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INTERNATIONAL STANDARD

colour
inside

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

IEC 60567:2023-12 CMV(en)

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

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This commented version (CMV) of the official standard IEC 60567:2023 edition 5.0 allows the user to identify the changes made to the previous IEC 60567:2011 edition 4.0. Furthermore, comments from IEC TC 10 experts are provided to explain the reasons of the most relevant changes, or to clarify any part of the content.

A vertical bar appears in the margin wherever a change has been made. Additions are in green text, deletions are in strikethrough red text. Experts' comments are identified by a blue-background number. Mouse over a number to display a pop-up note with the comment.

This publication contains the CMV and the official standard. The full list of comments is available at the end of the CMV.

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. 1

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. The main document types developed by IEC are described in greater detail at www.iec.ch/publications.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn, or
- revised.

IMPORTANT – The "colour inside" logo on the cover page of this document indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

INTRODUCTION

Gases ~~may~~ 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 ~~may~~ 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 ~~may~~ 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 ~~may~~ 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 ~~may~~ 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 ~~may~~ 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 ~~could~~ 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. ~~Consult local regulations~~ 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 ~~should be carried out strictly according to local regulations~~ 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:~~2011~~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 ~~may~~ can be by un-pressurized air freight and where considerable differences in ambient temperature ~~may~~ 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 –* ~~*Unused Mineral insulating oils for transformers and switchgear*~~ *Mineral insulating oils for electrical equipment*

IEC 60475:~~2011~~2022, *Method of sampling insulating liquids*

~~IEC 60599, *Mineral oil-impregnated electrical equipment in service – Guide to the interpretation of dissolved and free gases analysis*~~

~~ISO 5725 (all parts), *Accuracy (trueness and precision) of measurement methods and results*~~

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

~~ASTM D2780, *Standard Test Method for Solubility of Fixed Gases in Liquids*~~

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 ~~(Buchholz)~~ 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 ~~may~~ 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 ~~should~~ 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, ~~may~~ 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 ~~may need to be taken into account~~ 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 ~~may~~ 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:

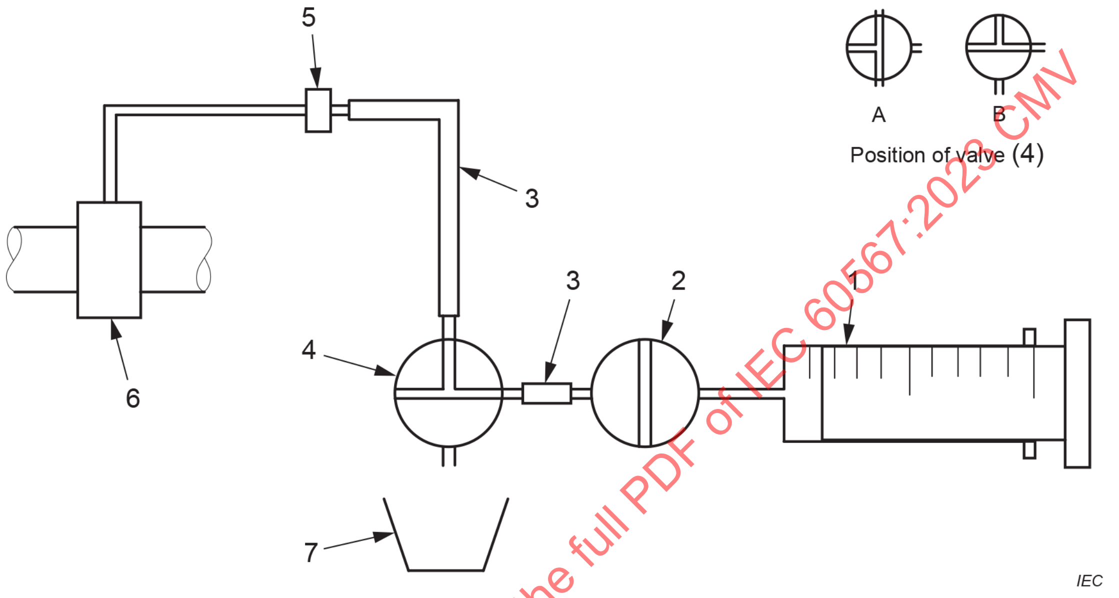
a) Impermeable oil-resistant plastic or rubber tubing (3) provided with a connector to fit onto a suitable sampling connection of the gas-collecting relay. To avoid cross-contamination, the tubing should be used only once.

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:~~2011~~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:~~2011~~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

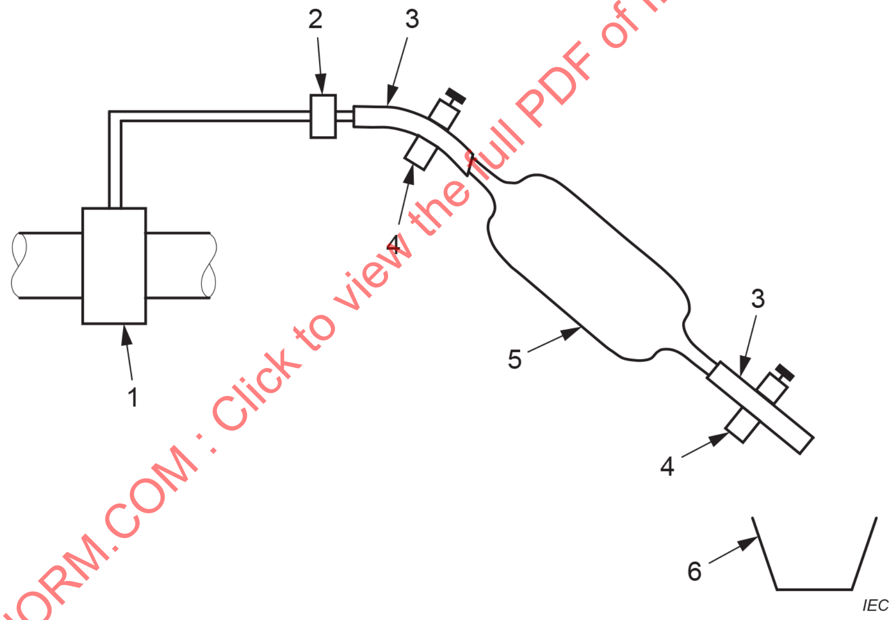
This method is reliable only where the gas sample is at or above atmospheric pressure. The apparatus is shown in Figure 2.

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

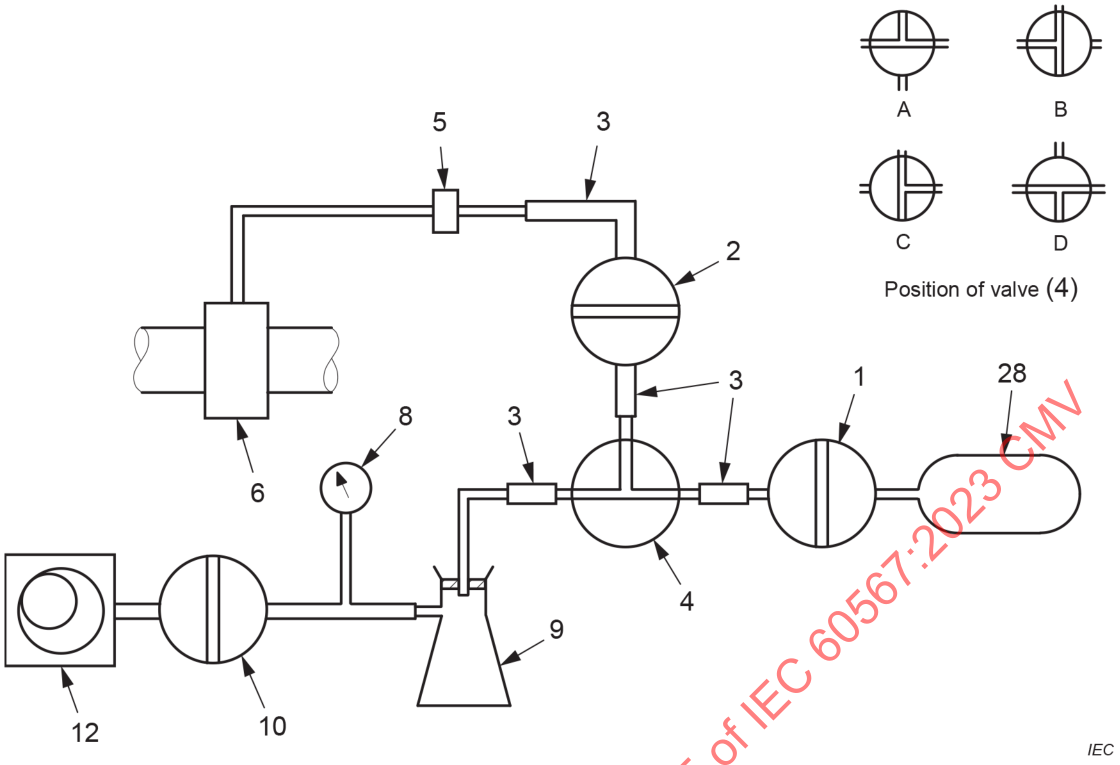
4.4 Sampling of free gases by vacuum

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.



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:~~2011~~2022, 4.2.

5 Labelling of gas samples

Gas samples ~~should~~ 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	
Oil	
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:~~2011~~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:~~2011~~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:~~2011~~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 ~~may~~ 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.

~~NOTE~~ 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.

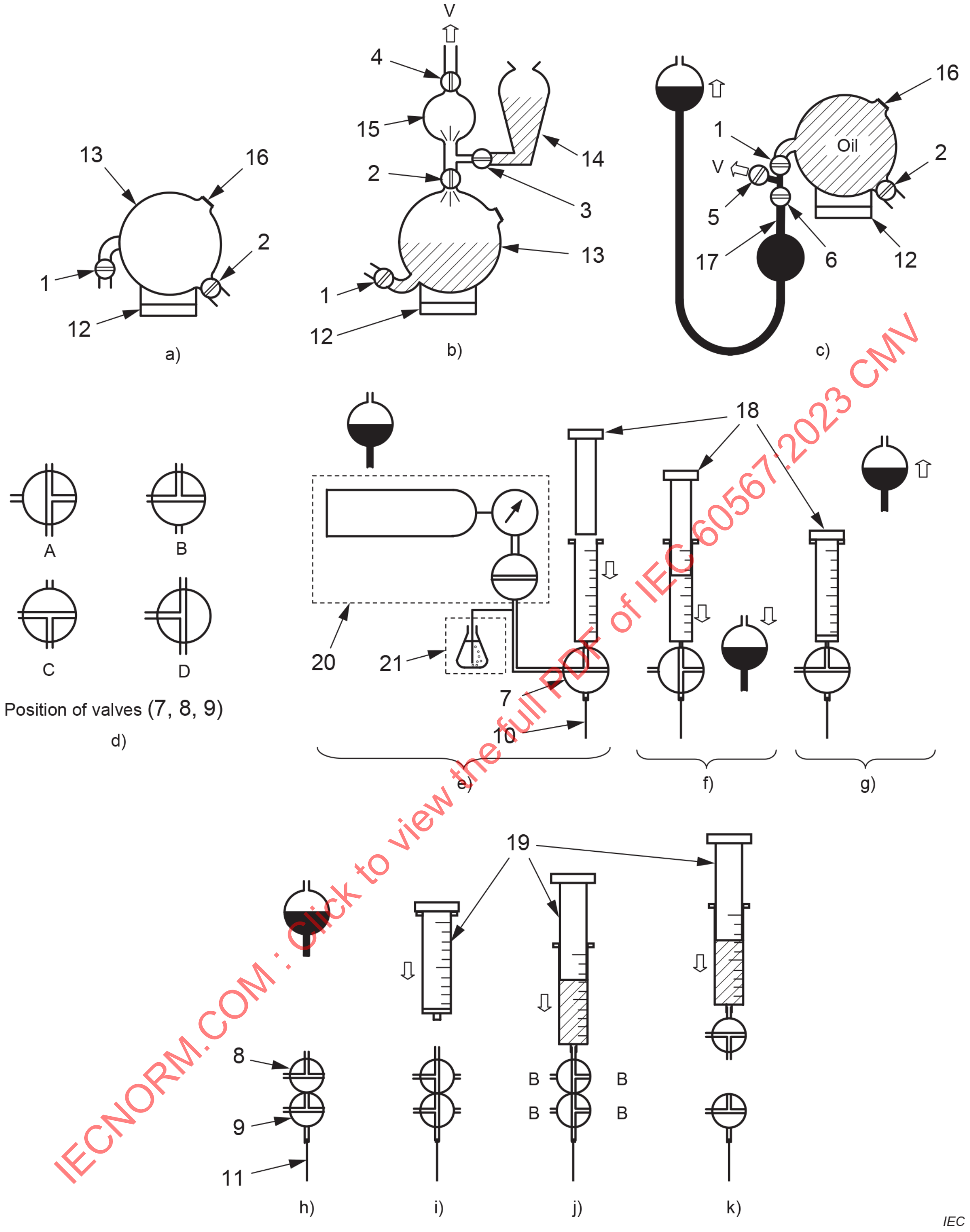
d) Adapt the oil reservoir (14), the splash bulb (15) and stopcocks (4) to the 5 l vessel (13). Connect the system to the vacuum pump (V) and evacuate the splash bulb (15) and the 5 l oil vessel (13) by opening stopcocks (2) and (4).

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).



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:

$$C_\mathrm{i} = V_\mathrm{i} / V \times 10^6$$

where

C_i is the concentration of gas "i", in µl/l;

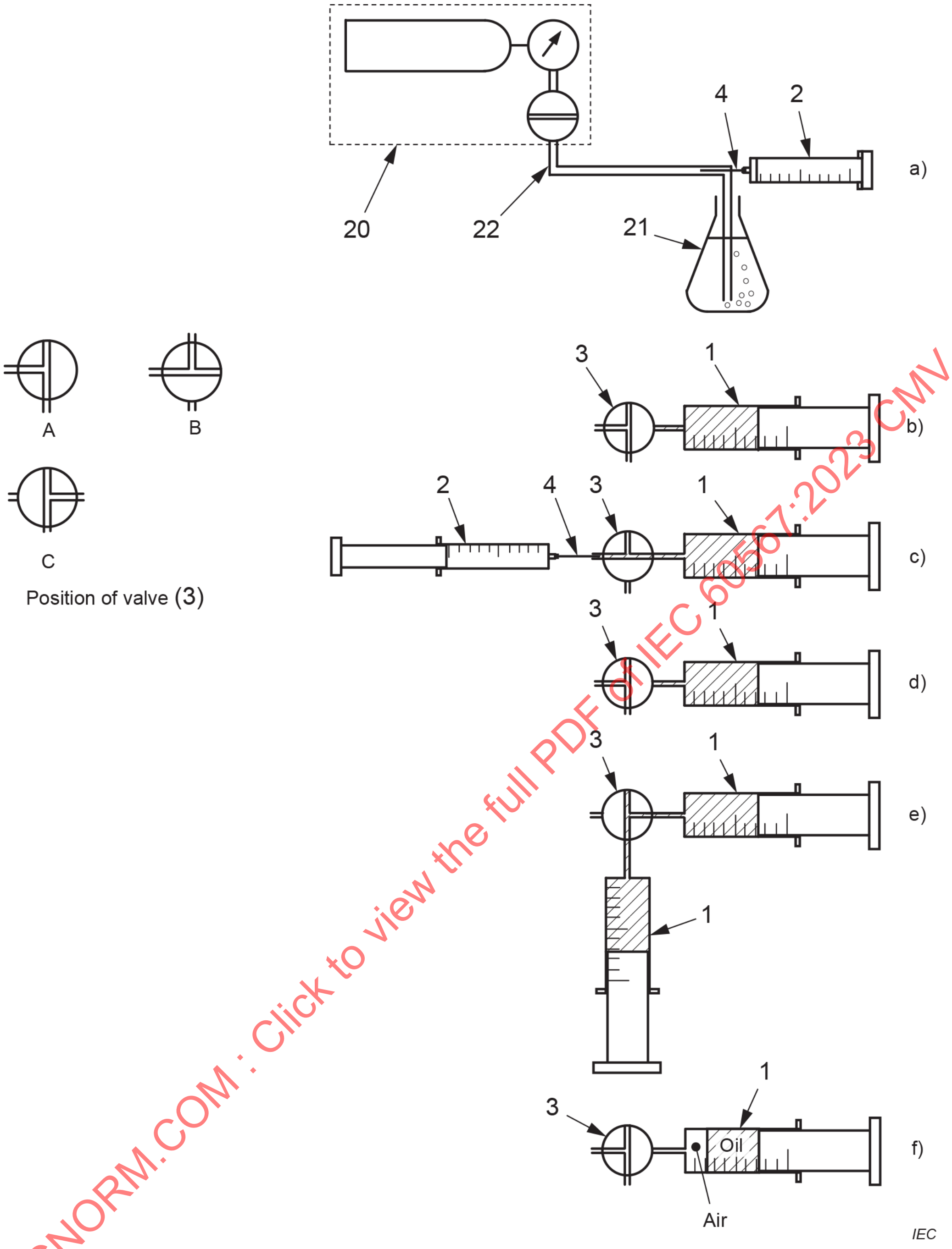
V_i is the volume of gas "i" injected, corrected to 20 °C and 101,3 kPa in ml;

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).



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 ~~may~~ 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_2 and 2 000 µl/l N_2 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_2-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 ~~may~~ can be used instead of a syringe. The vial is filled with the same amount of degassed oil as ~~that needed~~ 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 ~~should be~~ 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 ~~may~~ 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.

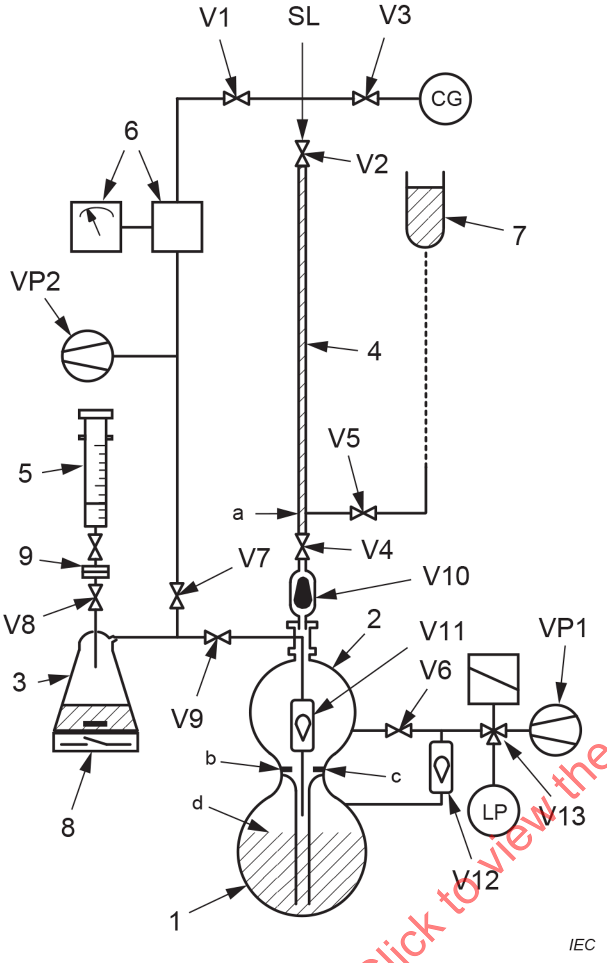
Since the detailed design of this apparatus is not standardized, it is necessary to establish an operation that will ensure adequate extraction of all components of the dissolved gas. The main parameters ~~that need~~ to be established are the number of degassing cycles (strokes) of the Toepler pump 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.

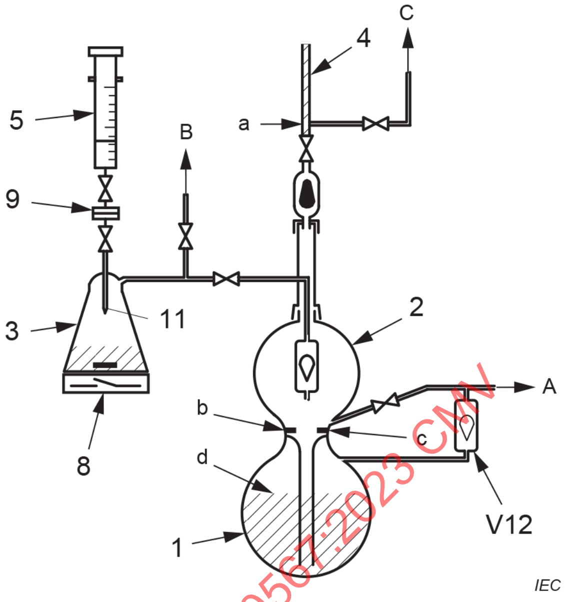
Degas successive standards until a number of cycles of the Toepler pump, together with a degassing time on each stroke, has been established so that the area or height of each peak on the chromatogram of the extracted gases is within 95 % of the area or height of that peak on the chromatogram of the 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).

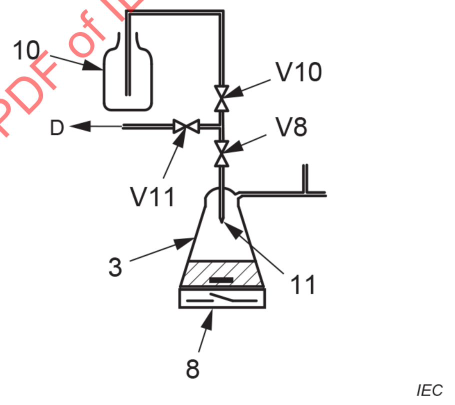
The above procedure serves to establish a routine of operation, which will apply until any major changes are made to the equipment and will also apply to other equipment of the same design. It is recommended that the overall calibration of the complete equipment (degassing equipment plus chromatograph) 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.



a) General view of a Toepler pump extraction apparatus



b) Recommended volumes of several parts of a Toepler pump



c) Example of oil introduction by bottle

Key

1	mercury reservoir – 2 l
2	gas collection flask – 1 l
3	degassing flask – 250 ml or 500 ml
4	gas-collecting burette – 25 ml (0,05 ml divisions)
5	introduction of oil sample via syringe
6	Pirani vacuum gauge
7	mercury-levelling vessel
8	magnetic stirrer
9	septum
10	oil-sampling bottle
11	jet

V1 to V11	hand stopcocks
V10 to V12	non-return valves
V13	electromagnetic three-way valve
VP1	rough vacuum pump
VP2	main vacuum pump
LP	connection to low pressure air (±110 kPa)
SL	connection to GC sample loop
CG	connection to calibration gas cylinder
a b c	electrical contacts
d	mercury level mark on tube
A	connection to rough vacuum pump and air
B	connection to main vacuum pump
C	connection to mercury-levelling vessel
D	connection to waste oil reservoir and rough vacuum pump

[a] Item 6 of Figure 6 a) ~~should read~~ 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 ~~may~~ can be ~~needed~~ 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, ~~ensure that~~ 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 ~~may~~ can be used to increase the precision of the analysis. For oil from a factory test, a modification ~~may be needed~~ 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 ~~may be~~ 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 µl/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 ~~may~~ 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:

a) 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.

b) 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.

c) 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.

d) 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.

e) 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.

f) 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 $V_{\mathrm{c}}/V_{\mathrm{t}}$, 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 ~~may~~ 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.

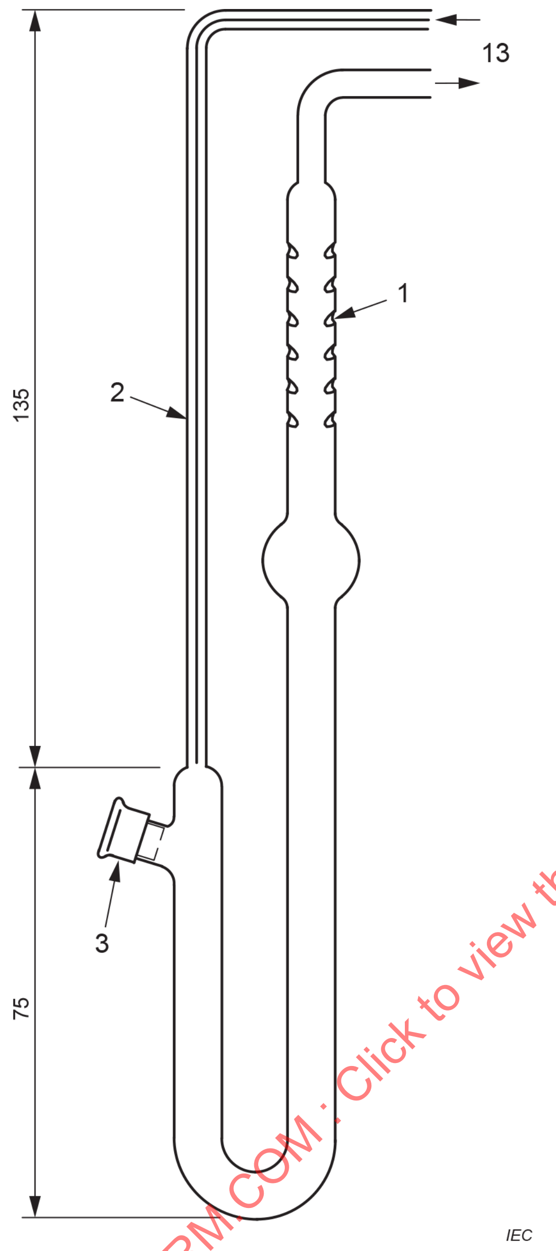
8.4.2 Stripping apparatus

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.

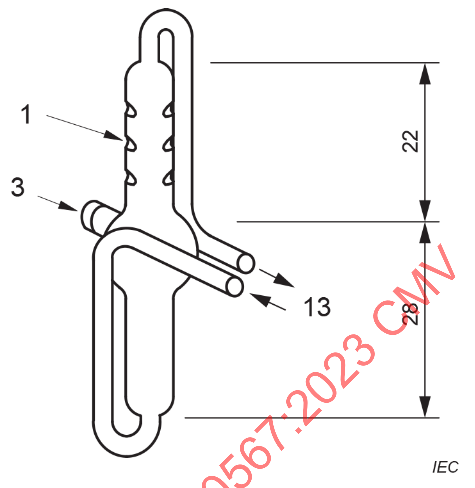
A design of a stripper made of stainless steel is shown in Figure 8. A needle with a cock and interchangeable syringe connection is permanently fixed into the base of the stripper and a syringe containing oil is attached to the fixed needle. The oil is injected by the movement of a pneumatic actuator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

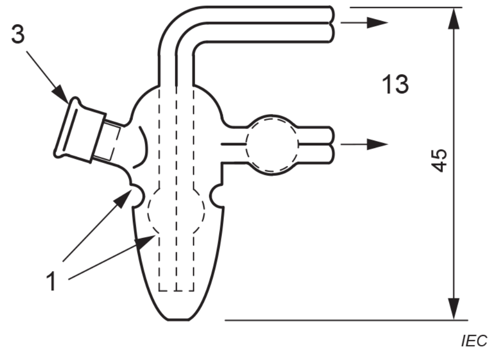
Dimensions in millimetres



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

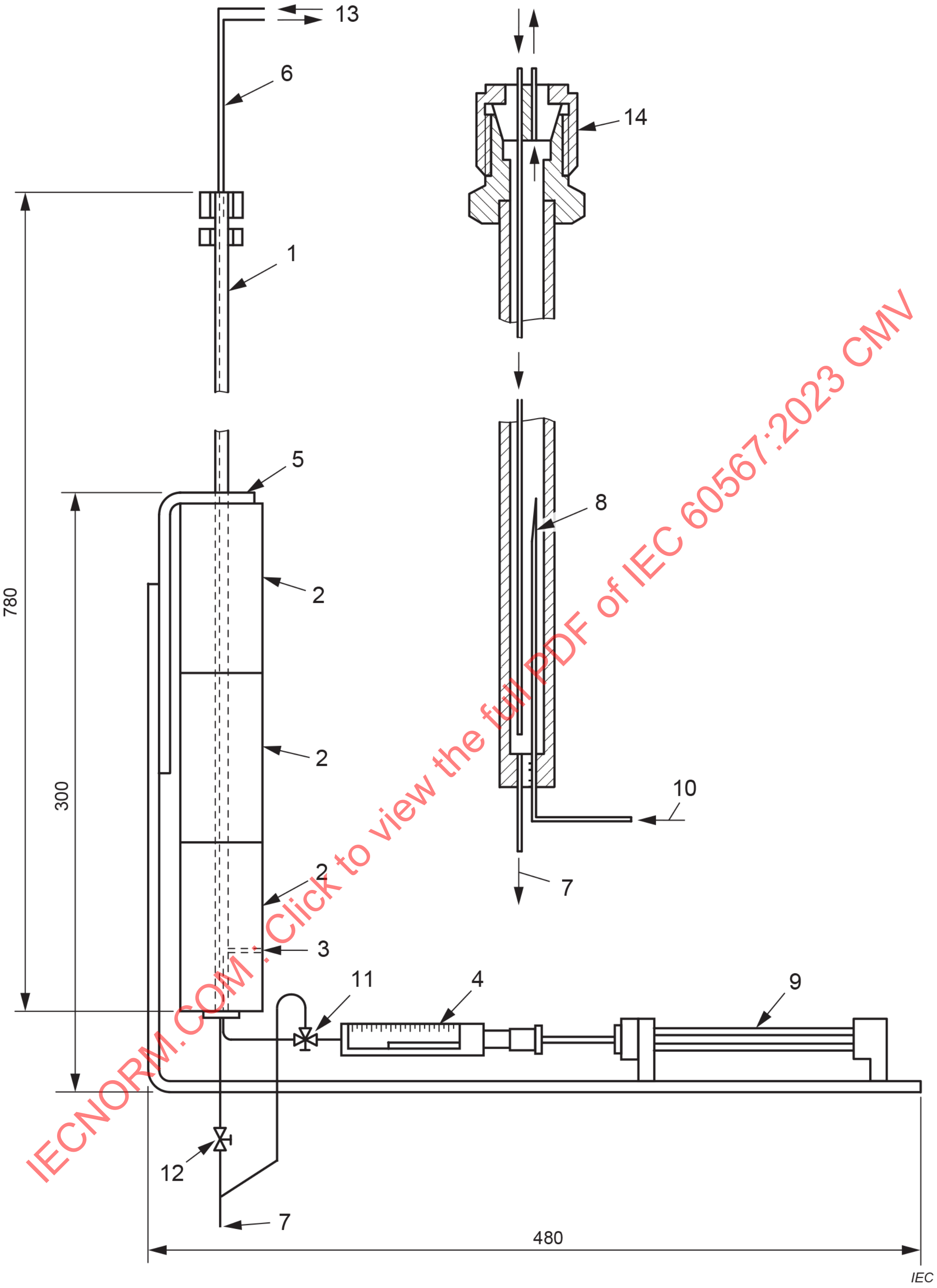
2 capillary tube

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



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

a) 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.

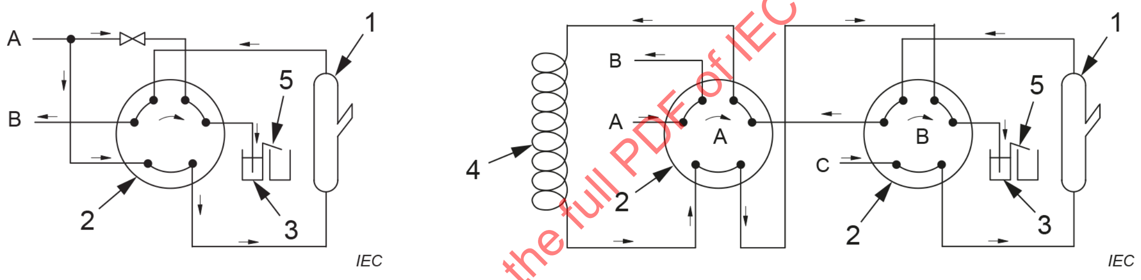
b) Maintain the stripper at a controlled temperature between 20 °C and 80 °C. Indeed, elevated temperatures reduce oil viscosity and facilitate gas stripping.

c) Allow the carrier gas to flow through the stripper.

d) 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.

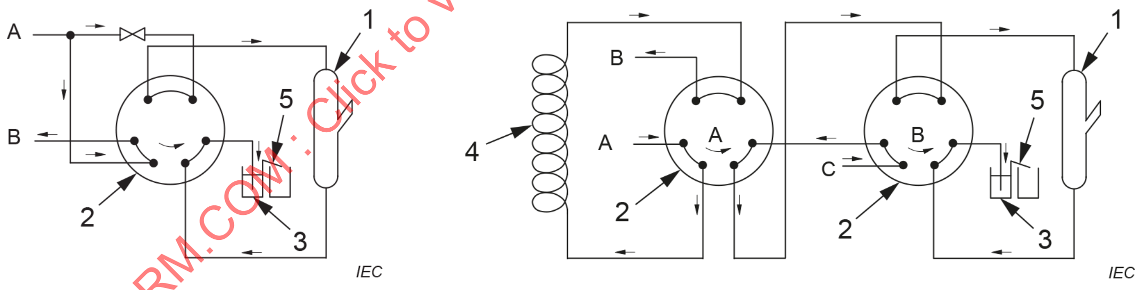
e) Inject the oil to be analysed into the stripper. The volume of oil to be injected will depend upon the type of stripper used and the expected gas content. During this operation, the carrier gas flow through the stripper shall be maintained.

f) 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.



