Designation: D3612 – 02 (Reapproved 2009)

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

This standard is issued under the fixed designation D3612; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers three 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 warning statements see 6.1.8, 30.2.2 and 30.3.1.

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D2140 Practice for Calculating Carbon-Type Composition of Insulating Oils of Petroleum Origin

D2300 Test Method for Gassing of Electrical Insulating Liquids Under Electrical Stress and Ionization (Modified Pirelli Method)

D2779 Test Method for Estimation of Solubility of Gases in Petroleum Liquids

D2780 Test Method for Solubility of Fixed Gases in Liquids (Withdrawn 2010)[3]

D3613 Practice for Sampling Insulating Liquids for Gas Analysis and Determination of Water Content (Withdrawn 2007)[3]

D4051 Practice for Preparation of Low-Pressure Gas Blends

E260 Practice for Packed Column Gas Chromatography

2.2 *IEEE Standard:*

C 57.104 Guide for the Interpretation of Gases Generated in Oil-Immersed Transformers[4]

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[5]

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 Methods B and C, 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 *headspace—*a volume of gas phase in contact with a volume of oil in a closed vessel. The vessel is a headspace vial of 20-mL nominal capacity.

3.1.2.1 *Discussion—*Other vessel volumes may also be used, but the analytical performance may be somewhat different than that specified in Method C.

3.1.3 *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.

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

3.1.5 *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 *Method C*—Method C consists of bringing an oil sample in contact with a gas phase (headspace) in a closed vessel purged with argon. The dissolved gases contained in the oil are then equilibrated in the two phases in contact under controlled conditions (in accordance with Henry's law). At equilibrium, the headspace is overpressurized with argon and then the content of a loop is filled by the depressurization of the headspace against the ambient atmospheric pressure. The gases contained in the loop are then introduced into a gas chromatograph.

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

4.5 A portion of the extracted gases (Method A) or all of the extracted gases (Method B) or a portion of the headspace gases (Method C) is introduced into a gas chromatograph. Calibration curves are used in Method C to establish the concentration of each species. The 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[6] 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 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.

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. A 500-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.

6.1.8 *Reservoir of Mercury,* sufficient to fill the collection flask and collection tube. (**Warning**—Mercury vapor is extremely toxic. Appropriate precautions should be taken.)

7. Sampling

7.1 Obtain samples in accordance with the procedure described in Test Methods D3613 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

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[6] 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.

EXTRACT GAS SAMPLE
WITH SYRINGE

SEPTUM

GAS COLLECTION
TUBE

REFERENCE
COLUMN

FLEXIBLE PTFE TUBING

VACUUM
GAUGE

SAMPLE SYRINGE

COLLECTION
FLASK
(APPROX.
500 ML.)

DEGASSING FLASK

MAGNETIC STIRRER

VENT

MERCURY
RESERVOIR

HAND PUMP

TO VACUUM

FIG. 1 Extraction of Gas from Insulating Oil

EXTRACT GAS SAMPLE
WITH SYRINGE

FLEXIBLE
PTFE
TUBING

SEPTUM

GAS COLLECTION
TUBE

REFERENCE COLUMN

MERCURY
LEVELLING
BOTTLE

VACUUM
GAUGE

COLLECTION
FLASK (APPROX.
500 ML.)

