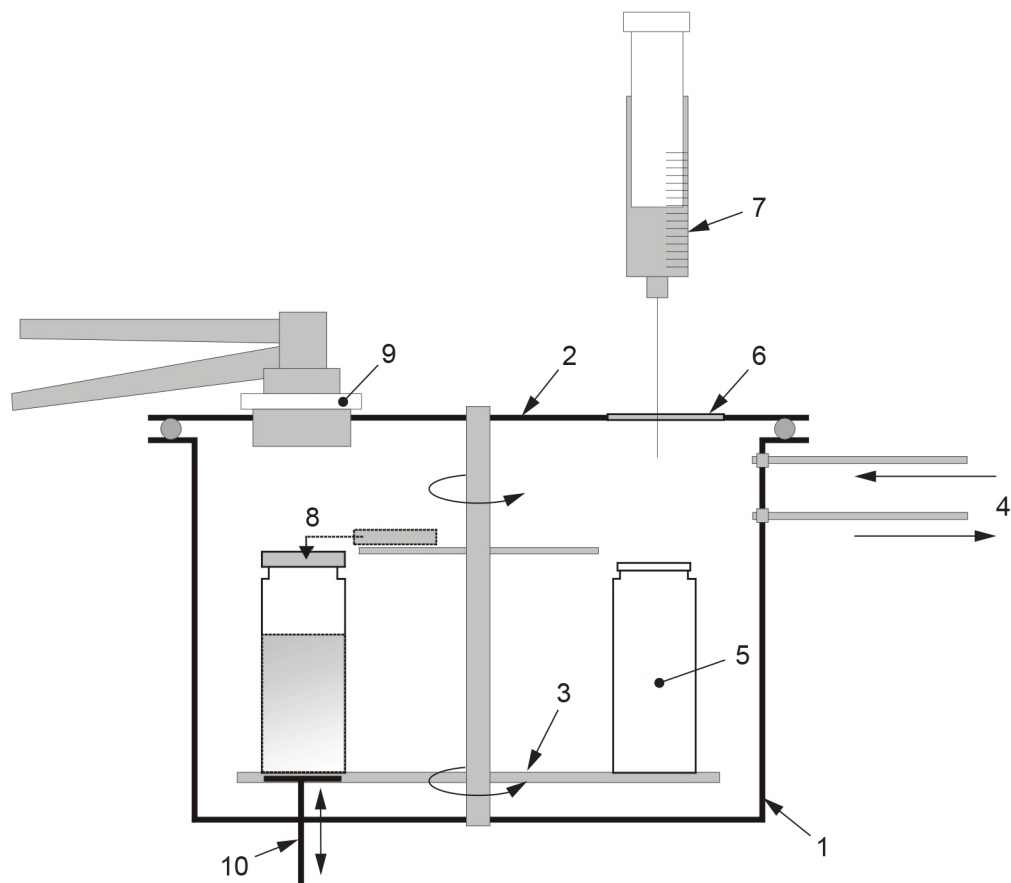
The glove box and its lock chamber should be purged with at least five times its volume of argon (typically, at 400 ml/min). Alternatively, a plastic glove bag, filled with all the necessary equipment (syringes, vials, etc), then purged with argon, may be used.

#### 8.5.2.6.3 Revolving table

The "revolving table" is described in Figure 12: a carousel carrying 20 empty vials is placed in a circular housing, hermetically covered by a transparent removable lid. The carousel can be rotated from outside with a knob.

A septum is attached to one side of the lid, and a vial crimper on the other side, both facing the mouth of the vials.

The revolving table is continuously flushed with inert gas (the same used as carrier gas) at a known and constant flow rate and pressure, to ensure constant operation conditions.



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**Key**

- 1 housing
- 2 lid
- 3 rotating carousel
- 4 argon purge
- 5 vial
- 6 lid septum
- 7 oil syringe
- 8 vial septum and cap
- 9 vial crimper
- 10 vial lifter

**Figure 12 – Revolving table****8.5.2.7 Headspace operational conditions**

See Table 2. The same conditions can be used for mineral and non-mineral oils.