Position A: analysis

Position A1: trapping of gases



Position B: purge (emptying of tripper)

Position B1: injection + purge (emptying of stripper)

a) Usual arrangement for degassing up to about 2,5 ml of oil

b) Arrangement with cold trap added for use with larger quantities of oil

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

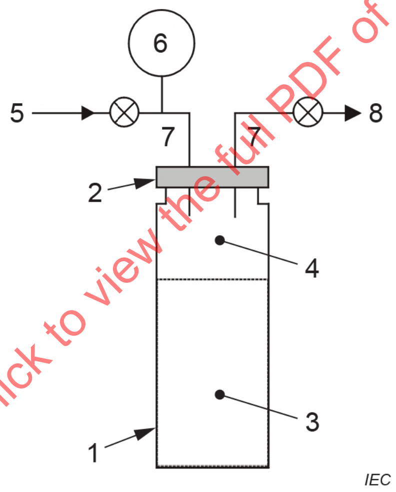
8.5 Headspace method

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 ~~may~~ 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 ~~should be~~ is adapted to the type of columns in order to avoid broadening of peaks. If injection loops larger than 1 ml are used, ~~it should be verified that the~~ an overpressure ~~is~~ high enough to adequately flush the sample loop is used and ~~fill it~~ 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 ~~may~~ 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 ~~Buchholz~~ the gas collecting relay analysis. These operations are also possible using the headspace sampler, after transferring the calibrated gas mixture or the ~~Buchholz~~ 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 ~~may~~ 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.

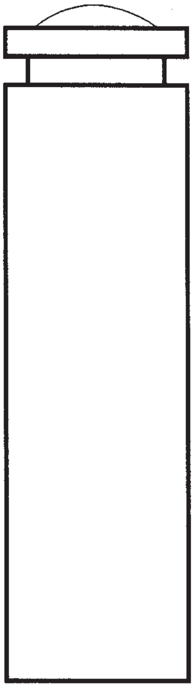


Figure 11 – Vial filled with water

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 µl/l O_2 and 350 µl/l 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 µl/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 ~~should be~~ are used, preferably of the chlorobutyl rubber, high-temperature type ~~(PTFE = polytetrafluoroethylene = Teflon ®)~~. Silicone rubber septa have been found to leak and ~~should be~~ are best avoided.

In any case, new types of septa ~~should be~~ 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, ~~it is recommended that~~ a subprocedure 8.5.3.1.2 (preparation of vials in an inert box) ~~be~~ 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

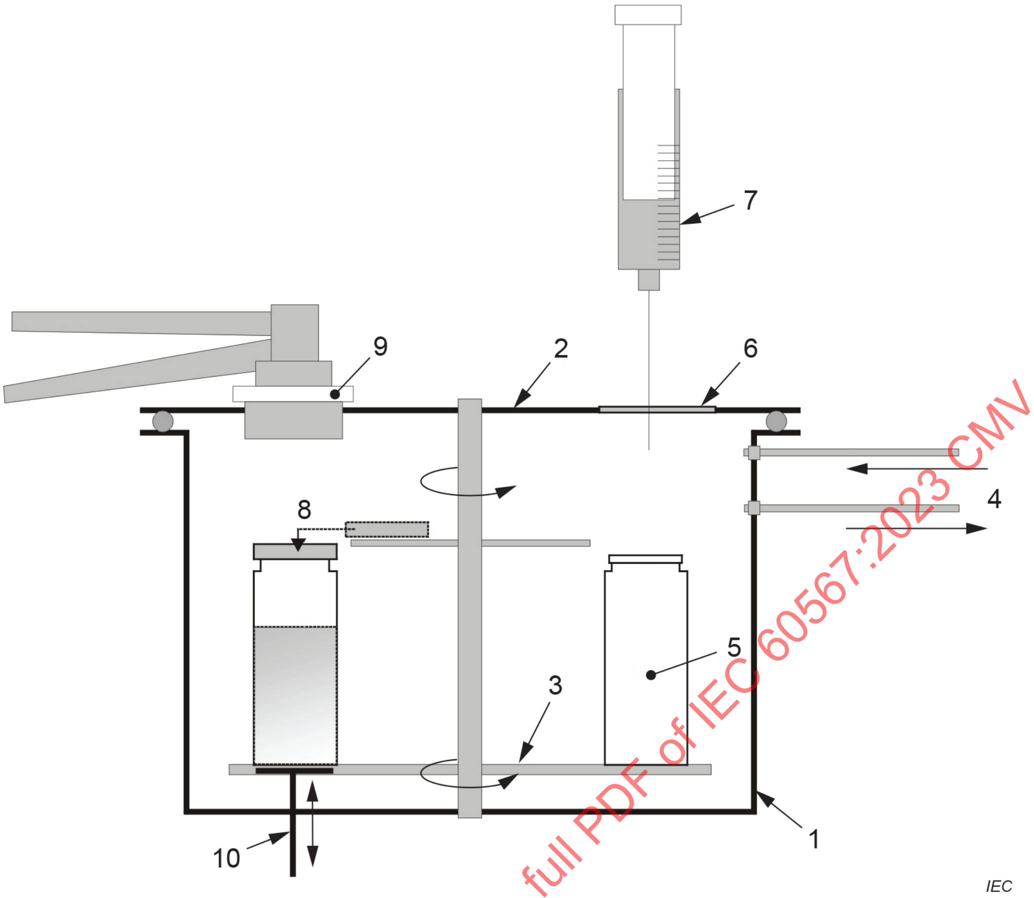
The glove box and its lock chamber should be purged with at least five times its volume of argon (typically, at 400 ml/min). Alternatively, a plastic glove bag, filled with all the necessary equipment (syringes, vials, etc), then purged with argon, may be used.

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 carrousel 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.



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 ~~should~~ is not ~~be~~ used to speed up equilibrium times as it ~~may~~ 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 ±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. ~~This may need~~ 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 ±0,5 %, to be able to calculate actual quantities of gases introduced at the various steps of the procedure and~~/or~~ 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 ±1 %, if available, or at worst ±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 carrousel. 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 ~~should be~~ is done within 45 s after the vial has been filled with oil; otherwise, the sample ~~should be~~ 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) ~~should be~~ 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) ~~should be~~ 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®)[1] 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~~/or~~ 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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[1] 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.

Fill up the vial with the chosen amount of oil. Remove the two needles together, to make sure that the pressure in the vial at this stage is atmospheric pressure.

Weigh the oil-filled vial and subtract the weight of the empty vial to get the mass of oil in the vial. Divide by the density of the oil to get the exact volume of oil in the vial.

The same procedure applies for vials of gas-in-oil standards.

8.5.3.2 Headspace analyses

Place the vials inside the headspace sampler and begin the analysis using operational conditions such as those given in Table 2 as examples. As shown in Table 2, a large range of temperatures is possible for the transfer line and the injection valve, as well as for the equilibration times ~~needed~~, depending on the exact type of equipment used.

NOTE Pressure in the vials at this stage ~~should~~ is always ~~be~~ below the injection pressure (140 kPa). Pressure in the glove box ~~may~~ can exceed this, in which case it ~~should be~~ is measured (in the glove box, or in the vial, with the gauge on the headspace equipment) and reduced if necessary. Ideally, it ~~should be~~ is close to atmospheric pressure and ~~should be~~ known with precision in order to make the corrections and calculations indicated in 8.5.4.2 and 8.5.4.3.

Record the actual atmospheric pressure throughout the run, since it ~~may~~ can vary by several per cent over an extended run, especially if unattended, and it ~~may~~ can be necessary to make corrections to total pressure in the vial.

8.5.3.3 Procedure for analysis at low concentration levels

The procedures described in 8.5.3.1 and 8.5.3.2 provide the detection limits specified in Table 5 for service tests. More sensitive procedures (and special attention to avoid contamination) are required to obtain the detection limits specified for acceptance tests, where extracted gases in the headspace of the vials are in the nl/l range.

Toepler and partial degassing, where extracted gases are in the µl/l range at these levels, are more recommended for acceptance tests. However, if headspace is to be used for low concentration levels and acceptance tests, the more sensitive equipment and procedures described below are required:

- capillary GC columns such as the PLOT columns described in 9.3.2;
- reduced dead volumes between the vial and the GC detectors;
- calibration with different calibration curves;
- manual (rather than electronic) integration of the baseline of GC peaks. This will lower the detection limits to typically 0,2 µl/l for hydrocarbons;
- for the still lower detection limits of acceptance tests, a larger injection loop of 1,5 ml, followed by a split of the gas sample between the vial and the GC columns (typically, of 1/50 to 1/100). This will result in much sharper GC peaks (particularly for hydrogen);

  NOTE The equipment ~~may~~ can be instructed to automatically choose the splitter option (e.g. 1/100 for acceptance tests and 1/10 for service tests).
- alternatively, a syringe may be used to manually transfer a gas sample from the vial to the injection port of the GC. This will eliminate the gas dilution resulting from argon pressurization of the vial.

8.5.3.4 Procedure for analysis at high concentration levels

It has been observed that when hydrogen concentration levels are too high, the measured values are considerably below actual values. In such cases, a smaller volume of the oil sample should be used to obtain accurate results.

It has been found that when the hydrogen content is typically above 6 000 µl/l, a second sample with 7 ml of the oil sample in the vial and a third measurement with 3 ml in the vial should be performed. Valid results are obtained when identical values with two different dilution factors are measured.

When using the procedure in 8.5.4.2 (calibration with gas-in-oil standards), introduce the reduced volume of oil sample (7 ml or 3 ml) in a syringe, complete to 15 ml with degassed oil, then transfer into a vial and proceed as with regular oil samples. Multiply the measured values of gas in oil by the proper oil dilution factor (15/7 or 15/3).

When using the procedure in 8.5.4.3 (calibration with gas standards), introduce the reduced volume of oil in a vial and proceed as with regular oil samples. Calculate gas concentrations in the oil sample using the equation indicated in 8.5.4.3 and the proper values of V_{G} and V_{L}.

NOTE This non-linearity has been observed mainly with hydrogen dissolved in oil, but samples with high concentrations of the other dissolved gases ~~should~~ can also be measured following a similar procedure.

8.5.4 Calibration of the headspace extractor

8.5.4.1 General remark

Two different calibration methods are available.

8.5.4.2 Calibration with gas-in-oil standards

This is the preferred method of calibration recommended by CIGRE TF D1.01.15 and CIGRE WG A2/D1.47.

The advantage of this method is that knowledge of precise partition coefficients ~~need~~ is not ~~be determined~~ necessary. Neither is it affected by the linearity problems evidenced by the scatter of results observed during CIGRE inter-laboratory tests using partition coefficients.

Three gas-in-oil standards (GIOS) at different concentrations, prepared according to the methods described in 7.2 or 7.3, are run at least once a month or each time an operational parameter has changed (argon overpressure, new batches of vials or syringes) or if calibration of GC detectors with gas standards indicate a change in the response of detectors.

Direct calibration curves are drawn, relating peak height or peak area to the concentration of gases in the ~~gas-in-oil standard~~ GIOS.

When an unknown oil sample is run under exactly the same operational conditions, its dissolved gas concentrations C_{L}^{0*} can be obtained by using these calibration curves. ~~A small correction for the differences of atmospheric pressure and temperature when the gas-in-oil standard and unknown oil samples were analysed should be made:~~

~~$C_{\mathrm{L}}^{0} = C_{\mathrm{L}}^{0*} \times (P/P_{\mathrm{s}}) \times [(273 + t_{\mathrm{s}})/(273 + t)]$~~

~~(see 7.5.2 for abbreviations).~~

For the storage of gas-in-oil standards, see CIGRE TB 783-2019, section E3, p.44.

8.5.4.3 Calibration with gas standards

It has been confirmed in CIGRE TB 783-2019 that laboratories using the calibration method in 8.5.4.3 have less accurate and more disperse results than those using the preferred method in 8.5.4.2, based on numerous round robin tests and proficiency test programmes.

The advantage of this method is that there is no requirement to prepare gas-in-oil standards for direct calibration of the headspace extractor.

Partition coefficients ~~need~~ are to be determined accurately, however, under exactly the same operational conditions as the oil samples (see 8.5.4.4).

A vial containing the gas standard, prepared according to 8.5.3.1.3.3, is placed in the headspace sampler and analysed through the headspace injection loop.

Calibration curves relating peak height or peak area to the concentration of the gases in the gas standard are drawn. When an oil sample is run under exactly the same operational conditions, the concentration of the gases in the gas phase C_G can be obtained by using this calibration curve.

The concentrations in the oil sample are then determined using the following equation, based on Henry's law, which requires that the partition coefficients K and the actual vial volume ratio (V_G/V_L) for each oil sample be precisely determined.

$$C_L^0 = C_G \times (K + V_G / V_L)$$

NOTE 1 V_L and V_G are calculated according to 8.5.2.3.2 and 8.5.2.5.

~~A correction for atmospheric pressure and temperature should be made using Equation (1) (see 7.5.5.2), replacing "gas-in-oil standard" by "gas standard".~~ Generally, gas standards are prepared together with oil samples and so the temperature and pressure inside the vials before headspace extraction should be the same. Concerning the atmospheric pressure, it can vary during the time ~~needed for analysing~~ several samples are analysed; as a consequence, in some systems equipped with sample loops in equilibrium with atmospheric pressure, the amount of gas (number of moles) going to the detector through the sample loop can change. Because of this, a correction for atmospheric pressure should be made.

NOTE 2 ~~Although it is not needed for calibration, it is recommended~~ When using this procedure ~~that~~, the overall performance of the extractor ~~be~~ is verified regularly by running gas-in-oil standards.

8.5.4.4 Determination of partition coefficients

The recommended method of determination of partition (or Ostwald or solubility) coefficients is the CIGRE TF D1.01.15 method consisting of bubbling pure gases in the oil ~~according to ASTM Method D2780,~~ or bubbling a standard mixture of gases in the oil.

It has been shown by CIGRE that partition coefficients measured by different laboratories using the headspace method and gas-in-oil standards, and~~/or~~ the so-called slope ~~/~~intercept method, are not reliable and reproducible.

Examples of headspace partition coefficients measured experimentally at 70 °C in a mineral insulating oil of density d = 0,864 are given in Table 3.

Table 3 – Examples of headspace partition coefficients at 70 °C in mineral insulating oil

Headspace partition coefficients at 70 °C in mineral insulating oil	
	~~**Mineral oil**~~
~~**Density**~~	~~0,864~~
H_2	0,074
O_2	0,17
N_2	0,11
CH_4	0,44
CO	0,12
CO_2	1,02
C_2H_2	0,93
C_2H_4	1,47
C_2H_6	2,09
C_3H_6	5,04
C_3H_8	5,37
C_4H_6	10,10

Shake test and mechanical oscillation versions of the headspace gas extraction method are described in Annex B.

9 Gas analysis by gas-solid chromatography

9.1 General remarks

Gas samples, whether obtained from gas-collecting relays or removed from an oil sample, are analysed by gas chromatography. The gases to be determined are as follows:

– hydrogen	H_2
– oxygen	O_2
– nitrogen	N_2
– methane	CH_4
– ethane	C_2H_6
– ethylene	C_2H_4
– acetylene	C_2H_2
– carbon monoxide	CO
– carbon dioxide	CO_2

For the purposes of this document, C_3 hydrocarbons are not required, but they ~~may~~ can on occasion give useful information.

A number of methods may be used for the analyses; the two methods detailed in Table 4 are given as examples that have been found suitable for all extraction techniques.

The following assumes a measure of competence in the techniques of gas chromatography and omits, for brevity, many details that ~~may~~ can be found in practical manuals on these techniques.

Table 4 – Examples of gas chromatographic operating conditions

	Example 1	**Example 2**
Type of columns	**Packed**	**PLOT**
Column 1	Porapak N®[2] or Haysep N®[3], L = 3; D = 3	Carboxen 1 006®[4] or Carboplot P7 ®[5], L = 30; D = 0,5
Column 2	Molecular sieve 5A or 13x L = 0,5; D = 3	Molecular sieve 5A (50 µm) L = 30; D = 0,5
Temperature (°C) of:		
Column bypass valve	120	90
FID	250	250
HID	250	250
TCD	200	200
Methanator	400	350
Oven	35 to 180	40 to 100
Gases separated		
On column 1	CO_2 (TCD) CO_2^a, C_nH_n, (FID)	C_2H_4, C_2H_2, C_2H_6, CO_2^a (FID)
On column 2	H_2, O_2, N_2, CO (TCD) CO^a (FID)	H_2, O_2, N_2, CO (TCD) CH_4, CO^a (FID)
Argon carrier gas	25 ml/min	6 ml/min

~~NOTE~~

Key

PLOT	porous large open tubular
FID	flame ionization detector
HID	helium ionization detector
TCD	thermal conductivity detector
L	length (in m)
D	diameter (in mm)
[a]	CO and CO_2 converted into CH_4 by methanator.

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[2] Porapak® is the trade name of products supplied by Water Associates. (Porapaks® are porous polymer beads modified to give different retention characteristics. Eight types are available; in order of increasing polarity these are Porapak® P, PS, Q, QS, R, S, N, and T). Haysep® products are polymers of a similar type. 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.

[3] Haysep N® is the trade name of products supplied by VICI Valco Instruments. 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.

[4] Carboxen® is the trade name of products supplied by Sigma-Aldrich. 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.

[5] Carboplot® is the trade name of products supplied by Agilent Technologies. 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.

9.2 Outline of suitable methods using Table 4

In example 1 of Table 4, two separate runs are made, one with a Porapak® column and the other with a molecular sieve column. A single detector having adequate sensitivity for all the gases to be detected is not available; thus, the gases eluted from the column in use are passed over both a thermal conductivity detector which detects atmospheric gases, CO, CO_2 and H_2 and a flame ionization detector which detects hydrocarbons.

To determine CO and CO_2 with improved sensitivity, a methanator may be fitted at the inlet of the flame ionization detector to convert CO and CO_2 to methane, which is then detected by the flame ionization detector.

In example 2 of Table 4, more sensitive porous large open tubular (PLOT) columns are used, particularly in the case of headspace extraction.

When using a stripping extraction method, it may not be possible to achieve the sensitivity and precision for hydrocarbons required for factory tests using less than 5 ml of oil. Larger volumes of oil (10 ml) require longer stripping times to extract the dissolved gases, which would give unacceptable gas chromatograms unless the extracted gases were to be concentrated by cold trapping.

The method in 9.3 is written for an apparatus in which the outputs from the detectors are switched electrically so that they may be dealt with by a single channel integrator or single channel chart recorder. Use of a dual channel integrator or recorder eliminates the need for switching.

9.3 Apparatus

9.3.1 Gas chromatograph

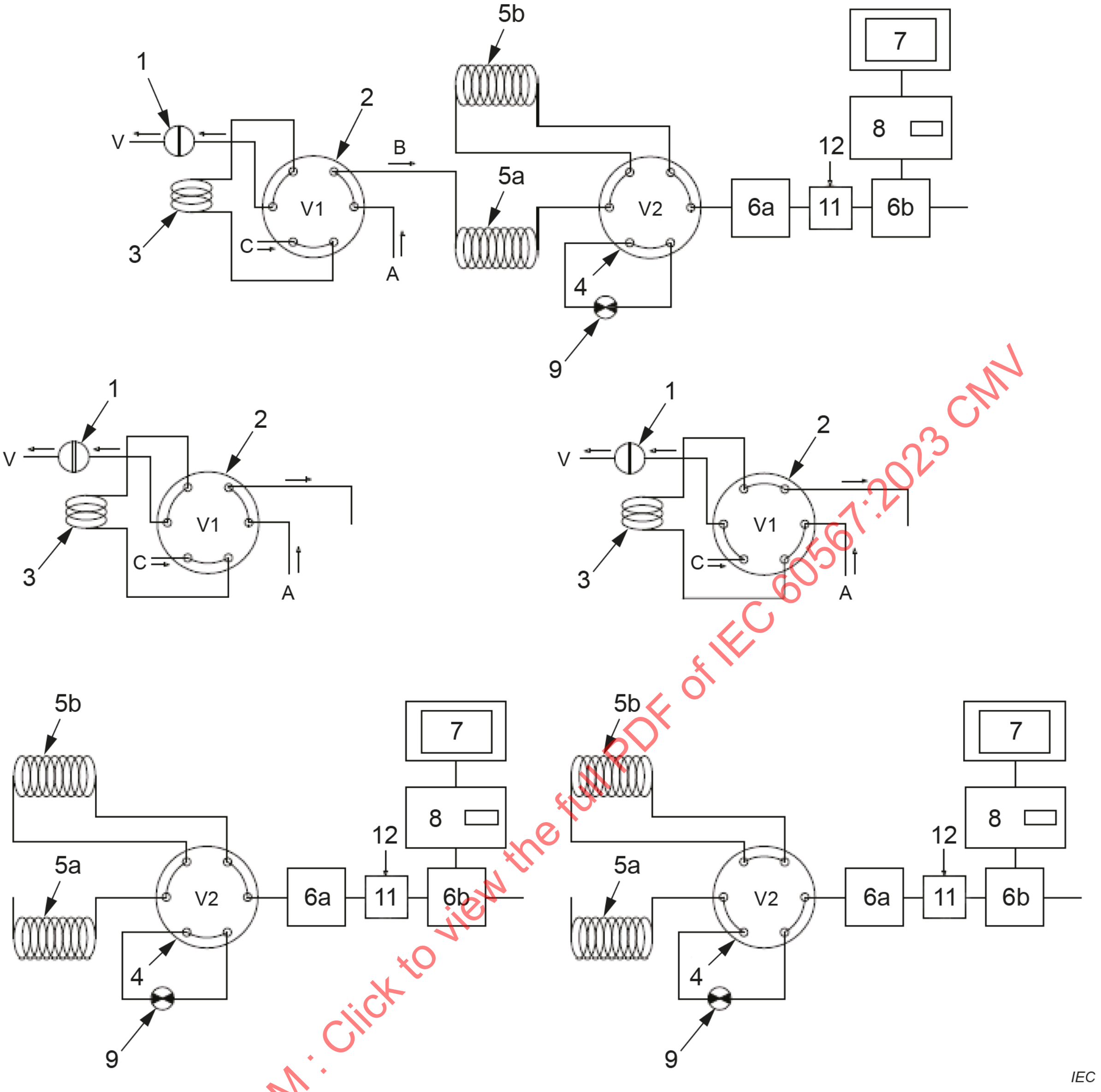
Figure 13 is an example of the layout of an instrument that has been used and found acceptable. Injection arrangements shall suit the method by which gas is transferred from gas extraction equipment into the chromatograph.

Thus, the vacuum extraction equipment described in Figure 6 and used for both Toepler pump and partial degassing methods transfers the gas via a gas sample valve and calibrated sample loop, a method recommended to improve repeatability.

Alternatively, gas samples may be transferred and injected into the chromatograph using a precision gas-tight syringe, and this latter method is generally used for gas samples from gas-collecting relays.

In the case of extraction by stripping (see Figure 9), a sampling valve is used, with the stripper inserted in place of the sample loop as shown in Figure 9 a). Arrangements where a stripper plus cold trap are used are shown in Figure 9 b).

In the case of the headspace method, the headspace accessories described in 8.5.2.2, a bypass valve, and a zero-dead volume adapter (0,53 mm ID) for the column connections are used for injecting extracted gases.



Key

Position A: Sample loop filling

1	stopcock	
2	chromatograph gas sample valve	
3	sample loop	
4	column selector valve	
5	columns	a) column 1 b) column 2
6	detectors	a) thermal conductivity b) flame ionization
7	recorder	

Position B: Injection

8	integrator
9	optional restriction valve for pressure compensation
11	methanator
12	H_2 for catalysis

A	inlet carrier gas
B	outlet carrier gas (to GC)
C	injection of gas sample
V	connection to vacuum

Figure 13 – Schematic arrangement for gas chromatography

9.3.2 Columns

In the present examples of Table 4, two columns are used with a two-way valve enabling selection between the columns.

However, the important requirement for all columns is that they should achieve good separation in as short a time as possible, while giving all elutions on a stable baseline. The columns indicated in Table 4 are given only by way of examples and other columns meeting these general requirements may be used.

In the case of the headspace method, the packed columns described in example 1 of Table 4 can be used for the routine analysis of oils; however, at low gas-in-oil concentration levels, gases shall be detected in the headspace phase at the nl/l level. This requires the use of the PLOT columns of example 2 of Table 4. At these nl/l gas levels, special care should be taken to prevent contamination and in the control of the GC detectors.

9.3.3 Carrier gas

The carrier gas is, preferably, gas chromatograph grade argon.

9.3.4 Detectors

The gases eluted from the columns are passed over a thermal conductivity detector (TCD) and a flame ionization detector (FID). A helium ionization detector (HID) can be used instead of the FID and TCD. The HID is 10 times more sensitive than the FID, using helium as a carrier gas, and does not require the use of a methanator.

9.3.5 Methanator

In the present examples, a methanator is fitted at the inlet to the flame ionization detector to improve the sensitivity with which CO and CO_2 can be detected by converting these gases to methane.

NOTE The activity of the methanator ~~may~~ can be impaired by the presence of sulphur hexafluoride (this gas is sometimes used in cable terminal boxes and ~~may~~ can diffuse into the equipment filling oil). In this case, a different analytical arrangement ~~should be~~ is used which is not described in this document.

The methanator ~~may~~ can lose some sensitivity (and the CO_2/C_2H_4 and CO/CH_4 ratios decrease) with time, but ~~may~~ can be recalibrated.

9.3.6 Cold trap

When the stripping method is used, a cold trap may be fitted at the outlet of the stripper to improve the sensitivity for hydrocarbons.

Figure 9 b) shows an example of the method of inclusion of a cold trap. A typical device used consists of a 130 mm long, 6 mm OD, stainless steel tube packed with 100/120 mesh Porapak Q® or equivalent, maintained below −54 °C in a suitable freezing mixture such as solid carbon dioxide and alcohol.

During stripping, a separate carrier gas stream circulates in the cold trap while the main carrier gas flows directly to the gas chromatograph. After stripping, a valve is switched to direct the carrier gas flow through the cold trap. Then the trap is rapidly heated to 80 °C, injecting the trapped gases onto the analytical columns.

9.3.7 Integrator and recorder

The electrical outputs from the detectors are fed to an integrator. Additionally or alternatively, a chart recorder may be used.

9.4 Preparation of apparatus

a) Set up the chromatograph and allow the flow of carrier gas and the temperature to stabilize as shown by the production of a steady baseline.

b) For the vacuum extraction methods, either inject the gas sample using a syringe or with the gas sample loop previously evacuated.

c) For the stripping method, introduce the oil sample into the stripper by means of a precision syringe.

d) For the headspace method, inject the extracted gases using accessories indicated in 9.3.1.

9.5 Analysis

See Figure 13.

A possible procedure using one chromatograph fitted with two columns, a gas-sampling valve and a methanator is given below (example 1 of Table 4).

a) Adjust the selector valve (4) (position A) to bring the Porapak® (5a) or equivalent column into use.

b) Turn the sample valve (2) to introduce the gas sample.

c) Use ~~the~~ another switch ~~(10)~~ to select the flame ionization detector (6b). The first peak to emerge will be CO converted to CH_4 by the methanator. The second peak will be CH_4. The third peak is CO_2 converted to CH_4 by the methanator, and this is followed by C_2H_4, C_2H_6 and C_2H_2.

NOTE The CO and CO_2, having been converted to CH_4 by the methanator, are detected at high sensitivity by the flame ionization detector. High concentrations of these gases ~~may~~ can well exceed the linear range of this detector. In this case, use ~~may~~ can be made of a thermal conductivity detector to evaluate the CO_2 before methanation.

d) Adjust the selector valve (4) (position B) to bring the molecular sieve column into use. Obtain a stable baseline.

e) Refill the gas sample loop according to step j) of 8.2.3.

f) Turn the sample valve (2) to introduce the gas sample.

g) Use ~~the~~ another switch ~~(10)~~ to select the thermal conductivity detector (6a). Peaks will emerge in the following order: H_2, O_2 and N_2.

h) Use ~~the~~ another switch ~~(10)~~ to select the flame ionization detector (6b). The next peak will be CH_4; the last peak to emerge will be CO converted to CH_4 by the methanator.

i) Purge any retained gases from both columns.

j) One determination per gas sample is normally sufficient.

9.6 Calibration of the chromatograph

Retention times are established by injection of dilutions of individual gases in the carrier gas into the columns. The response factors of the detectors, however, are preferably determined using a standard gas mixture diluted with the carrier gas, containing known concentrations of all gas components to be determined, in proportions resembling those found in oils from transformers. Such a standard mixture should be used periodically, depending upon the stability of the equipment. For better precision, calibration should be undertaken immediately before analysis of the oil sample.

The minimum number of standard gas mixtures ~~needed~~ for calibration of the chromatograph varies from one to three. Only one is ~~needed~~ necessary when performance of analysis equipment has been found linear (by verification of the entire system) in the concentration range of gases usually found in transformer oil.

A different standard for verification of GC detectors should be run at least once a day.

9.7 Calculations

a) Identify the gas corresponding to each peak by comparison with the chromatograms obtained during calibration.

b) Measure the area or height of each peak, note its retention time and apply the calibration data to obtain the gas volumes.

c) When dealing with analyses of gases taken from gas collecting relays, calculate the concentration of each gas in per cent by volume.

d) When dealing with analyses of gases extracted from oil, calculate the concentration in microlitres of each gas per litre of the oil from which it was extracted (or micromole of each gas per litre of oil).

Dissolved gas concentrations in the oil sample should be converted to these standard conditions (101,325 kPa and 20 °C), using the following equation:

$$C_{\mathrm{L}}^{0}(\text{corrected}) = C_{\mathrm{L}}^{0} \times (P/101{,}325) \times (293/(273+t))$$

where

C_{L}^{0} is the concentration of gases in the oil sample at ambient temperature and pressure;

t is the ambient temperature, in °C;

P is the atmospheric pressure, in kPa.

NOTE 1 1 µl/ l corresponds to one part per million (1 ppm) by volume and 0,042 µmol/l at 20 °C and 101,3 kPa.

NOTE 2 Concentrations in µmol/l can be converted to µl/l or ppm, under the standard conditions of Note 1, by multiplying by 22,4 (293/273).

NOTE 3 The total gas content of oil by volume, expressed as a percentage, in the case of partial degassing, stripping and headspace methods, can be estimated by the sum of the individual gas concentrations expressed in µl/l under the standard conditions of Note 1.

The correction for incomplete gas extraction in partial degassing method is described in Annex A.

The correction for gas bubbles in oil syringe or air gap in rigid bottles is described in Annex D.

10 Quality control

10.1 Verification of the entire analytical system

The preferred method of ensuring that the entire system (extraction and chromatography) gives stable and accurate results is by analysing a known quantity of gas-in-oil standards (containing all the gases listed in 9.1 in proportions resembling those found in oils taken from transformers) in place of an oil sample and carrying out all the procedures detailed in Clause 10.

In the case of the Toepler pump extraction method, it has been confirmed that the extraction efficiency and performance of the whole analysis equipment can be verified by the daily analysis of an air-saturated oil standard (see Annex C) and one standard gas mixture with average gas concentrations in the range usually found in transformer oil samples.

It is recommended to use at least two gas-in-oil standards, one containing low concentrations of gases (resembling oils in factory tests) and the other containing higher concentrations (resembling oils from equipment in the field) to check the quality of the results produced by the analytical system in the entire linearity range. The chromatogram peak areas or heights can then be related directly to the quantities of gases present in the oil, compensating automatically for incomplete extraction and other operational factors.

It is good practice to repeat this procedure at intervals of calibration of not more than six months or following changes in apparatus or operating conditions.

10.2 Limits of detection and quantification

The basic requirement is that the analytical system, consisting of degassing equipment and gas chromatograph, shall have adequate sensitivity for the task for which it is designed.

Not only the detection limit, but also the sensitivity, the repeatability and the accuracy of results depend on many details of the overall procedure, in particular the method of extraction and the design and method of operation of the gas chromatograph and its ancillaries.

For example, by using a methanator combined with a flame ionization detector, instead of using a thermal conductivity detector, the sensitivity and detection limit for the carbon oxides are considerably improved.

Tests on equipment in service where the dissolved gas concentration is often high do not require the same detection limits as factory tests where gas concentrations are usually very low.

In the case of headspace, extraction efficiency is low, and the concentration of gases in the extracted gas phase is typically 100 times lower than with the other extraction methods. At low gas-in-oil concentration levels, detection limits in the nl/l range in the gas phase of the headspace are therefore necessary, requiring the use of more sensitive equipment and procedures (see 8.5.3.3).

It is necessary that each laboratory determines overall procedures that will give suitable sensitivities for all gases. For guidance, experience indicates that the entire analytical system should be capable of detecting gases dissolved in oil at the concentrations indicated in Table 5.

For the analysis of gas samples taken from gas-collecting relays, a detection limit equivalent to that obtained for the analyses of gases extracted from the oil for service tests is adequate.