SAMPLE
SYRINGE

DEGASSING
FLASK

VENT

MAGNETIC
STIRRER
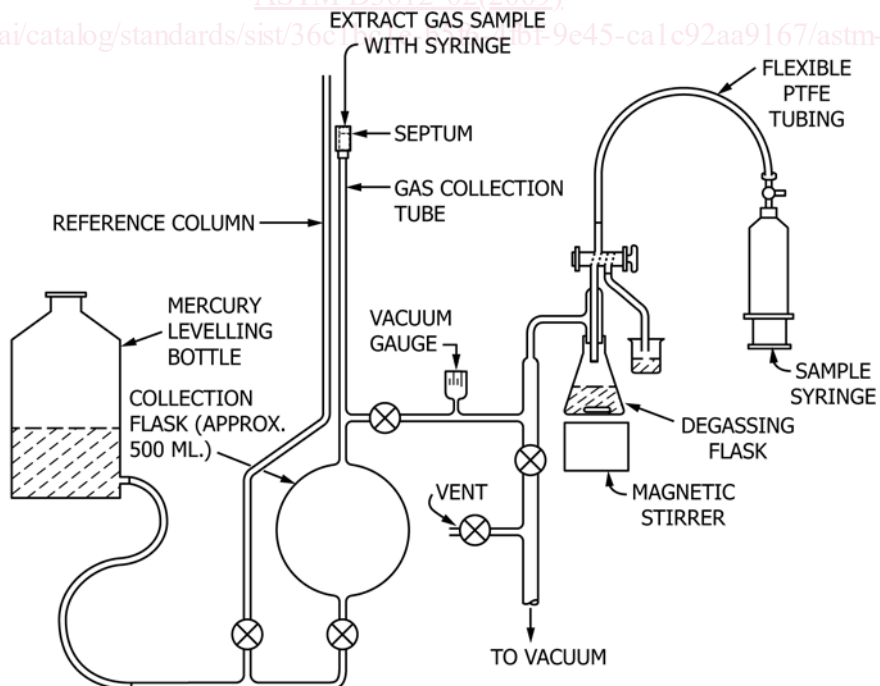
TO VACUUM

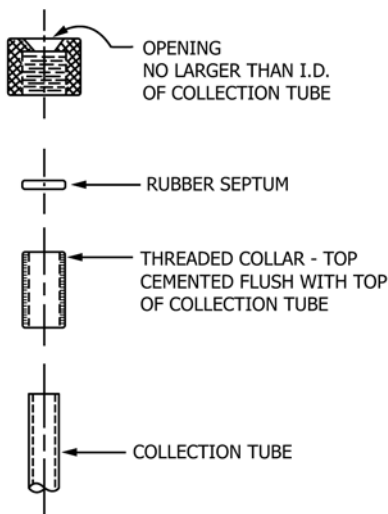FIG. 2 Extraction of Gas from Insulating Oil

FIG. 3 Retaining Rubber Septum for Gas Collection Tube

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 4—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:

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

where V_o = the volume of oil to be added.

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

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

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 D2780.

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 D2779.

Component Gas	Ostwald Solubility [7] (Note 5) 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 5—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/cm³ used in the original determination. Ostwald coefficients for mineral oils of different density may be calculated as follows:

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

where, *density* = density of the oil of interest, g/cm³ at 15.5°C (60°F). This equation is derived from the equation in Test Method D2779. 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.

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

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.

NOTE 6—Use Practice E260 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 7). 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 7—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*[8], 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.[9] 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.

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[8] 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.

