Designation: D 3612 – 96

Standard Test Method for
Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography [1]

1. Scope

1.1 This test method covers two procedures for extraction and measurement of gases dissolved in electrical insulating oil having a viscosity of 20 cSt (100 SUS) or less at 40°C (104°F), and the identification and determination of the individual component gases extracted. Other methods have been used to perform this analysis.

1.2 The individual component gases that may be identified and determined include:

Hydrogen—H_2
Oxygen—O_2
Nitrogen—N_2
Carbon monoxide—CO
Carbon dioxide—CO_2
Methane—CH_4
Ethane—C_2H_6
Ethylene—C_2H_4
Acetylene—C_2H_2
Propane—C_3H_8
Propylene—C_3H_6

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements see 6.1.8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2779 Test Method for Estimation of Solubility of Gases in Petroleum Liquids [2]

D 2780 Test Method for Solubility of Fixed Gases in Liquids [2]

D 3613 Test Methods of Sampling Electrical Insulating Oils for Gas Analysis and Determination of Water Content [3]

D 4051 Practice for Preparation of Low-Pressure Gas Blends [2]

E 260 Practice for Packed Column Gas Chromatography [4]

2.2 *IEEE Standard:*

C 57.104 Guide for the Interpretation of Gases Generated in Oil-Immersed Transformers [5]

2.3 *IEC Standard:*

Publication No. 567 Guide for the Sampling of Gases and of Oil from Oil-Filled Electrical Equipment and for the Analysis of Free and Dissolved Gases [6]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *gas content of oil by volume—in Method A*, the total volume of gases, corrected to 760 torr (101.325 kPa) and 0°C, contained in a given volume of oil, expressed as a percentage. *In Method B*, the sum of the individual gas concentrations corrected to 760 torr (101.325 kPa) and 0°C, expressed in percent or parts per million.

3.1.2 *parts per million (ppm) by volume of (specific gas) in oil*—the volume of that gas corrected to 760 torr (101.325 kPa) and 0°C, contained in 10^6 volume of oil.

3.1.3 *sparging, v*—agitating the liquid sample using a gas to strip other gases free.

3.1.4 *volume concentration of (specific gas) in the gas sample*—the volume of the specific gas contained in a given volume of the gas sample at the same temperature and pressure (as the measured total volume), expressed either as a percentage or in parts per million.

4. Summary of Test Method

4.1 *Method A*—Dissolved gases are extracted from a sample of oil by introduction of the oil sample into a pre-evacuated known volume. The evolved gases are compressed to atmospheric pressure and the total volume measured.

4.2 *Method B*—Dissolved gases are extracted from a sample of oil by sparging the oil with the carrier gas on a stripper column containing a high surface area bead.

4.3 There may be some differences in limits of detection and precision and bias between Methods A and B for the various gases.

4.4 A portion of the extracted gases (Method A) or all of the gases extracted (Method B) are introduced into a gas chromatograph equipped with suitable adsorption column(s). The

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[1] This test method is under the jurisdiction of ASTM Committee D-27 on Electrical Insulating Liquids and Gases and is the direct responsibility of Subcommittee D27.03 on Analytical Tests.

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[2] *Annual Book of ASTM Standards*, Vol 05.02.

[3] *Annual Book of ASTM Standards*, Vol 10.03.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

[5] Available from IEEE, 345 E. 47th St., New York, NY 10017.

[6] Available from IEC.

composition of the sample is calculated from its chromatogram by comparing the area of the peak of each component with the area of the peak of the same component on a reference chromatogram made on a standard mixture of known composition.

5. Significance and Use

5.1 Oil and oil-immersed electrical insulation materials may decompose under the influence of thermal and electrical stresses, and in doing so, generate gaseous decomposition products of varying composition which dissolve in the oil. The nature and amount of the individual component gases that may be recovered and analyzed may be indicative of the type and degree of the abnormality responsible for the gas generation. The rate of gas generation and changes in concentration of specific gases over time are also used to evaluate the condition of the electric apparatus.

NOTE 1—Guidelines for the interpretation of gas-in-oil data are given in IEEE C57.104.

6. Apparatus

6.1 Apparatus [7] of the type shown in Fig. 1 or Fig. 2 is suitable for use with up to 50-mL samples of oil and consists of the following components:

NOTE 2—This sample size has been found to be sufficient for most oils. However, oil that has had only limited exposure to air may contain much smaller amounts of nitrogen and oxygen. For these oils it may be desirable to increase the size of the sample and the extraction apparatus.

NOTE 3—Alternative apparatus designs including the use of a Toepler pump have also been found successful.

6.1.1 *Polytetrafluoroethylene (PTFE) Tubing*, narrow-bore, terminated with a Luer-Lock fitted glass syringe, and leading to a a solid plug, three-way, high-vacuum stopcock.

6.1.2 *Degassing Flask*, with a glass inlet tube, of sufficient volume to contain up to 50 mL of oil below the inlet tube, capable of being evacuated through a vacuum pump, containing a PTFE-coated magnetic spin bar, and mounted on a magnetic stirrer.

6.1.3 *Means of Measuring Absolute Pressure* within the apparatus.