NOTE The limit of detection is defined as the lowest concentration that can be identified. The limit of quantification is defined as the lowest concentration that can be quantified with a reasonable precision and accuracy.

Table 5 – Required limits of detection in oil

Gases	Acceptance tests		Service tests	
	Concentrations at 20 °C			
	µl/l	µmol/l	µl/l	µmol/l
Hydrogen	2	0,08	5	0,2
Hydrocarbons	0,1	0,004	1	0,042
Carbon monoxide	5,0	0,2	25	1,0
Carbon dioxide	10	0,4	25	1,0
Oxygen	500	21	500	21
Nitrogen	2 000	84	2 000	84

10.3 Repeatability, reproducibility and accuracy

10.3.1 General remark

Repeatability (r), reproducibility (R) and accuracy are defined in detail in ISO 5725-1.

10.3.2 Repeatability

Repeatability is related to the differences that are observed when the same oil sample is analysed several times by the same laboratory over the same day or a short period of time.

Having established methods that give adequate overall detection limits, each laboratory shall confirm that these methods give adequate repeatability following the procedure described in ISO 5725-1.

For gas concentration levels greater than 10 µl/l the repeatability of a laboratory shall be considered as acceptable if the absolute difference (A – B) of two measurements A and B satisfies the following equation:

$$r = (\mathrm{A} - \mathrm{B}) < k \times (\mathrm{A} + \mathrm{B})\ /2$$

which means that the repeatability of the laboratory, at 95 % confidence limit, is lower than k times the mean concentration of the gas analysed. The k coefficient depends on the nature of the gas analysed.

A general acceptable value, calculated from an international IEC inter-laboratory test is: k = ~~0,07~~ 0,15 for concentrations > 10 µl/l and < 1 000 µl/l, and k = 0,10 for concentrations > 1 000 µl/l.

For low gas concentrations (e.g. < 10 µl/l), the required repeatability ~~is given by the following equation: $r = S$ (where S = detection limit), whatever the concentration, as deduced from the same international IEC inter-laboratory test~~ can be of the same order of magnitude of the detection limit S.

It is recommended that each laboratory checks its own individual repeatability at both concentration levels at appropriate time intervals or after major changes on its system (gas extractor and gas chromatograph). To do that, a sufficient number of analyses on multiple samples of the same oil are run within a short period of time (less than one day), then the repeatability of results r is determined according to ISO 5725-1.

10.3.3 Reproducibility

Reproducibility is related to the differences which are observed when the same oil sample is analysed by different laboratories (inter-laboratory reproducibility), or when it is analysed by the same laboratory over long periods of time (after several days, weeks or months) (intra-laboratory reproducibility).

Inter-laboratory reproducibility has been evaluated by CIGRE as around ±20 % at medium concentration levels.

It is recommended that each laboratory checks its own intra-laboratory reproducibility at different concentration levels at appropriate time intervals or after major changes on its system (gas extractor and gas chromatograph). To do that, analyse multiple samples of the same oil at regular intervals of time, for instance each week or each month over a period of several months, then determine the reproducibility of results R according to ISO 5725-1.

A good conservation of the samples is necessary between analyses. Storing the samples in a refrigerator is recommended to avoid reactions with light and oxygen present in the oil.

10.3.4 Accuracy

Accuracy is related to the differences that are observed between the values analysed by a laboratory and the true values of dissolved gases contained in the oil sample.

Inaccurate DGA results ~~may~~ can lead to wrong fault diagnoses, especially if gas ratios are close to a fault zone boundary, or to inappropriate actions on the equipment, if concentration values are close to the typical or alarm values defined in IEC 60599.

To be able to determine accuracy, the nominal values of dissolved gas concentrations have to be known. The mean of several measured values has been shown by inter-laboratory tests to be different from the nominal values. Determination of accuracy shall be carried out with gas-in-oil standards prepared according to Clause 7, or through participation to round robin tests using such standards, or with certified gas-in-oil standards prepared according to ISO 5725-1.

Examples of accuracies that can be obtained using the overall experimental procedure are given in Table 6. These values are deduced from IEC and CIGRE inter-laboratory tests made on two gas-in-oil standards (prepared according to 7.2) and involving 44 laboratories worldwide. One standard sample contained medium gas concentration levels (hydrocarbons between 9 µl/l and 60 µl/l, CO and CO_2 between 100 µl/l and 500 µl/l). The other one contained low gas concentration levels (hydrocarbons between 1 µl/l and 10 µl/l, CO and CO_2 between 30 µl/l and 100 µl/l).

It is recommended that each laboratory determines its own accuracy, which ~~may~~ can differ from the values in Table 6. To do that, analyse a gas-in-oil standard according to Clause 7, then determine the accuracy according to ISO 5725-1.

Table 6 – Examples of accuracy of extraction methods

	Accuracy, in percentage of the nominal value	
Extraction procedure	**Medium concentration**	**Low concentration**
Toepler	13	35
Partial degassing	13	30
Stripping	18	23
Headspace	18	37
Mercury-free Toepler	15[a]	14[a]
Mercury-free partial degassing	11[a]	
Shake test	15	44
[a] Based on a limited number of analyses.		

The preparation of oil standards saturated with air is described in Annex C.

The procedure for comparing gas monitor readings to laboratory results is described in Annex E.

11 Report of results

The report for DGA shall include

- a reference to this document;
- information on the gas or oil sample (see Clause 5 of this document or IEC 60475:~~2011~~2022, 4.4, respectively);
- the sampling procedure used (e.g. syringe, bottle) (see Clause 4 of this document and IEC 60475:~~2011~~2022, Clause 4, respectively);
  - the extraction procedure used (e.g. Toepler, headspace) (see Clause 8 and Annex B);

  - for headspace analysis, reference for the Ostwald coefficients used in case of calibration with gas standards (see 8.5.4.3);
- the detection limits for each gas with the analysis procedure used (see 10.2);
- for each gas analysed, the results in µl/l or in µmol/l (see 9.7).

NOTE 1 When available, it ~~may~~ can be useful for diagnosis purposes to indicate the average accuracies obtained by the laboratory at these gas levels with the analysis procedure used (see 10.3.4).

NOTE 2 Guidelines for drafting the report in terms of quality assurance can be found in ISO/IEC 17025.

Annex A
(informative)

Correction for incomplete gas extraction in partial degassing method by calculation

From the chromatogram, the sample oil volume, the calculated total volume of gas extracted and the volume of the aliquot of gas passed into the chromatograph, determine the apparent volume concentration C_i of each component gas extracted from the oil.

Calculate the equilibrium extraction efficiency for each component gas from

$$E_i = 1/(1 + a_i V_0/V_t)$$

where

E_i is the extraction efficiency for component i;

V_0 is the volume of the oil sample, in ml;

V_t is the total expansion volume, in ml (see 8.3.3);

a_i is the Ostwald solubility coefficient of component i.

Examples of solubility coefficients for typical mineral oils of 2006 are shown in Table A.1. Values in more recent types of oils can differ significantly.

Table A.1 – Examples of solubility coefficients a_i (at 25 °C) reported by CIGRE TF D1.01.15 in 2006

Gas	Mineral oils	Natural esters	Synthetic esters	Silicone oils
Hydrogen	0,055 6	0,047 0	0,051 0	0,092 4
Nitrogen	0,090 7	0,072 8	0,087 2	0,157
Carbon monoxide	0,132	0,111	0,127	0,204
Oxygen	0,172	0,134	0,152	0,266
Methane	0,429	0,341	0,381	0,569
Carbon dioxide	1,09	1,54	2,05	1,63
Acetylene	1,24	2,68	4,38	2,04
Ethylene	1,84	1,69	1,87	2,18
Ethane	2,82	2,16	2,19	3,10

The data given in Table A.1 represent mean values obtained by bubbling the pure gases in some of the current types of transformer oils.

The actual data on specific types of oils ~~may~~ can differ a little from these figures.

~~The data given in the above table represent mean values obtained on some of the current types of transformer oils. The actual data may differ a little from these figures.~~

Calculate the corrected volume concentration of each gas in the oil from:

$$C_i \text{ (corrected)} = C_i \text{ (apparent)}/E_i$$

NOTE 1 Solubility coefficients are functions of temperature and of oil density.

NOTE 2 Instead of correcting for incomplete gas extraction by calculation, calibration of the partial degassing method with several gas-in-oil standards at different concentration levels ~~may~~ can be used.

~~NOTE 3 When using the partial degassing method, the measurement of total gas content may need to be corrected (by a factor of up to 60 %) in order to take into account the vapour pressure of water, which depends on the water content in oil.~~

~~Annex B~~
~~(informative)~~

~~Mercury-free and shake test versions of the standard extraction methods~~

~~A mercury-free version of the Toepler method is available commercially. In this equipment, mechanical pistons are used instead of the mercury piston to extract the dissolved gases and recompress them.~~

~~A typical schematic representation of this equipment is indicated in Figure B.1a. Some versions can be automated with an oil sample carousel so that large numbers of samples can be injected and analysed on a 24 h basis with unattended operation.~~

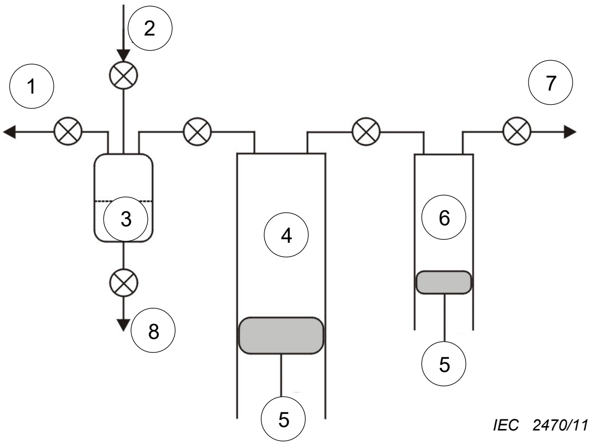
~~A mercury-free version of the partial degassing method is available commercially. In this equipment, mechanical pistons are used instead of the mercury piston to extract the dissolved gases and recompress them.~~

~~A typical schematic representation of this equipment is indicated in Figure B.1b.~~

~~A simplified version of the headspace method is available commercially (the so-called “shake-test” method). In this version, an oil sample (90 ml) is introduced in a 100 ml precision glass syringe rather than in a glass vial. 10 ml of air are then introduced in the syringe. The syringe is shaken vigorously by hand to extract the dissolved gases. Equilibrium is reached in less than 2 min because of the high shaking efficiency. An aliquot of the extracted gases is then injected in a portable chromatograph for on-site analysis, or in a standard laboratory chromatograph. A typical schematic representation of this equipment is indicated in Figure B.1d.~~

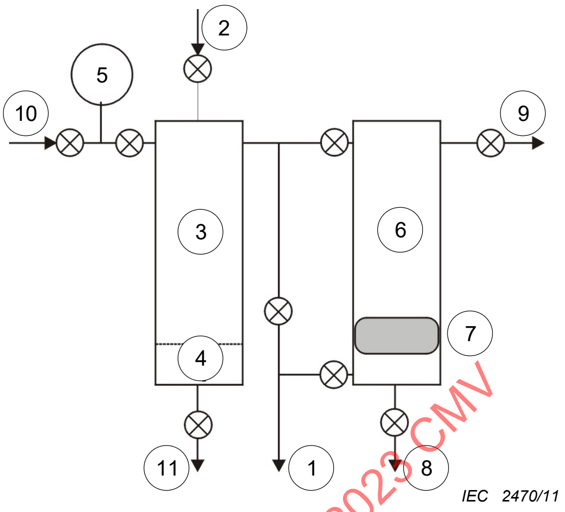
~~Examples of accuracies that can be obtained using these methods are given in Table 6.~~

~~These values are deduced from inter-laboratory tests made on two gas-in-oil standards prepared as in 9.3 and involving 10 laboratories world wide (2 for mercury-free Toepler, 1 for mercury-free partial degassing, and 7 for the shake test).~~



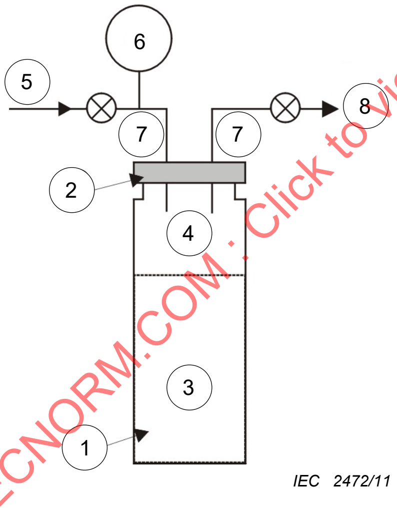
Key
1 vacuum pump
2 oil inlet
3 oil sample
4 gas extraction chamber
5 piston
6 gas compression chamber
7 to GC injection loop and detectors
8 oil purge

Figure B.1a – Mercury-free Toepler



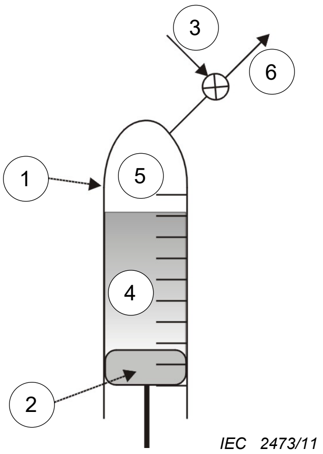
Key
1 vacuum pump
2 oil inlet
3 gas extraction chamber (glass)
4 oil sample
5 pressure gauge
6 gas compression chamber (glass)
7 piston
8 atmospheric air
9 to GC injection loop and detectors
10 calibration gas
11 oil purge

Figure B.1b – Mercury-free partial degassing



Key
1 vial
2 septum
3 oil sample
4 gas phase (Ar or He)
5 carrier gas (Ar or He)
6 pressurization gauge
7 needle
8 to GC injection loop and detectors

Figure B.1c – Headspace



Key
1 precision syringe
2 piston
3 oil/air inlet
4 oil sample
5 gas phase (air)
6 to GC injection loop and detectors

Figure B.1d – Shake test

~~Figure B.1 – Schematic representation of methods in Annex B~~

Annex B

(informative)

Alternative gas extraction methods 2

B.1 Mercury-free versions of the vacuum extraction methods

B.1.1 Mercury-free version of the Toepler method

In the equipment used in the mercury-free version of the Toepler method, mechanical pistons are used instead of the mercury piston to extract the dissolved gases and recompress them.

A typical schematic representation of this equipment is indicated in Figure B.1.

B.1.2 Mercury-free version of the partial degassing method

B.1.2.1 In the equipment used in the mercury-free version of the partial degassing method, mechanical pistons are used instead of the mercury piston to extract the dissolved gases and recompress them.

A typical schematic representation of this equipment is indicated in Figure B.2.

The procedure used is the following.

B.1.2.2 Rinse with the analysed oil by opening valve 2 under vacuum through the built-in sintered filter. Then drain the rinsing oil through valve 11.

B.1.2.3 Evacuate the whole apparatus with the vacuum pump during 15 min.

B.1.2.4 Slowly suck the oil sample over the sintered filter by opening valve 2, until a pressure of 500 Pa to 600 Pa is reached.

B.1.2.5 Open valve 8 to push the mechanical piston up to a pressure of 18 kPa. Open valve 9 to transfer the compressed gas to the transfer line of the GC. The low pressure injection valve is connected to a vacuum pump to allow further pressure reduction to a defined value, at which injection in the GC takes place.

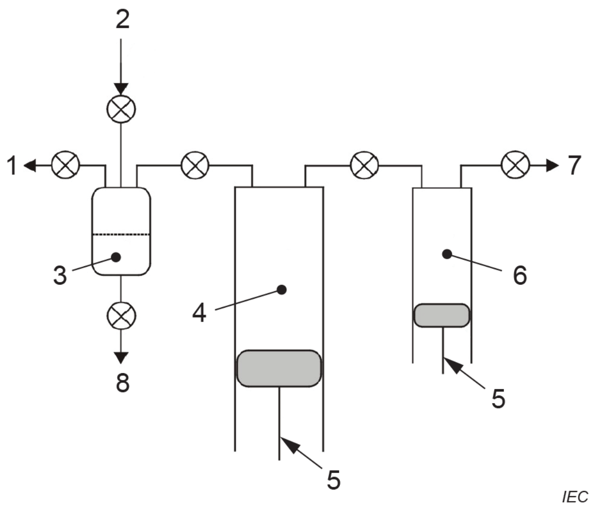
The total gas content is calculated according to gas laws.

Correction for incomplete gas extraction should be made as indicated in Annex A.

B.2 Syringe versions of the headspace method

B.2.1 Shake test method

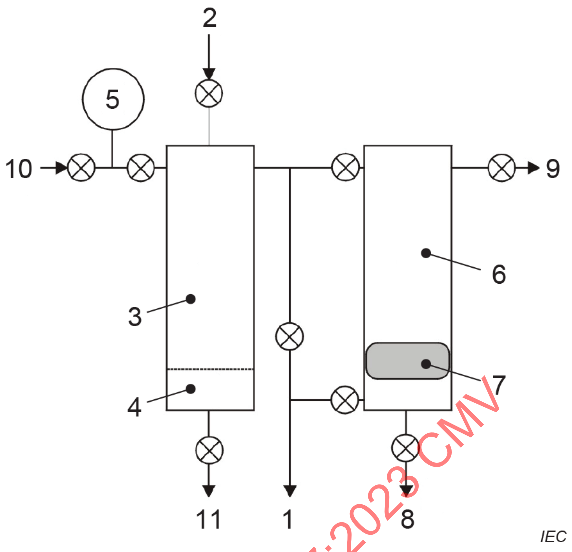
In this version, an oil sample (90 ml) is introduced in a 100 ml precision glass syringe rather than in a glass vial. 10 ml of air are then introduced in the syringe. The syringe is shaken vigorously by hand to extract the dissolved gases. Equilibrium is reached in less than 2 min because of the high shaking efficiency. An aliquot of the extracted gases is then injected in a portable chromatograph for on-site analysis, or in a standard laboratory chromatograph. A typical schematic representation of this equipment is indicated in Figure B.3.



Key

1	vacuum pump
2	oil inlet
3	oil sample
4	gas extraction chamber
5	piston
6	gas compression chamber
7	to GC injection loop and detectors
8	oil purge

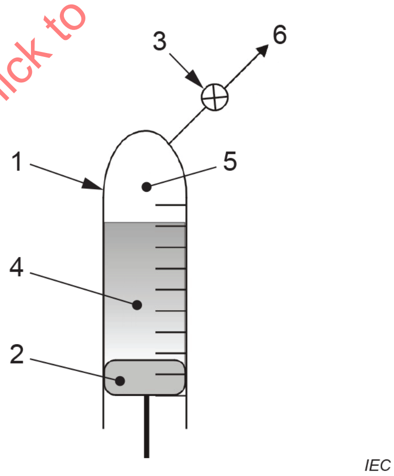
Figure B.1 – Schematic representation of mercury-free Toepler method



Key

1	vacuum pump
2	oil inlet
3	gas extraction chamber (glass)
4	oil sample
5	pressure gauge
6	gas compression chamber (glass)
7	piston
8	atmospheric air
9	to GC injection loop and detectors
10	calibration gas
11	oil purge

Figure B.2 – Schematic representation of mercury-free partial degassing method



Key

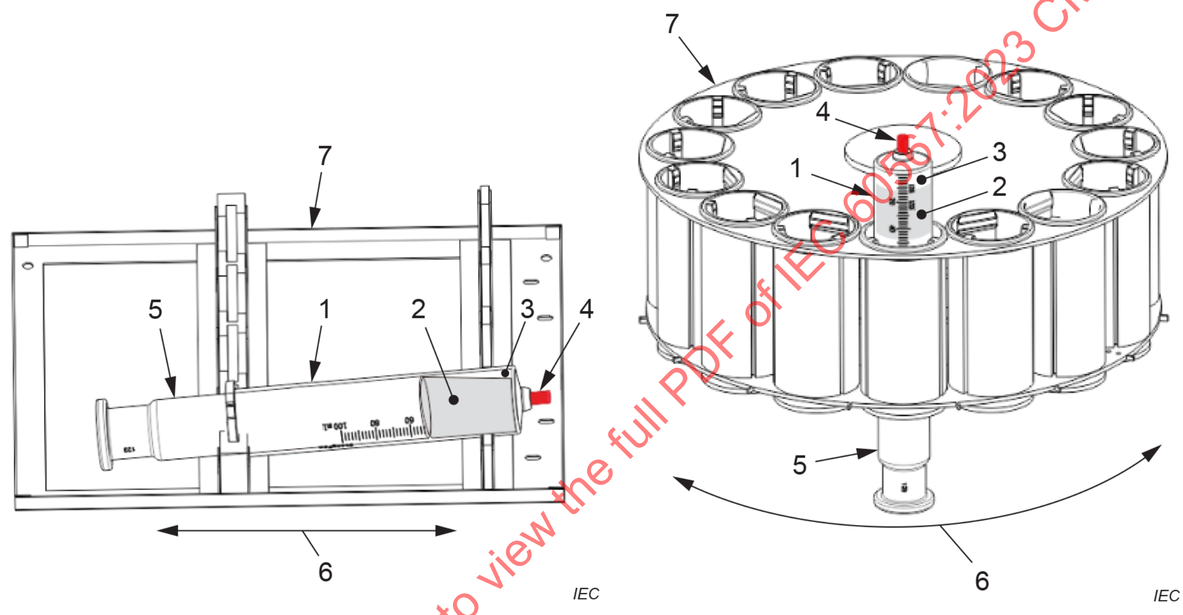
1	precision syringe
2	piston
3	oil/air inlet
4	oil sample
5	gas phase (air)
6	to GC injection loop and detectors

Figure B.3 – Schematic representation of shake test method

B.2.2 Mechanical oscillation method

The mechanical oscillation degassing method uses a piston syringe whose volume can be adjusted according to the ambient atmospheric pressure. It simplifies the operation steps of filling the sample bottle with carrier gas in advance when using vials to prepare the oil sample bottle for oil analysis. Since both sample degassing and sample gas transfer are carried out at atmospheric pressure, no additional monitoring and correction of the pressure in the degassing container is necessary.

A typical schematic representation of this equipment is shown in Figure B.4 a) and Figure B.4 b). Figure B.4 a) is applied to the scene where manual sample gas transfer is required, and Figure B.4 b) is applied to the scene where instrument automation is used for sample gas transfer and analysis.



a) Manual gas transfer mode **b) Automatic gas transfer mode**

Key

1	precision syringe
2	oil sample
3	gas phase (Ar or N_2)
4	rubber cap
5	movable core of syringe
6	oscillation direction
7	oscillating sample disc

Figure B.4 – Schematic representations of mechanical oscillation method

Examples of accuracies that can be obtained using these methods are given in Table 6.

These values are deduced from inter-laboratory tests made in 2006 on two gas-in-oil standards prepared as in 10.3 and involving 10 laboratories worldwide (two for the mercury-free Toepler method, one for the mercury-free partial degassing method, and seven for the shake test).

Annex C
(informative)

Preparation of air-saturated standards

Keep a batch of new transformer mineral or non-mineral oil in an open container at room temperature for at least one week. Measure the oxygen and nitrogen content in the oil, using any one of the gas extraction methods, then the air content of the oil at saturation.

The gas extraction equipment is checked with this air-saturated oil standard (see 10.1) and found correct if the average total gas content measured corresponds to the value measured for this type of oil, with a standard deviation of 3 %.

The gas extractor and the gas chromatograph are checked by the retention times and concentrations of O_2, N_2 and CO_2 in this air-saturated oil standard. All three retention times should be in accordance with those obtained with gas standard mixtures.

The solubility of air in oil at saturation depends on the atmospheric pressure and temperature and on the type of oil used. Examples of solubility values of air for different types of oils, as reported by CIGRE TF D1.01.15 in 2006, are indicated in Table C.1.

Table C.1 – Examples of solubility values of air for different oil types

Fluid	Density at 20 °C	µl/l at 20 °C			
		O_2	N_2	CO_2	Air
Mineral oil 1	0,851 8	29 980	65 320	569	95 869
Mineral oil 2	0,888 2	32 080	61 780	537	94 397
Natural ester 1	0,921 0	21 995	49 613	647	72 255
Natural ester 2	0,915 8	24 507	50 177	625	75 309
Synthetic ester	0,919 7	21 705	45 269	555	67 529
Silicone oil	0,964 5	54 938	113 078	763	168 779

Examples of variations with temperature of the solubility of oxygen and nitrogen in a mineral oil as reported by CIGRE TF D1.01.15 are given in Table C.2.

Table C.2 – Examples of temperature variations for oxygen and nitrogen solubility in mineral oil

Temperature °C	O_2	N_2
13	32 937	62 798
21,5	32 750	63 728
25	32 483	64 061
50	31 465	66 141

Annex D
(informative)

Correction for gas bubbles in syringes and air gap in rigid bottles

It has been found by CIGRE TF D1.01.15 that gas bubbles are observed in oil in about 20 % of syringes on average (this value ~~may~~ can be lower or higher depending on the experience of samplers).

When using the Toepler, partial degassing and stripping methods, the bubble is introduced into the extraction vessel (see 8.2.3, item e), Note 1), and no correction is necessary. When using the headspace method, the bubble should not be introduced in the vial, and a correction for the gases having migrated into the bubble should be made as indicated in 9.7.

In glass or rigid metal bottles, the air gap volume used as an oil expansion device is about 2 ml to 5 ml depending on the size of the bottle (1 l or 2 l). A correction for the gases having migrated into the air gap should also be made as indicated in 9.7.

The following equation can be used for that purpose, for each gas measured:

$$C_\mathrm{C} = C_\mathrm{m}\ (1 + V_\mathrm{G}\ /\ (kV_\mathrm{L} + V_\mathrm{G}))$$

where

C_C is the corrected concentration, in µl/l;

C_m is the measured concentration, in µl/l;

V_G is the volume of bubble in the syringe, or volume of air gap in the glass bottle, in ml;

V_L is the volume of oil in the syringe or glass bottle, in ml;

k is the Ostwald (solubility) coefficient.

NOTE In general, the corrections (10 % to 5 %) are significant only for the less soluble gases (H_2, CO).

Annex E
(informative)

Procedure for comparing gas monitor readings to laboratory results

Gas monitors (installed on-line on electrical equipment in service or used as portable instruments) are increasingly used in industry. In some cases, monitors readings do not quite agree with laboratory results for the same equipment, and it is not possible to know for sure which is right, monitors readings or laboratory results.

The following procedure has been developed by CIGRE TF 15 to make such an evaluation (see CIGRE TB 409).

- Purchase a sample of gas-in-oil standard from an appropriate vendor, or prepare one according to IEC 60567 (this document) or ASTM D3612.
- Take a reading on one or several on-line gas monitors installed on transformers in service.
- Take four duplicate samples of oil from the sampling point of the monitor(s), immediately after having taken the reading.
- For portable gas monitors, take five duplicate samples of oil from a transformer. Using one of the five samples, take a reading of the portable monitor.
- Send all the above samples of oil to the DGA laboratory.
- Analyse all samples on the same day (or over no more than a few days), using the same analytical equipment for all samples.
- Convert all DGA results and monitor readings to the same units (IEC or STP µl/l).
- Calculate the bias of the laboratory by comparing its results for the gas-in-oil standard sample to what was actually prepared.
- Correct all other DGA laboratory results using the bias calculated above.
- Calculate the average values (A) of each set of four duplicate samples, in µl/l.
- Calculate the repeatability (R) of laboratory results as the difference between results for the individual four samples and average values (A), and express it as a percentage.
- Calculate the difference (D) between gas monitor readings and average values (A), and express it as a percentage.
- The maximum accuracy of the gas monitor as measured by the laboratory is ($D – R – 2$), in per cent, where 2 % is the uncertainty on the gas-in-oil standard.

For example, if

- gas-in-oil standard S = 100 µl/l, laboratory result for S = 90 µl/l;
- laboratory results for four duplicate samples = 250 µl/l, 230 µl/l, 210 µl/l, 240 µl/l;
- laboratory results corrected for bias = 275 µl/l, 253 µl/l, 231 µl/l, 264 µl/l;
- average value (A) = 256 µl/l, repeatability (R) = 9 %;
- monitor reading = 300 µl/l, difference (D) = +17 %;
- maximum accuracy of gas monitor = (17 – 9 – 2) = +6 %.

Annex F
(normative)

Insulating liquids based on synthetic and natural esters and silicones 3

The general methods used for mineral oils in Clause 6 to Clause 11 apply to insulating liquids based on synthetic and natural esters and silicones (thereafter called "liquids"), with the following differences:

- in 8.2 (Toepler pump method), and 8.3 (partial degassing method), exposure to vacuum is up to 10 min for the liquids, depending on their viscosity, as compared to 3 min for mineral oils. Calculation of the correction for incomplete extraction of the partial degassing method is indicated in Annex A, using the Ostwald coefficients of the liquids indicated in Table A.1, or more precise values if available.
- in 8.2.3 k) (Toepler pump method), and 8.3 (partial degassing method), the total volume of (gas + water vapour) V_{gw} extracted from mineral oil and the liquids is measured directly in the burette. With mineral oil, the amount of water vapour extracted V_w is negligible. With an ester liquid, the amounts of moisture in the ester liquid and of water vapour extracted from the ester liquid V_w are large and calculated. The actual total volume of gas V_g can then be calculated as $V_g = (V_{gw} - V_w)$.
- in Annex B (mercury-free partial degassing method, described in Figure B.2), the total volume of (gas + water vapour) V_{gw} extracted from the ester liquid can be deduced indirectly from the increase in pressure in the vacuum vessel.

In the above vacuum methods, in the case of ester liquids with large amounts of dissolved water, values of V_w, V_{gw} and V_g are calculated as follows:

Calculation of the volume of (water vapour) V_w extracted from the ester liquid:

v	is the volume of ester liquid introduced, in ml;
d	is the density of ester liquid;
W_1	is the mass of water in the ester liquid before being subjected to vacuum, measured by KF or another device, in ppm ($W_1 \times 10^{-6}$ in g/g);
W_2	is the mass of water in the ester liquid after being subjected to vacuum, measured by KF or another device, in ppm ($W_2 \times 10^{-6}$ in g/g);
m	is the mass of water vapour extracted from the ester liquid by vacuum = $(W_1 - W_2)10^{-6}$ vd, in g.

Water vapour and individual gases extracted from the ester liquid can also be measured simultaneously with the HID detector described in 9.3.4.

n_w	is the number of moles of water vapour extracted from the ester liquid = m/18;
V_w	is the volume of water vapour extracted from the ester liquid = $n_w \times 22\,400$, in ml.

Calculation of the volume of (gas + water vapour) V_{gw} extracted from the ester liquid, using gas law $PV = n\mathrm{R}T$, where:

P	is the pressure increase in the pressure gauge, in mbar (1 mbar = 101 kPa), due to the (gas + water vapour) extracted;
V	is the volume of the vacuum chamber with ester liquid, in ml = $(V_1 - V_2)$;
V_1	is the volume of the vacuum chamber without ester liquid, in ml;
V_2	is the volume of ester liquid introduced in the vacuum chamber, in ml;
R	is a gas constant = 83 144, in mbar, ml;
T	is the temperature in K;

n = n_{gw} is the number of moles of (gas + water vapour) extracted = $(P (V_1 - V_2) / RT)$;

V_{gw} is the volume of (gas + water vapour) extracted = $n_{gw} \times 22\,400$, in ml;

V_g is the volume of gas extracted = $(V_{gw} - V_w)$, in ml.

– in 8.5.4 (headspace method), calibration of the headspace extractor with gas-in-oil standards (GIOS) or gas-in-liquid standards (GILS) is the preferred method of calibration recommended for both mineral oils and the liquids. Calibration with gas standards, although not forbidden, is not recommended. The same recommendation is made in CIGRE TB 783-2019.

Each laboratory should preferably calculate its own calibration curves and partition coefficients, using GIOS or GILS. Home-made GIOS or GILS prepared in accordance with 7.3, and NIST-traceable commercial GIOS or GILS prepared by weight, both qualify as analytical chemistry standards.

They should be prepared in the same type of oil or liquid as the unknown oil or liquid sample, and they should contain similar amounts of air or nitrogen (near saturation or at partial saturation), similar individual gas concentrations (low or high), and similar moisture contents in the case of ester liquids.

Bibliography

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I. Hoehlein-Atanasova and C. Schutt, "Gas-In-Oil Analysis and Evaluation Criteria for Synthetic Esters in Offshore and Traction Transformers", IEEE-EI Magazine, 36, 6, pp.32-36, 2020

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J. Jalbert, R. Gilbert and P. Tetrault, "Simultaneous Determination of Dissolved Gases and Moisture in Mineral Insulating Oils by Static Headspace Gas Chromatography with Helium Photoionization Pulsed Discharge Detection, Analytical Chemistry, 73, 4, pp.3382-3391, 2001

List of comments

1 Insulating liquids based on natural and synthetic esters are increasingly used in wind turbine, traction and distribution transformers, because they are less flammable than mineral oils and less damaging to the environment in case of spills. When faults occur in these transformers, gases are formed that can be used to detect these faults and prevent costly failures.