[9] *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. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.
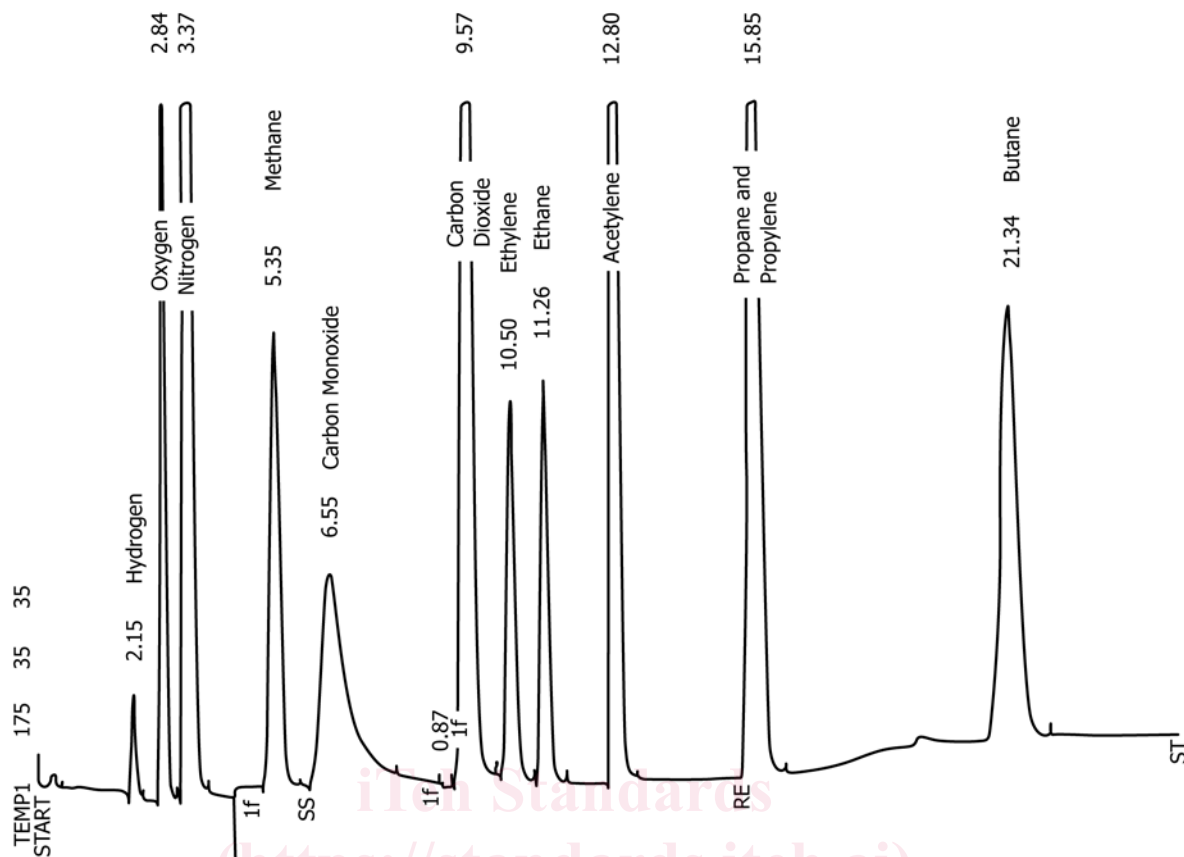
Gas Chromatograph Conditions:
Argon carrier gas, flow rate 30 mL/min

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

12.3 *Helium, Argon, or Nitrogen Carrier Gas,* having a minimum purity of 99.95 mol % (see Note 7).

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 D4051 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.[10]

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

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.

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.

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

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.

$$\frac{C_i}{E_i} \qquad (5)$$

16. Report

16.1 Report the following information:

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 The precision, bias and lower limit of detection of Method A have been evaluated by a statistical examination of the results of an inter-laboratory test of mineral oil test specimens.[11] A lower limit of repetition is defined here as an aid in the testing of transformers in factories.

17.2 *Precision – Repeatability*—The expected difference between successive results obtained on identical test specimens by the same operator using the same apparatus and normal and correct operation of the test method.

17.2.1 *Combustible Gases and Carbon Dioxide*—Repeatability of the determination of each individual combustible gas and of carbon dioxide was found to vary linearly with individual gas concentration level. The repeatability interval at the 95 % confidence level for the determination of a combustible gas n or of CO_2, $l_n(r)_{95\%}$ can be represented by:

$$l_n(r)_{95\%} = k_n(r)_{95\%} \times C_n \qquad (6)$$

where $l_n(r)_{95\%}$ is the value of the repeatability coefficient for the determination of that combustible gas or of carbon dioxide. C_n is the concentration level of the gas of interest (ppm). The repeatability coefficients at the 95 % level for each of the combustible gases and for CO_2 and the concentration ranges tested are given in Table 1.

17.2.2 *Oxygen and Nitrogen*—The ranges of concentrations of oxygen and nitrogen in the test specimens analyzed in the inter-laboratory test were relatively narrow. Therefore the relationships between repeatability intervals and concentrations of dissolved O_2 or of N_2 are not well defined. The coefficients of variation, $S(r)$, at the 50 % confidence level for the repeatability of the determination of O_2 and of N_2 and the concentration ranges tested are given in Table 1.

17.3 *Precision – Reproducibility*—The expected difference between two results obtained on identical test specimens by

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[11] Available from ASTM Headquarters. Request RR:D27-1016.