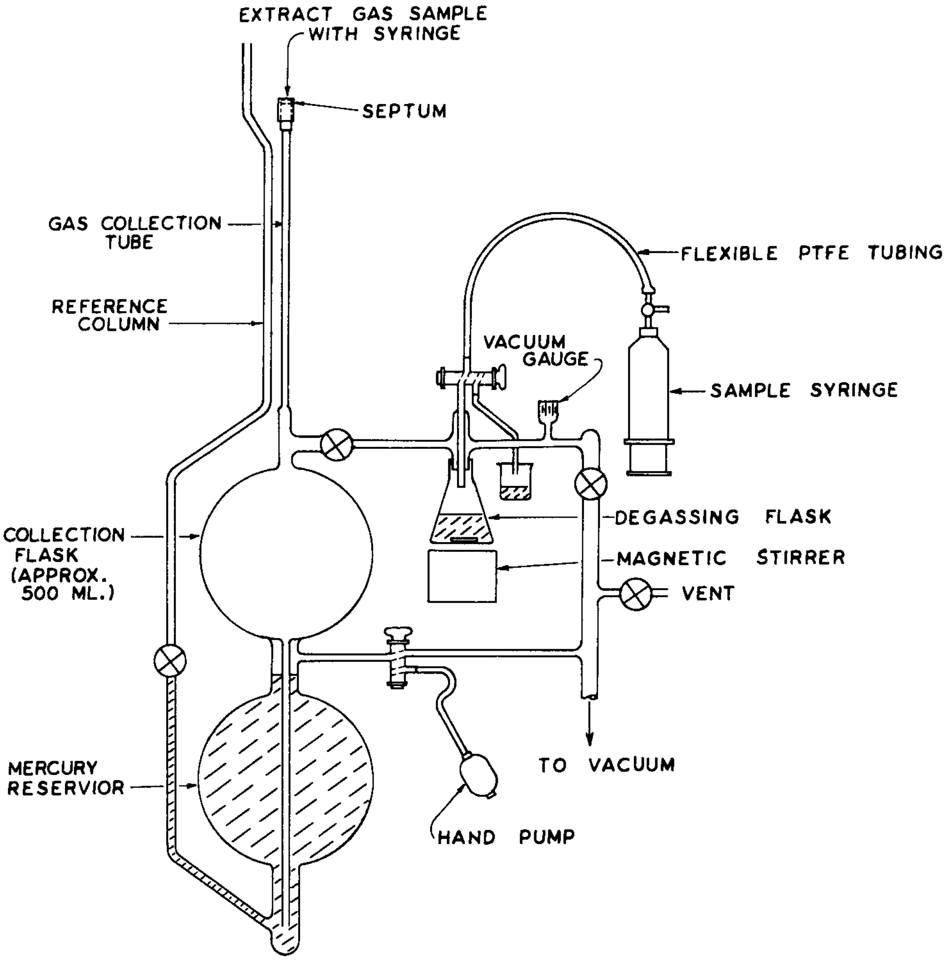

FIG. 1 Extraction of Gas from Insulating Oil

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[7] Ace Glass and Lurex Glass manufacture glass extractors. For Ace Glass, the glass apparatus conforming to Fig. 1 is Part E-13099-99-99 and Fig. 2 is Part E-1400-99. Available from P.O. Box 688, 1430 Northwest Blvd., Vineland, NJ 08360 or Lurex Glass, 1298 Northwest Blvd., Vineland, NJ 08360.

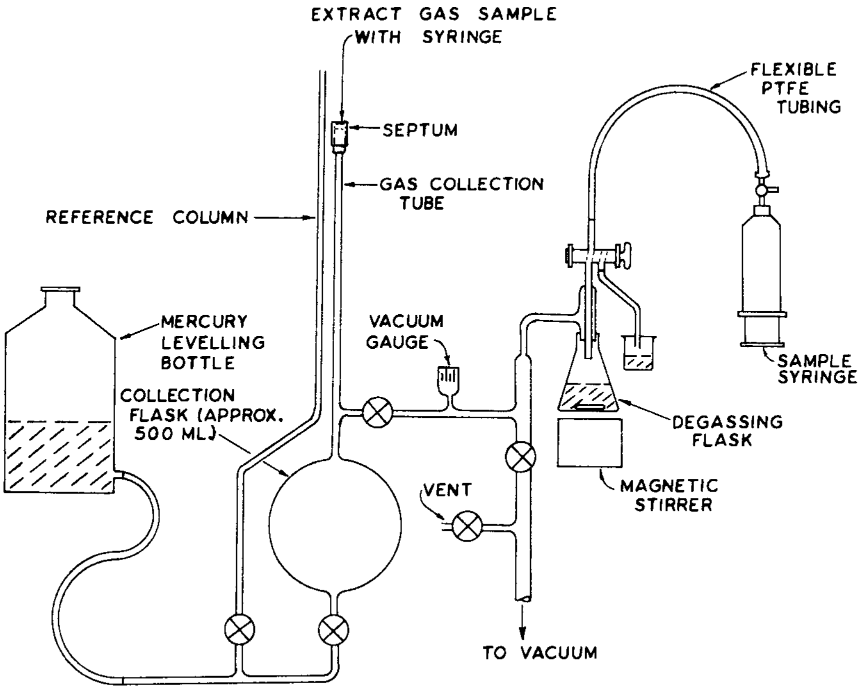

FIG. 2 Extraction of Gas from Insulating Oil

6.1.4 *Vacuum Pumping System*, capable of evacuating the glassware to an absolute pressure of 1×10^{-3} torr (130 mPa) or lower.

6.1.5 *Vacuum Glassware*, sufficiently large compared to the volume of the oil sample, so that virtually complete degassing is obtained and that the volumetric collection ratio is as large as possible. A500-mL gas collecting flask has been found suitable.

6.1.6 *High-Vacuum Valves or Stopcocks*, employing the minimum necessary amounts of high-vacuum stopcock grease are used throughout the apparatus.

6.1.7 *Gas Collection Tube*, calibrated in 0.01-mL divisions, capable of containing up to 5 mL of gas, terminated with a silicone rubber retaining septum. A suitable arrangement is shown in Fig. 3.

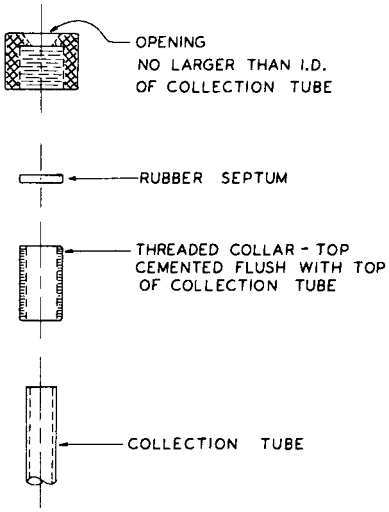

FIG. 3 Retaining Rubber Septum for Gas Collection Tube

6.1.8 *Reservoir of Mercury*, sufficient to fill the collection flask and collection tube.

NOTE 4—**Caution:** Mercury vapor is extremely toxic. Appropriate precautions should be taken.

7. Sampling

7.1 Obtain samples in accordance with the procedure described in Test Method D 3613 for sampling with syringetype devices or rigid metal cylinders. The use of rigid metal cylinders is not recommended for use with Method B.

7.2 The procurement of representative samples without loss of dissolved gases or exposure to air is very important. It is also important that the quantity and composition of dissolved gases remain unchanged during transport to the laboratory. Avoid prolonged exposure to light by immediately placing drawn samples into light-proof containers and retaining them there until the start of testing.

7.2.1 To maintain the integrity of the sample, keep the time between sampling and testing as short as possible. Evaluate containers for maximum storage time. Samples have been stored in syringes and metal cylinders for four weeks with no appreciable change in gas content.

NOTE 5—Additional sampling procedures using flexible metal cans are currently being studied for use with Method A.

METHOD A—VACUUM EXTRACTION

8. Method A—Vacuum Extraction

8.1 Method A employs vacuum extraction to separate the gases from the oil. The evolved gases are compressed to atmospheric pressure and the total volume measured. The gases are then analyzed by gas chromatography.

9. Preparation of Apparatus

9.1 Check the apparatus carefully for vacuum tightness of all joints and stopcocks.

9.2 Measure the total volume of the extraction apparatus, V_T, and the volume of the collection space, V_c, and calculate the ratio as the volumetric collection ratio:

$$\frac{V_c}{V_T - V_o} \quad (1)$$

where V_o = the volume of oil to be added.