In 2021, IEC 60599 on the interpretation of gases dissolved in transformer liquids was revised to include the amounts of gases considered as acceptable in service in these specific pieces of equipment. In 2022, National Committees of IEC TC 10 decided to also revise IEC 60567, on the laboratory analysis of gases dissolved in transformer oils, in order to include the analysis in ester liquids in a separate part of this Standard, to make sure that the results in ester liquids provided by laboratories are accurate and reliable.

Comments on the specific changes made to IEC 60567 are indicated on pages 58 (Annex B) and 64 (Annex F) of this new Standard.

Future revision of IEC 60567 is recommended to evaluate the reliability of its second method of preparation of gas-in-oil standards, using syringes or vials, for the calibration of the headspace method of gas extraction applied to the large number of different ester liquids on the market today.

2 Informative Annex B has been revised to include a more precise procedure for the mercury-free version of the partial degassing method, used under differential pressure vacuum.

The mechanical oscillation version of the shake test method, widely used in China, has also been included in Annex B.

3 New normative Annex F contains detailed calculations taking into account the much larger amounts of water dissolved in ester liquids than in mineral oils when using the vacuum extraction methods.

Preparation of gas-in-ester standards remains the preferred method of calibration when using the headspace method of gas extraction from ester liquids.

IEC 60567

Edition 5.0 2023-12

INTERNATIONAL STANDARD

NORME INTERNATIONALE

colour inside

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

IEC 60567:2023-12(en-fr)

CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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

FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as "IEC Publication(s)"). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.

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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;

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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. The main document types developed by IEC are described in greater detail at www.iec.ch/publications.

The committee has decided that the contents of this document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn, or
- revised.

IMPORTANT – The "colour inside" logo on the cover page of this document indicates that it contains colours which are considered to be useful for the correct understanding of its contents. Users should therefore print this document using a colour printer.

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:

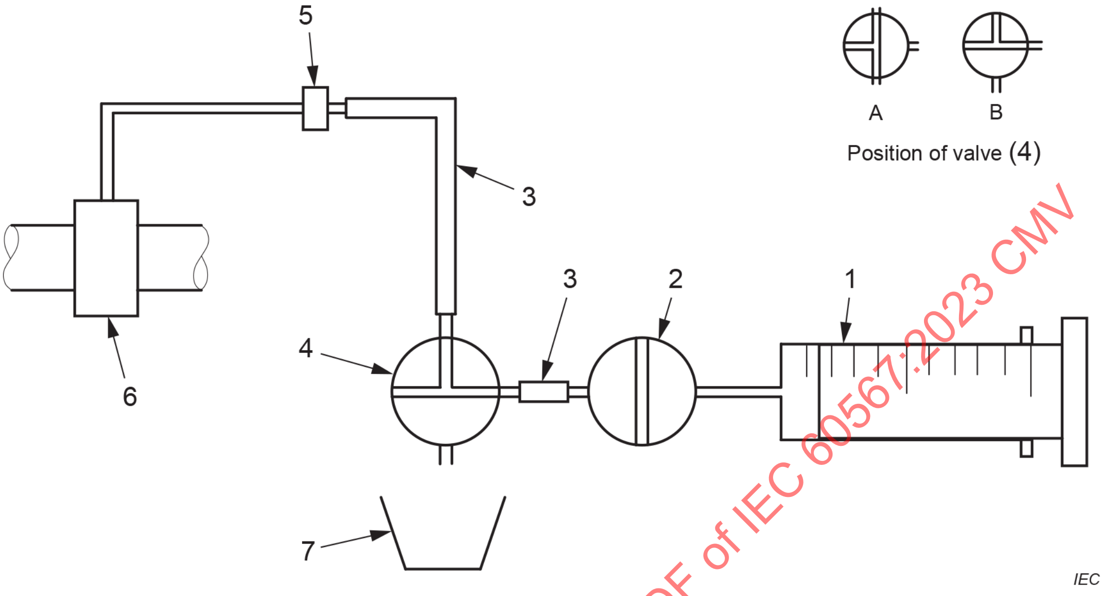
a) Impermeable oil-resistant plastic or rubber tubing (3) provided with a connector to fit onto a suitable sampling connection of the gas-collecting relay. To avoid cross-contamination, the tubing should be used only once.

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

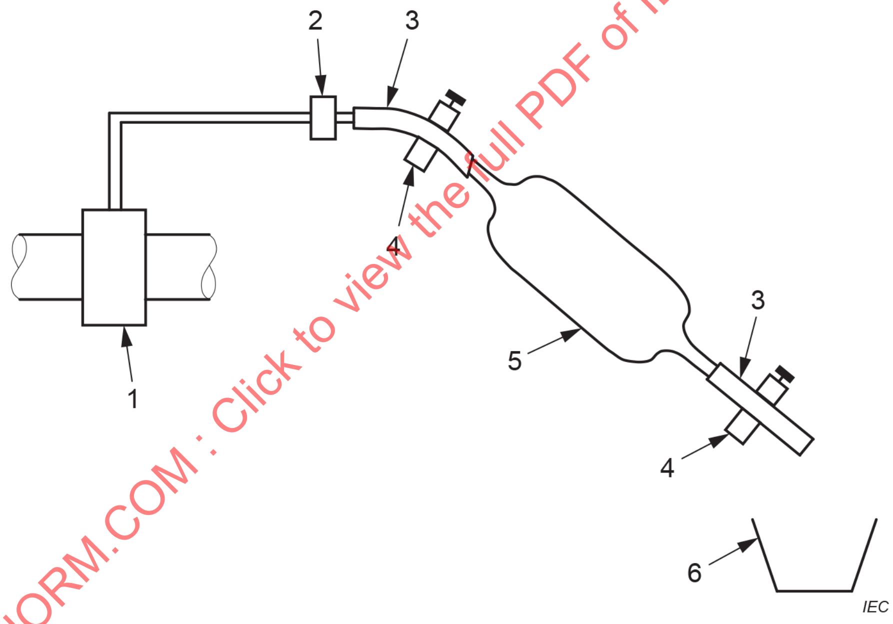
This method is reliable only where the gas sample is at or above atmospheric pressure. The apparatus is shown in Figure 2.

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

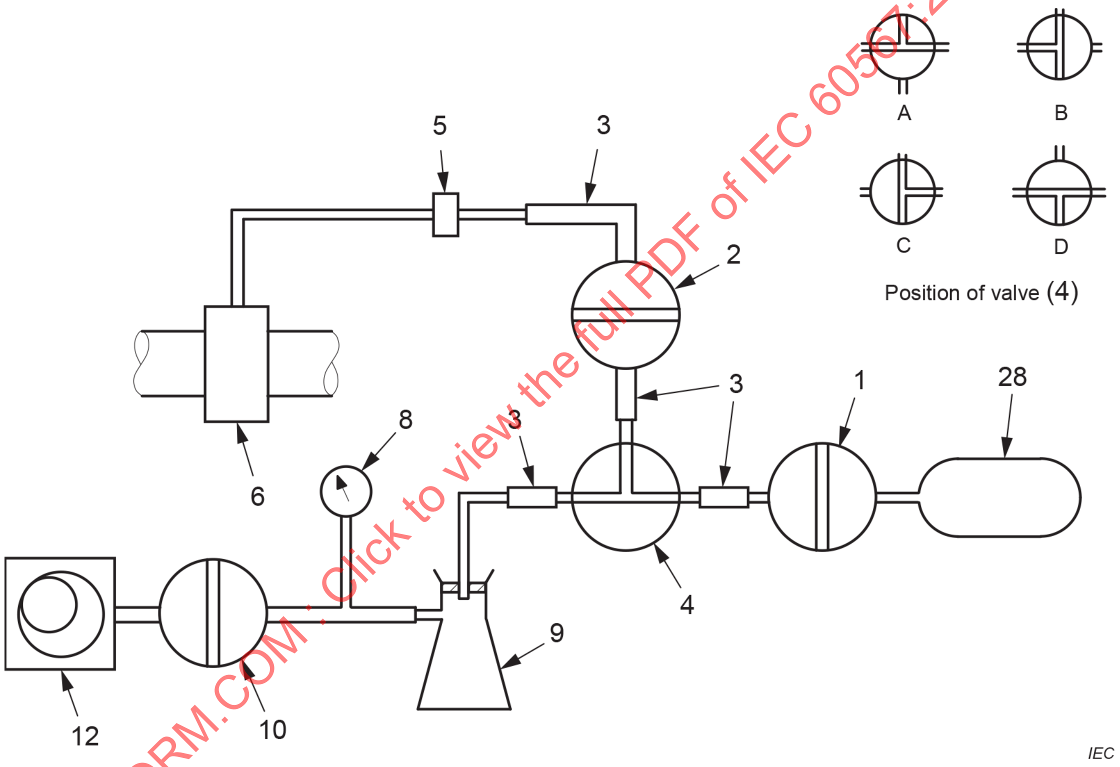
4.4 Sampling of free gases by vacuum

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.



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	
Oil	
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.

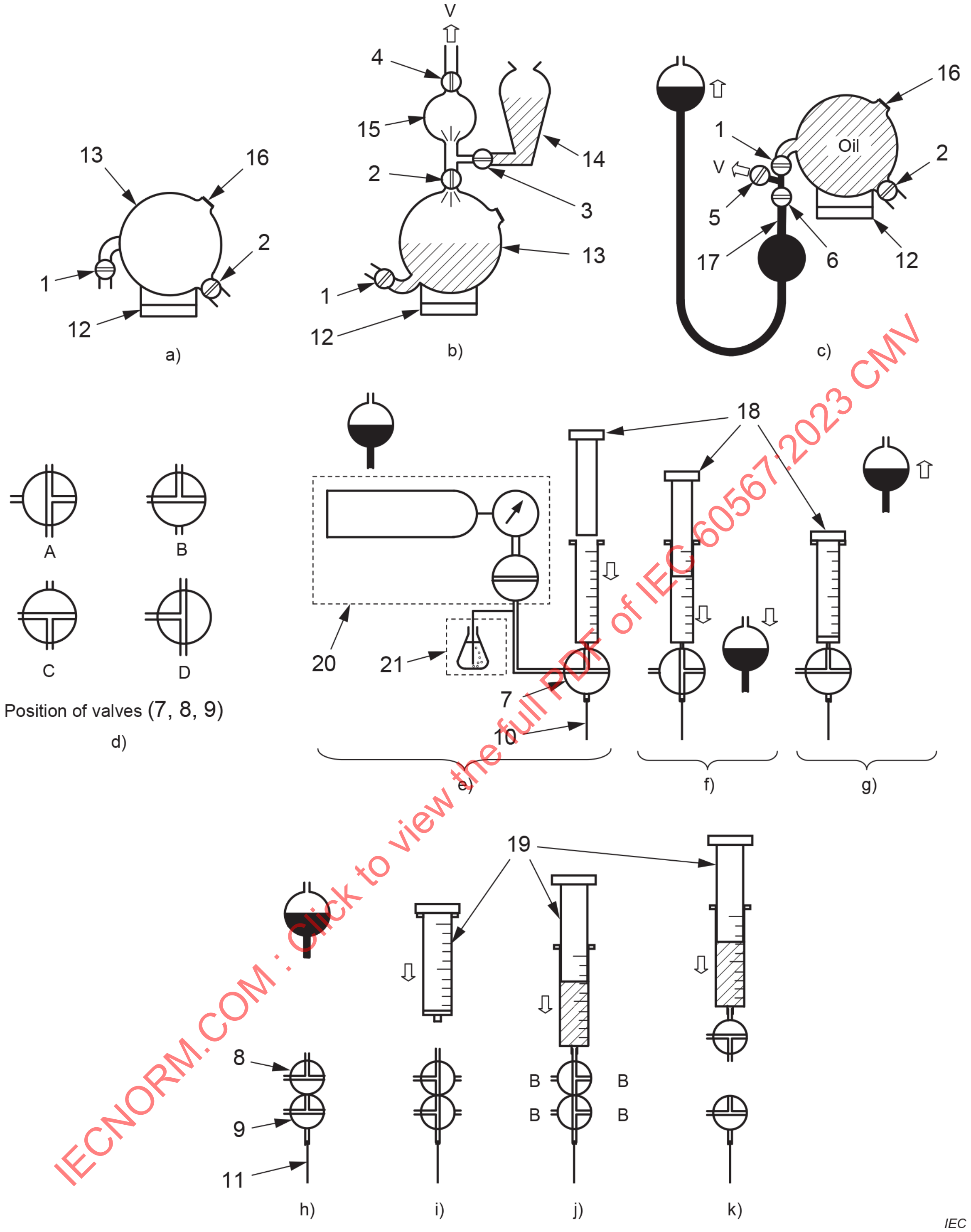
d) Adapt the oil reservoir (14), the splash bulb (15) and stopcocks (4) to the 5 l vessel (13). Connect the system to the vacuum pump (V) and evacuate the splash bulb (15) and the 5 l oil vessel (13) by opening stopcocks (2) and (4).

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).



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:

$$C_\mathrm{i} = V_\mathrm{i} / V \times 10^6$$

where

C_i is the concentration of gas "i", in µl/l;

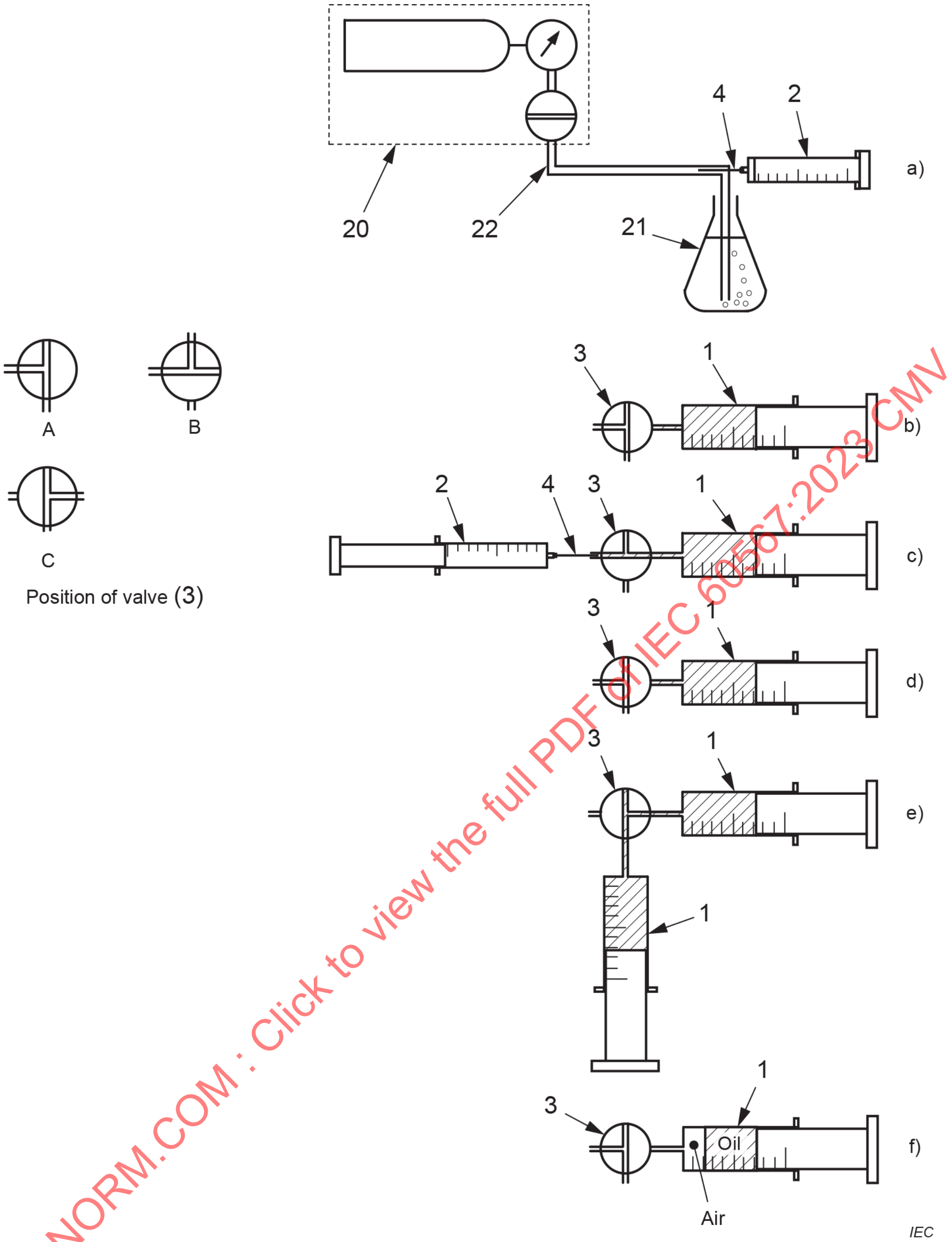
V_i is the volume of gas "i" injected, corrected to 20 °C and 101,3 kPa in ml;

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).



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_2 and 2 000 µl/l N_2 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_2-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.

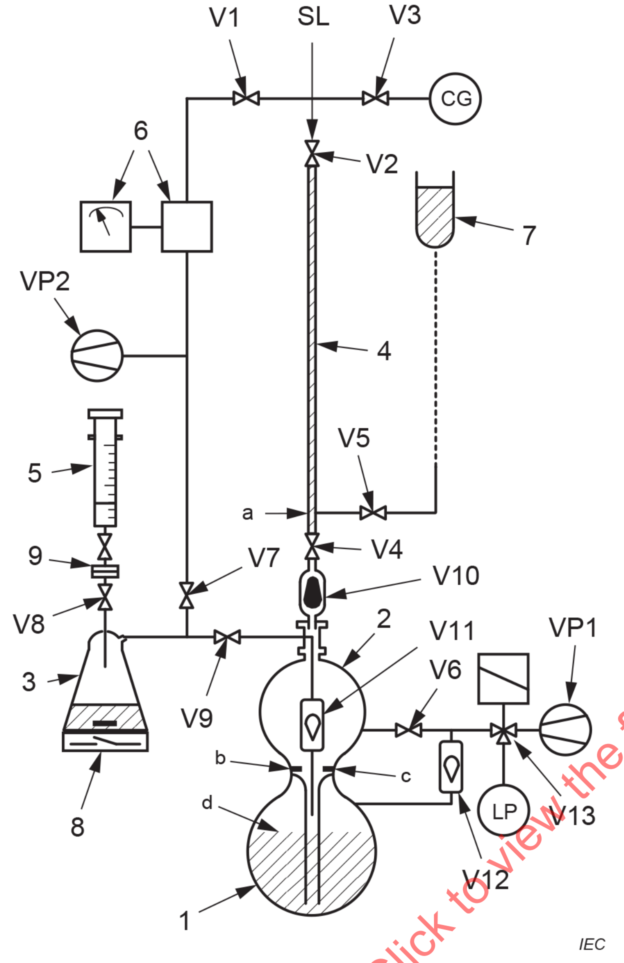
Since the detailed design of this apparatus is not standardized, it is necessary to establish an operation that will ensure adequate extraction of all components of the dissolved gas. The main parameters to be established are the number of degassing cycles (strokes) of the Toepler pump that should be 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.

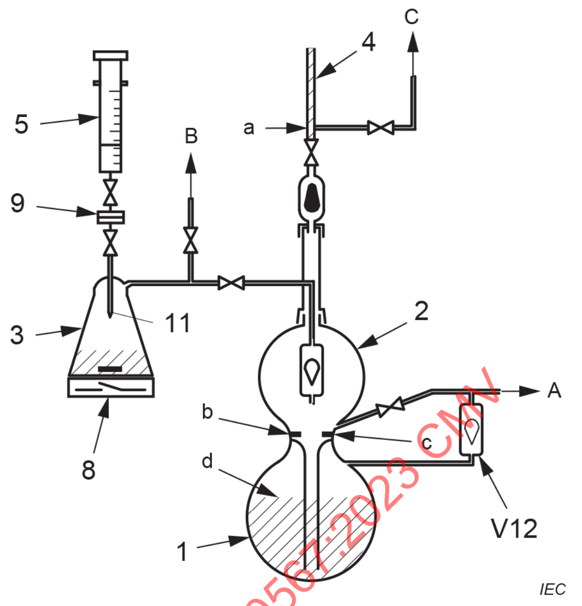
Degas successive standards until a number of cycles of the Toepler pump, together with a degassing time on each stroke, has been established so that the area or height of each peak on the chromatogram of the extracted gases is within 95 % of the area or height of that peak on the chromatogram of the 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).

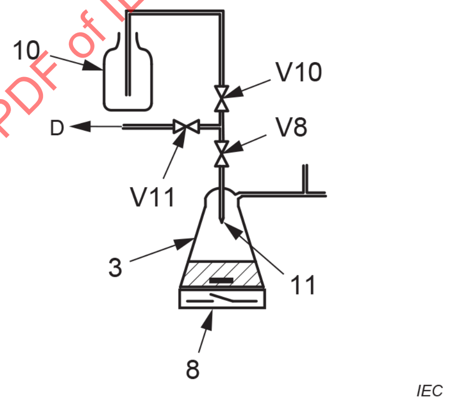
The above procedure serves to establish a routine of operation, which will apply until any major changes are made to the equipment and will also apply to other equipment of the same design. It is recommended that the overall calibration of the complete equipment (degassing equipment plus chromatograph) 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.



a) General view of a Toepler pump extraction apparatus



b) Recommended volumes of several parts of a Toepler pump



c) Example of oil introduction by bottle

Key

1	mercury reservoir – 2 l
2	gas collection flask – 1 l
3	degassing flask – 250 ml or 500 ml
4	gas-collecting burette – 25 ml (0,05 ml divisions)
5	introduction of oil sample via syringe
6	Pirani vacuum gauge
7	mercury-levelling vessel
8	magnetic stirrer
9	septum
10	oil-sampling bottle
11	jet

V1 to V11	hand stopcocks
V10 to V12	non-return valves
V13	electromagnetic three-way valve
VP1	rough vacuum pump
VP2	main vacuum pump
LP	connection to low pressure air (±110 kPa)
SL	connection to GC sample loop
CG	connection to calibration gas cylinder
a b c	electrical contacts
d	mercury level mark on tube
A	connection to rough vacuum pump and air
B	connection to main vacuum pump
C	connection to mercury-levelling vessel
D	connection to waste oil reservoir and rough vacuum pump

[a] 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 µl/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:

a) 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.

b) 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.

c) 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.

d) 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.

e) 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.

f) 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.

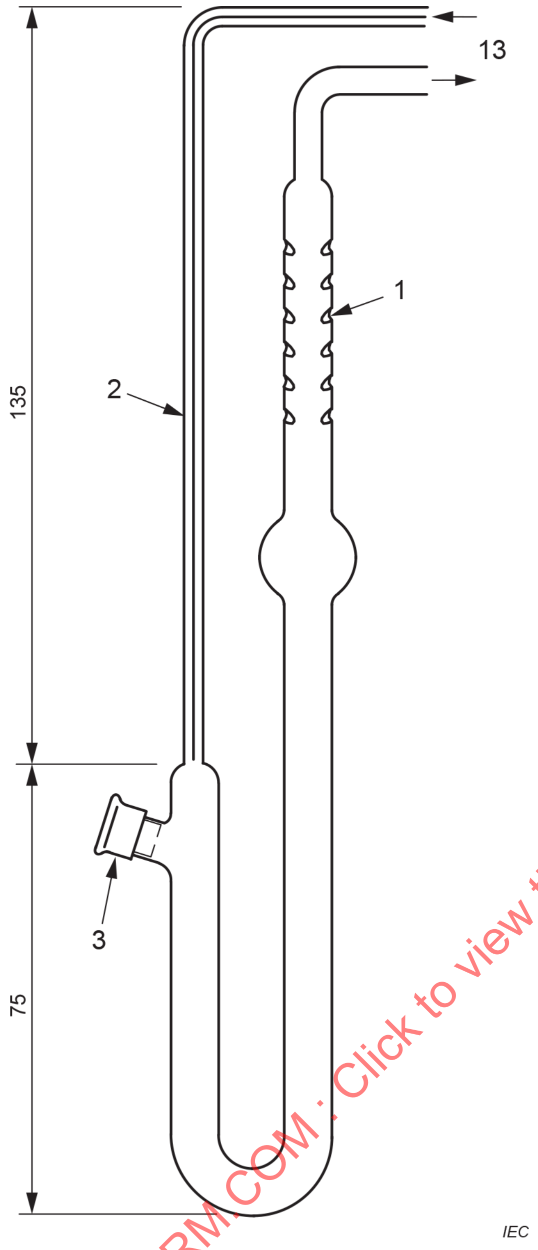
8.4.2 Stripping apparatus

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.

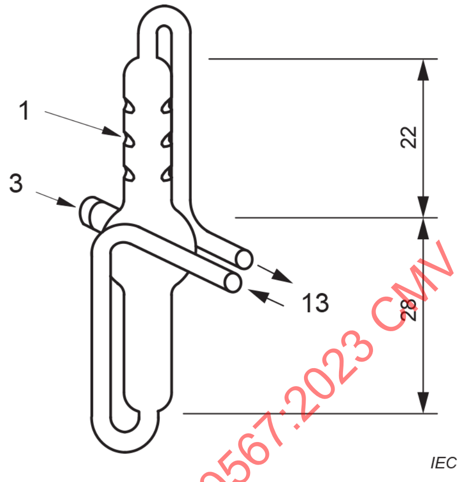
A design of a stripper made of stainless steel is shown in Figure 8. A needle with a cock and interchangeable syringe connection is permanently fixed into the base of the stripper and a syringe containing oil is attached to the fixed needle. The oil is injected by the movement of a pneumatic actuator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

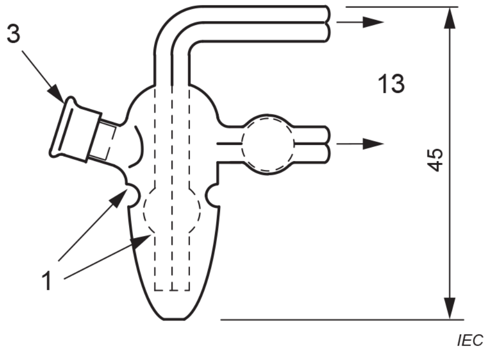
Dimensions in millimetres



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

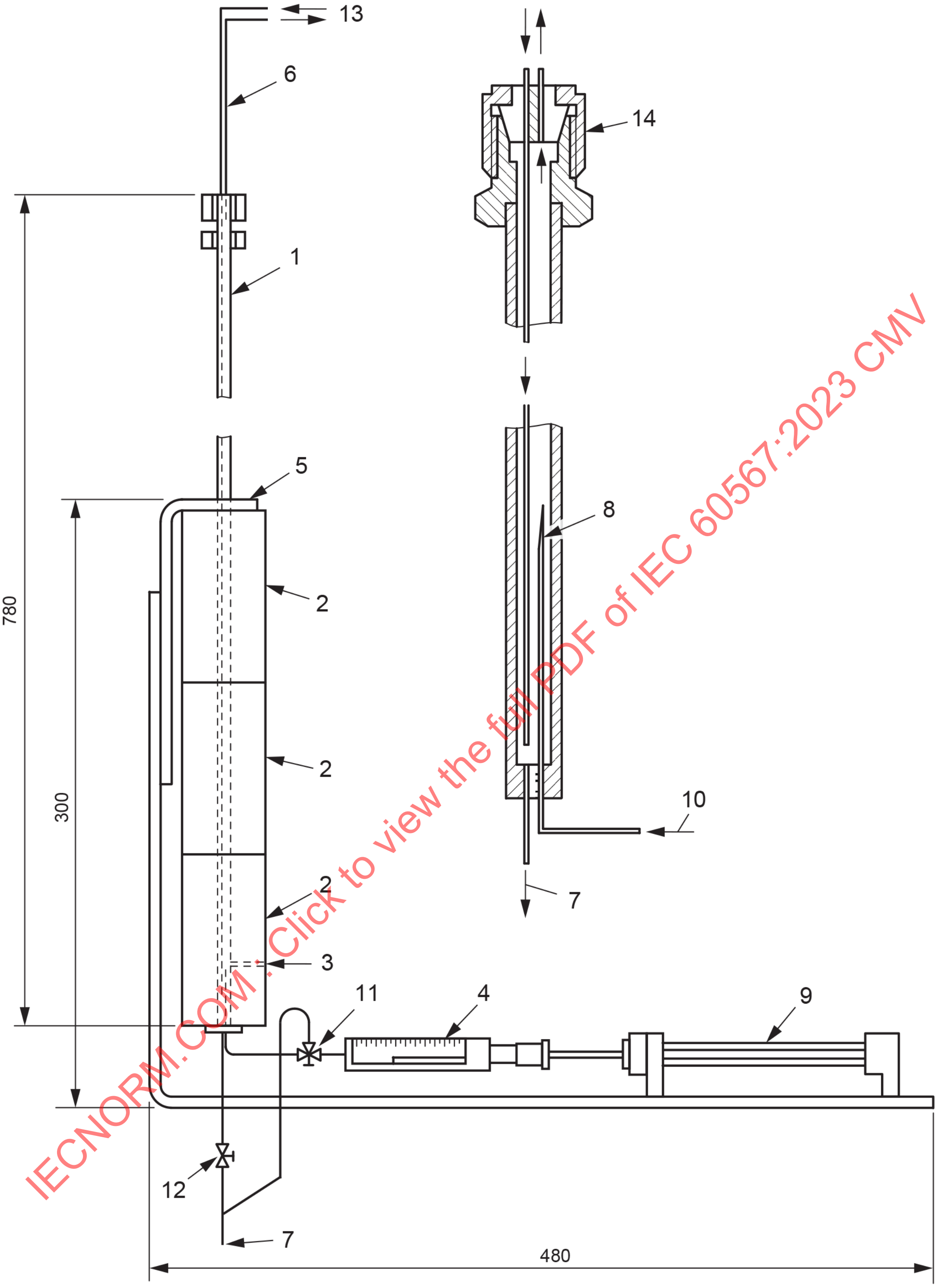
2 capillary tube

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



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

a) 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.

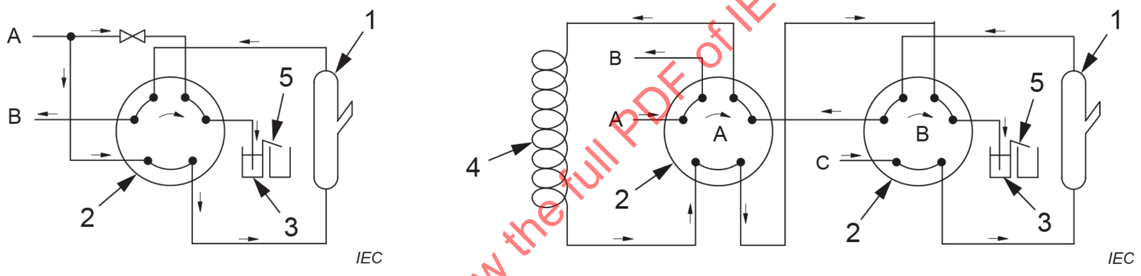
b) Maintain the stripper at a controlled temperature between 20 °C and 80 °C. Indeed, elevated temperatures reduce oil viscosity and facilitate gas stripping.

c) Allow the carrier gas to flow through the stripper.

d) 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.

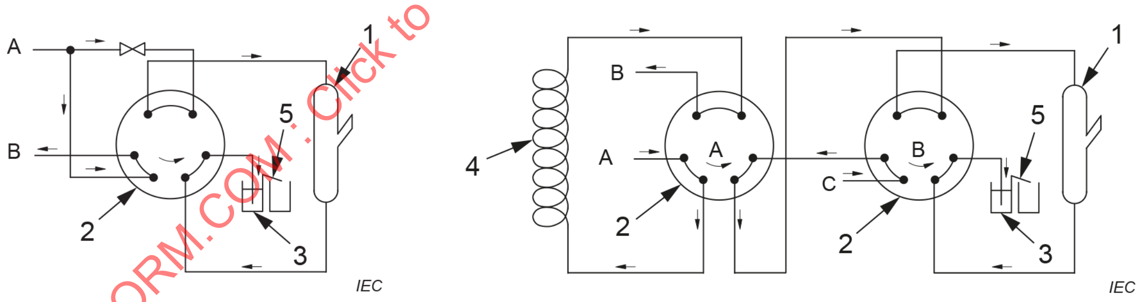
e) Inject the oil to be analysed into the stripper. The volume of oil to be injected will depend upon the type of stripper used and the expected gas content. During this operation, the carrier gas flow through the stripper shall be maintained.

f) 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.



Position A: analysis

Position A1: trapping of gases



Position B: purge (emptying of tripper)

Position B1: injection + purge (emptying of stripper)

a) Usual arrangement for degassing up to about 2,5 ml of oil

b) Arrangement with cold trap added for use with larger quantities of oil

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

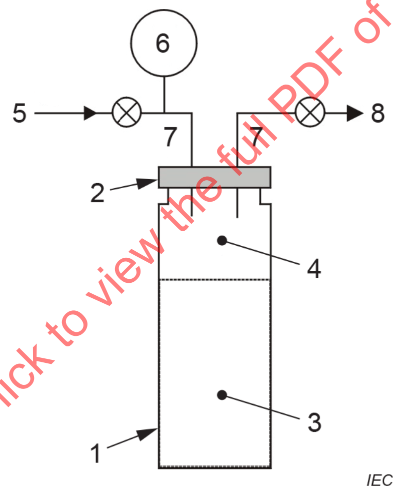
8.5 Headspace method

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.