TABLE 1 Summary of Precision and Bias for Method A

Gas	C° - Range	Repeatability	Reproducibility	Bias
		Combustible Gases and Carbon Dioxide		
n	ppm	$k_n(r)_{95\%}$	$k_n(R)_{95\%}$	B_n
H_2	90 – 710	0.31	0.38	−0.13
CO	110 – 930	0.28	0.79	−0.14
CH_4	35 – 620	0.25	0.72	−0.21
C_2H_6	40 – 400	0.37	0.75	−0.29
C_2H_4	30 – 800	0.28	0.82	−0.27
C_2H_2	25 – 335	0.29	0.64	−0.30
CO_2	45 – 9300	0.48	0.76	[A]
		Oxygen and Nitrogen		
n	ppm	$S_n(r)_{50\%}$	$S_n(R)_{50\%}$	B_n
O_2	4630 – 4670	0.25	0.35	0.07 – 0.53
N_2	27000 – 61000	0.14	0.27	0.47 – (−) 0.05

[A]See text.

different operators working in different laboratories under normal and correct operation of the test method.

17.3.1 *Combustible Gases and Carbon Dioxide*— Reproducibility of the determination of each individual combustible gas and of carbon dioxide was found to vary linearly with individual gas concentration level. The reproducibility interval at the 95 % confidence level for the determination of a combustible gas n or of CO_2, $l_n(R)_{95\%}$ can be represented by:

$$l_n(R)_{95\%} = K_n(R)_{95\%} \times C_n \quad (7)$$

where $l_n(R)_{95\%}$ is the value of the reproducibility coefficient for the determination of that combustible gas or of carbon dioxide. C_n is the concentration level of the gas of interest (ppm). The reproducibility coefficients at the 95 % level for each of the combustible gases and CO_2 and the concentration ranges tested are given in Table 1.

17.3.2 *Oxygen and Nitrogen*—The ranges of concentrations of oxygen and of nitrogen contained were relatively narrow in the specimens analyzed in the interlaboratory test. Therefore the relationships between reproducibility intervals and concentration of dissolved O_2 or N_2 are not well defined. The coefficients of variation, $S(R)$, at the 50 % confidence level for the reproducibility of the determination of O_2 and of N_2 and the concentration ranges tested are given in Table 1.

17.4 *Bias*—The difference between the mean of results obtained for a gas in a test specimen and the "true" (that is, spiked) value of the concentration of that gas in the tested material.[11]

17.4.1 *Combustible Gases*—Bias of the determination of each individual combustible gas was found to vary linearly with individual gas concentration level. The relative bias, B_n, for the determination of a combustible gas, n, can be represented by:

$$B_n = (C_n - C_n^o)/C_n^o \quad (8)$$

where C_n is the concentration level of the gas of interest (ppm) and C_n^o is the "true" (spiked) value of the concentration of that gas in that test material. The bias and the concentration ranges tested are given in Table 1 for each of the combustible gases. The biases in results from Method A for the combustible gases are uniformly negative.

17.4.2 *Carbon Dioxide*—Bias for the determination of carbon dioxide decrease with increasing CO_2. No analytical

transformation adequately fits the results; these results are shown graphically in Fig. 5. It is possible that the positive bias at lower concentrations results, in part, from contamination by air.

17.4.3 *Oxygen and Nitrogen*—The bias for determinations of O_2 and of N_2 are positive and variable. It is possible that positive bias is, in part, the result of contamination by air. Also, the ranges of concentrations of oxygen and of nitrogen in the test specimens analyzed in the interlaboratory test were relatively narrow. The relationships between bias and dissolved concentration of O_2 or of N_2 then are not well defined. The coefficients of variation $S(R)$ at the 50 % confidence level for the reproducibility of the determination of O_2 and of N_2 and the concentration ranges tested are given in Table 1.

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.