9.3 Calculate the degassing efficiencies for each individual component gas as follows:

$$E_i = \frac{1}{1 + \frac{K_i V_o}{V_T - V_o}} \quad (2)$$

where:

E_i = degassing efficiency of component i,
V_o = volume of oil sample,
V_T = total internal volume of extraction apparatus before oil sample is introduced, and
K_i = Ostwald solubility coefficient of component i.

9.4 Determine the Ostwald solubility coefficients of fixed gases in accordance with Test Method D 2780.

9.5 Ostwald solubility coefficients that have been determined for a number of gases in one specific electrical insulating oil at 25°C are shown as follows. Values for gases in other oils may be estimated by reference to Test Method D 2779.

Component Gas	Ostwald Solubility [8] (Note 6) Coefficient, K_i, 25°C, 760 mm Hg
Hydrogen	0.0558
Nitrogen	0.0968
Carbon monoxide	0.133
Oxygen	0.179
Methane	0.438
Carbon dioxide	1.17
Acetylene	1.22
Ethylene	1.76
Ethane	2.59
Propane	11.0

NOTE 6—The Ostwald coefficient values shown in this table are correct only for the specific mineral oil having a density at 15.5°C of 0.855 g/cm ^{3} used in the original determination. Ostwald coefficients for mineral oils of different density may be calculated as follows:

$$K_i\,(\text{corrected}) = K_i \frac{0.980 - \text{density}}{0.130} \quad (3)$$

where, *density* = density of the oil of interest, g/cm^3 at 15.5°C (60°F). This equation is derived from the equation in Test Method D 2779. Note especially that all of the Ostwald coefficients are changed by the same factor, meaning that though the absolute solubilities of each of the gases will change if a different oil is used, the ratio of the solubility of one gas to another gas will remain constant.

9.6 A procedure to check the extraction efficiency requires the use of prepared gas-in-oil standards of known concentration. The methods of preparation are outlined in Annex A1 and Annex A2.

10. Procedure

10.1 Lower the mercury level from the collection flask.

10.2 Evacuate the system of collection flask and degassing flask to an absolute pressure of 1×10^{-3} torr (130 mPa) or less. (In Fig. 1, the space above the mercury in the reservoir must also be evacuated.)

10.3 Connect the oil sample syringe by the PTFE tubing to the three-way stopcock leading to the degassing flask.

10.4 Flush a small quantity of oil from the syringe through the tubing and stopcock to waste, making sure that all the air in the connecting tubing is displaced by oil.

10.4.1 Any gas bubbles present in the syringe should be retained during this flushing operation. This may be accomplished by inverting the syringe so that the bubble remains at the plunger end of the syringe during the flushing operation.

10.5 Close the stopcocks to the vacuum pumps and then slowly open the three-way stopcock to allow oil and any gas bubbles that may be present from the sample syringe to enter the degassing flask.

10.6 Allow the desired amount of oil to enter the degassing flask and operate the magnetic stirrer vigorously for approximately 10 min. This is the volume, V_o used in the calculation in 15.4.

10.6.1 If a gas bubble is present in the syringe, either analyze the total content of the syringe including the bubble; or, if the gas bubble is large, and it is suspected that the concentration of dissolved gases is high, measure and analyze the gas bubble separately, extract an aliquot of the oil sample, and correct as applicable.

10.7 Close the stopcock isolating the collection flask, and allow mercury to flow into the collection flask.

10.8 Open the stopcock to the reference column and by means of the hand pump (Fig. 1) or leveling bottle (Fig. 2) bring the level of the mercury in the reference column even with the level in the collection tube.

10.9 Measure the volume of extracted gas in the collection tube, and correct for collection efficiency by dividing it by the volumetric collection ratio calculated in 9.2. Correct to 760 torr (101.325 kPa) and 0°C. Determine the volume of oil degassed in the degassing flask. Record the gas content as a percentage of the oil by volume.

10.10 Because the total concentration of gas is not extractable from the oil, a rinse step may be required when high quantities are present. The extractor can be rinsed with oil containing nondetectable quantities of gases, except for those present in air. The amount of rinsing needed will be dependent upon the gas concentration, type (solubility in oil), and efficiency of the extractor. To ensure that the combustible gases have been sufficiently removed from the extractor, the rinse oil may be treated as a sample. General rinse procedures may be established. However, for samples with very high concentrations of gases verify effectiveness of the rinse procedure.

GAS ANALYSIS

11. Apparatus

11.1 *Gas Chromatograph*, consisting essentially of a carrier gas source, a pressure regulator, a sample injection port and chromatography column(s), flow meter(s), detector(s), and recorder(s) or recording integrator(s).

11.2 Provide means for measuring and controlling temperatures of the adsorption column, the inlet port, and the detector to within ±0.5°C.

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[8] "Analysis of Gas Dissolved in Transformer Oils;" Daoust, R., Dind, J. E., Morgan, J., and Regis, J.; Doble Conference, 1971, Sections 6–110.

NOTE 7—Use Practice E 260 as a reference for good chromatographic techniques.

11.3 The apparatus shall be capable of sufficiently separating the component gases, at the sensitivity levels shown as follows, to ensure quantitative measurement of the respective peak areas:

Component Gas	Minimum Detection Limits for Gases Dissolved in Oil, ppm
Hydrogen	5
Hydrocarbons	1
Carbon oxides	25
Atmospheric gases	50

11.4 The apparatus shall provide sufficient repeatability so that successive runs of a reference standard agree within ±1 % with respect to area under the peaks for hydrocarbon and carbon oxide components.

11.5 A wide range of chromatographic conditions have been successfully employed. Both argon and helium have been used as carrier gases (see Note 8). In some cases, a separate GC or other device is used for the detection and quantification of hydrogen when helium is used as a carrier gas.

NOTE 8—If helium is used as a carrier gas with a thermal conductivity detector, medium to high concentrations of hydrogen may give a nonlinear response, due to the closed heat capacity values of helium and hydrogen. The limit of detection will be higher than with an argon carrier gas under similar conditions. If nitrogen is used as a carrier gas, nitrogen cannot be detected in the sample.

11.5.1 With the use of an argon carrier gas, a catalytic converter containing powdered nickel located after the chromatographic columns is used to convert carbon monoxide and carbon dioxide to methane for detection with a flame ionization detector for acceptable sensitivity. (The condition of the nickel catalyst can be evaluated by checking the linearity of the response to carbon dioxide.) With helium as a carrier gas, a catalytic converter is not necessary but may be used to enhance sensitivity.

11.5.2 A flame ionization detector, instead of a thermal conductivity detector, is often used to detect hydrocarbon gases due to its greater sensitivity for these components. A wide range of injector, column, and detector temperatures can be used. Both isothermal and temperature programs can be used to provide adequate separation and sensitivity. A typical chromatogram is shown in Fig. 4.

11.6 *Fixed Needle Gas-Tight Syringes*, [9] of suitable sizes are needed for transfer of the gases.