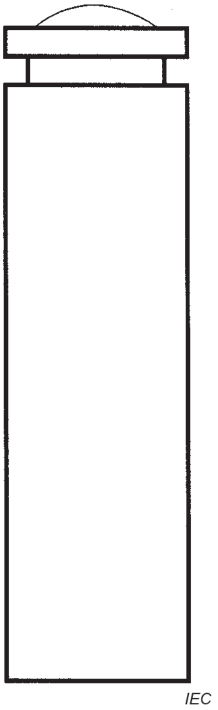


Figure 11 – Vial filled with water

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 µl/l O_2 and 350 µl/l 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 µl/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

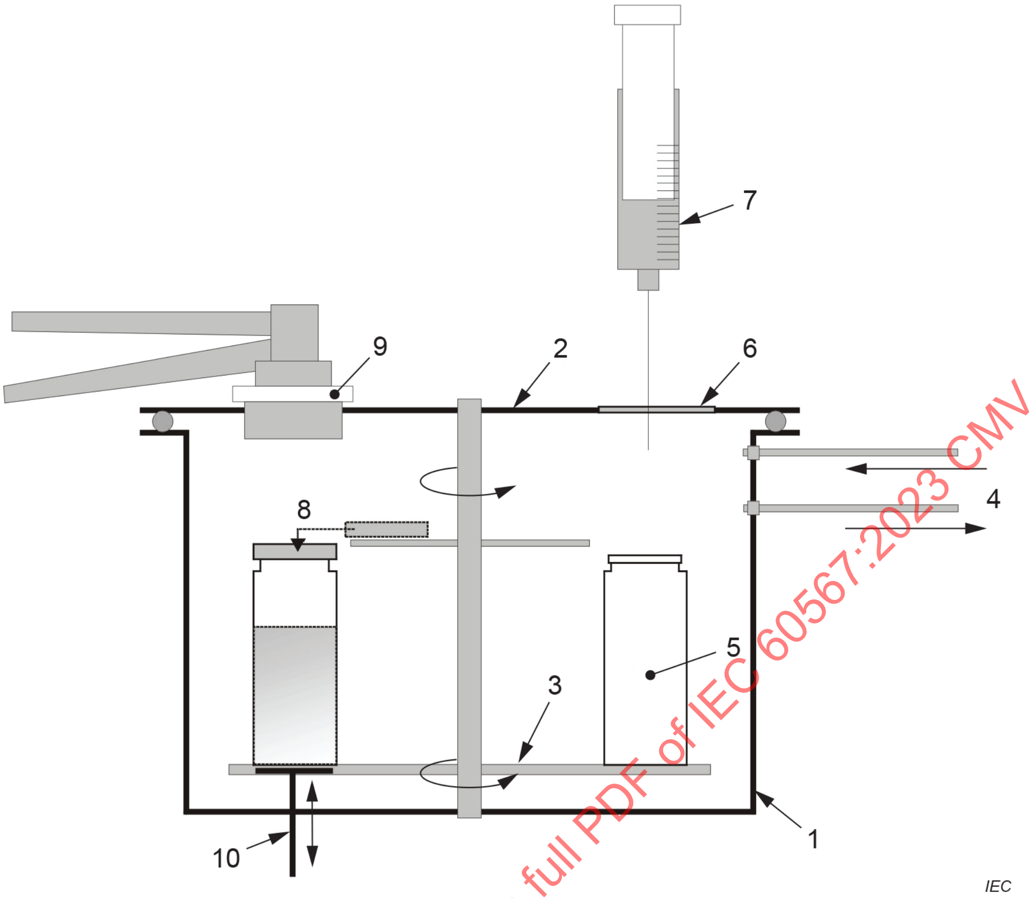
The glove box and its lock chamber should be purged with at least five times its volume of argon (typically, at 400 ml/min). Alternatively, a plastic glove bag, filled with all the necessary equipment (syringes, vials, etc), then purged with argon, may be used.

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 carrousel 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.



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 ±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 ±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 ±1 %, if available, or at worst ±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 carrousel. 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®)[1] 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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[1] 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.

Fill up the vial with the chosen amount of oil. Remove the two needles together, to make sure that the pressure in the vial at this stage is atmospheric pressure.

Weigh the oil-filled vial and subtract the weight of the empty vial to get the mass of oil in the vial. Divide by the density of the oil to get the exact volume of oil in the vial.

The same procedure applies for vials of gas-in-oil standards.

8.5.3.2 Headspace analyses

Place the vials inside the headspace sampler and begin the analysis using operational conditions such as those given in Table 2 as examples. As shown in Table 2, a large range of temperatures is possible for the transfer line and the injection valve, as well as for the equilibration times, depending on the exact type of equipment used.

NOTE Pressure in the vials at this stage is always below the injection pressure (140 kPa). Pressure in the glove box can exceed this, in which case it is measured (in the glove box, or in the vial, with the gauge on the headspace equipment) and reduced if necessary. Ideally, it is close to atmospheric pressure and known with precision in order to make the corrections and calculations indicated in 8.5.4.2 and 8.5.4.3.

Record the actual atmospheric pressure throughout the run, since it can vary by several per cent over an extended run, especially if unattended, and it can be necessary to make corrections to total pressure in the vial.

8.5.3.3 Procedure for analysis at low concentration levels

The procedures described in 8.5.3.1 and 8.5.3.2 provide the detection limits specified in Table 5 for service tests. More sensitive procedures (and special attention to avoid contamination) are required to obtain the detection limits specified for acceptance tests, where extracted gases in the headspace of the vials are in the nl/l range.

Toepler and partial degassing, where extracted gases are in the µl/l range at these levels, are more recommended for acceptance tests. However, if headspace is to be used for low concentration levels and acceptance tests, the more sensitive equipment and procedures described below are required:

- capillary GC columns such as the PLOT columns described in 9.3.2;
- reduced dead volumes between the vial and the GC detectors;
- calibration with different calibration curves;
- manual (rather than electronic) integration of the baseline of GC peaks. This will lower the detection limits to typically 0,2 µl/l for hydrocarbons;
- for the still lower detection limits of acceptance tests, a larger injection loop of 1,5 ml, followed by a split of the gas sample between the vial and the GC columns (typically, of 1/50 to 1/100). This will result in much sharper GC peaks (particularly for hydrogen);

  NOTE The equipment can be instructed to automatically choose the splitter option (e.g. 1/100 for acceptance tests and 1/10 for service tests).
- alternatively, a syringe may be used to manually transfer a gas sample from the vial to the injection port of the GC. This will eliminate the gas dilution resulting from argon pressurization of the vial.

8.5.3.4 Procedure for analysis at high concentration levels

It has been observed that when hydrogen concentration levels are too high, the measured values are considerably below actual values. In such cases, a smaller volume of the oil sample should be used to obtain accurate results.

It has been found that when the hydrogen content is typically above 6 000 µl/l, a second sample with 7 ml of the oil sample in the vial and a third measurement with 3 ml in the vial should be performed. Valid results are obtained when identical values with two different dilution factors are measured.

When using the procedure in 8.5.4.2 (calibration with gas-in-oil standards), introduce the reduced volume of oil sample (7 ml or 3 ml) in a syringe, complete to 15 ml with degassed oil, then transfer into a vial and proceed as with regular oil samples. Multiply the measured values of gas in oil by the proper oil dilution factor (15/7 or 15/3).

When using the procedure in 8.5.4.3 (calibration with gas standards), introduce the reduced volume of oil in a vial and proceed as with regular oil samples. Calculate gas concentrations in the oil sample using the equation indicated in 8.5.4.3 and the proper values of V_{G} and V_{L}.

NOTE This non-linearity has been observed mainly with hydrogen dissolved in oil, but samples with high concentrations of the other dissolved gases can also be measured following a similar procedure.

8.5.4 Calibration of the headspace extractor

8.5.4.1 General remark

Two different calibration methods are available.

8.5.4.2 Calibration with gas-in-oil standards

This is the preferred method of calibration recommended by CIGRE TF D1.01.15 and CIGRE WG A2/D1.47.

The advantage of this method is that knowledge of precise partition coefficients is not necessary. Neither is it affected by the linearity problems evidenced by the scatter of results observed during CIGRE inter-laboratory tests using partition coefficients.

Three gas-in-oil standards (GIOS) at different concentrations, prepared according to the methods described in 7.2 or 7.3, are run at least once a month or each time an operational parameter has changed (argon overpressure, new batches of vials or syringes) or if calibration of GC detectors with gas standards indicate a change in the response of detectors.

Direct calibration curves are drawn, relating peak height or peak area to the concentration of gases in the GIOS.

When an unknown oil sample is run under exactly the same operational conditions, its dissolved gas concentrations C_{L}^{0*} can be obtained by using these calibration curves.

For the storage of gas-in-oil standards, see CIGRE TB 783-2019, section E3, p.44.

8.5.4.3 Calibration with gas standards

It has been confirmed in CIGRE TB 783-2019 that laboratories using the calibration method in 8.5.4.3 have less accurate and more disperse results than those using the preferred method in 8.5.4.2, based on numerous round robin tests and proficiency test programmes.

The advantage of this method is that there is no requirement to prepare gas-in-oil standards for direct calibration of the headspace extractor.

Partition coefficients are to be determined accurately, however, under exactly the same operational conditions as the oil samples (see 8.5.4.4).

A vial containing the gas standard, prepared according to 8.5.3.1.3.3, is placed in the headspace sampler and analysed through the headspace injection loop.

Calibration curves relating peak height or peak area to the concentration of the gases in the gas standard are drawn. When an oil sample is run under exactly the same operational conditions, the concentration of the gases in the gas phase C_G can be obtained by using this calibration curve.

The concentrations in the oil sample are then determined using the following equation, based on Henry's law, which requires that the partition coefficients K and the actual vial volume ratio (V_G/V_L) for each oil sample be precisely determined.

$$C_L^0 = C_G \times (K + V_G / V_L)$$

NOTE 1 V_L and V_G are calculated according to 8.5.2.3.2 and 8.5.2.5.

Generally, gas standards are prepared together with oil samples and so the temperature and pressure inside the vials before headspace extraction should be the same. Concerning the atmospheric pressure, it can vary during the time several samples are analysed; as a consequence, in some systems equipped with sample loops in equilibrium with atmospheric pressure, the amount of gas (number of moles) going to the detector through the sample loop can change. Because of this, a correction for atmospheric pressure should be made.

NOTE 2 When using this procedure, the overall performance of the extractor is verified regularly by running gas-in-oil standards.

8.5.4.4 Determination of partition coefficients

The recommended method of determination of partition (or Ostwald or solubility) coefficients is the CIGRE TF D1.01.15 method consisting of bubbling pure gases in the oil or bubbling a standard mixture of gases in the oil.

It has been shown by CIGRE that partition coefficients measured by different laboratories using the headspace method and gas-in-oil standards, and the so-called slope intercept method, are not reliable and reproducible.

Examples of headspace partition coefficients measured experimentally at 70 °C in a mineral insulating oil of density d = 0,864 are given in Table 3.

Table 3 – Examples of headspace partition coefficients at 70 °C in mineral insulating oil

Headspace partition coefficients at 70 °C in mineral insulating oil	
H_2	0,074
O_2	0,17
N_2	0,11
CH_4	0,44
CO	0,12
CO_2	1,02
C_2H_2	0,93
C_2H_4	1,47
C_2H_6	2,09
C_3H_6	5,04
C_3H_8	5,37
C_4H_6	10,10

Shake test and mechanical oscillation versions of the headspace gas extraction method are described in Annex B.

9 Gas analysis by gas-solid chromatography

9.1 General remarks

Gas samples, whether obtained from gas-collecting relays or removed from an oil sample, are analysed by gas chromatography. The gases to be determined are as follows:

– hydrogen	H_2
– oxygen	O_2
– nitrogen	N_2
– methane	CH_4
– ethane	C_2H_6
– ethylene	C_2H_4
– acetylene	C_2H_2
– carbon monoxide	CO
– carbon dioxide	CO_2

For the purposes of this document, C_3 hydrocarbons are not required, but they can on occasion give useful information.

A number of methods may be used for the analyses; the two methods detailed in Table 4 are given as examples that have been found suitable for all extraction techniques.

The following assumes a measure of competence in the techniques of gas chromatography and omits, for brevity, many details that can be found in practical manuals on these techniques.

Table 4 – Examples of gas chromatographic operating conditions

	Example 1	**Example 2**
Type of columns	**Packed**	**PLOT**
Column 1	Porapak N®[2] or Haysep N®[3], L = 3; D = 3	Carboxen 1 006®[4] or Carboplot P7 ®[5], L = 30; D = 0,5
Column 2	Molecular sieve 5A or 13x L = 0,5; D = 3	Molecular sieve 5A (50 µm) L = 30; D = 0,5
Temperature (°C) of:		
Column bypass valve	120	90
FID	250	250
HID	250	250
TCD	200	200
Methanator	400	350
Oven	35 to 180	40 to 100
Gases separated		
On column 1	CO_2 (TCD) $CO_2{}^a$, C_nH_n, (FID)	C_2H_4, C_2H_2, C_2H_6, $CO_2{}^a$ (FID)
On column 2	H_2, O_2, N_2, CO (TCD) CO^a (FID)	H_2, O_2, N_2, CO (TCD) CH_4, CO^a (FID)
Argon carrier gas	25 ml/min	6 ml/min

Key

PLOT	porous large open tubular
FID	flame ionization detector
HID	helium ionization detector
TCD	thermal conductivity detector
L	length (in m)
D	diameter (in mm)
[a]	CO and CO_2 converted into CH_4 by methanator.

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[2] Porapak® is the trade name of products supplied by Water Associates. (Porapaks® are porous polymer beads modified to give different retention characteristics. Eight types are available; in order of increasing polarity these are Porapak® P, PS, Q, QS, R, S, N, and T). Haysep® products are polymers of a similar type. 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.

[3] Haysep N® is the trade name of products supplied by VICI Valco Instruments. 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.

[4] Carboxen® is the trade name of products supplied by Sigma-Aldrich. 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.

[5] Carboplot® is the trade name of products supplied by Agilent Technologies. 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.

9.2 Outline of suitable methods using Table 4

In example 1 of Table 4, two separate runs are made, one with a Porapak® column and the other with a molecular sieve column. A single detector having adequate sensitivity for all the gases to be detected is not available; thus, the gases eluted from the column in use are passed over both a thermal conductivity detector which detects atmospheric gases, CO, CO_2 and H_2 and a flame ionization detector which detects hydrocarbons.

To determine CO and CO_2 with improved sensitivity, a methanator may be fitted at the inlet of the flame ionization detector to convert CO and CO_2 to methane, which is then detected by the flame ionization detector.

In example 2 of Table 4, more sensitive porous large open tubular (PLOT) columns are used, particularly in the case of headspace extraction.

When using a stripping extraction method, it may not be possible to achieve the sensitivity and precision for hydrocarbons required for factory tests using less than 5 ml of oil. Larger volumes of oil (10 ml) require longer stripping times to extract the dissolved gases, which would give unacceptable gas chromatograms unless the extracted gases were to be concentrated by cold trapping.

The method in 9.3 is written for an apparatus in which the outputs from the detectors are switched electrically so that they may be dealt with by a single channel integrator or single channel chart recorder. Use of a dual channel integrator or recorder eliminates the need for switching.

9.3 Apparatus

9.3.1 Gas chromatograph

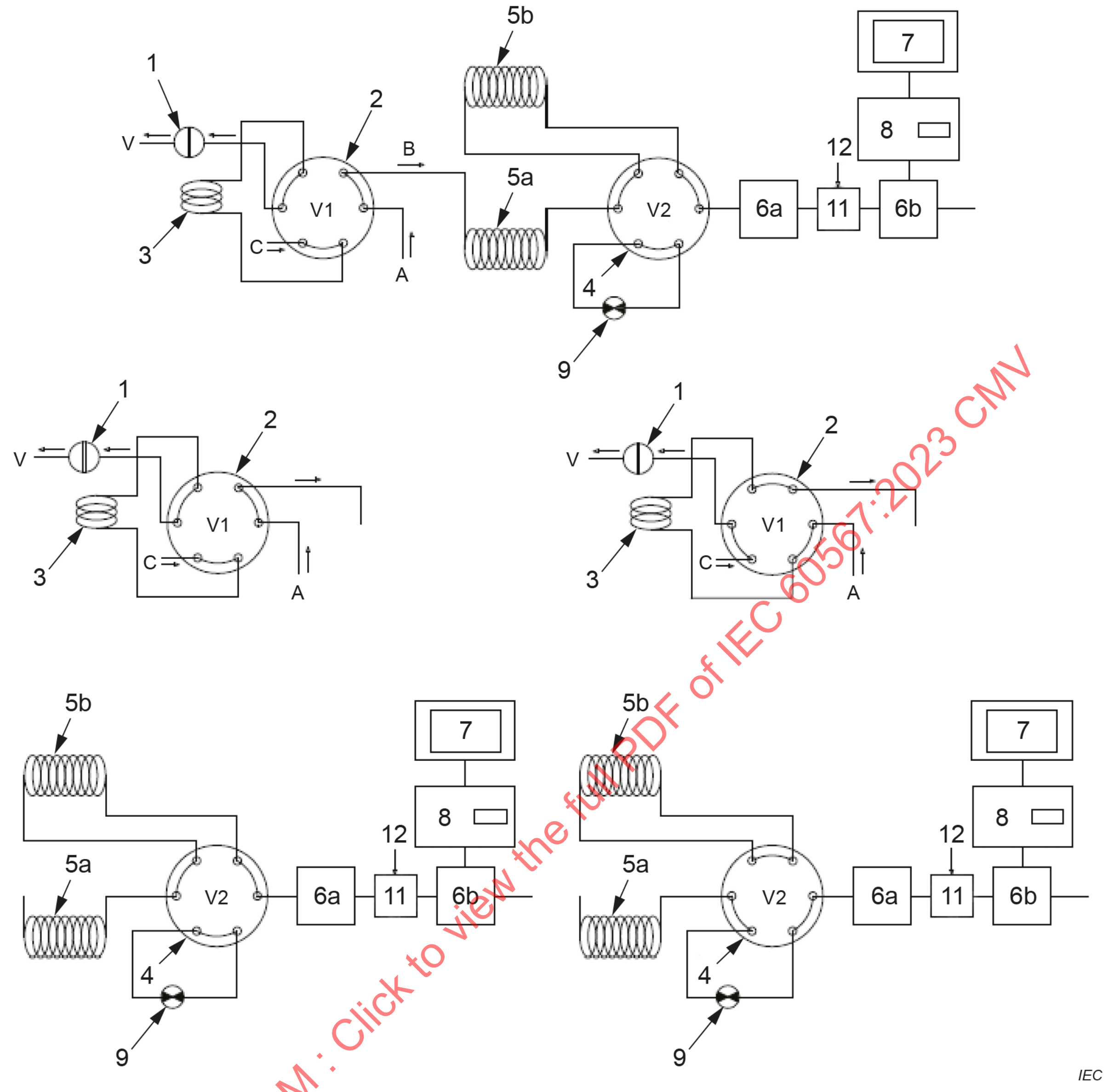
Figure 13 is an example of the layout of an instrument that has been used and found acceptable. Injection arrangements shall suit the method by which gas is transferred from gas extraction equipment into the chromatograph.

Thus, the vacuum extraction equipment described in Figure 6 and used for both Toepler pump and partial degassing methods transfers the gas via a gas sample valve and calibrated sample loop, a method recommended to improve repeatability.

Alternatively, gas samples may be transferred and injected into the chromatograph using a precision gas-tight syringe, and this latter method is generally used for gas samples from gas-collecting relays.

In the case of extraction by stripping (see Figure 9), a sampling valve is used, with the stripper inserted in place of the sample loop as shown in Figure 9 a). Arrangements where a stripper plus cold trap are used are shown in Figure 9 b).

In the case of the headspace method, the headspace accessories described in 8.5.2.2, a bypass valve, and a zero-dead volume adapter (0,53 mm ID) for the column connections are used for injecting extracted gases.



Key

Position A: Sample loop filling

1	stopcock	
2	chromatograph gas sample valve	
3	sample loop	
4	column selector valve	
5	columns	a) column 1 b) column 2
6	detectors	a) thermal conductivity b) flame ionization
7	recorder	

Position B: Injection

8	integrator
9	optional restriction valve for pressure compensation
11	methanator
12	H_2 for catalysis
A	inlet carrier gas
B	outlet carrier gas (to GC)
C	injection of gas sample
V	connection to vacuum

Figure 13 – Schematic arrangement for gas chromatography

9.3.2 Columns

In the present examples of Table 4, two columns are used with a two-way valve enabling selection between the columns.

However, the important requirement for all columns is that they should achieve good separation in as short a time as possible, while giving all elutions on a stable baseline. The columns indicated in Table 4 are given only by way of examples and other columns meeting these general requirements may be used.

In the case of the headspace method, the packed columns described in example 1 of Table 4 can be used for the routine analysis of oils; however, at low gas-in-oil concentration levels, gases shall be detected in the headspace phase at the nl/l level. This requires the use of the PLOT columns of example 2 of Table 4. At these nl/l gas levels, special care should be taken to prevent contamination and in the control of the GC detectors.

9.3.3 Carrier gas

The carrier gas is, preferably, gas chromatograph grade argon.

9.3.4 Detectors

The gases eluted from the columns are passed over a thermal conductivity detector (TCD) and a flame ionization detector (FID). A helium ionization detector (HID) can be used instead of the FID and TCD. The HID is 10 times more sensitive than the FID, using helium as a carrier gas, and does not require the use of a methanator.

9.3.5 Methanator

In the present examples, a methanator is fitted at the inlet to the flame ionization detector to improve the sensitivity with which CO and CO_2 can be detected by converting these gases to methane.

NOTE The activity of the methanator can be impaired by the presence of sulphur hexafluoride (this gas is sometimes used in cable terminal boxes and can diffuse into the equipment filling oil). In this case, a different analytical arrangement is used which is not described in this document.

The methanator can lose some sensitivity (and the CO_2/C_2H_4 and CO/CH_4 ratios decrease) with time, but can be recalibrated.

9.3.6 Cold trap

When the stripping method is used, a cold trap may be fitted at the outlet of the stripper to improve the sensitivity for hydrocarbons.

Figure 9 b) shows an example of the method of inclusion of a cold trap. A typical device used consists of a 130 mm long, 6 mm OD, stainless steel tube packed with 100/120 mesh Porapak Q® or equivalent, maintained below −54 °C in a suitable freezing mixture such as solid carbon dioxide and alcohol.

During stripping, a separate carrier gas stream circulates in the cold trap while the main carrier gas flows directly to the gas chromatograph. After stripping, a valve is switched to direct the carrier gas flow through the cold trap. Then the trap is rapidly heated to 80 °C, injecting the trapped gases onto the analytical columns.

9.3.7 Integrator and recorder

The electrical outputs from the detectors are fed to an integrator. Additionally or alternatively, a chart recorder may be used.

9.4 Preparation of apparatus

a) Set up the chromatograph and allow the flow of carrier gas and the temperature to stabilize as shown by the production of a steady baseline.

b) For the vacuum extraction methods, either inject the gas sample using a syringe or with the gas sample loop previously evacuated.

c) For the stripping method, introduce the oil sample into the stripper by means of a precision syringe.

d) For the headspace method, inject the extracted gases using accessories indicated in 9.3.1.

9.5 Analysis

See Figure 13.

A possible procedure using one chromatograph fitted with two columns, a gas-sampling valve and a methanator is given below (example 1 of Table 4).

a) Adjust the selector valve (4) (position A) to bring the Porapak® (5a) or equivalent column into use.

b) Turn the sample valve (2) to introduce the gas sample.

c) Use another switch to select the flame ionization detector (6b). The first peak to emerge will be CO converted to CH_4 by the methanator. The second peak will be CH_4. The third peak is CO_2 converted to CH_4 by the methanator, and this is followed by C_2H_4, C_2H_6 and C_2H_2.

NOTE The CO and CO_2, having been converted to CH_4 by the methanator, are detected at high sensitivity by the flame ionization detector. High concentrations of these gases can well exceed the linear range of this detector. In this case, use can be made of a thermal conductivity detector to evaluate the CO_2 before methanation.

d) Adjust the selector valve (4) (position B) to bring the molecular sieve column into use. Obtain a stable baseline.

e) Refill the gas sample loop according to step j) of 8.2.3.

f) Turn the sample valve (2) to introduce the gas sample.

g) Use another switch to select the thermal conductivity detector (6a). Peaks will emerge in the following order: H_2, O_2 and N_2.

h) Use another switch to select the flame ionization detector (6b). The next peak will be CH_4; the last peak to emerge will be CO converted to CH_4 by the methanator.

i) Purge any retained gases from both columns.

j) One determination per gas sample is normally sufficient.

9.6 Calibration of the chromatograph

Retention times are established by injection of dilutions of individual gases in the carrier gas into the columns. The response factors of the detectors, however, are preferably determined using a standard gas mixture diluted with the carrier gas, containing known concentrations of all gas components to be determined, in proportions resembling those found in oils from transformers. Such a standard mixture should be used periodically, depending upon the stability of the equipment. For better precision, calibration should be undertaken immediately before analysis of the oil sample.

The minimum number of standard gas mixtures for calibration of the chromatograph varies from one to three. Only one is necessary when performance of analysis equipment has been found linear (by verification of the entire system) in the concentration range of gases usually found in transformer oil.

A different standard for verification of GC detectors should be run at least once a day.

9.7 Calculations

a) Identify the gas corresponding to each peak by comparison with the chromatograms obtained during calibration.

b) Measure the area or height of each peak, note its retention time and apply the calibration data to obtain the gas volumes.

c) When dealing with analyses of gases taken from gas collecting relays, calculate the concentration of each gas in per cent by volume.

d) When dealing with analyses of gases extracted from oil, calculate the concentration in microlitres of each gas per litre of the oil from which it was extracted (or micromole of each gas per litre of oil).

Dissolved gas concentrations in the oil sample should be converted to these standard conditions (101,325 kPa and 20 °C), using the following equation:

$$C_{\mathrm{L}}^{0}(\text{corrected}) = C_{\mathrm{L}}^{0} \times (P/101{,}325) \times (293/(273+t))$$

where

C_{L}^{0} is the concentration of gases in the oil sample at ambient temperature and pressure;

t is the ambient temperature, in °C;

P is the atmospheric pressure, in kPa.

NOTE 1 1 µl/ l corresponds to one part per million (1 ppm) by volume and 0,042 µmol/l at 20 °C and 101,3 kPa.

NOTE 2 Concentrations in µmol/l can be converted to µl/l or ppm, under the standard conditions of Note 1, by multiplying by 22,4 (293/273).

NOTE 3 The total gas content of oil by volume, expressed as a percentage, in the case of partial degassing, stripping and headspace methods, can be estimated by the sum of the individual gas concentrations expressed in µl/l under the standard conditions of Note 1.

The correction for incomplete gas extraction in partial degassing method is described in Annex A.

The correction for gas bubbles in oil syringe or air gap in rigid bottles is described in Annex D.

10 Quality control

10.1 Verification of the entire analytical system

The preferred method of ensuring that the entire system (extraction and chromatography) gives stable and accurate results is by analysing a known quantity of gas-in-oil standards (containing all the gases listed in 9.1 in proportions resembling those found in oils taken from transformers) in place of an oil sample and carrying out all the procedures detailed in Clause 10.

In the case of the Toepler pump extraction method, it has been confirmed that the extraction efficiency and performance of the whole analysis equipment can be verified by the daily analysis of an air-saturated oil standard (see Annex C) and one standard gas mixture with average gas concentrations in the range usually found in transformer oil samples.

It is recommended to use at least two gas-in-oil standards, one containing low concentrations of gases (resembling oils in factory tests) and the other containing higher concentrations (resembling oils from equipment in the field) to check the quality of the results produced by the analytical system in the entire linearity range. The chromatogram peak areas or heights can then be related directly to the quantities of gases present in the oil, compensating automatically for incomplete extraction and other operational factors.

It is good practice to repeat this procedure at intervals of calibration of not more than six months or following changes in apparatus or operating conditions.

10.2 Limits of detection and quantification

The basic requirement is that the analytical system, consisting of degassing equipment and gas chromatograph, shall have adequate sensitivity for the task for which it is designed.

Not only the detection limit, but also the sensitivity, the repeatability and the accuracy of results depend on many details of the overall procedure, in particular the method of extraction and the design and method of operation of the gas chromatograph and its ancillaries.

For example, by using a methanator combined with a flame ionization detector, instead of using a thermal conductivity detector, the sensitivity and detection limit for the carbon oxides are considerably improved.

Tests on equipment in service where the dissolved gas concentration is often high do not require the same detection limits as factory tests where gas concentrations are usually very low.

In the case of headspace, extraction efficiency is low, and the concentration of gases in the extracted gas phase is typically 100 times lower than with the other extraction methods. At low gas-in-oil concentration levels, detection limits in the nl/l range in the gas phase of the headspace are therefore necessary, requiring the use of more sensitive equipment and procedures (see 8.5.3.3).

It is necessary that each laboratory determines overall procedures that will give suitable sensitivities for all gases. For guidance, experience indicates that the entire analytical system should be capable of detecting gases dissolved in oil at the concentrations indicated in Table 5.

For the analysis of gas samples taken from gas-collecting relays, a detection limit equivalent to that obtained for the analyses of gases extracted from the oil for service tests is adequate.

NOTE The limit of detection is defined as the lowest concentration that can be identified. The limit of quantification is defined as the lowest concentration that can be quantified with a reasonable precision and accuracy.

Table 5 – Required limits of detection in oil

Gases	**Acceptance tests**		**Service tests**	
	Concentrations at 20 °C			
	µl/l	µmol/l	µl/l	µmol/l
Hydrogen	2	0,08	5	0,2
Hydrocarbons	0,1	0,004	1	0,042
Carbon monoxide	5,0	0,2	25	1,0
Carbon dioxide	10	0,4	25	1,0
Oxygen	500	21	500	21
Nitrogen	2 000	84	2 000	84

10.3 Repeatability, reproducibility and accuracy

10.3.1 General remark

Repeatability (r), reproducibility (R) and accuracy are defined in detail in ISO 5725-1.

10.3.2 Repeatability

Repeatability is related to the differences that are observed when the same oil sample is analysed several times by the same laboratory over the same day or a short period of time.

Having established methods that give adequate overall detection limits, each laboratory shall confirm that these methods give adequate repeatability following the procedure described in ISO 5725-1.

For gas concentration levels greater than 10 µl/l the repeatability of a laboratory shall be considered as acceptable if the absolute difference (A – B) of two measurements A and B satisfies the following equation:

$$r = (\mathrm{A} - \mathrm{B}) < k \times (\mathrm{A} + \mathrm{B})/2$$

which means that the repeatability of the laboratory, at 95 % confidence limit, is lower than k times the mean concentration of the gas analysed. The k coefficient depends on the nature of the gas analysed.

A general acceptable value, calculated from an international IEC inter-laboratory test is: $k = 0{,}15$ for concentrations > 10 µl/l and < 1 000 µl/l, and $k = 0{,}10$ for concentrations > 1 000 µl/l.

For low gas concentrations (e.g. < 10 µl/l), the required repeatability can be of the same order of magnitude of the detection limit S.

It is recommended that each laboratory checks its own individual repeatability at both concentration levels at appropriate time intervals or after major changes on its system (gas extractor and gas chromatograph). To do that, a sufficient number of analyses on multiple samples of the same oil are run within a short period of time (less than one day), then the repeatability of results r is determined according to ISO 5725-1.

10.3.3 Reproducibility

Reproducibility is related to the differences which are observed when the same oil sample is analysed by different laboratories (inter-laboratory reproducibility), or when it is analysed by the same laboratory over long periods of time (after several days, weeks or months) (intra-laboratory reproducibility).

Inter-laboratory reproducibility has been evaluated by CIGRE as around ±20 % at medium concentration levels.

It is recommended that each laboratory checks its own intra-laboratory reproducibility at different concentration levels at appropriate time intervals or after major changes on its system (gas extractor and gas chromatograph). To do that, analyse multiple samples of the same oil at regular intervals of time, for instance each week or each month over a period of several months, then determine the reproducibility of results R according to ISO 5725-1.

A good conservation of the samples is necessary between analyses. Storing the samples in a refrigerator is recommended to avoid reactions with light and oxygen present in the oil.

10.3.4 Accuracy

Accuracy is related to the differences that are observed between the values analysed by a laboratory and the true values of dissolved gases contained in the oil sample.

Inaccurate DGA results can lead to wrong fault diagnoses, especially if gas ratios are close to a fault zone boundary, or to inappropriate actions on the equipment, if concentration values are close to the typical or alarm values defined in IEC 60599.

To be able to determine accuracy, the nominal values of dissolved gas concentrations have to be known. The mean of several measured values has been shown by inter-laboratory tests to be different from the nominal values. Determination of accuracy shall be carried out with gas-in-oil standards prepared according to Clause 7, or through participation to round robin tests using such standards, or with certified gas-in-oil standards prepared according to ISO 5725-1.