**Table 2 – Examples of headspace operating conditions**

| Headspace operating conditions                                                                                                        |                          |              |
|---------------------------------------------------------------------------------------------------------------------------------------|--------------------------|--------------|
| Carrier gas                                                                                                                           |                          | Argon        |
| Temperatures, in °C                                                                                                                   | Vial                     | 70           |
|                                                                                                                                       | Transfer line            | 70 to 150    |
|                                                                                                                                       | Injector                 | 150          |
| Pressure, in kPa                                                                                                                      | Overpressure in vial     | 35 to 40     |
| Volume, in ml                                                                                                                         | Sampling loop            | 0,25 to 1    |
| Times, in min                                                                                                                         | Equilibration            | 10 to 180    |
|                                                                                                                                       | Pressurization           | 0,05 to 0,25 |
|                                                                                                                                       | Pressure equilibrium     | 0,05 to 0,25 |
|                                                                                                                                       | Expansion in sample loop | 0,20 to 0,25 |
|                                                                                                                                       | Injection                | 0,20 to 1,00 |
| Mixing power                                                                                                                          |                          | High         |
| NOTE 1 Ultrasonic agitation is not used to speed up equilibrium times as it can produce hydrogen.                                     |                          |              |
| NOTE 2 "High" (or "maximum") mixing power refers to the position on the headspace equipment (about 100 shaking movements per minute). |                          |              |
| NOTE 3 The pressurization time used is the shortest one to get equilibrium.                                                           |                          |              |

Monitoring or recording of measurable parameters (argon overpressure, temperature, etc.) within a precision of  $\pm 0,5$  % is advisable to verify if they have not changed accidentally during an extended run.

This can be done by recording or printing the electronic reading of pressure available within the headspace equipment during the analysis. Important modifications are used for some headspace samplers that have only mechanical reading of the pressure.

The atmospheric pressure and ambient temperature shall be recorded when filling the vials, within a precision of  $\pm 0,5$  %, to be able to calculate actual quantities of gases introduced at the various steps of the procedure and to convert to the conditions of this document.

### 8.5.2.8 Gases

The argon used shall be chromatography graded (typically, > 99,999 % pure).

Standard gas mixtures supplied with a calibration certificate of  $\pm 1$  %, if available, or at worst  $\pm 2$  %, are used to establish a calibration curve for each dissolved gas. The concentrations of the mixtures should be chosen in order to fully cover the expected concentration range of field samples, which depends on the type of equipment to be monitored.

Different levels of concentrations in the calibration curve may be obtained by injecting different volumes of the same standard mixture or by using different standard mixtures in a suitable concentration range.

## 8.5.3 Headspace extraction procedure

### 8.5.3.1 Preparation of vials

#### 8.5.3.1.1 General

Two alternate methods are possible, using either an inert box or needles.

### 8.5.3.1.2 Preparation of vials in an inert box

#### 8.5.3.1.2.1 General

This method has the advantage that septa are never punctured before being placed in the headspace carousel. The risk of septa leak (with its dramatic effect on analysis results) is therefore much reduced.

#### 8.5.3.1.2.2 Pre-purging of vials

Pre-purging can be carried out

- a) in the glove box: for practical reasons, series of 10 samples are prepared. Label and weigh 10 vials with their corresponding perforated aluminium caps and septa (uncrimped) to the nearest 0,01 g. Place the 10 weighed vials, 10 glass syringes of 20 ml, and 10 oil samples in their glass syringes or glass ampoules in the lock chamber of the glove box. Purge the lock chamber with argon. Transfer the content of the lock chamber into the glove box filled with argon;
- b) in the revolving table: up to 20 empty vials weighted as above and their corresponding caps and septa (of known average weight) are placed in the closed housing. Purge with argon for 10 min to 15 min.

#### 8.5.3.1.2.3 Preparation of vials with oil samples

Vials with oil samples can be prepared as follows:

- a) in the glove box: with a 3-way valve transfer about 5 ml of the first oil sample into a glass syringe and rinse the entire body of the syringe with the oil. Release the 5 ml oil to waste and fill the glass syringe with 20 ml of oil. Disconnect the oil syringe or glass ampoule and fix a needle to the glass syringe.

Release about 5 ml of oil into the waste vessel, then fill an empty vial with the remaining 15 ml of oil with the tip of the needle to the bottom of the vial. Adjust the volumes if a lower final oil volume (between 10 ml and 15 ml) has been chosen.

Close the vial with its septum and crimping cap and crimp with the help of the crimping bead, making sure that the lined side is turned towards the inside of the vial.