12. Reagent and Materials

12.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[10] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

12.2 *Suitable Chromatography Columns*—Several combinations have been found to be suitable, including molecular sieve, Porapak Q, Porapak S, diisodecyl phthalate A, Silica Gel J, Chromosorb 102, and Carbosieve B.

12.3 *Helium, Argon, or Nitrogen Carrier Gas*, having a minimum purity of 99.95 mol % (see Note 8).

12.4 *Reference Standard Gas Mixture*, containing known percentages of the gases shown in 11.3.

12.4.1 A round robin performed for this test method showed considerable variation in gas standards when compared to a supplied primary standard. It is strongly recommended that only primary standards (each component prepared gravimetrically) be used. Refer to Practice D 4051 for procedures used to prepare a blend of standard gases. The National Institute of Standards and Technology (NIST) has some gas standards available which can be used to calibrate working standards.[11]

12.4.2 Individual gases can range from detectable levels to thousands of parts per million in actual samples. However, in most samples the concentration of gases (except oxygen, nitrogen, and carbon dioxide) is tens to hundreds of parts per million. Normally, the gas standard is prepared at concentrations of 5 to 10 times that seen in the oil due to the concentration effect of extracting the gas from the oil and because higher concentrations can be prepared with greater accuracy. Some laboratories use more than one concentration of standards. Acetylene is of greater concern at lower concentration levels than the other hydrocarbon gases.

13. Calibration

13.1 Prepare the gas chromatograph for use as directed by the manufacturer, and establish a set of operating conditions capable of separation of the indicated component gases.

13.2 Inject a pre-established volume of the reference standard gas mixture into the chromatograph and establish a pattern of elution times for the gas components known to be in the mixture, at an established set of operating conditions and sample size. Repeat the analysis until consistent operating conditions provide consistent chromatograms as specified in 11.4. Repeat calibration daily when analyses are being conducted.

14. Procedure

14.1 Increase the pressure on the extracted gas contained in the collection tube, described in 6.1.7 to slightly above atmospheric pressure by raising the level of mercury in the reference column slightly above the level of mercury in the gas collection tube.

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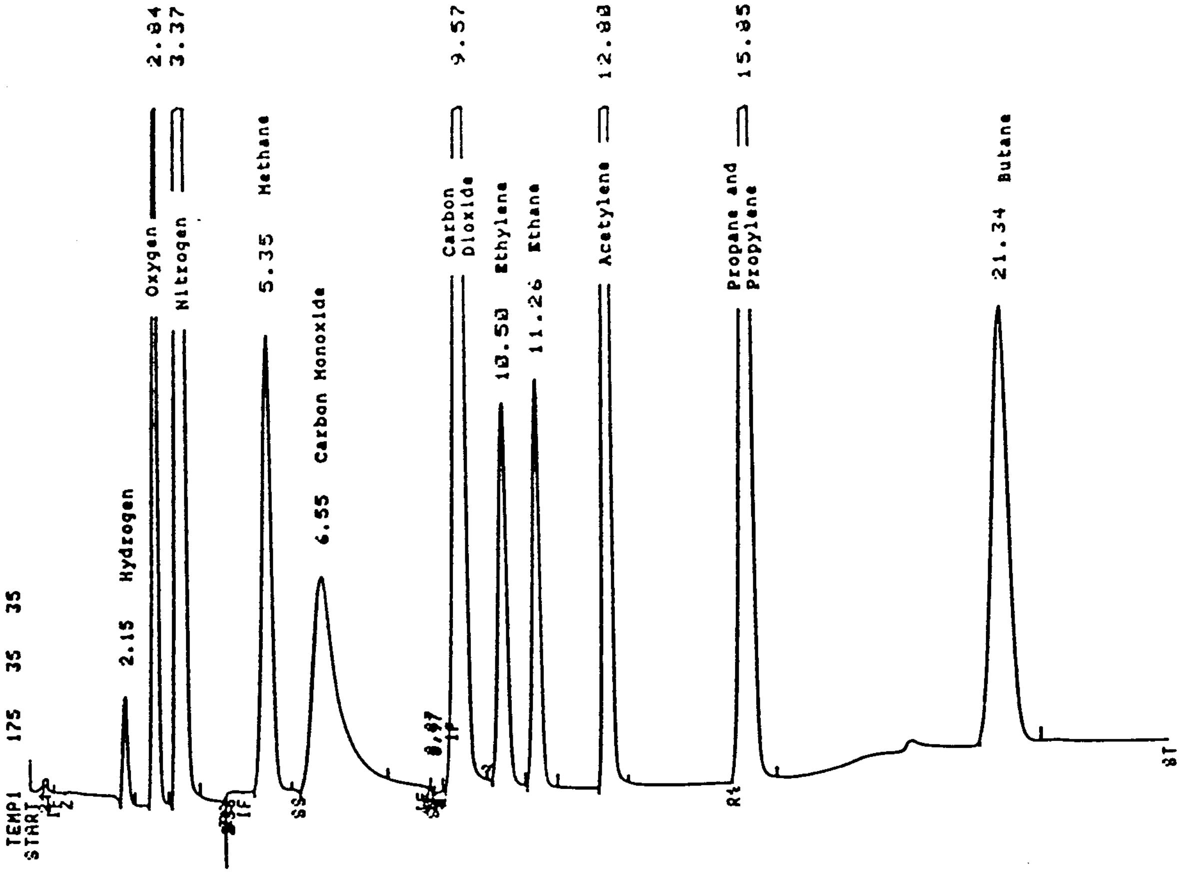
[9] Syringes that have been found suitable include those from the Hamilton Co., P.O. Box 307, Whittier, CA 90608; Pressure-Lok Syringes made by Precision Sampling Corp., P.O. Box 15119, Baton Rouge, LA 70815; and Popper and Sons, Inc., 300 Denton Ave., New Hyde Park, NY 11040.

[10] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.

[11] Available from U.S. Department of Commerce, National Institute of Standards and Technology, Standard Reference Materials Program, Bldg. 202, Room 204, Gaithersburg, MD 20899.



Gas Chromatograph Conditions:

Argon carrier gas, flow rate 30 mL/min

Columns:	Porapak N, 80–100 mesh, 13 ft × ⅛ in. Molecular sieve, 13×, 40–60 mesh, 3 ft × ⅛ in.
Catalytic converter for detection of CO and CO_2	
Detectors:	Thermal conductivity: H_2, O_2, N_2 Flame ionization: CH_4, CO, CO_2, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6, C_4H_{10}
Temperatures:	Injection 200°C TCD 150°C FID 300°C Column: Isothermal 35°C for 8 min 35–132°C ramp at 20°C/min, hold until 15.5 min 132–150°C ramp at 25°C/min, hold

NOTE 1—Propane and propylene are not separated under these conditions.

FIG. 4 Sample Chromatogram

14.2 Insert the needle of the gas-tight injection syringe through the septum of the collection tube, and withdraw a suitable volume of gas into the syringe. Adjust the gas pressure, as indicated by the reference column, precisely to atmospheric pressure before closing the syringe or withdrawing the needle from the septum.