Examples of accuracies that can be obtained using the overall experimental procedure are given in Table 6. These values are deduced from IEC and CIGRE inter-laboratory tests made on two gas-in-oil standards (prepared according to 7.2) and involving 44 laboratories worldwide. One standard sample contained medium gas concentration levels (hydrocarbons between 9 µl/l and 60 µl/l, CO and CO_2 between 100 µl/l and 500 µl/l). The other one contained low gas concentration levels (hydrocarbons between 1 µl/l and 10 µl/l, CO and CO_2 between 30 µl/l and 100 µl/l).

It is recommended that each laboratory determines its own accuracy, which can differ from the values in Table 6. To do that, analyse a gas-in-oil standard according to Clause 7, then determine the accuracy according to ISO 5725-1.

Table 6 – Examples of accuracy of extraction methods

	Accuracy, in percentage of the nominal value	
Extraction procedure	**Medium concentration**	**Low concentration**
Toepler	13	35
Partial degassing	13	30
Stripping	18	23
Headspace	18	37
Mercury-free Toepler	15[a]	14[a]
Mercury-free partial degassing	11[a]	
Shake test	15	44

[a] Based on a limited number of analyses.

The preparation of oil standards saturated with air is described in Annex C.

The procedure for comparing gas monitor readings to laboratory results is described in Annex E.

11 Report of results

The report for DGA shall include

- a reference to this document;
- information on the gas or oil sample (see Clause 5 of this document or IEC 60475:2022, 4.4, respectively);
- the sampling procedure used (e.g. syringe, bottle) (see Clause 4 of this document and IEC 60475:2022, Clause 4, respectively);
  - the extraction procedure used (e.g. Toepler, headspace) (see Clause 8 and Annex B);

  - for headspace analysis, reference for the Ostwald coefficients used in case of calibration with gas standards (see 8.5.4.3);

- the detection limits for each gas with the analysis procedure used (see 10.2);
- for each gas analysed, the results in µl/l or in µmol/l (see 9.7).

NOTE 1 When available, it can be useful for diagnosis purposes to indicate the average accuracies obtained by the laboratory at these gas levels with the analysis procedure used (see 10.3.4).

NOTE 2 Guidelines for drafting the report in terms of quality assurance can be found in ISO/IEC 17025.

Annex A
(informative)

Correction for incomplete gas extraction in partial degassing method by calculation

From the chromatogram, the sample oil volume, the calculated total volume of gas extracted and the volume of the aliquot of gas passed into the chromatograph, determine the apparent volume concentration C_i of each component gas extracted from the oil.

Calculate the equilibrium extraction efficiency for each component gas from

$$E_\mathrm{i} = 1/(1 + a_\mathrm{i}V_0/V_\mathrm{t})$$

where

E_i is the extraction efficiency for component i;

V_0 is the volume of the oil sample, in ml;

V_t is the total expansion volume, in ml (see 8.3.3);

a_i is the Ostwald solubility coefficient of component i.

Examples of solubility coefficients for typical mineral oils of 2006 are shown in Table A.1. Values in more recent types of oils can differ significantly.

Table A.1 – Examples of solubility coefficients a_i (at 25 °C) reported by CIGRE TF D1.01.15 in 2006

Gas	Mineral oils	Natural esters	Synthetic esters	Silicone oils
Hydrogen	0,055 6	0,047 0	0,051 0	0,092 4
Nitrogen	0,090 7	0,072 8	0,087 2	0,157
Carbon monoxide	0,132	0,111	0,127	0,204
Oxygen	0,172	0,134	0,152	0,266
Methane	0,429	0,341	0,381	0,569
Carbon dioxide	1,09	1,54	2,05	1,63
Acetylene	1,24	2,68	4,38	2,04
Ethylene	1,84	1,69	1,87	2,18
Ethane	2,82	2,16	2,19	3,10

The data given in Table A.1 represent mean values obtained by bubbling the pure gases in some of the current types of transformer oils. The actual data on specific types of oils can differ a little from these figures.

Calculate the corrected volume concentration of each gas in the oil from:

$$C_\mathrm{i}\ (\text{corrected}) = C_\mathrm{i}\ (\text{apparent})/E_\mathrm{i}$$

NOTE 1 Solubility coefficients are functions of temperature and of oil density.

NOTE 2 Instead of correcting for incomplete gas extraction by calculation, calibration of the partial degassing method with several gas-in-oil standards at different concentration levels can be used.

Annex B
(informative)

Alternative gas extraction methods

B.1 Mercury-free versions of the vacuum extraction methods

B.1.1 Mercury-free version of the Toepler method

In the equipment used in the mercury-free version of the Toepler method, mechanical pistons are used instead of the mercury piston to extract the dissolved gases and recompress them.

A typical schematic representation of this equipment is indicated in Figure B.1.

B.1.2 Mercury-free version of the partial degassing method

B.1.2.1 In the equipment used in the mercury-free version of the partial degassing method, mechanical pistons are used instead of the mercury piston to extract the dissolved gases and recompress them.

A typical schematic representation of this equipment is indicated in Figure B.2.

The procedure used is the following.

B.1.2.2 Rinse with the analysed oil by opening valve 2 under vacuum through the built-in sintered filter. Then drain the rinsing oil through valve 11.

B.1.2.3 Evacuate the whole apparatus with the vacuum pump during 15 min.

B.1.2.4 Slowly suck the oil sample over the sintered filter by opening valve 2, until a pressure of 500 Pa to 600 Pa is reached.

B.1.2.5 Open valve 8 to push the mechanical piston up to a pressure of 18 kPa. Open valve 9 to transfer the compressed gas to the transfer line of the GC. The low pressure injection valve is connected to a vacuum pump to allow further pressure reduction to a defined value, at which injection in the GC takes place.

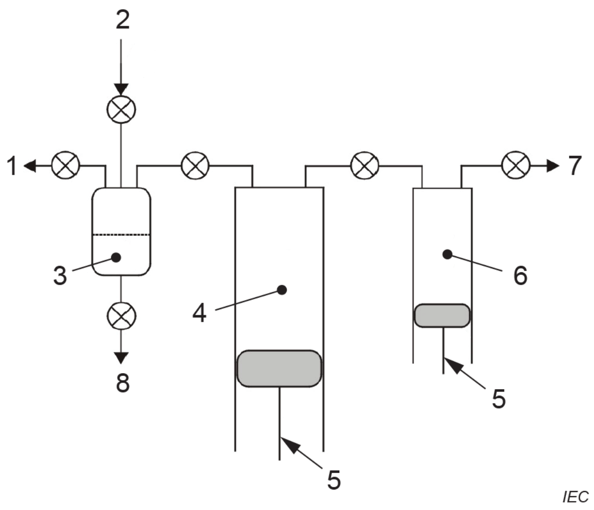
The total gas content is calculated according to gas laws.

Correction for incomplete gas extraction should be made as indicated in Annex A.

B.2 Syringe versions of the headspace method

B.2.1 Shake test method

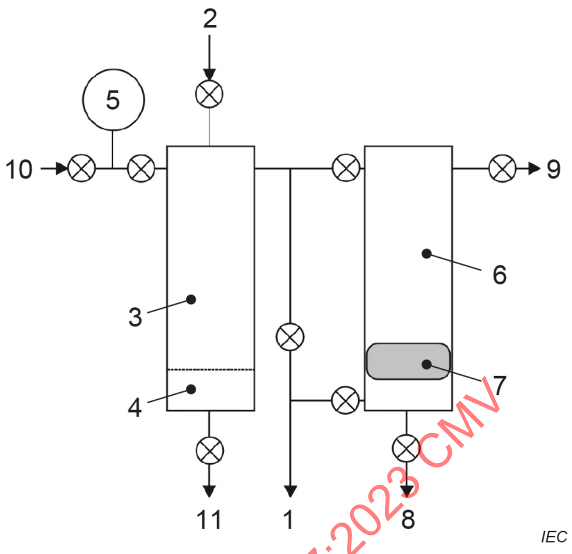
In this version, an oil sample (90 ml) is introduced in a 100 ml precision glass syringe rather than in a glass vial. 10 ml of air are then introduced in the syringe. The syringe is shaken vigorously by hand to extract the dissolved gases. Equilibrium is reached in less than 2 min because of the high shaking efficiency. An aliquot of the extracted gases is then injected in a portable chromatograph for on-site analysis, or in a standard laboratory chromatograph. A typical schematic representation of this equipment is indicated in Figure B.3.



Key

1	vacuum pump
2	oil inlet
3	oil sample
4	gas extraction chamber
5	piston
6	gas compression chamber
7	to GC injection loop and detectors
8	oil purge

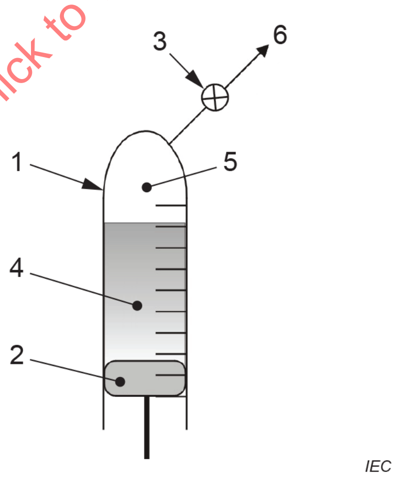
Figure B.1 – Schematic representation of mercury-free Toepler method



Key

1	vacuum pump
2	oil inlet
3	gas extraction chamber (glass)
4	oil sample
5	pressure gauge
6	gas compression chamber (glass)
7	piston
8	atmospheric air
9	to GC injection loop and detectors
10	calibration gas
11	oil purge

Figure B.2 – Schematic representation of mercury-free partial degassing method



Key

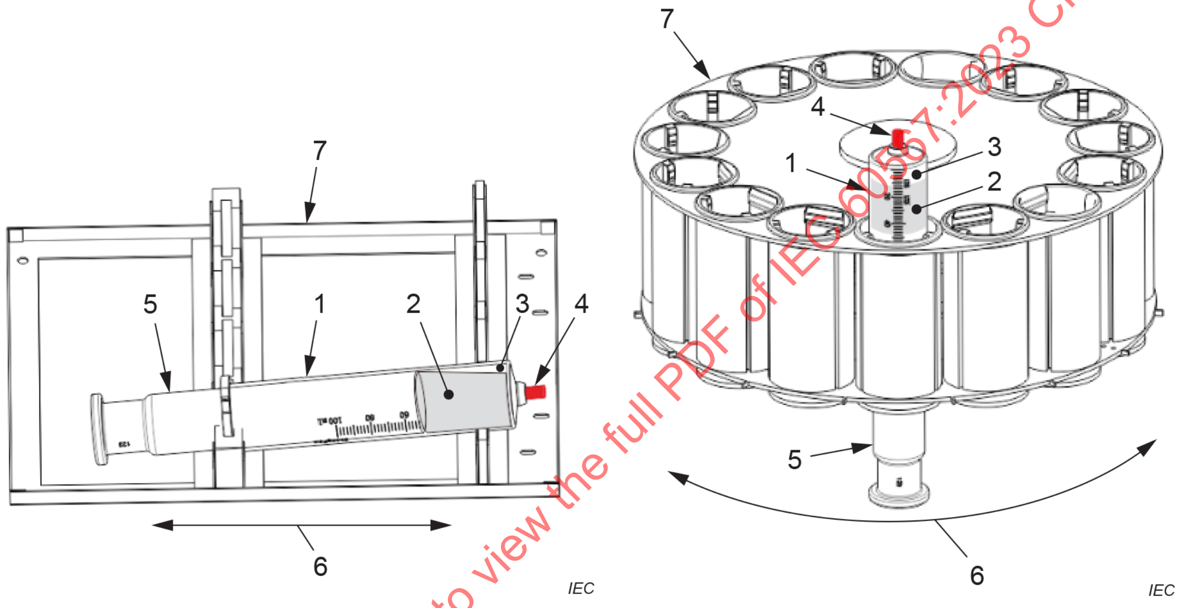
1	precision syringe
2	piston
3	oil/air inlet
4	oil sample
5	gas phase (air)
6	to GC injection loop and detectors

Figure B.3 – Schematic representation of shake test method

B.2.2 Mechanical oscillation method

The mechanical oscillation degassing method uses a piston syringe whose volume can be adjusted according to the ambient atmospheric pressure. It simplifies the operation steps of filling the sample bottle with carrier gas in advance when using vials to prepare the oil sample bottle for oil analysis. Since both sample degassing and sample gas transfer are carried out at atmospheric pressure, no additional monitoring and correction of the pressure in the degassing container is necessary.

A typical schematic representation of this equipment is shown in Figure B.4 a) and Figure B.4 b). Figure B.4 a) is applied to the scene where manual sample gas transfer is required, and Figure B.4 b) is applied to the scene where instrument automation is used for sample gas transfer and analysis.



a) **Manual gas transfer mode**

b) **Automatic gas transfer mode**

Key

1 precision syringe
2 oil sample
3 gas phase (Ar or N_2)
4 rubber cap
5 movable core of syringe
6 oscillation direction
7 oscillating sample disc

Figure B.4 – Schematic representations of mechanical oscillation method

Examples of accuracies that can be obtained using these methods are given in Table 6.

These values are deduced from inter-laboratory tests made in 2006 on two gas-in-oil standards prepared as in 10.3 and involving 10 laboratories worldwide (two for the mercury-free Toepler method, one for the mercury-free partial degassing method, and seven for the shake test).

Annex C
(informative)

Preparation of air-saturated standards

Keep a batch of new transformer mineral or non-mineral oil in an open container at room temperature for at least one week. Measure the oxygen and nitrogen content in the oil, using any one of the gas extraction methods, then the air content of the oil at saturation.

The gas extraction equipment is checked with this air-saturated oil standard (see 10.1) and found correct if the average total gas content measured corresponds to the value measured for this type of oil, with a standard deviation of 3 %.

The gas extractor and the gas chromatograph are checked by the retention times and concentrations of O_2, N_2 and CO_2 in this air-saturated oil standard. All three retention times should be in accordance with those obtained with gas standard mixtures.

The solubility of air in oil at saturation depends on the atmospheric pressure and temperature and on the type of oil used. Examples of solubility values of air for different types of oils, as reported by CIGRE TF D1.01.15 in 2006, are indicated in Table C.1.

Table C.1 – Examples of solubility values of air for different oil types

Fluid	**Density at 20 °C**	**µl/l at 20 °C**			
		O_2	**N_2**	**CO_2**	**Air**
Mineral oil 1	0,851 8	29 980	65 320	569	95 869
Mineral oil 2	0,888 2	32 080	61 780	537	94 397
Natural ester 1	0,921 0	21 995	49 613	647	72 255
Natural ester 2	0,915 8	24 507	50 177	625	75 309
Synthetic ester	0,919 7	21 705	45 269	555	67 529
Silicone oil	0,964 5	54 938	113 078	763	168 779

Examples of variations with temperature of the solubility of oxygen and nitrogen in a mineral oil as reported by CIGRE TF D1.01.15 are given in Table C.2.

Table C.2 – Examples of temperature variations for oxygen and nitrogen solubility in mineral oil

Temperature °C	**O_2**	**N_2**
13	32 937	62 798
21,5	32 750	63 728
25	32 483	64 061
50	31 465	66 141

Annex D
(informative)

Correction for gas bubbles in syringes and air gap in rigid bottles

It has been found by CIGRE TF D1.01.15 that gas bubbles are observed in oil in about 20 % of syringes on average (this value can be lower or higher depending on the experience of samplers).

When using the Toepler, partial degassing and stripping methods, the bubble is introduced into the extraction vessel (see 8.2.3, item e), Note 1), and no correction is necessary. When using the headspace method, the bubble should not be introduced in the vial, and a correction for the gases having migrated into the bubble should be made as indicated in 9.7.

In glass or rigid metal bottles, the air gap volume used as an oil expansion device is about 2 ml to 5 ml depending on the size of the bottle (1 l or 2 l). A correction for the gases having migrated into the air gap should also be made as indicated in 9.7.

The following equation can be used for that purpose, for each gas measured:

$$C_\mathrm{C} = C_\mathrm{m}\ (1 + V_\mathrm{G}\ /\ (kV_\mathrm{L} + V_\mathrm{G}))$$

where

C_C is the corrected concentration, in µl/l;

C_m is the measured concentration, in µl/l;

V_G is the volume of bubble in the syringe, or volume of air gap in the glass bottle, in ml;

V_L is the volume of oil in the syringe or glass bottle, in ml;

k is the Ostwald (solubility) coefficient.

NOTE In general, the corrections (10 % to 5 %) are significant only for the less soluble gases (H_2, CO).

Annex E
(informative)

Procedure for comparing gas monitor readings to laboratory results

Gas monitors (installed on-line on electrical equipment in service or used as portable instruments) are increasingly used in industry. In some cases, monitors readings do not quite agree with laboratory results for the same equipment, and it is not possible to know for sure which is right, monitors readings or laboratory results.

The following procedure has been developed by CIGRE TF 15 to make such an evaluation (see CIGRE TB 409).

- Purchase a sample of gas-in-oil standard from an appropriate vendor, or prepare one according to IEC 60567 (this document) or ASTM D3612.
- Take a reading on one or several on-line gas monitors installed on transformers in service.
- Take four duplicate samples of oil from the sampling point of the monitor(s), immediately after having taken the reading.
- For portable gas monitors, take five duplicate samples of oil from a transformer. Using one of the five samples, take a reading of the portable monitor.
- Send all the above samples of oil to the DGA laboratory.
- Analyse all samples on the same day (or over no more than a few days), using the same analytical equipment for all samples.
- Convert all DGA results and monitor readings to the same units (IEC or STP µl/l).
- Calculate the bias of the laboratory by comparing its results for the gas-in-oil standard sample to what was actually prepared.
- Correct all other DGA laboratory results using the bias calculated above.
- Calculate the average values (A) of each set of four duplicate samples, in µl/l.
- Calculate the repeatability (R) of laboratory results as the difference between results for the individual four samples and average values (A), and express it as a percentage.
- Calculate the difference (D) between gas monitor readings and average values (A), and express it as a percentage.
- The maximum accuracy of the gas monitor as measured by the laboratory is ($D – R – 2$), in per cent, where 2 % is the uncertainty on the gas-in-oil standard.

For example, if

- gas-in-oil standard S = 100 µl/l, laboratory result for S = 90 µl/l;
- laboratory results for four duplicate samples = 250 µl/l, 230 µl/l, 210 µl/l, 240 µl/l;
- laboratory results corrected for bias = 275 µl/l, 253 µl/l, 231 µl/l, 264 µl/l;
- average value (A) = 256 µl/l, repeatability (R) = 9 %;
- monitor reading = 300 µl/l, difference (D) = +17 %;
- maximum accuracy of gas monitor = (17 – 9 – 2) = +6 %.

Annex F
(normative)

Insulating liquids based on synthetic and natural esters and silicones

The general methods used for mineral oils in Clause 6 to Clause 11 apply to insulating liquids based on synthetic and natural esters and silicones (thereafter called "liquids"), with the following differences:

- in 8.2 (Toepler pump method), and 8.3 (partial degassing method), exposure to vacuum is up to 10 min for the liquids, depending on their viscosity, as compared to 3 min for mineral oils. Calculation of the correction for incomplete extraction of the partial degassing method is indicated in Annex A, using the Ostwald coefficients of the liquids indicated in Table A.1, or more precise values if available.
- in 8.2.3 k) (Toepler pump method), and 8.3 (partial degassing method), the total volume of (gas + water vapour) V_{gw} extracted from mineral oil and the liquids is measured directly in the burette. With mineral oil, the amount of water vapour extracted V_w is negligible. With an ester liquid, the amounts of moisture in the ester liquid and of water vapour extracted from the ester liquid V_w are large and calculated. The actual total volume of gas V_g can then be calculated as $V_g = (V_{gw} - V_w)$.
- in Annex B (mercury-free partial degassing method, described in Figure B.2), the total volume of (gas + water vapour) V_{gw} extracted from the ester liquid can be deduced indirectly from the increase in pressure in the vacuum vessel.

In the above vacuum methods, in the case of ester liquids with large amounts of dissolved water, values of V_w, V_{gw} and V_g are calculated as follows:

Calculation of the volume of (water vapour) V_w extracted from the ester liquid:

v	is the volume of ester liquid introduced, in ml;
d	is the density of ester liquid;
W_1	is the mass of water in the ester liquid before being subjected to vacuum, measured by KF or another device, in ppm ($W_1 \times 10^{-6}$ in g/g);
W_2	is the mass of water in the ester liquid after being subjected to vacuum, measured by KF or another device, in ppm ($W_2 \times 10^{-6}$ in g/g);
m	is the mass of water vapour extracted from the ester liquid by vacuum = $(W_1 - W_2)10^{-6}$ vd, in g.

Water vapour and individual gases extracted from the ester liquid can also be measured simultaneously with the HID detector described in 9.3.4.

n_w	is the number of moles of water vapour extracted from the ester liquid = m/18;
V_w	is the volume of water vapour extracted from the ester liquid = $n_w \times 22\,400$, in ml.

Calculation of the volume of (gas + water vapour) V_{gw} extracted from the ester liquid, using gas law $PV = n\mathrm{R}T$, where:

P	is the pressure increase in the pressure gauge, in mbar (1 mbar = 101 kPa), due to the (gas + water vapour) extracted;
V	is the volume of the vacuum chamber with ester liquid, in ml = $(V_1 - V_2)$;
V_1	is the volume of the vacuum chamber without ester liquid, in ml;
V_2	is the volume of ester liquid introduced in the vacuum chamber, in ml;
R	is a gas constant = 83 144, in mbar, ml;
T	is the temperature in K;

n = n_{gw} is the number of moles of (gas + water vapour) extracted = $(P\,(V_1 - V_2) / \mathrm{R}T)$;

V_{gw} is the volume of (gas + water vapour) extracted = $n_{gw} \times 22\,400$, in ml;

V_g is the volume of gas extracted = $(V_{gw} - V_w)$, in ml.

- in 8.5.4 (headspace method), calibration of the headspace extractor with gas-in-oil standards (GIOS) or gas-in-liquid standards (GILS) is the preferred method of calibration recommended for both mineral oils and the liquids. Calibration with gas standards, although not forbidden, is not recommended. The same recommendation is made in CIGRE TB 783-2019.

Each laboratory should preferably calculate its own calibration curves and partition coefficients, using GIOS or GILS. Home-made GIOS or GILS prepared in accordance with 7.3, and NIST-traceable commercial GIOS or GILS prepared by weight, both qualify as analytical chemistry standards.

They should be prepared in the same type of oil or liquid as the unknown oil or liquid sample, and they should contain similar amounts of air or nitrogen (near saturation or at partial saturation), similar individual gas concentrations (low or high), and similar moisture contents in the case of ester liquids.

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SOMMAIRE

COMMISSION ÉLECTROTECHNIQUE INTERNATIONALE

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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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L'IEC 60567 a été établie par le comité d'études 10 de l'IEC: Fluides pour applications électrotechniques. Il s'agit d'une Norme internationale.

Cette cinquième édition annule et remplace la quatrième édition parue en 2011. Cette édition constitue une révision technique.

Cette édition inclut les modifications techniques majeures suivantes par rapport à l'édition précédente:

a) une nouvelle Annexe F normative concernant l'analyse AGD des liquides isolants autres que les huiles minérales (esters et silicones) a été ajoutée;
b) les Articles 4 à 11 et les Annexe A à Annexe E informatives restent consacrés aux huiles minérales;
c) deux nouvelles méthodes d'extraction de gaz sans mercure sont décrites à l'Annexe B (extraction sous vide à basse pression et oscillation mécanique).

Le texte de cette Norme internationale est issu des documents suivants:

Projet	Rapport de vote
10/1207/FDIS	10/1211/RVD

Le rapport de vote indiqué dans le tableau ci-dessus donne toute information sur le vote ayant abouti à son approbation.

La langue employée pour l'élaboration de cette Norme internationale est l'anglais.

Le présent document a été rédigé selon les Directives ISO/IEC, Partie 2, il a été développé selon les Directives ISO/IEC, Partie 1 et les Directives ISO/IEC, Supplément IEC, disponibles sous www.iec.ch/members_experts/refdocs. Les principaux types de documents développés par l'IEC sont décrits plus en détail sous www.iec.ch/publications.

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INTRODUCTION

Les processus naturels de vieillissement dans les matériels électriques immergés dans l'huile forment des gaz, mais il peut s'en produire beaucoup plus en cas de défauts.

Le fonctionnement en présence de défauts peut sérieusement endommager les matériels, et il est important de pouvoir détecter ces défauts au tout début de leur apparition.

Si ces défauts ne sont pas importants, les gaz formés se dissolvent normalement dans l'huile et diffusent éventuellement, dans une faible proportion, du liquide dans toute la phase gazeuse au-dessus du liquide. L'extraction des gaz dissous à partir d'un échantillon d'huile et la détermination de leur teneur et de leur composition sont des moyens de détecter de tels défauts. Le type et la sévérité de tout type de défaut peuvent alors souvent être déduits à partir de la composition des gaz et de leur vitesse de formation.

Dans le cas de défauts suffisamment importants, les gaz libres traversent l'huile et sont recueillis au relais de protection (Buchholz), le cas échéant; en cas de nécessité, ces gaz peuvent être analysés pour déterminer le type de défaut qui les a créés. Au fur et à mesure du déplacement des bulles dans l'huile vers le relais de protection, la composition des gaz dans ces bulles varie.

Cela peut être utilisé à bon escient, puisque les informations concernant la vitesse de formation des gaz peuvent souvent être déduites en comparant la composition des gaz libres recueillis à la concentration des gaz qui restent dissous dans le liquide.

L'interprétation de l'analyse des gaz fait l'objet de l'IEC 60599.

À tous les stades de la vie des matériels immergés dans l'huile, ces techniques sont précieuses. Lors des essais de réception des transformateurs en usine, la comparaison des analyses de gaz dissous dans l'huile avant, pendant et après un essai d'échauffement peut révéler la présence de points chauds; de même, après les essais électriques, les analyses peuvent fournir des informations complémentaires concernant la présence de décharges partielles ou disruptives. Lors du fonctionnement sur site, des prélèvements périodiques d'échantillons d'huile, pour l'analyse des teneurs en gaz, servent à surveiller l'état des transformateurs et autres matériels immergés dans l'huile.

L'importance de ces techniques a conduit à l'établissement du présent document, qui donne les modes opératoires utilisés pour l'échantillonnage des gaz et de l'huile contenant des gaz dans les matériels électriques immergés dans l'huile, pour les analyses ultérieures.

NOTE Les méthodes décrites dans le présent document s'appliquent aux huiles isolantes, car l'expérience, à ce jour, a presque entièrement été obtenue sur de telles huiles. Ces méthodes peuvent également être appliquées à d'autres liquides isolants, sous réserves de modifications éventuelles.

Précautions générales, protection de la santé, de la sécurité et de l'environnement

AVERTISSEMENT – Le présent document ne prétend pas couvrir tous les problèmes de sécurité liés à son utilisation. Il incombe à l'utilisateur du présent document d'établir, avant de l'utiliser, des pratiques d'hygiène et de sécurité appropriées et de déterminer l'applicabilité des restrictions réglementaires.

Il convient de manipuler les huiles isolantes dont traite le présent document en respectant l'hygiène personnelle. Un contact direct avec les yeux peut provoquer une irritation. En cas de contact oculaire, il convient d'effectuer un lavage avec une grande quantité d'eau courante propre et de consulter un médecin. Certains des essais spécifiés dans le présent document impliquent l'emploi de procédés qui peuvent conduire à une situation dangereuse. Les recommandations des normes correspondantes sont prises en compte.

Le mercure présente un risque pour l'environnement et pour la santé. Il convient de nettoyer et d'éliminer immédiatement tout déversement de façon appropriée. Des exigences réglementaires concernant l'utilisation et la manipulation du mercure peuvent s'appliquer. Des méthodes qui n'utilisent pas de mercure peuvent être exigées dans certains pays.

Environnement

AVERTISSEMENT – Le présent document s'applique aux huiles isolantes, aux produits chimiques et aux récipients d'échantillons usagés.

L'attention est attirée sur le fait que, au moment de la rédaction du présent document, de nombreuses huiles isolantes en service sont connues pour être contaminées dans une certaine mesure par des polychlorobiphényles (PCB). Si tel est le cas, il convient de prendre des contre-mesures de sécurité afin d'éviter les risques pour les travailleurs, le public et l'environnement au cours de la durée de vie du matériel, en contrôlant rigoureusement les débordements et les émissions. L'élimination ou la décontamination de ces huiles peut être soumise à des exigences réglementaires. Il convient de prendre toutes les précautions afin d'empêcher le déversement de tout type d'huile isolante dans l'environnement, y compris celles qui sont partiellement biodégradables dans le temps.

MATÉRIELS ÉLECTRIQUES IMMERGÉS – ÉCHANTILLONNAGE DE GAZ LIBRES ET ANALYSE DES GAZ LIBRES ET DISSOUS DANS LES HUILES MINÉRALES ET D'AUTRES LIQUIDES ISOLANTS – RECOMMANDATIONS

1 Domaine d'application

Le présent document traite des techniques d'échantillonnage de gaz libres au niveau des relais de protection des transformateurs de puissance. Trois méthodes d'échantillonnage des gaz libres sont décrites.

Les techniques d'échantillonnage de l'huile dans les matériels immergés dans l'huile, tels que les transformateurs de puissance et de mesure, les bobines d'inductances, les traversées de transformateurs, les câbles à huile fluide et les condensateurs de puissance ne sont plus couverts par le présent document, mais se trouvent dorénavant dans l'IEC 60475:2022, 4.2.

Avant d'analyser les gaz dissous dans l'huile, ils sont en premier lieu extraits de l'huile. Trois méthodes de base sont décrites, l'une utilisant l'extraction sous vide (Toepler et dégazage partiel), une autre par déplacement des gaz dissous par barbotage d'un gaz vecteur dans l'échantillon d'huile (entraînement) et la dernière par partition des gaz entre l'échantillon d'huile et un faible volume du gaz vecteur (espace de tête). Après extraction, l'analyse quantitative des gaz s'effectue par chromatographie en phase gazeuse; une méthode d'analyse est décrite. Les gaz libres prélevés au niveau des relais de protection sont analysés sans traitement préalable.

La méthode préférentielle pour assurer le fonctionnement des matériels d'extraction des gaz et d'analyse, étudiés ensemble comme un seul et même système, consiste à extraire les gaz d'échantillons d'huile préparés au laboratoire qui contiennent des concentrations en gaz connues ("étalons de gaz dissous dans l'huile") et qui sont analysés quantitativement. Deux méthodes sont décrites pour l'obtention d'étalons de gaz dissous dans l'huile.

Lors de vérifications quotidiennes de l'étalonnage du chromatographe, il est commode d'utiliser un mélange de gaz étalons dont les teneurs en chacun des composants sont connues et appropriées, et dans un rapport similaire aux teneurs habituelles des gaz extraits des huiles des transformateurs.

Les techniques décrites tiennent compte, d'une part, des problèmes spécifiques à l'analyse liés aux essais de réception en usine, pour lesquels les teneurs en gaz sont généralement très faibles, et, d'autre part, des problèmes rencontrés dans la surveillance du matériel sur site, le transport des échantillons pouvant se faire par fret aérien non pressurisé et des différences importantes de températures pouvant exister entre le site de prélèvement et le laboratoire d'analyse.

2 Références normatives

Les documents suivants sont cités dans le texte de sorte qu'ils constituent, pour tout ou partie de leur contenu, des exigences du présent document. Pour les références datées, seule l'édition citée s'applique. Pour les références non datées, la dernière édition du document de référence s'applique (y compris les éventuels amendements).

IEC 60296, *Fluides pour applications électrotechniques – Huiles minérales isolantes pour matériel électrique*

IEC 60475:2022, *Méthode d'échantillonnage des liquides isolants*

ISO 5725-1, *Exactitude (justesse et fidélité) des résultats et méthodes de mesure – Partie 1: Principes généraux et définitions*

3 Termes, définitions, symboles et abréviations

3.1 Termes et définitions

Aucun terme n'est défini dans le présent document.

L'ISO et l'IEC tiennent à jour des bases de données terminologiques destinées à être utilisées en normalisation, consultables aux adresses suivantes:

- IEC Electropedia: disponible à l'adresse https://www.electropedia.org/
- ISO Online browsing platform: disponible à l'adresse https://www.iso.org/obp

3.2 Symboles et abréviations

3.2.1 Symboles

Les symboles utilisés en 8.5.2 sont les suivants:

V	volume total du flacon;
V_{G}	volume de la phase gazeuse dans le flacon;
V_{L}	volume de la phase d'huile dans le flacon;
C_{G}	concentration de gaz (i) dans la phase gazeuse du flacon, obtenue par chromatographie en phase gazeuse (GC, *Gas Chromatography*);
C_{L}^{0*}	concentration de gaz (i) dans l'échantillon d'huile, obtenue directement à partir de C_{G}, en utilisant des courbes d'étalonnage avec des étalons de gaz dissous dans l'huile;
P, t	pression atmosphérique et température au moment où l'échantillon d'huile a été analysé (P en kPa; t en °C);
P_{s}, t_{s}	pression atmosphérique et température au moment où l'étalon de gaz dissous dans l'huile, ou l'étalon de gaz, a été analysé (P_{s} en kPa; t_{s} en °C);
K	coefficient de partage du gaz (i), pour le calcul de C_{L}^{0} en utilisant des étalons de gaz;
C_{L}^{0}	concentration de gaz (i) dans l'échantillon d'huile.