NOTE 1 Closing the vial is done within 45 s after the vial has been filled with oil; otherwise, the sample is discarded and a new one prepared.

Repeat the same procedure for the other nine samples.

- b) in the revolving table: connect a needle to the syringe containing the oil sample. Release about 5 ml of the oil sample into the waste vessel, to condition the needle and remove traces of air bubbles. Introduce an aliquot (10 ml to 15 ml) of the oil sample in a vial through the septum of the lid. Rotate the carousel and move the caps on the top of the vials. Rotate the carousel again and crimp the vial using the crimper and vial lifter. Repeat the same procedure for the 20 vials, then stop the flushing, open the lid and remove the vials from the carousel.
- c) Take the crimped vials out of the glove box or revolving table and weigh them to the nearest 0,01 g. Calculate the mass of oil by subtracting the weight of the empty vials from the weight of the filled vials and calculate their volumes by dividing the mass by the density of the oil.

NOTE 2 The actual density of oil (measured according to ISO 3675 or other standardized method) is used for the calibration procedure with gas-in-oil standards. For sample analysis, an average density of the oil type (e.g. one for paraffinic oils and one for naphthenic oils) is used.

Measure the pressure and the ambient temperature in the glove box or revolving table precisely. Place the oil-filled vials in the headspace carousel for analysis.

The same procedures apply to gas-in-oil standards.

#### **8.5.3.1.2.4 Preparation of vials with gas standards**

This is effected outside the glove box or revolving table. Place a piece of paraffin film (Parafilm®)<sup>1</sup> on the mouth of a vial. Insert two needles through the film. Purge with calibrating gas mixture so that the purging volume of the vial is at least five times the volume of the vial (typically, 1 min at 100 ml/min). Remove the needle and close the vial with a septum and crimp cap, without removing the film.

#### **8.5.3.1.3 Preparation of vials with needles**

##### **8.5.3.1.3.1 General**

Crimp a series of vials using perforated aluminium caps fitted with a PTFE-lined septum. Ensure that the lined side is turned towards the inside of the vial and that the latter is properly sealed by trying to turn the cap. If the cap is not tightly fixed, repeat the process.

##### **8.5.3.1.3.2 Pre-purging of vials**

Insert two needles A (8.5.2.5) through the vial septum, one to be used as inlet gas and the other as outlet gas, on the sides of the septum, not in its centre. Purge each vial with argon at least five times the vial volume (e.g. at a rate of 1 l/min for 0,1 min at 120 kPa or 120 ml/min for 1 min).

First remove the outlet needle and then the inlet needle, to build up some argon overpressure in the vial. Removal of the outlet and inlet needle should be done with a minimum of delay in order to avoid excessive overpressure if high flushing rates are used.

The efficiency of this preparation technique can be checked by analysis of one of these vials containing only argon. This has also been used to test the quality of septa (see 8.5.2.4). Very low quantities of oxygen and nitrogen should be found (see Note 2 of 8.5.2.4).

##### **8.5.3.1.3.3 Preparation of vials with gas standards**

Insert two needles A (8.5.2.5) through the vial septum, one to be used as inlet gas and the other as outlet gas. Purge one vial with each calibration gas mixture at the same rate used in 8.5.3.1.3.2.

First remove the outlet needle (overpressure will take place in the vial). Remove the inlet needle. Using a 10 ml syringe with a type B needle remove the overpressure in the vial by inserting the needle of the syringe through the septum. After equilibrium, the atmospheric pressure will be obtained. If not, the dilution factor, and the results, will be affected when argon overpressure is applied at the next stage.

Measure the ambient temperature and atmospheric pressure precisely in order to determine the exact quantities of gases present in the vial and to convert to normal conditions (20 °C; 101,3 kPa).

##### **8.5.3.1.3.4 Preparation of vials with oil samples**

Weigh a pre-purged crimped vial. Attach a type A needle to the syringe stopcock. Insert the needle through the septum and insert simultaneously a second type B needle to release the argon overpressure.

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<sup>1</sup> Parafilm® is the trade name of products supplied by Pechiney Plastic Packaging Company. This information is given for the convenience of users of this document and does not constitute an endorsement by IEC of the products named. Equivalent products may be used if they can be shown to lead to the same results.