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 Guide 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 Dissolved 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.
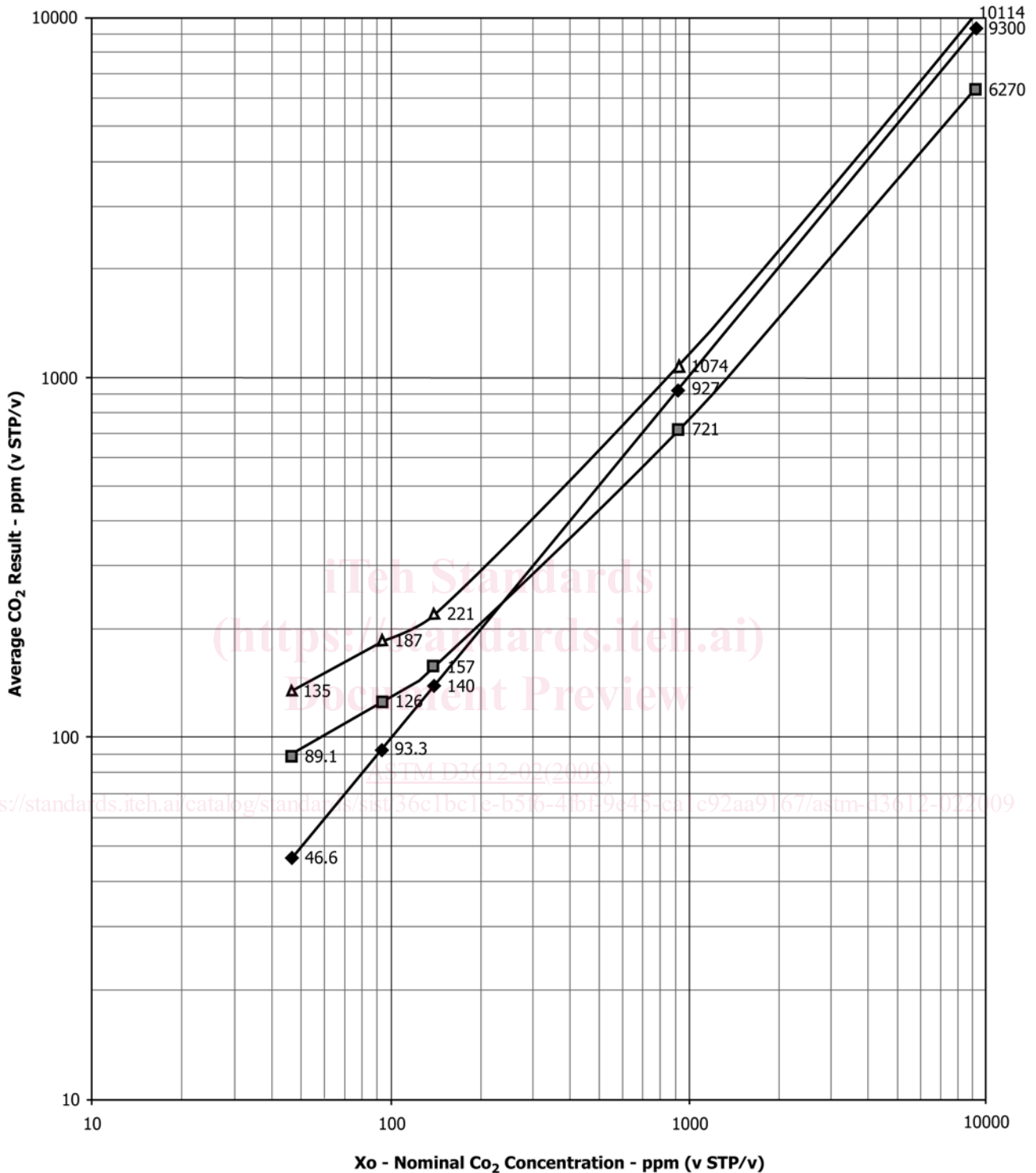
20. Reagent and Materials

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

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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.

FIG. 5 CO$_2$ in Oil — D3612 A&B Interlaboratory Test - Average Result versus Nominal Concentration

Note 1—Co = Calculated CO$_2$
C$_A$ = Average of CO$_2$ Method A
C = Average of CO$_2$ Method B

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$_2$H$_4$, C$_2$H$_6$, C$_2$H$_2$, C$_3$H$_6$, C$_3$H$_6$, and C$_4$H$_{10}$. 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 7.)

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 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 preestablished 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:

$$D_i (C_{aoi} - C_{boi})/C_{oi} \qquad (9)$$

where:

D_i = 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:

$$C_{ci} = C_{aoi}/D_i \qquad (10)$$

where:

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