14.3 When the apparatus conditions are equal to those established during the calibration procedure, quickly inject the known volume of gas into the chromatograph through the injection port.

14.4 Periodically, chromatography columns require baking out at elevated temperatures. The frequency and duration will depend upon such factors as type of column, amount of use, and concentration of materials tested. Peaks which are not as sharp as usual may be from compounds retained on the column from a previous run, and may indicate a need for baking out the columns. Another indicator that the molecular sieve column needs conditioning is that the methane and carbon monoxide peaks begin to lose baseline separation.

15. Calculation

15.1 Determine the integrated area of each peak of the chromatogram.

15.2 Identify the gases represented by each peak by comparison of elution times with those obtained for the reference standard gas mixture in the calibration procedure.

15.3 Determine the amount of each identified gas component by comparing respective peak areas with those obtained for the reference standard gas mixture in the calibration procedure.

15.4 Calculate the volume concentration of each specific gas with respect to the volume of oil degassed in the degassing flask. Correct to 760 torr (101.325 kPa) and 0°C, and express as parts per million of (specific gas) in oil, by volume.

$$C_i = \frac{V_g A_i C_{si} P_a \, 273 \times 10^4}{A_{si} V_o \, 760 \, T_a} \tag{4}$$

where:
V_g = volume of gas extracted,
C_i = concentration of gas in ppm, vol/vol,
A_i = area count or peak height for gas i in sample,
A_{si} = area count or peak height for gas i in standard,
C_{si} = concentration of gas i in standard in percent vol/vol,
V_o = volume of oil,
P_a = atmospheric pressure, in torr, and
T_a = ambient temperature, in Kelvin.

15.5 Correct each experimental value obtained in 15.4 for incomplete degassing by dividing each value by its respective degassing efficiency derived from 9.3.

$$\frac{C_i}{E_i} \tag{5}$$

16. Report

16.1 Report the following:

16.1.1 Identification of oil sample,

16.1.2 Temperature of oil at time of sampling,

16.1.3 Gas content of oil by volume, expressed as a percentage,

16.1.4 Volume concentration in the oil, for each component gas, expressed in parts per million, and

16.1.5 Test method used (for example, D3612, Part A).

17. Precision and Bias

17.1 Precision and bias statements for this test method have not been established but are being developed.

NOTE 9—An interlaboratory test program was conducted in which a total of 50 individual specimens of oil were sampled, at the same time, by the same experienced operator, from a 40 000-L forced-oil-cooled transformer while the transformer was in operation under full load. Individual specimens varying in number from 1 to 8 were shipped to 13 laboratories throughout North America for extraction and analysis of the dissolved gases in accordance with this method. The test results exhibited the coefficients of variation (see Table 1) related to the type of gas and the type of sample container used.

METHOD B—STRIPPER COLUMN EXTRACTION

18. Method B—Stripper Column Extraction

18.1 Dissolved gases are extracted from a sample of oil by sparging the oil with the carrier gas on a stripper column containing a high surface area bead. The gases are then flushed from the stripper column into a gas chromatograph for analysis. Testing of silicone liquids by this test method is not recommended for systems which are also used to test mineral oil, as excessive foaming should cause contamination of columns after the stripper.

TABLE 1 Coefficients of Variation

Gas	Syringe	Cylinder	Can
H_2	34	64	39
O_2	38	45	74
N_2	19	45	27
CO	21	74	27
CO_2	19	42	31
CH_4	28	50	30
C_2H_6	29	26	28
C_2H_4	21	30	25
C_2H_2	65	33	23
Total	18	33	35

19. Apparatus

19.1 *Gas Chromatograph*, [12] capable of separating and detecting the gases of interest using a direct injection of a portion of the liquid samples. Alternative gas strippers are given in IEC Method 567.

19.2 The apparatus must be capable of sufficiently separating the component gases, at the sensitivity levels shown as follows, to ensure quantitative measurement of the respective peak areas:

Component Gas	Minimum Detection Limits for Gases Dis solved in Oil, ppm
Hydrogen	20
Hydrocarbons	1
Carbon oxides	2
Atmospheric gases	500

The limit of detection for hydrogen specified in Method B is higher than that specified for Method A. This could affect the interpretation of results when low levels of gases are present.

19.3 The apparatus shall be capable of providing data for successive runs of a reference standard that are repeatable within 1 %, with respect to area under the peaks, for hydrogen and carbon oxide components.

20. Reagent and Materials

20.1 *Suitable Chromatography Columns*— Several combinations have been found to be suitable including molecular sieve, Porapak Q, Porapak N, diisodecyl phthalate A, Silica Gel J, Chromosorb 102, Carbosieve B, and Sperocarb. Molecular sieve is used to separate H_2, O_2, N_2, CH_4, and CO. Porapak N, Q, or combinations of both are used to separate CO_2, C_2H_4, C_2H_6, C_2H_2, C_3H_6, C_3H_6, and C_4H_{10}. Sperocarb is used to separate the carbon oxide and hydrocarbon gases.

20.2 *Argon, or Nitrogen Carrier Gas*, having a minimum purity of 99.95 mol % with total hydrocarbons of less than 0.5 ppm and CO_2 of less than 1 ppm. (See Note 8.)

20.2.1 With the use of an argon carrier gas, a catalytic converter containing powdered nickel, located after the separating columns, is used to convert carbon monoxide and carbon dioxide to methane for detection with a flame ionization detector for acceptable sensitivity. (The condition of the nickel catalyst can be evaluated by checking the linearity of the response to carbon dioxide.)

20.3 *Flame Ionization Detector Gases*—Hydrogen having a purity of 99.99 mol % with total hydrocarbons of less than 0.5 ppm and air having a purity of less than 1 ppm total hydrocarbons.

20.4 *Reference Standard Gas Mixtures*—Low-concentration standard containing known percentages of the gases in 1.2 at

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[12] Suitable equipment includes that from Shimadzu Scientific Instruments, Inc., 7102 Riverwood Road, Columbia, MD. This equipment uses a patented process for the sparger.

concentrations approximately the magnitude of the values normally encountered. The high-concentration gas standard should contain levels approximately one order of magnitude higher than contained in the low-concentration gas standard. The gas standards should be a primary grade (each component added gravimetrically). The high gas standard is used for preparing gas in oil standards as outlined in Annex A1.

21. Calibration (Gases)

21.1 Prepare the gas chromatograph for use as directed by the manufacturer, and establish a set of operating conditions capable of separating the indicated component gases.

21.2 Inject a pre-established volume of the reference standard (low concentration) gas mixture into the chromatograph and establish a pattern of elution times for the gas components known to be in the mixture, at an established set of operating conditions and sample sizes. Repeat the analysis until consistent operating conditions provide consistent chromatograms. Repeat calibration daily when analyses are being conducted.