3.2.2 Abréviations

AGD	analyse des gaz dissous
FID (Flame Ionization Detector)	détecteur à ionisation de flamme
GC (Gas Chromatography)	chromatographie en phase gazeuse
GILS (Gas-In-Liquid Standards)	étalons de gaz dissous dans les liquides
GIOS (Gas-In-Oil Standards)	étalons de gaz dissous dans l'huile
HID (Helium Ionization Detector)	détecteur à ionisation d'hélium
DI	diamètre intérieur
NIST	National Institute of Standards and Technology
DE	diamètre extérieur
OLTC (On-Load Tap-Changer)	changeur de prises en charge
PLOT (Porous Large Open Tubular)	tubulaires, ouvertes, de grande taille et poreuses

PTFE	polytétrafluoroéthylène
TCD (Thermal Conductivity Detector)	détecteur à conductibilité thermique

4 Échantillonnage des gaz aux relais de protection

4.1 Remarques générales

Il est important de garder à l'esprit que le fait de recevoir un échantillon qualitatif et représentatif est crucial pour obtenir un diagnostic fiable du matériel électrique. Même les méthodes d'extraction ou de diagnostic les plus sophistiquées ne peuvent pas rattraper un échantillonnage défectueux.

Il convient de prélever sur le matériel les échantillons de gaz accumulés au niveau des relais, dans le plus bref délai après le signalement de l'accumulation. Des variations de la composition des gaz, dues à la réabsorption sélective des composants, peuvent se produire si les gaz libres restent en contact avec l'huile.

Il est nécessaire de prendre certaines précautions lors du prélèvement des gaz. La liaison entre le dispositif de prélèvement et le récipient d'échantillonnage doit éviter toute entrée d'air. Il convient que les raccordements provisoires soient aussi courts que possible. Il convient aussi que l'imperméabilité aux gaz de tous les tuyaux en plastique ou en caoutchouc utilisés ait été vérifiée.

Les échantillons de gaz doivent être convenablement étiquetés (voir Article 5) et être analysés dans les plus brefs délais pour réduire le plus possible les pertes d'hydrogène de la seringue utilisée pour l'échantillonnage du gaz (délai maximal d'une semaine, par exemple).

S'il y a de l'oxygène, il peut réagir avec l'huile échantillonnée. Cette réaction est retardée en empêchant l'action de la lumière sur l'échantillon, par exemple en enveloppant le récipient de prélèvement avec une feuille d'aluminium ou tout autre matériau opaque.

Des trois méthodes décrites en 4.2, en 4.3 et en 4.4, la méthode de prélèvement en seringue est recommandée. Les deux autres méthodes sont des alternatives à utiliser seulement en cas de problème sérieux.

L'échantillonnage en ampoule de prélèvement par déplacement de liquide, en utilisant de l'huile pour transformateurs comme liquide de transfert, est simple, mais il exige de tenir compte des différences de solubilité des composants gazeux, si la quantité de gaz recueillie est telle qu'il reste de l'huile dans le tube.

La méthode d'échantillonnage sous vide demande une certaine maîtrise pour éviter que les fuites du système contaminent l'échantillon. Cela est particulièrement vrai dans les cas où le gaz à échantillonner peut être à une pression inférieure à la pression atmosphérique (cas de transformateurs hermétiques, par exemple).

4.2 Échantillonnage de gaz libres en seringue

4.2.1 Matériel de prélèvement

NOTE Les nombres entre parenthèses se réfèrent aux nombres encerclés sur la figure en question.

Voir Figure 1. Le matériel doit consister en ce qui suit:

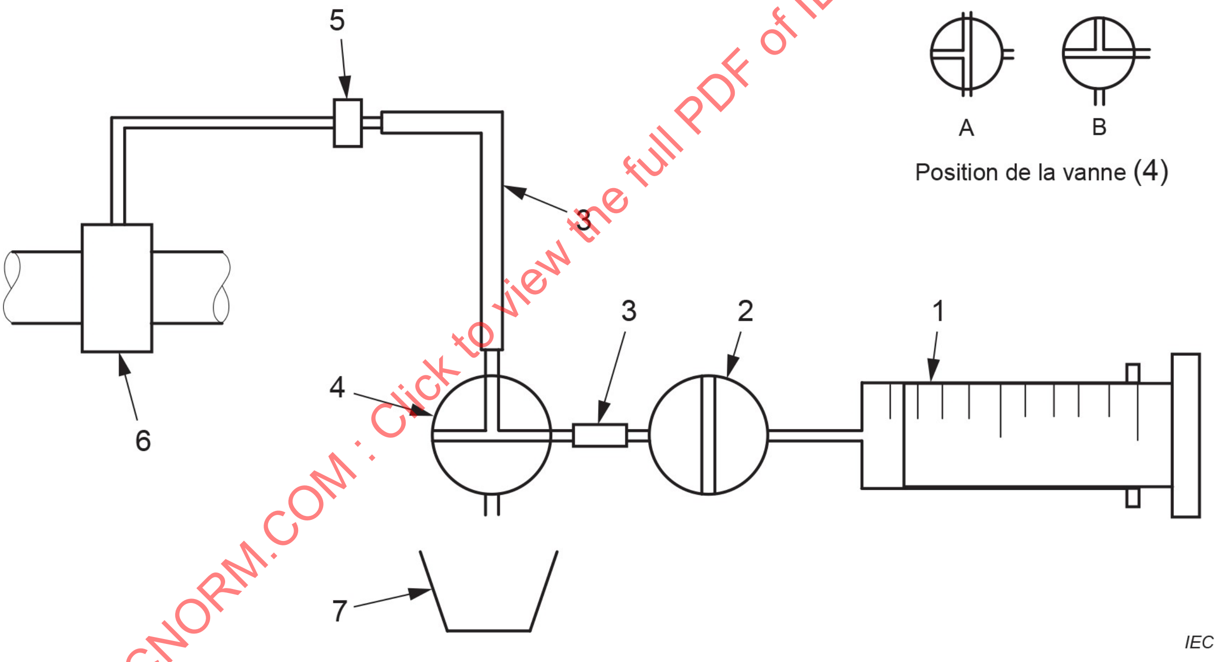
a) un tuyau en caoutchouc ou en plastique, imperméable aux gaz et résistant à l'huile (3), équipé d'un raccord adaptable sur la prise d'échantillonnage appropriée du relais de protection. Afin d'éviter la contamination croisée, il convient de n'utiliser le tuyau qu'une seule fois;

b) des seringues étanches aux gaz, de volume adéquat (1) (25 ml à 250 ml). Des seringues en verre, du type médical ou vétérinaire, avec des pistons en verre dépoli, peuvent être appropriées; sinon des seringues avec joints étanches à l'huile peuvent être utilisées. Il convient d'obturer les seringues par un embout ou un robinet adapté. Il est souvent commode d'utiliser les mêmes seringues à la fois pour l'échantillonnage du gaz et de l'huile (voir l'IEC 60475:2022, 4.2.2).

   L'étanchéité au gaz d'une seringue en verre utilisée pour l'échantillonnage du gaz peut être vérifiée en conservant, pendant deux semaines au moins, un échantillon d'huile qui contient une quantité mesurable d'hydrogène et en analysant l'hydrogène sur des parties aliquotes, au début et à la fin de cette période. Une seringue est considérée comme acceptable si les pertes d'hydrogène sont inférieures à 2,5 % par semaine. L'expérience générale révèle que les seringues entièrement en verre présentent moins de fuites que les seringues qui utilisent des joints plastiques. L'amélioration de l'étanchéité au gaz peut être obtenue en utilisant un lubrifiant tel qu'une graisse légère ou de l'huile pour transformateurs.

   Une bonne pratique consiste à soumettre aux essais l'intégrité des seringues et du système de soupape avant l'échantillonnage. Un mode opératoire recommandé est décrit dans l'IEC 60475:2022, Annexe B;

c) il convient de réaliser des mallettes d'expédition de façon à maintenir fermement les seringues durant le transport, tout en permettant au piston de se déplacer librement, et en empêchant que son extrémité ne soit en contact avec la mallette, quelle que soit sa position au cours du transport.



Légende

1 seringue

2 robinet

3 raccord en caoutchouc

4 vanne à trois voies

5 vanne d'échantillonnage du matériel

6 vanne du relais de protection

7 récipient de vidange

Figure 1 – Échantillonnage de gaz en seringue

4.2.2 Mode de prélèvement

Le dispositif est raccordé comme cela est indiqué à la Figure 1. Il convient que les raccordements soient aussi courts que possible et soient remplis d'huile au début du prélèvement.

La vanne d'échantillonnage (5) est ouverte. L'échantillonnage à partir du relais de protection d'un transformateur à conservateur se fait en surpression; mettre alors avec précaution la vanne à trois voies (4) en position A et laisser couler l'huile du tuyau de raccordement (3) dans le bac de vidange (7). Quand les gaz atteignent la valve à trois voies (4), tourner ce dernier en position B pour raccorder la seringue prélubrifiée (1). Ouvrir alors le robinet (2) et, sous l'effet de la pression hydrostatique, remplir la seringue en veillant à ne pas chasser son piston. Après avoir prélevé le volume suffisant, fermer le robinet (2) et la vanne d'échantillonnage (5), puis démonter le dispositif.

Chasser toute l'huile de la seringue en retournant la seringue et en repoussant lentement le piston.

Étiqueter avec soin l'échantillon (voir Article 5).

4.3 Échantillonnage des gaz libres par déplacement d'huile

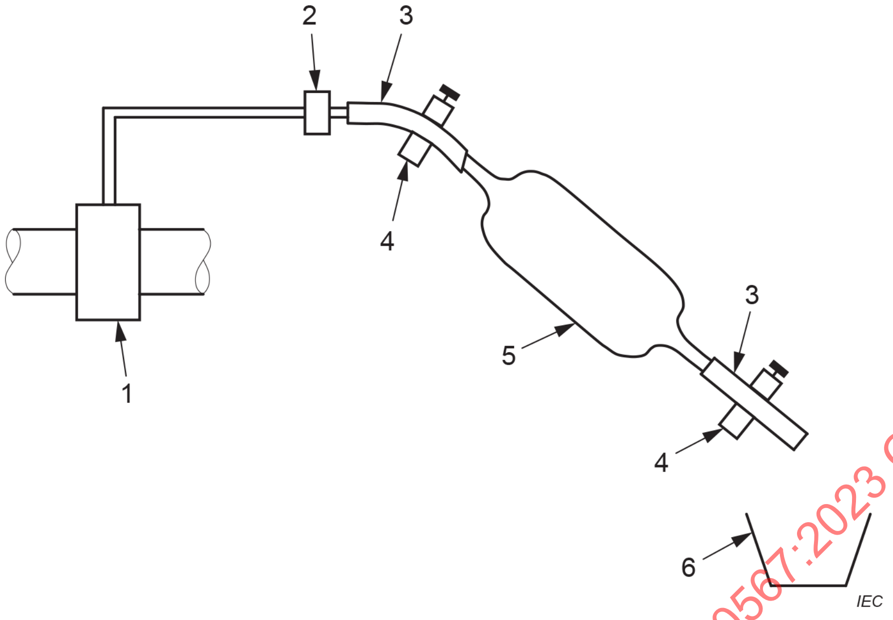
Cette méthode n'est fiable que si les gaz à prélever sont à pression égale ou supérieure à la pression atmosphérique. Le dispositif est représenté à la Figure 2.

L'ampoule de prélèvement (5), habituellement de volume 100 ml, est de préférence en verre, afin que l'opérateur puisse voir la quantité d'huile qui reste durant le prélèvement des gaz. L'ampoule de prélèvement est remplie d'huile provenant du transformateur sur site. Il convient que le tuyau de raccordement (3), décrit ci-après, soit également rempli d'huile avant son emploi.

Adapter l'extrémité libre du tuyau de raccordement (3) à la vanne à gaz d'échantillonnage (2). La vanne d'échantillonnage et le robinet d'entrée de l'ampoule de prélèvement sont ouverts. Incliner l'ampoule de prélèvement, de telle sorte que son extrémité fermée soit le plus bas possible. Ensuite, ouvrir le robinet de sortie de l'ampoule de prélèvement afin de permettre l'écoulement de l'huile dans le bac de vidange (6), provoquant l'entraînement en premier lieu de toute l'huile des tubulures de raccordement entre le relais et la vanne d'échantillonnage, puis des gaz du relais dans l'ampoule de prélèvement.

Le prélèvement est terminé quand le relais de protection est complètement rempli d'huile ou quand presque toute l'huile de l'ampoule de prélèvement s'est écoulée.

Fermer les deux robinets (4) de l'ampoule de prélèvement et la vanne d'échantillonnage (2), puis enlever les tuyaux de raccordement.



Légende

1	vanne du relais de protection
2	vanne d'échantillonnage du matériel
3	tuyau de raccordement résistant à l'huile
4	robinet
5	ampoule de prélèvement
6	récipient de vidange

Figure 2 – Échantillonnage des gaz libres par déplacement d'huile

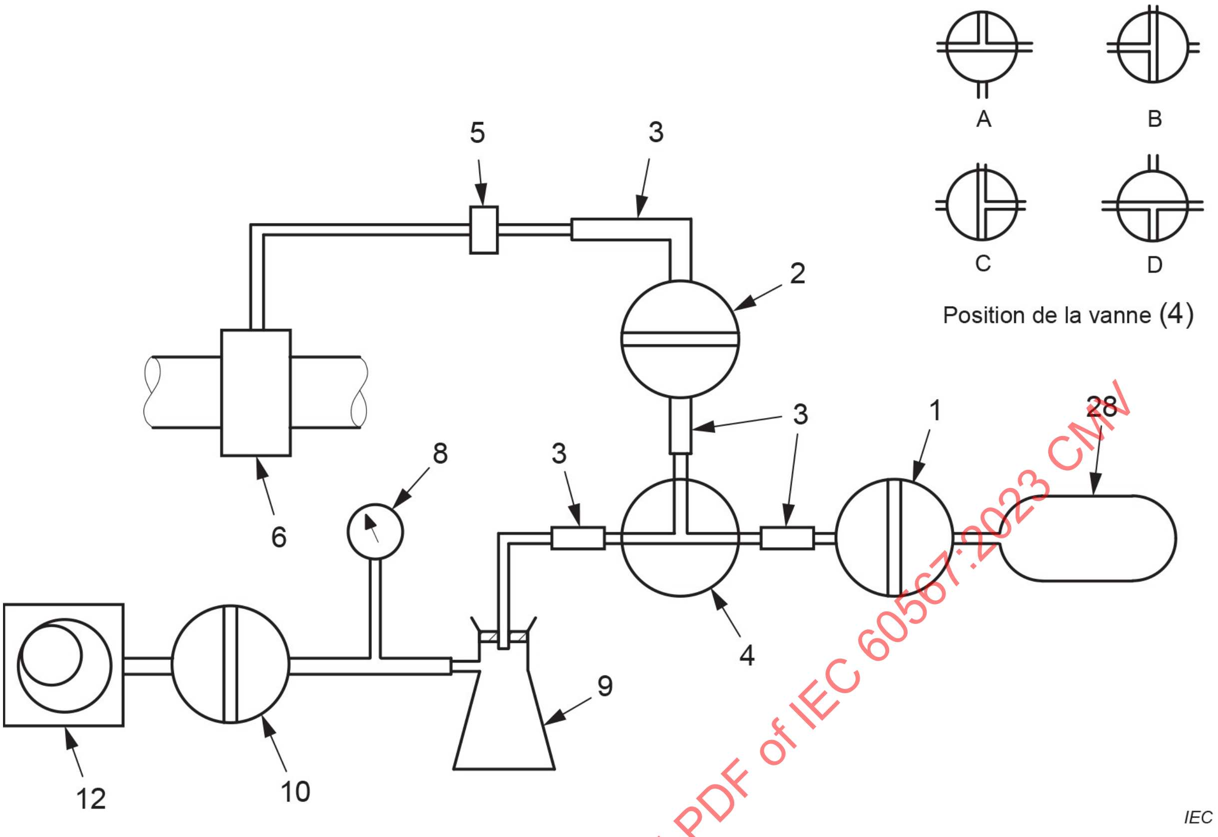
4.4 Échantillonnage sous vide des gaz libres

Le dispositif est raccordé comme cela est indiqué à la Figure 3. Mettre en route la pompe à vide (12) pour évacuer les tuyaux de raccordement, le piège et le récipient d'échantillonnage, les robinets (1), (2) et (10) étant ouverts, la vanne à trois voies (4) étant dans la position A et la vanne d'échantillonnage du matériel étant fermée.

Le vide obtenu est considéré comme satisfaisant s'il est inférieur à 100 Pa. Il convient de contrôler les fuites du système de prélèvement en fermant le robinet d'aspiration (10) de la pompe et en observant qu'il n'y a pas de variation appréciable du vide obtenu. Sur une durée égale à celle nécessaire au prélèvement, il convient que la pression n'augmente pas de plus de 100 Pa. De manière analogue, il convient que le robinet (1) de l'ampoule de prélèvement soit aussi étanche au vide durant plusieurs semaines.

Si le tuyau de raccordement entre la vanne d'échantillonnage du matériel (5) et le relais de protection est rempli d'huile, mettre la vanne à trois voies (4) en position B. Ouvrir la vanne d'échantillonnage du matériel (5) avec soin afin de laisser s'écouler l'huile dans le piège (9). Quand la fin de l'écoulement de l'huile arrive au niveau de la vanne à trois voies (4), placer celui-ci en position D, pour le vidanger. Remettre alors la vanne (4) en position C. Le prélèvement terminé, fermer le robinet (1) en premier, puis la vanne d'échantillonnage du matériel (5) et enlever le dispositif de prélèvement.

Dans le cas où le tuyau de raccordement entre le matériel et la vanne d'échantillonnage est vide d'huile, ne pas appliquer le mode opératoire de vidange de l'huile et placer la vanne à trois voies (4) dans la position C, après avoir évacué le dispositif de prélèvement et avoir vérifié qu'il est étanche aux fuites.



Légende

1 robinet étanche au vide
2 robinet étanche au vide
3 raccord en caoutchouc
4 vanne à trois voies étanche au vide
5 vanne d'échantillonnage du matériel
6 vanne du relais de protection
8 manomètre de mesure du vide
9 piège
10 robinet étanche au vide
12 pompe à vide
28 ampoule de prélèvement

Figure 3 – Échantillonnage sous vide des gaz libres

4.5 Échantillonnage de l'huile dans les matériels immergés dans l'huile

Voir l'IEC 60475:2022, 4.2.

5 Identification des échantillons de gaz

Les échantillons de gaz doivent être convenablement étiquetés avant leur envoi au laboratoire.

Les informations indiquées dans le Tableau 1 sont nécessaires (lorsqu'elles sont connues).

Tableau 1 – Informations nécessaires pour les échantillons de gaz

Transformateur	Échantillonnage
Client	Date du prélèvement et temps écoulé après l'alarme de gaz
Emplacement	Point d'échantillonnage
Numéro d'identification	Personne qui réalise le prélèvement
Fabricant	Raison de l'analyse
Type général (de puissance, de mesure ou industriel)	Transformateur hors tension, sous tension hors charge ou en charge
MVA en valeur assignée	
Rapport de tension	
Type et emplacement du CPC	
Date de mise en service	
Huile	
Type d'huile (minérale ou non minérale)	Poids (ou volume) d'huile
Nom du produit	Date du dernier traitement de l'huile

Les informations additionnelles ci-après sont souhaitables:

- température ambiante, lecture des MVA, du courant de charge ou du pourcentage de charge, fonctionnement des pompes, mode de communication du changeur de prises avec la cuve de l'appareil, système de protection de l'huile (conservateur, matelas d'azote, etc.) et toutes les variations des conditions de fonctionnement ou toutes les interventions de maintenance depuis le dernier prélèvement;
- heure de l'échantillonnage en cas de prélèvement de plusieurs échantillons.

6 Échantillonnage, étiquetage et transfert de l'huile dans les matériels immergés dans l'huile

6.1 Échantillonnage et étiquetage de l'huile

Consulter l'IEC 60475:2022, 4.2 à 4.4, pour connaître le matériel d'échantillonnage, les modes de prélèvement et l'étiquetage à utiliser.

6.2 Transfert de l'huile pour analyse AGD

6.2.1 Généralités

Pour transférer de l'huile de son flacon d'échantillonnage dans les récipients d'extraction de gaz spécifiés à l'Article 8, il convient d'utiliser les modes opératoires suivants.

6.2.2 Transfert à partir des seringues à huile

Introduire une partie de l'échantillon d'huile de la seringue dans le récipient d'extraction des gaz en tournant la vanne à trois voies de la seringue en position B, représentée dans l'IEC 60475:2022, Figure 5.

6.2.3 Transfert à partir des ampoules

Fixer l'ampoule en position verticale. Installer une vanne à trois voies en plastique entre le tuyau en plastique inférieur de l'ampoule et un autre élément de ce tuyau pour vidanger le réceptacle d'huile. Fixer une seringue en verre à la vanne à trois voies en plastique. Ouvrir le robinet supérieur, puis le robinet inférieur de l'ampoule. Remplir la seringue d'huile selon les modes opératoires indiqués dans l'IEC 60475:2022, 4.2.2.2. Transférer une partie de l'échantillon d'huile de la seringue dans le récipient d'extraction des gaz (voir 6.2.2 ci-dessus).

6.2.4 Transfert à partir de bouteilles métalliques flexibles

Ouvrir le bouchon à vis de la bouteille, introduire une longue aiguille jusqu'au fond de la bouteille, fixer une seringue en verre équipée d'une vanne à trois voies à l'aiguille, puis prélever doucement (afin de ne pas créer de bulles de gaz en raison de la pression négative) un échantillon d'huile dans la seringue. Détacher la vanne à trois voies de l'aiguille, puis inverser la seringue pour expulser toutes les bulles de gaz présentes dans l'huile. Ensuite, introduire une partie de l'échantillon d'huile de la seringue dans la chambre d'extraction des gaz (voir 6.2.2 ci-dessus). En variante, un élément du tuyau peut être utilisé pour placer l'huile directement dans le récipient d'extraction des gaz (Toepler ou dégazage partiel) sous vide.

Il convient de toujours utiliser le premier échantillon prélevé de la bouteille pour analyse AGD. Il convient de ne prélever aucun autre échantillon pour analyse AGD, une perte de gaz significative pouvant se produire dans l'espace de tête de la bouteille.

6.2.5 Transfert à partir de bouteilles en verre et en métal rigide

Le mode opératoire utilisé pour les bouteilles métalliques flexibles en 6.2.4 convient pour les bouteilles en verre et en métal rigide.

7 Préparation d'étalon de gaz dissous dans l'huile

7.1 Remarques générales

Comme cela est indiqué à l'Article 1, la méthode préférentielle pour assurer le fonctionnement du système d'extraction des gaz et d'analyse dans son ensemble repose sur l'analyse d'huiles contenant des concentrations connues de gaz (étalons de gaz dissous dans l'huile).

Deux méthodes de préparation de ces étalons de gaz dissous dans l'huile sont décrites en 7.2 et en 7.3, une méthode générale et une méthode simplifiée. L'intérêt de la première méthode est de fournir des volumes d'huile beaucoup plus importants.

Si des étalons de gaz dissous dans l'huile sont disponibles dans le commerce, ils peuvent être utilisés, à condition qu'ils répondent aux exigences d'assurance de la qualité. S'ils sont fournis dans les conditions normalisées ASTM (0 °C), ils doivent être convertis aux conditions IEC (20 °C).

7.2 Première méthode: préparation d'un grand volume d'étalon de gaz dissous dans l'huile

7.2.1 Matériel

Un dispositif approprié se compose (voir Figure 4 a), Figure 4 b) et Figure 4 c)):

- d'un agitateur magnétique (12);
- d'un réservoir d'huile de 5 l (13) à trois sorties latérales, dont deux équipées de robinets à vide poussé (1) et (2) et la troisième d'un septum en caoutchouc (16);
- d'un réservoir de 6 l (14) équipé d'un robinet à vide poussé (3) et relié à un ballon de sécurité (15) de 75 ml, monté sur un robinet à vide poussé (4);

– d'un système de déplacement à mercure (17) composé de deux ballons en verre qui contiennent 500 ml de mercure, reliés par un tuyau en caoutchouc flexible résistant à l'huile, à vide poussé.

Le système d'injection de gaz (Figure 4 e), Figure 4 f) et Figure 4 g)) se compose:

– d'un jeu de seringues étanches aux gaz de volumes adéquats (18);

– d'une vanne à trois voies en plastique de type normalisé (7), modifiée pour réduire le plus possible les volumes morts, en insérant des bouts de tube en acier inoxydable (environ 0,4 mm de diamètre intérieur (DI) et 1,5 mm de diamètre extérieur (DE)) dans les voies et relié à une aiguille d'injection de gaz (10) (environ 10 cm de longueur et 0,25 mm de diamètre extérieur) pour perforer le septum en caoutchouc du récipient à huile (16);

– des bouteilles de gaz comprimé équipées d'un détendeur et d'une vanne (20);

NOTE 1 Des bouteilles de gaz comprimé qui contiennent chacun des gaz à injecter peuvent être utilisées. Des mélanges de ces gaz prêts à l'emploi peuvent également être obtenus auprès des fournisseurs de gaz.

– d'une certaine longueur de tuyau flexible résistant à l'huile qui relie la bouteille de gaz comprimé à la vanne à trois voies (7), le tuyau étant équipé d'une aiguille hypodermique (environ 0,3 mm de DI et 0,6 mm de DE). Celle-ci permet de provoquer une fuite vers un barboteur à eau (21) utilisé pour vérifier l'absence de refoulement.

NOTE 2 La longueur de tuyau qui relie la bouteille de gaz comprimé à la vanne à trois voies est remplacée après chaque changement de gaz.

Le système d'échantillonnage de l'huile (Figure 4 h) à Figure 4 k)) se compose de seringues en verre (19) de volume adéquat, équipées de deux vannes à trois voies en plastique (8) et (9) et d'aiguilles hypodermiques (11) (environ 0,6 mm de DI, 1,0 mm de DE et 120 mm de longueur).

7.2.2 Mode opératoire

NOTE Les nombres entre parenthèses se réfèrent aux nombres encerclés sur la Figure 4. Les positions A à D des vannes à trois voies (7, 8 et 9) sont indiquées à la Figure 4 d).

7.2.2.1 Dégazage de l'huile

a) Nettoyer soigneusement la verrerie avant montage.

b) Fixer le septum en caoutchouc et les raccords souples avec des colliers métalliques.

c) Laver, si nécessaire, environ 1 l de mercure avec du pentane et le filtrer au moyen d'un filtre fin en papier, percé d'un trou.

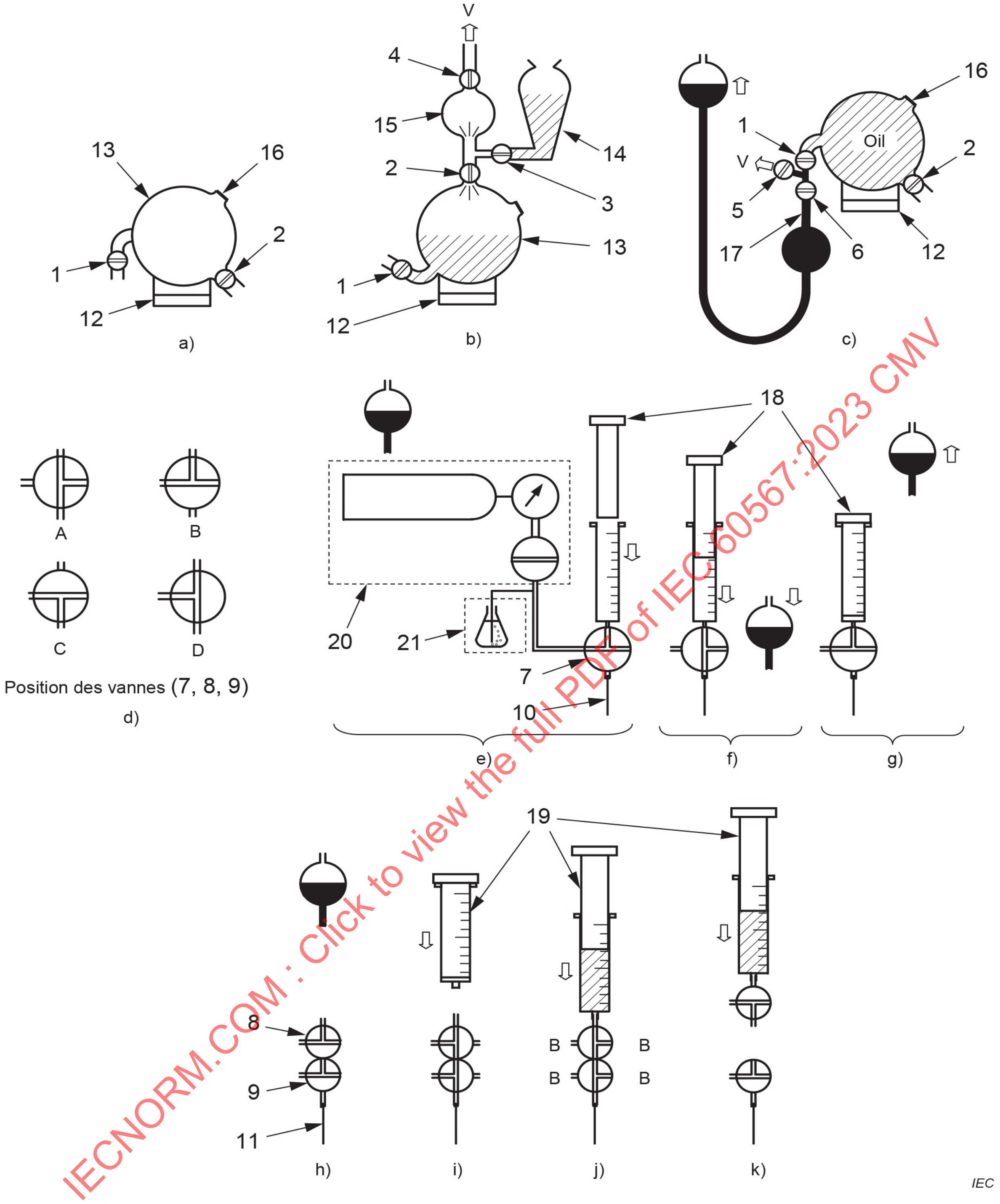
d) Adapter le réservoir d'huile (14), le ballon de sécurité (15) et les robinets (4) au réservoir de 5 l (13). Relier le système à une pompe à vide (V) et faire le vide dans le ballon de sécurité (15) et le réservoir d'huile de 5 l (13) en ouvrant les robinets (2) et (4).

e) Remplir le réservoir (14) d'huile minérale isolante conforme aux spécifications de l'IEC 60296 et introduire lentement l'huile par le robinet (3) dans le réservoir de 5 l (13) en le remplissant totalement. Ensuite, fermer le robinet (2), puis démonter le réservoir d'huile (14) et le ballon de sécurité.

NOTE Si ce mode opératoire est suivi scrupuleusement (durée de remplissage de 4 h environ), l'huile est pratiquement dégazée.

f) Basculer le réservoir d'huile comme cela est indiqué à la Figure 4 c). Mettre un linge humide sur le réservoir pour que sa température ne s'élève pas et fixer le système de déplacement à mercure (17) au robinet (1). Introduire 750 ml de mercure, le robinet (6) étant fermé.

g) Relier le système de déplacement à la canalisation de vide (V), ouvrir le robinet (5) et mettre sous vide la partie comprise entre les robinets (1) et (6). Ouvrir le robinet (6) pour faire monter le mercure jusqu'aux robinets (1) et (5), puis fermer le robinet (5). Élever l'ampoule de gauche du système de déplacement (voir Figure 7 c)), de sorte que le niveau de mercure soit plus haut que celui de l'huile dans le ballon. Ouvrir le robinet (1). Enlever le linge humide et mettre en route l'agitateur magnétique (12).



Légende

1	robinets à vide	9	vannes à trois voies	17	système de déplacement à mercure
2	robinets à vide	10	aiguille d'injection de gaz	18	seringue de précision étanche au gaz
3	robinets à vide	11	aiguille de prélèvement d'huile	19	seringue en verre
4	robinets à vide	12	agitateur magnétique	20	bouteille de gaz comprimé équipée d'un détendeur et d'une vanne
5	robinets à vide	13	réservoir d'huile de 5 l	21	fuite vers le barboteur à eau
6	robinets à vide	14	réservoir d'huile de 6 l	V	liaison à la pompe à vide
7	vannes à trois voies	15	boule de sécurité de 75 ml		
8	vannes à trois voies	16	septum en caoutchouc		

Figure 4 – Première méthode de préparation d'étalons de gaz dissous dans l'huile

7.2.2.2 Préparation d'étalon de gaz dissous dans l'huile

Voir Figure 4 c) à Figure 4 g).

a) Pour injecter les gaz, fixer la vanne à trois voies modifiée (7) en position B à l'aiguille d'injection de gaz (10). Introduire l'aiguille à travers le septum en caoutchouc (16) dans l'huile. Tourner la vanne à trois voies dans la position D pour purger l'aiguille et la vanne avec l'huile, puis la remettre en position B. Fixer le corps d'une seringue de précision étalonnée, étanche au gaz (18) de volume convenable (d'une précision de 1 %) et le tuyau de raccordement de la bouteille de gaz comprimé (voir Figure 4 e)) à la vanne (7). Balayer le corps de seringue par un courant modéré de gaz puis, lentement, introduire plusieurs fois le piston dans le cylindre, pour finalement l'arrêter au volume de gaz à injecter en s'assurant qu'il y a un barbotage continu à travers l'aiguille de fuite (21).

b) Placer la vanne (7) en position d'injection A, abaisser le niveau du mercure au-dessous de la pointe de l'aiguille et repousser le piston pour injecter le volume de gaz dans l'huile. Mettre la vanne (7) en position B et élever la cuve à mercure au-dessus du réservoir d'huile.

c) Répéter le même mode opératoire pour chaque gaz à mettre en solution, puis enlever l'aiguille d'injection de gaz et la vanne (7).