22. Efficiency Determination

22.1 Inject the oil standard prepared from one of the procedures in the Annexes into the system. Determine the dissolved gas content of this oil chromatographically based upon the low-concentration gas standard. The difference between the calculated concentration and the observed concentration is the degassing efficiency of a given component and may be calculated as follows:

$$D_i (C_{aoi} - C_{boi}) / C_{oi} \tag{6}$$

where:

D_i = the degassing efficiency of component i,

C_{aoi} = observed concentration of component i in the oil standard,

C_{boi} = observed concentration of component i in the blank oil, and

C_{oi} = calculated concentration of component i in the oil standard.

22.2 The degassing efficiency factor is used to correct the determined concentration values for incomplete extraction. Repeat the procedure until consistent results are obtained. Conduct this efficiency determination weekly for at least one concentration of standard gas. Whenever there are changes in the chromatographic system, redetermine the extraction efficiency.

22.3 Determine the linearity of the detector response monthly by testing a range of gas concentrations expected to be encountered in actual samples. Extraction efficiencies should also be determined over a corresponding range to ensure they are linear and constant over time. Samples can be prepared by simple dilution of pure gases with either nitrogen or carrier gas (for gas standards) or degassed oil (for gas-in-oil standards). If commercially supplied standard mixtures are used, they may be checked using this method. Check efficiencies and linearity whenever chromatographic conditions are changed.

23. Procedure for Direct Injection

23.1 Prepare the gas chromatograph as outlined by the manufacturer.

23.2 Prepare the sample for injection by first dissolving any gas bubble present into the volume of oil by compressing the plunger into the barrel of the syringe and agitating the gas by tipping the syringe up and down. Any bubble present in the syringe must be dissolved to obtain a representative aliquot of the sample for injection. Small volumes of oil are needed for flushing and sample, typically a total of several millitres. Flushing is required to displace the previous sample from the column.

23.3 Once the sample is connected to the gas chromatograph, flush enough oil through the injection system to ensure that no gas bubbles remain in the line.

23.4 If high concentrations of the more soluble gases are found, in particular C_2H_2, the injection column can be back flushed. Use a blank run of degassed insulating oil to check that no residual gases remain.

24. Calculation

24.1 Determine the integrated area of each peak of the chromatogram.

24.2 Identify the gases represented by each peak by comparison of elution times with those obtained for the reference standard gas mixture in the calibration procedure.

24.3 Determine the amount of each identified gas component by comparing respective peak areas with those obtained for the reference standard gas mixture in the calibration procedure.

24.4 Correct the values obtained based on the efficiency values obtained in the efficiency determination procedure, and express as parts per million of (specific gas) in oil, by volume as shown in the following calculation:

$$C_{ci} = C_{aoi} / D_i \tag{7}$$

where:

C_{aoi} = observed concentration of component i in the oil sample, and

C_{ci} = corrected concentration of component i in the oil sample.

24.5 Estimate the total gas content in oil by volume by summing the concentration of all of the individual gases detected. The error in this calculation occurs when gases present are not detected and therefore not included. The total gas content is determined by a different technique than given in Method A, but the results are usually similar.

25. Report

25.1 Report the following information:

25.1.1 Identification of oil sample,

25.1.2 Temperature of oil at time of sampling,

25.1.3 Volume concentration in the oil, for each component gas, expressed in parts per million, and

25.1.4 The test method used (for example, D3612, Part B).

26. Precision and Bias

26.1 A round-robin is being run to determine the precision and bias of this test method. An interim statement of repeatability for two laboratories is provided in Annex A3.

27. Keywords

27.1 combustible gases; dissolved gases; gases; insulating oil; oil; transformer oil

ANNEXES

(Mandatory Information)

A1. PREPARATION OF SMALL QUANTITIES OF GAS-IN-OIL STANDARDS (Mandatory Information—Method B)

A1.1 Calibration Apparatus

A1.1.1 *Syringes*, fixed needle gas-tight, of suitable size, and a rubber slip-on septum.

A1.1.2 *Vacuum Pumping System*, capable of evacuating the glassware to an absolute pressure of 1×10^{-3} torr (130 mPa) or lower.

A1.1.3 *Erlenmeyer Vacuum Flask*, 1-L with a glass inlet tube, capable of being evacuated through a vacuum pump, containing a PTFE-coated magnetic spin bar, and a magnetic stirrer.

A1.1.4 *Gas-Tight Chromatography Syringe*, 2.0 mL.

A1.1.5 *Lab Bench Vacuum Pump*, small, attached to 6 in. piece of vacuum tubing containing a needle end.

A1.2 Procedure

A1.2.1 Using a 1-L Erlenmeyer flask attached by vacuum tubing to a mechanical vacuum pump, degas approximately 500 mL of clean oil by stirring the oil under vacuum with a TFE-fluorocarbon stir bar and magnetic stirrer for approximately 2 h, or until no more noticeable air is being drawn out of the oil.

A1.2.2 Rapidly transfer 75 mL of the "blank oil" from the flask to a gas-tight pre-calibrated 100-mL syringe containing a Luer lock valve, breaking vacuum with the same gas as the carrier gas. Air can be used to break vacuum if there is sufficient oil to determine a baseline for oxygen, nitrogen, and carbon dioxide for each syringe. Expel any bubbles that might be present.

A1.2.3 Using the blank oil, determine the quantity of remaining gases in the oil by analyzing an aliquot of the oil from the gas-tight syringe. The 75 mL initial volume provides enough volume for this analysis to be repeated (in some cases 2 or 3 times) to ensure repeatable results.

A1.2.4 Adjust the oil volume in the syringe to 50 mL by holding the syringe vertically with the tip pointed upwards and insert a slip-on septum on the tip of the syringe.

A1.2.5 Turn the syringe so that the tip is facing downward, and inject 1.0 mL of the high-concentration gas standard taken under known conditions of temperature and pressure into the blank oil through the septum seal contained on the syringe valve. If the "high" gas standard is taken from a pressurized container, the syringe should be filled to capacity and then allowed to bleed down slowly to atmospheric pressure before adjusting to the desired volume. Rapid decompression of a gas sample results in adiabatic cooling leading to an unknown temperature of the gas sample. Record ambient temperature and for use in calculating the concentration of the gas-in-oil standard. The injection is performed using a 2.50 mL gas-tight syringe.

A1.2.6 Shake the syringe with a back and forth motion, while applying a slight positive pressure with the syringe barrel, until the bubble containing gas standard is completely dissolved. The use of a thin, flat washer can facilitate the stirring action and aid in homogenizing the sample.

A1.2.7 Determine the calculated concentration of the gases dissolved in the standard as follows:

$$C_{oi} = V_{sg}\,(P_a / 760)(273 / T_a) / V_{bo}C_{sgi}10^4$$

where:

C_{oi} = calculated concentration of component i in the oil, ppm,
P_a = ambient pressure when "high" gas standard sampled,
T_a = ambient temperature when "high" gas standard sampled,
C_{sgi} = concentration of component i in the high concentration gas standard, %,
V_{sg} = volume of the high concentration gas standard, and
V_{bo} = volume of the blank oil.

A2. PREPARATION OF LARGE QUANTITIES OF GAS-IN-OIL STANDARDS (Mandatory Information—Method B)

A2.1 Apparatus

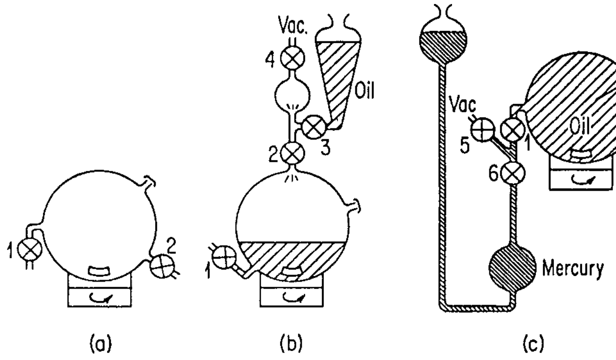
A2.1.1 *Oil Vessel (*Fig. A2.1*(a))*, 5-L equipped with one sidearm septum holder, two sidearm outlets, one egg-shaped TFE-fluorocarbon-coated stirring bar, a cork ring to support the vessel, and a magnetic stirrer.

A2.1.2 *Oil-Degassing System (*Fig. A2.1*(b))*, consisting of one 4-L oil reservoir, one 75-mL splash bulb, two high-vacuum stopcocks, one *T*-type glass connector and a vacuum mechanical pump.

A2.1.3 *Mercury Displacement System (*Fig. A2.1*(c))*, to compensate for oil volume variations, consisting of two 500-mL glass bulbs, two high-vacuum stopcocks, and one *Y*-type glass connector.

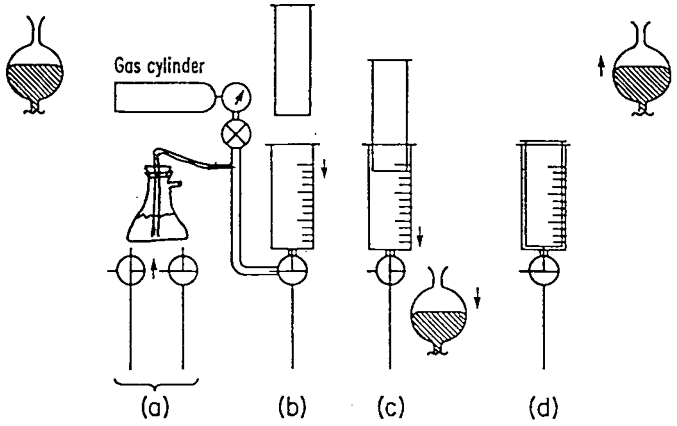
A2.1.4 *Rigid Stands*, with clamps to secure the various elements, and a large plastic tank to contain accidental mercury spills. All connections between these components are of high-vacuum oil resistant flexible tubing.

A2.1.5 *Gas-Injection System (*Fig. A2.2*)*, consisting of a set



(*a*) Oil Vessel
(*b*) Set-Up for Degassing Oil
(*c*) Set-Up for Injecting Gases and Sampling Oil

FIG. A2.1 Apparatus



(*a*) Purging Needle and Valve with Oil
(*b*) Purging and Filling Gas Syringe with Gas
(*c*) Injecting Gas Volume in Oil Under Reduced Pressure
(*d*) Final Syringe Position

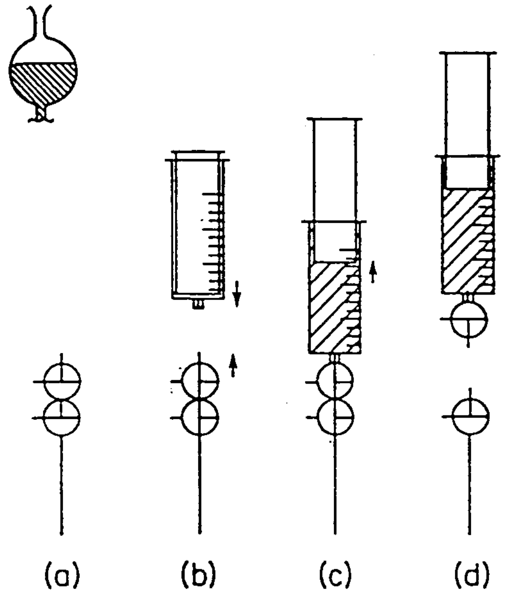
FIG. A2.2 Gas-Injection System

of calibrated gas tight syringes of appropriate volumes, a plastic three-way stopcock (standard medical type) modified to minimize dead volumes by inserting pieces of 0.4 mm inside diameter, 1.5 mm outside diameter steel tubing in the inner branches of the barrel and syringe port (filling up with epoxy resin where necessary), a 0.25-mm inside diameter side-port "gas" injecting needle (10 cm long) to go through the rubber septum into the oil vessel, gas cylinders containing the gases or calibrated gas mixtures to be dissolved in the oil equipped with the proper regulators and valves, a length of flexible tubing connecting the cylinder to the stopcock. A 23-gage needle pierced into this tubing to act as a leak, is connected to a water bubbler to check the absence of back diffusion of air.

A2.1.6 *Oil-Sampling System (*Fig. A2.3*)*, consisting of a 19-gage oil-withdrawing needle (12 cm long), and glass syringes of suitable capacity equipped with two three-way plastic stopcocks.

A2.2 Materials

A2.2.1 Approximately 1 L of clean mercury is needed. Oil-contaminated mercury can be cleaned with pentane and filtered through a finely pierced filter paper.



(*a*) Starting Position
(*b*) Purging Needle, Valve, and Syringe Tip with Oil
(*c*) Filling Oil Syringe
(*d*) Removing Oil Syringe

FIG. A2.3 Oil-Sampling System

A2.2.2 *Gases* (H_2, O_2, N_2, CO, CO_2, CH_4, C_2H_4, C_2H_2, C_2H_6, etc.) of technical purity, in pressure cylinders, or a mixed commercially prepared primary standard of the gases of interest in appropriate concentrations. The primary standard should have each component prepared gravimetrically.

A2.2.3 *High-Vacuum Grease,* for stopcocks.

A2.3 Preparation of Apparatus

A2.3.1 Clean all glassware thoroughly, first with detergent, then with a good solvent (methanol, for example), and dry. Pay special attention to the sidearm septum holder. Secure the rubber septum and the flexible connections with pieces of twisted metal wire.

A2.4 Procedure

A2.4.1 *Degassing the Oil (*Fig. A2.1*(b))*:

A2.4.1.1 Evacuate the splash bulb and the 5-L oil vessel by opening stopcocks 2 and 4.