   Quand tous les gaz sont mis en solution, arrêter l'agitateur magnétique. Noter la pression atmosphérique et la température.

   NOTE Au lieu d'ajouter individuellement les gaz, il est plus commode d'utiliser un mélange de gaz étalons qui contient de préférence tous ceux cités en 9.1, dont les concentrations sont représentatives de celles de l'huile échantillonnée.

7.2.2.3 Échantillonnage d'étalon de gaz dissous dans l'huile

Voir Figure 4 h) à Figure 4 k).

a) Pour prélever des échantillons d'huile du réservoir de 5 l (13), adapter deux vannes à trois voies (8) et (9) suivant la Figure 4 b), toutes deux en position B, et fixer l'ensemble à l'aiguille de prélèvement d'huile (11), puis introduire cette aiguille dans l'huile à travers le septum en caoutchouc (16). Le niveau du mercure étant en position haute, fermer les vannes (8) et (9) en position D d'aspiration pour les purger avec de l'huile (voir Figure 4 i)).

b) Fixer une seringue (19) et tourner simultanément les deux vannes (8) et (9) en position A, puis aspirer un volume adéquat d'huile (voir Figure 4 j)). Placer ensuite la vanne (8) en position C et la vanne (9) en position B, puis retirer la seringue équipée de la vanne (8) (voir Figure 4 k)).

Pour prélever plus d'huile, du mercure doit être rajouté au système de déplacement à mercure.

7.2.3 Calcul

Calculer la concentration de chaque gaz "i" dissous comme suit:

$$C_\mathrm{i} = V_\mathrm{i} / V \times 10^6$$

où

C_i est la concentration de gaz "i", en µl/l;

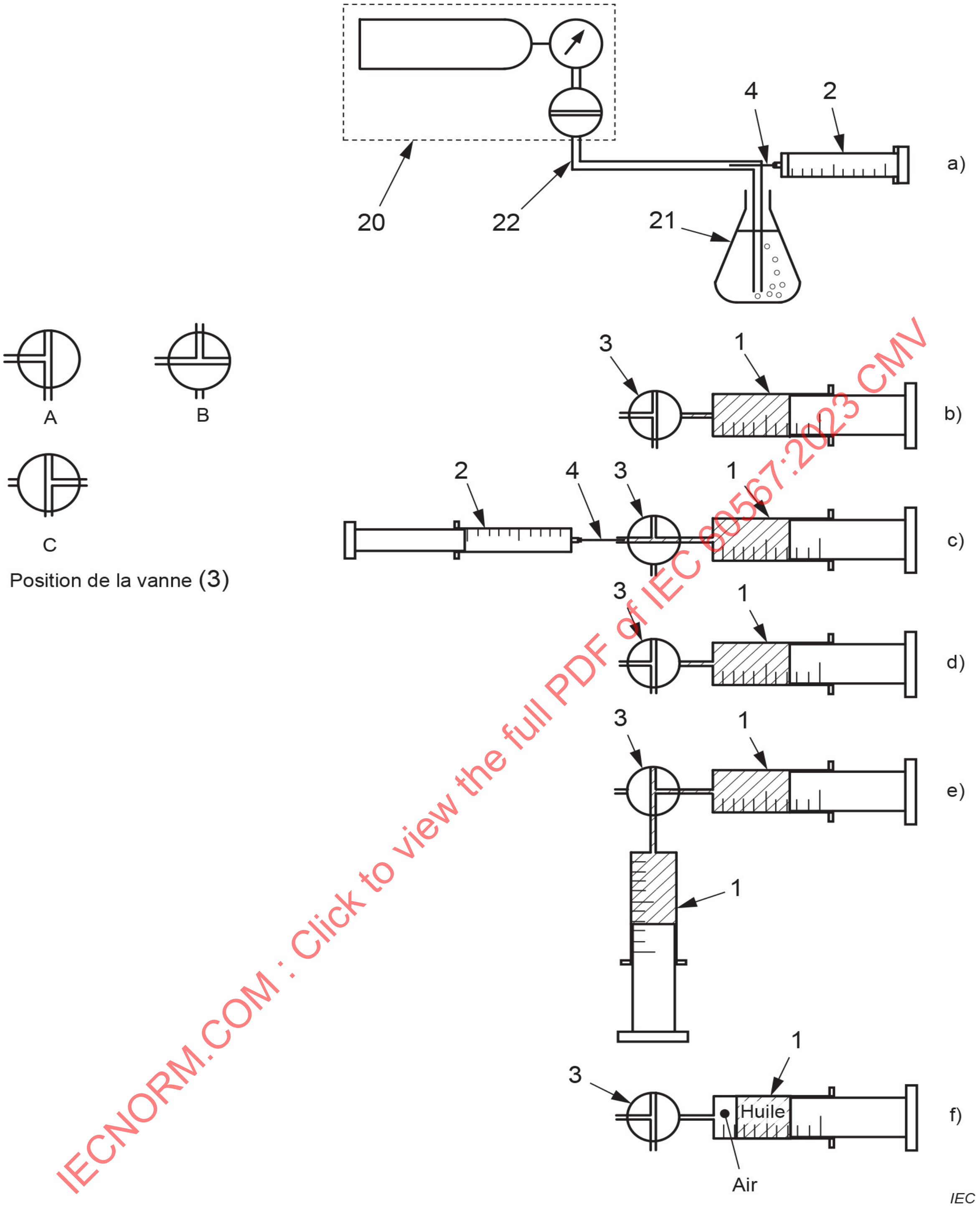
V_i est le volume de gaz "i" injecté, en ml, ramené à 20 °C et 101,3 kPa;

V est le volume exact d'huile contenu dans le réservoir de 5 l, en ml.

7.3 Deuxième méthode: préparation d'étalon de gaz dissous dans l'huile dans une seringue ou un flacon

7.3.1 Généralités

Voir Figure 5 a) à Figure 5 f).



Légende

1 seringue en verre

2 seringue de précision étanche au gaz

3 vanne à trois voies

4 aiguille d'injection de gaz

20 bouteille de gaz comprimé équipée d'un détendeur et d'une vanne

21 fuite vers le barboteur à eau

22 tuyau en caoutchouc silicone

Figure 5 – Deuxième méthode de préparation d'étalons de gaz dissous dans l'huile

7.3.2 Matériel

Le matériel se compose:

- d'un jeu de seringues étanches au gaz de volume adéquat (2);
- d'un jeu de seringues en verre de volume adéquat (1);
- d'un jeu d'aiguilles d'injection de gaz (4);
- de vannes à trois voies en plastique (3);
- de bouteilles de gaz comprimé équipées d'un détendeur et d'une vanne (20).

NOTE Des bouteilles de gaz comprimé qui contiennent chacun des gaz à injecter peuvent être utilisées. Des mélanges de ces gaz prêts à l'emploi peuvent également être obtenus auprès des fournisseurs de gaz.

7.3.3 Mode opératoire

a) Barboter de l'argon dans 1 l d'huile pendant 1 h en agitant, en ajustant le flux de gaz pour maintenir l'agitation de l'huile, afin de purger tous les autres gaz dissous. Extraire les gaz de cette huile saturée en argon sous vide jusqu'à 1 Pa à travers un filtre de 8 µm dans un récipient de 2 l (des teneurs résiduelles de 500 µl/l O_2 et 2 000 µl/l N_2 sont acceptables). Lorsque l'huile est complètement dégazée, couper le vide avec de l'argon jusqu'à 20 kPa.

b) Peser une seringue en verre de 100 ml contenant 10 ml de billes de verre. Relier la seringue au fond du récipient de 2 l et purger la seringue deux fois avec 20 ml d'huile. S'assurer que le cylindre et le piston sont complètement mouillés avec de l'huile. Remplir la seringue avec 90 ml d'huile dégazée.

c) Relier une seringue étanche au gaz du volume exigé avec une aiguille suffisamment longue pour introduire un mélange gazeux dans la partie cylindrique de la seringue, par exemple d'une longueur de 115 mm, à un cylindre qui contient un mélange de gaz étalons, et purger quatre fois avec le gaz étalon. Remplir la seringue avec un volume connu de gaz étalon. Insérer l'aiguille à travers la pointe de la seringue à huile, et transférer le volume de gaz étalon dans la seringue à huile. Peser à nouveau, pour déterminer le volume d'huile réel. Envelopper la seringue à huile avec un feuille d'aluminium afin d'éviter les dégradations dues à la lumière du jour et la fixer à un agitateur tridimensionnel de laboratoire. Secouer pendant 1 h ou jusqu'à dissolution de tous les gaz.

   NOTE 1 Toute autre mode opératoire qui aide à la dissolution des gaz dans l'huile (mélange avec agitateur magnétique ou autre, par exemple) est adaptée et peut être utilisée.

d) Noter la pression atmosphérique et la température; de même, se reporter à la note en 7.2.2.2. Calculer la concentration en gaz dissous à partir du volume d'huile, du volume de gaz étalon introduit, de la température et de la pression atmosphérique, comme en 7.2.3. Exprimer les quantités de gaz injectées en µmol, ou en µl converties aux conditions normales (20 °C; 101,3 kPa).

e) Répéter le mode opératoire pour obtenir au moins trois échantillons de gaz dissous dans l'huile (uniquement dans le cas de la méthode d'espace de tête) dont les concentrations permettent de tracer une courbe d'étalonnage qui couvre les valeurs prévues dans les échantillons inconnus.

   NOTE 2 Si un mélange totalement saturé est souhaité, introduire de l'air ou de l'azote sec exempt de CO_2 dans la seringue pour obtenir, avec les gaz précédemment injectés, un volume total de gaz de 10 % à 8 % du volume d'huile, selon le gaz choisi (voir Figure 5 f)).

   Tourner la vanne à trois voies (3) en position A et agiter de nouveau la seringue jusqu'à dissolution totale de l'air ou de l'azote. La dissolution du gaz dans l'huile est accélérée en plaçant la seringue dans un réfrigérateur.

   NOTE 3 Un flacon peut être utilisé au lieu d'une seringue. Le flacon est rempli de la même quantité d'huile dégazée que lorsque l'analyse ordinaire est réalisée, avec le volume exact d'huile mesurée par pesée. Dans ce flacon, des quantités connues d'un mélange de gaz étalons sont introduites, de telle sorte que les concentrations dans l'huile soient dans la même plage que dans l'échantillon inconnu prélevé sur site.

8 Extraction des gaz de l'huile

8.1 Remarques générales

L'extraction des gaz dissous de l'huile à analyser peut être obtenue sous vide, par entraînement ou par la méthode d'espace de tête.

La méthode d'extraction sous vide par cycles successifs (Toepler) est décrite en 8.2.

La méthode d'extraction sous vide en un seul cycle (dégazage partiel) est décrite en 8.3.

La méthode par entraînement est décrite en 8.4.

La méthode d'espace de tête est décrite en 8.5.

8.2 Dispositif d'extraction sous vide, par cycles successifs, qui utilise une pompe de Toepler

8.2.1 Généralités

Dans cette méthode, le mode opératoire utilisé a pour objectif d'extraire le plus possible de gaz dissous dans l'huile. Il est normalement possible de retirer environ 97 % des gaz les plus solubles, voire plus pour les gaz les moins solubles. Cette extraction incomplète est souvent négligeable comparée à l'exactitude globale de la méthode d'analyse, mais la méthode d'échantillonnage préférentielle, à partir d'étalons de gaz dissous dans l'huile, tient compte dans tous les cas de cette extraction incomplète.

NOTE Pour étalonner cette méthode avec des étalons de gaz dissous dans l'huile, le mode opératoire décrit en 7.2 pour la préparation d'étalons exempts d'argon est utilisé, le calcul étant influencé par la quantité d'argon dissous extraite, mais non détectée par le chromatographe en phase gazeuse.

8.2.2 Dispositif d'extraction à la pompe de Toepler

La Figure 6 a) représente un exemple de dispositif approprié. En outre, la Figure 6 b) indique les volumes recommandés. Dans ce dispositif, l'huile qui contient les gaz dissous est injectée à travers un septum (9). En variante, l'huile peut être introduite dans le matériel d'extraction mis sous vide à partir d'une bouteille d'échantillonnage reliée à la vanne (V8) par un tuyau préalablement rempli d'huile (voir Figure 6 c)).

Le dispositif d'extraction à l'aide d'une pompe de Toepler doit:

a) être capable de dégazer le liquide sous un vide inférieur à 10 Pa;
b) être étanche au vide. L'étanchéité totale du système peut être vérifiée en appliquant, sans introduire l'huile, le mode opératoire d'extraction suivant:

   effectuer les étapes b), c) et d) du 8.2.3. Ne pas réaliser l'étape e). Poursuivre par les étapes f), g) et h) comme s'il y avait de l'huile. Après avoir comprimé les gaz à la pression atmosphérique en suivant l'étape h), il convient que le volume de gaz soit inférieur à 0,1 ml;
c) permettre de mesurer les volumes de gaz extraits à 0,05 ml près ou mieux, dans les conditions normales de température et de pression.

De plus:

d) tous les tuyaux qui relient le récipient de dégazage (3) au récipient de collecte des gaz (2) (voir Figure 6 a)) doivent avoir un diamètre intérieur important, au minimum de 5 mm, et être aussi courts que possible;

e) la jauge à vide employée ne peut pas être d'un type qui fonctionne à température élevée ou qui utilise des radiations ionisantes (jauges de Penning, à ionisation ou à thermocouple), ces types pouvant être à l'origine de gaz analogues à ceux à analyser par craquage des vapeurs d'huile présentes dans le système. Une jauge Pirani n'est pas non plus satisfaisante, étant donné qu'elle peut réagir avec des gaz extraits. Un capteur qui repose sur les variations de capacité électrique entre deux chambres est approprié. Il est recommandé d'utiliser deux capteurs, l'un dans la chambre à vide, l'autre pour mesurer les volumes de gaz à la pression atmosphérique.

Des exigences supplémentaires sont données en 8.3, qui décrivent la méthode de dégazage partiel.

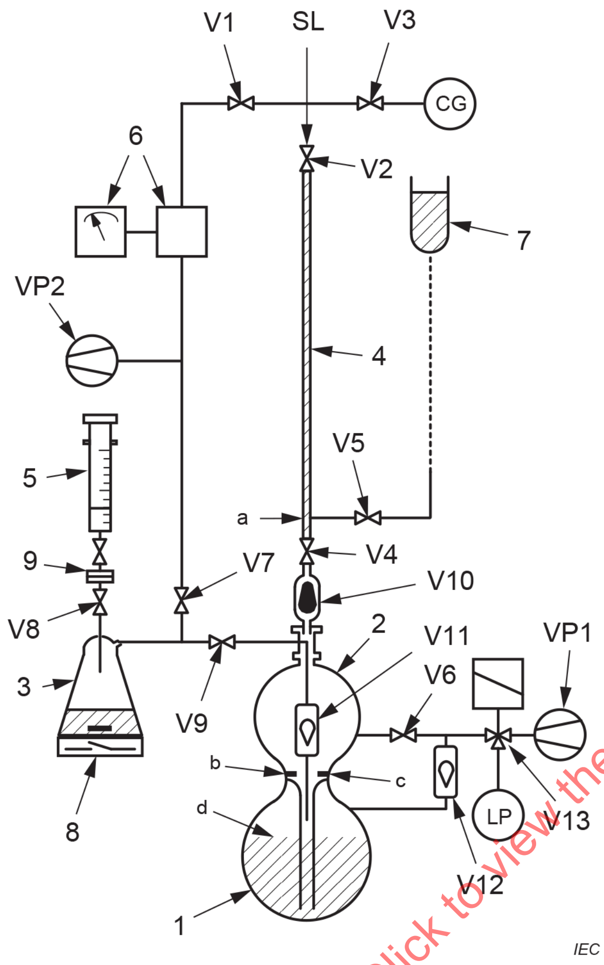
La conception détaillée du dispositif n'étant pas normalisée, il est nécessaire de définir un fonctionnement qui assure une bonne extraction de tous les composants des gaz dissous. Le nombre de cycles de dégazage (ou mouvements de mercure) de la pompe de Toepler qu'il convient d'utiliser et la durée de chacun de ces cycles sont les paramètres principaux à fixer. Ce fonctionnement est de préférence obtenu en dégazant des étalons de gaz dissous dans l'huile, de la façon suivante.

Appliquer le mode opératoire d'extraction des gaz décrit en 8.2.3, en remplaçant l'échantillon d'huile de teneurs en gaz inconnues par un étalon de gaz dissous dans l'huile, qui contient tous les gaz indiqués en 9.1, avec le volume d'huile normalement utilisé.

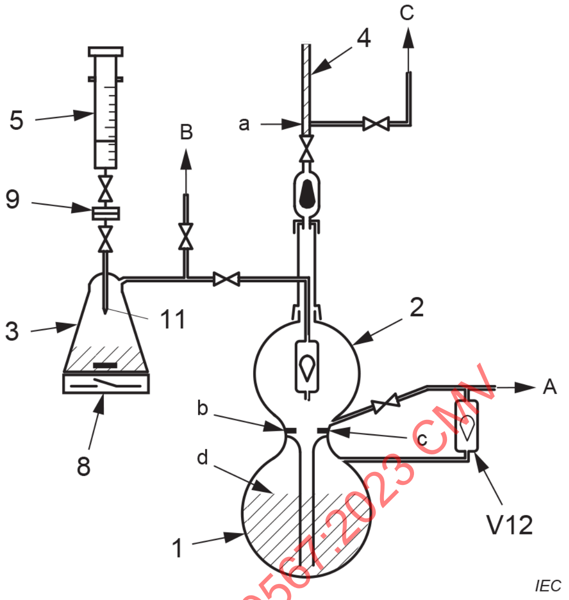
Effectuer plusieurs dégazages successifs, en variant le nombre de cycles de la pompe de Toepler, ainsi que la durée de chaque mouvement, jusqu'à ce que la surface ou les hauteurs de pics du chromatogramme des gaz extraits soient dans la limite de 95 % de la surface ou de la hauteur des pics du chromatogramme obtenu avec les mêmes volumes de gaz injectés directement dans le chromatographe, à partir d'un mélange de gaz étalons (voir 9.6).

Il est courant d'utiliser un temps de dégazage par cycle de 1 min à 3 min pour les huiles minérales; plus ce temps est court, plus le nombre de cycles exigé est susceptible d'augmenter. Des temps de dégazage similaires peuvent être utilisés pour les huiles non minérales qui présentent une viscosité analogue, et des temps plus longs pour les huiles qui présentent une viscosité plus importante (5 min à 10 min pour les huiles de silicone, par exemple; voir Annexe F).

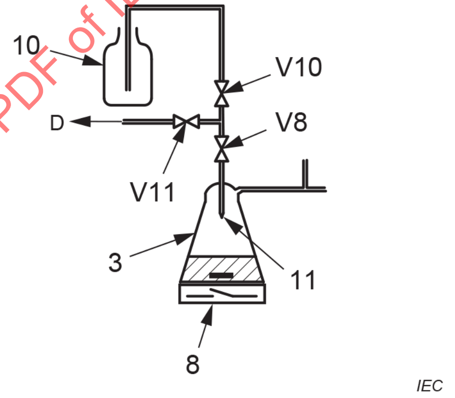
Le mode opératoire ci-dessus sert à établir un fonctionnement de routine, utilisé tant qu'aucune modification importante du matériel n'est apportée et également utilisé pour tout autre matériel de même conception. Il est recommandé de contrôler l'étalonnage global de l'appareil (matériel de dégazage plus chromatographe) de façon périodique (tous les six mois, par exemple), en employant des solutions étalons de gaz dissous dans l'huile qui donnent les facteurs de correction à appliquer aux surfaces ou hauteurs de pics des chromatogrammes.



a) Vue générale d'un dispositif d'extraction à la pompe de Toepler



b) Volumes recommandés de différentes parties d'une pompe de Toepler



c) Exemple d'introduction d'huile au moyen d'une bouteille

Légende

1	cuve à mercure de 2 l
2	récipient de collecte du gaz de 1 l
3	récipient de dégazage de 250 ml ou 500 ml
4	burette à gaz de 25 ml (graduation de 0,05 ml)
5	introduction de l'huile en seringue
6	jauge de Pirani
7	réservoir de mise à niveau à mercure
8	agitateur magnétique
9	septum
10	bouteille d'échantillonnage d'huile
11	ajutage

V1 à V11	robinets manuels
V10 à V12	vannes antiretour
V13	vanne à trois voies électromagnétique
VP1	pompe à vide primaire
VP2	pompe à vide principale
LP	liaison à l'air basse pression (±110 kPa)
SL	liaison à la boucle d'échantillon du chromatographe
CG	liaison à la bouteille de gaz comprimé étalon
a b c	contacts électriques
d	marque du niveau de mercure sur le tube
A	liaison au vide primaire et à l'air
B	liaison au vide principal
C	liaison au réservoir de mise à niveau à mercure
D	liaison au bac de vidange d'huile et au vide primaire

[a] L'élément 6 de la Figure 6 a) est un "appareil de mesure de la capacité".

Figure 6 – Exemple de dispositif d'extraction à la pompe de Toepler

8.2.3 Mode opératoire d'extraction

Le mode opératoire d'extraction décrit ci-après est un mode opératoire type, employé dans le cas d'un échantillonnage en seringue. Il est décrit à partir du dispositif représenté à la Figure 6 a) et à la Figure 6 b). Des modifications du mode opératoire peuvent être utilisées dans le cas de dispositifs de conception différente.

a) Peser la seringue (5) qui contient l'échantillon d'huile et la relier au récipient de dégazage (3). Si une bouteille est utilisée (Figure 9 c)), déterminer la masse d'huile dégazée en pesant le récipient de dégazage avant et après l'introduction de l'huile.

b) Ouvrir les vannes V1, V2, V4, V6, V7 et V9. Fermer les vannes V3, V5 et V8. La vanne V13 est une électrovanne à trois voies qui, à ce stade du mode opératoire, n'est pas sous tension et relie la pompe à vide VP1 au système.

c) Mettre en route les pompes à vide VP1 et VP2 ainsi que l'agitateur magnétique (8).

d) Quand la pression atteint 10 Pa, fermer les vannes V2, V6 et V7.

e) Ouvrir la vanne V8 et introduire une quantité suffisante d'huile par le septum (9), dans le récipient de dégazage (3). Cela est le début du premier cycle de dégazage de la pompe de Toepler.

NOTE 1 S'il y a une bulle de gaz dans la seringue, cela suggère que le piston a grippé; il est alors souhaitable de refaire un prélèvement. Si cela ne peut pas se faire, la bulle est introduite avec toute l'huile ou est de nouveau dissoute dans l'huile en agitant la seringue.

NOTE 2 Le volume d'huile minimal utilisé est le volume nécessaire pour produire suffisamment de volume de gaz pour injection dans le chromatographe en phase gazeuse. Lorsque cela est possible, des volumes d'huile plus importants peuvent être utilisés pour augmenter la précision de l'analyse. Dans le cas d'un échantillon d'huile issu d'un essai en usine, une modification est apportée à la méthode; voir la Note 3 du point j) ci-après.

f) Après le temps fixé pour le dégazage (par exemple, 1 min à 3 min), poursuivre le premier cycle de la pompe de Toepler en fermant la vanne V13 afin d'admettre de l'air comprimé à basse pression au-dessus du mercure qui s'élève jusqu'au contact (a), en comprimant les gaz du récipient de collecte dans la burette. En inversant la vanne V13, afin de relier la pompe à vide à la cuve à mercure (1), le retour du mercure est assuré (les gaz recueillis dans la burette sont retenus par la vanne antiretour V10) ce qui permet d'extraire davantage de gaz de l'huile. Les contacts rendent possible l'automatisation de ce cycle. Des électrovannes à induction peuvent alors être utilisées.

Il est utile de disposer d'un compteur pour déterminer le nombre de cycles et arrêter l'opération après le nombre exigé, tel qu'il a été normalisé pour le dispositif utilisé. Le fonctionnement automatique du matériel, pendant un temps normalisé (par exemple 10 min avec un cycle d'une durée de 1 min), peut constituer une variante.

Il convient que le nombre de mouvements soit tel que le vide à la fin de l'extraction s'approche de la valeur initiale avant l'extraction. Le nombre de mouvements nécessaires dépend du rapport entre le volume total du matériel et le volume de la pompe. Généralement, il a été établi que 4 à 20 mouvements sont adaptés pour atteindre une extraction de 97 % pour les gaz plus solubles, en fonction du matériel utilisé.

g) Arrêter la commande automatique de cycles (si elle est employée) et mettre la vanne V13 en position d'admission d'air. Laisser monter le mercure, dans la burette, au-dessus du niveau de la vanne V5. Fermer la vanne V4.

h) Ouvrir la vanne V6 et, à l'aide du réservoir de mercure (7), ajuster les niveaux de mercure. Lire le volume total de gaz recueillis dans la burette. Noter la température et la pression ambiantes.

i) Enlever la seringue d'huile et la peser à nouveau pour obtenir la masse d'huile dégazée. Déterminer la masse volumique de l'huile à température ambiante.

j) Fermer la vanne V1, ouvrir la vanne V2 et transférer les gaz extraits dans la boucle d'échantillon. Ajuster à nouveau les niveaux de mercure, à l'aide du réservoir de mercure, au nouveau niveau, puis fermer la vanne.

NOTE 3 Un autre procédé fréquemment utilisé consiste à adapter un septum au sommet de la burette, à la place de la vanne V2, à prélever une partie aliquote des gaz à l'aide d'une seringue de précision étanche aux gaz et à l'injecter dans le chromatographe. Dans ce cas, il est de bonne pratique de changer le septum à chaque fois.

NOTE 4 Si une quantité de gaz insuffisante résulte du premier dégazage de l'échantillon d'huile, le récipient de dégazage est enlevé et vidé, et la méthode répétée avec un nouvel échantillon d'huile. Conserver les gaz de la première extraction dans la burette en fermant la vanne V4, jusqu'à ce que le vide soit à nouveau refait dans le reste du système (point d) ci-dessus).

En variante, si des concentrations en gaz faibles sont prévues, un récipient de dégazage plus grand peut être utilisé, jusqu'à 2 l, avec un volume d'huile inférieur ou égal à 500 ml. Introduire l'échantillon d'huile lentement, afin de faciliter l'extraction des gaz.

k) Calculer la teneur totale en gaz extraits C_T de l'échantillon d'huile, exprimée en µl/l, à 20 °C et 101,3 kPa, par l'expression:

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

où

P est la pression locale de l'air, en kPa;

t est la température ambiante, en °C;

V est le volume total de gaz extraits, à température et pression ambiantes, en ml;

d est la masse volumique de l'huile ramenée à 20 °C, en g/ml;

m est la masse d'huile dégazée, en g.

l) Effectuer l'analyse selon l'Article 9.

NOTE 5 Dans la mesure où le gaz n'est pas complètement extrait de l'huile, une étape de rinçage peut être nécessaire après avoir effectué une analyse à concentration élevée (après analyse de l'échantillon d'huile à partir du changeur de prises, par exemple). L'extracteur peut être rincé avec de l'huile qui contient des quantités non détectables de gaz, sauf pour les gaz présents dans l'air.

8.3 Extraction sous vide par la méthode de dégazage partiel

8.3.1 Remarques générales

Dans cette méthode, l'extraction des gaz est obtenue en soumettant l'échantillon d'huile à une seule mise sous vide (entre 3 min pour les huiles minérales et 10 min pour les huiles de silicone qui présentent une viscosité plus importante; voir Annexe F). Le coefficient d'extraction dépend de la solubilité des composants gazeux. Pour tenir compte de cette extraction incomplète, une correction peut être effectuée en partant des coefficients de solubilité d'Ostwald de chaque gaz dans l'huile pour transformateurs, qu'elle soit minérale ou non (voir Annexe A).

8.3.2 Dispositif de dégazage partiel

Pour cette méthode, le matériel représenté à la Figure 6 a) et à la Figure 6 b) est également approprié, avec les modifications suivantes:

a) les dispositifs de commande automatique utilisés en mode pompe de Toepler (vannes V10 et contacts électriques a, b et c) ne sont pas nécessaires. Une simple pompe à main (poire et refoulante) peut être utilisée à la place du système d'air comprimé basse pression;

b) il convient que le volume total de détente (récipient de dégazage (3), plus récipient de collecte (2) et tubes de liaison, non compris le volume d'huile) soit au moins égal à 20 fois le volume d'huile. Dans le dispositif de la Figure 6 b), un récipient de collecte de 500 ml et un récipient de dégazage de 150 ml sont appropriés pour un volume d'huile de 25 ml à 30 ml;

c) il convient que le volume de la cuve à mercure n'excède pas trop le volume du récipient de collecte; dans le dispositif de la Figure 6 b), le volume recommandé de la cuve est approximativement de 600 ml à 700 ml. Il convient de la remplir de mercure de façon à ménager un volume d'air de 100 ml à 150 ml au maximum;

d) il convient de fixer un repère sur le tube plongeur de la cuve à mercure (repère d sur la Figure 6 a) et la Figure 6 b)) de sorte que, lorsque le matériel est utilisé en dégazage partiel, le niveau de mercure puisse être arrêté à cette marque, définissant ainsi, avec exactitude, le volume de détente;

e) le dispositif doit être exempt de fuites et doit pouvoir être mis sous un vide de 0,1 Pa. La burette, généralement de volume 3,5 ml, doit être graduée en 0,01 ml; les tuyaux de jonction et la jauge à vide doivent être conformes à ceux décrits aux points d) et f) du 8.2.2;

f) en lieu et place de la seringue, de l'aiguille et du septum, un tuyau souple en polytétrafluoroéthylène (PTFE) relié à la vanne peut être utilisé pour introduire des échantillons d'huile.

8.3.3 Mode opératoire d'extraction

a) Peser la seringue (5) qui contient l'échantillon d'huile et la relier au récipient de dégazage (3).

b) Continuer comme cela est indiqué aux points b) à e) du 8.2.3, en ayant réalisé un vide de 0,1 Pa.

c) Poursuivre le dégazage pendant 5 min à 10 min, en fonction de la viscosité de l'huile, l'agitateur fonctionnant énergiquement. Fermer alors la vanne V9.

d) Continuer comme cela est indiqué aux points g) et h) du 8.2.3.

e) Calculer le volume total de gaz extrait, en divisant le volume de gaz recueilli dans la burette par le rapport volumétrique V_c/V_t, où

   - V_c (volume de collecte) est le volume de la burette et du récipient de collecte (2), du repère "d" aux vannes V9, V6, V5 et V2;
   - V_t (volume total de détente) est le volume V_c plus le volume du récipient de dégazage (3) et des tuyaux de jonction aux vannes V9, V8 et V7, diminué du volume de l'huile admise.

f) Enlever la seringue et la peser à nouveau pour obtenir la masse d'huile dégazée. Déterminer la masse volumique de l'huile à température ambiante.

g) Ramener le volume total calculé des gaz extraits à 20 °C et 101,3 kPa, selon le point k) du 8.2.3.

h) Injecter une partie aliquote des gaz extraits dans le chromatographe, suivant le point j) du 8.2.3.

i) Effectuer l'analyse selon l'Article 9.

j) Calculer la concentration réelle de chacun des composants gazeux présents dans l'échantillon d'huile, en divisant la concentration déterminée par chromatographie par le coefficient d'extraction E_i (voir Annexe A).

NOTE Dans la mesure où le gaz n'est pas complètement extrait de l'huile, une étape de rinçage peut être nécessaire après avoir effectué une analyse à concentration élevée (après analyse de l'échantillon d'huile à partir du changeur de prises, par exemple). L'extracteur peut être rincé avec de l'huile qui contient des quantités non détectables de gaz, sauf pour les gaz présents dans l'air.

Des versions sans mercure des méthodes de Toepler et de dégazage partiel sont décrites à l'Annexe B.

8.4 Méthode d'extraction des gaz par entraînement

8.4.1 Généralités

L'extraction des gaz dissous dans l'huile est réalisée par barbotage du gaz vecteur lui-même dans un faible volume d'huile. Des volumes d'huile compris entre 0,25 ml et 5 ml sont généralement utilisés.

Le temps nécessaire pour extraire les gaz de volumes d'huile plus importants que ceux-ci conduit à des chromatogrammes inacceptables, sauf dans le cas de l'emploi de pièges à froid ou pour l'analyse de l'hydrogène seul.