A2.4.1.2 Fill the reservoir with oil, and allow oil to flow slowly through stopcock 3 in the 5-L oil vessel with stirrer on, until this vessel is full. Close stopcock 2 and remove the oil-degassing system. If the procedure is followed carefully (filling time, about 4 h), the oil in the vessel will be virtually gas-free.

A2.4.2 *Attaching the Mercury-Displacement System (*Fig. A2.1*(c))*:

A2.4.2.1 Turn the oil vessel to bring it into the position, shown in Fig. A2.1(*c*). Place a wet cloth over the oil vessel to prevent its temperature from rising and attach the mercury-displacement system to stopcock 1. Introduce 750 mL of mercury into the system so that the mercury level rises just above stopcock 6, then close the stopcock. From stopcock 5, evacuate sections between stopcock 5 and 1. Open 6 to allow mercury to rise up to stopcocks 1 and 5 and then close stopcock 5. Raise the left bulb so that the mercury level is slightly above the oil and open stopcock 1. Remove the wet cloth. Switch on the stirrer.

A2.4.3 *Injection of the Gases (*Fig. A2.1*(c) and* Fig. A2.2*)*

Attach the modified three-way stopcock 7 (in the closed position) to the gas-injecting needle. With the mercury level above the oil vessel, push the needle through the rubber septum into the oil (Fig. A2.1(*c*)).

A2.4.3.1 Open stopcock 7 to purge the needle and stopcock with oil, then close it (Fig. A2.2). Attach to stopcock the barrel of a gas-tight syringe of appropriate volume and the gas cylinder connection tubing (Fig. A2.2(*b*)).

A2.4.3.2 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.

A2.4.3.3 Switch stopcock 7 to the inject position (Fig. A2.2(*c*)), lower the mercury level below the needle tip, and push the plunger to inject the gas volume into the oil.

A2.4.3.4 Switch stopcock 7 to the closed position (Fig. A2.2(*d*)) and raise the mercury bulb above the oil vessel. Depending on the volume and solubility of the gas injected, it takes from a few minutes to several hours to dissolve completely. As the gas dissolves, the mercury-oil interface resumes its original position.

A2.4.3.5 Repeat the same procedure with each of the gases to be dissolved, changing the gas cylinder connection tube. Instead of adding individual gases, it may be convenient to use calibrated gas mixtures. When all the gases have been injected, remove the gas needle stopcock 7.

A2.4.4 *Removal of Oil Samples (*Fig. A2.3*)*:

A2.4.4.1 When all the gases are dissolved, switch off the stirrer. Attach two regular three-way stopcocks in the closed position to the oil withdrawing needle and push the needle through the rubber septum (Fig. A2.3(*a*)). With the mercury level up, switch the two three-way stopcocks to the draw-off position (Fig. A2.3(*b*)) to purge them with oil.

A2.4.4.2 Attach an oil syringe and draw out a suitable volume of oil (Fig. A2.3(*c*)). Then switch the two three-way stopcocks to the closed position and remove the syringe leaving the upper stopcock (Fig. A2.3(*d*)). This oil sample is ready for analysis.

A2.4.4.3 To remove several samples of oil, additional mercury may have to be introduced the mercury bulb.

A2.5 Calculation

A2.5.1 Calculate the concentration of each dissolved gas "*i*" as follows:

$$C_i = \frac{V_i}{V} \times 10^{\ 6}$$

where:

C_i = concentration of gas "*i*", ppm,

V_i = volume of gas " *i*", injected, mL, (corrected to 0°C (101.325 KPa)),

V = exact volume of oil in the 5-L oil flask, mL.

A2.6 Precision and Bias

A2.6.1 The main error comes from the measurement of the volume of gas injected $V_L$which can be obtained with an accuracy of 1 % using calibrated gas-tight syringes. The volume of oil V is obtained more accurately by weighing water in the glass vessel. Correction for dead volume in the injection needle and modified three-way stopcock (approximately 5 mL corresponding to 1 ppm in the dissolved state for the last gas injected) can be made negligible by a last injection of air or nitrogen. The expected overall accuracy therefore is ±1 %.

A3. INTERIM PRECISION STATEMENT FOR REPEATABILITY BY TWO LABORATORIES

A3.1 Data is given from two laboratories using Method B to determine the concentration of gases in oil. The results are provided in Table A3.1 and Table A3.2.

TABLE A3.1 Interim Precision Statement for Repeatability for Laboratory 1 [A]

	Hydrogen	Oxygen	Nitrogen	Methane	Carbon Monoxide	Carbon Dioxide	Ethylene	Thane	Acetylene
Theoretical concentration, ppm	98	2460	16678	74	98	394	74	68	54
Run #1	102	2392	17257	77	99	397	69	65	53
Run #2	110	2257	17125	76	101	396	70	64	52
Run #3	96	2253	16884	77	96	381	67	63	52
Run #4	100	2282	16971	77	98	400	72	68	54
Run #5	98	2273	17213	76	100	397	71	65	53
Average		2291 [B]	17090 [B]						
Standard Deviation (SD)		57 [B]	159 [B]						
RSD,%		1 [B]	2 [B]						
Run #6	105	4254	23588	70	94	367	63	58	47
Run #7	87	3103	17297	70	90	366	63	60	49
Run #8	94	3207	17265	70	89	360	62	58	47
Run #9	87	2770	16998	69	91	364	65	60	48
Run #10	96	3153	16974	69	86	361	60	57	47
Average	98	3297 [B]	18424 [B]	73	94	379	66	62	50
Standard deviation (SD)	7	561 [B]	2890 [B]	4	5	16	4	4	3
RSD,%	7	17 [B]	16 [B]	5	5	4	6	6	5

[A] Results given in parts per million (vol/vol) for analysis of two standards of the same concentration of gases in oil tested five times each.

[B] The data for these gases was not poolable and is based on the five runs for each sample.

TABLE A3.2 Interim Precision Statement for Repeatability of Laboratory 2 [A]

Trial	Hydrogen	Oxygen	Nitrogen	Methane	Carbon Monoxide	Carbon Dioxide	Ethylene	Ethane	Acetylene
#1	91	5763	40584	105	97	494	72	61	31
#2	48	5425	39989	95	89	458	67	57	28
#3	46	4979	39980	88	84	416	60	51	26
#4	39	4098	34396	86	82	420	60	51	26
#5	52	5372	38555	96	89	467	69	57	29
#6	51	4935	38536	93	88	448	65	54	28
#7	62	4541	38969	97	92	466	68	57	29
#8	52	4630	38690	97	93	471	68	57	29
#9	86	4913	40953	97	95	476	70	58	30
#10	57	4748	39075	95	91	468	69	57	29
Average	58.4	4940.4	38972.7	94.9	90.0	458.4	66.8	56.0	28.5
Standard deviation (SD)	17.0	483.3	1824.7	5.2	4.6	24.4	4.0	3.1	1.6
RSD,%	29	10	5	5	5	5	6	6	6

[A] Results given in parts per million (vol/vol) for ten consecutive runs of the same sample.