



Standard Test Method for Analysis of Gases Dissolved in Electrical Insulating Oil by Gas Chromatography¹

This standard is issued under the fixed designation D 3612; 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 reappraisal. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reappraisal.

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—H₂
Oxygen—O₂
Nitrogen—N₂
Carbon monoxide—CO
Carbon dioxide—CO₂
Methane—CH₄
Ethane—C₂H₆
Ethylene—C₂H₄
Acetylene—C₂H₂
Propane—C₃H₈
Propylene—C₃H₆

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 2140 Test Method for Carbon-Type Composition of Insulating Oils of Petroleum Origin²
- D 2300 Test Method for Gassing of Insulating Oils Under Electrical Stress and Ionization Modified Pirelli Method²
- D 2779 Test Method for Estimation of Solubility of Gases in Petroleum Liquids³
- D 2780 Test Method for Solubility of Fixed Gases in Liquids³
- D 3613 Test Methods of Sampling Electrical Insulating Oils for Gas Analysis and Determination of Water Content²

¹ This test method is under the jurisdiction of ASTM Committee D27 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 10.03.

³ Annual Book of ASTM Standards, Vol 05.02.

D 4051 Practice for Preparation of Low-Pressure Gas Blends³

E 260 Practice for Packed Column Gas Chromatography⁴

2.2 IEEE Standard:

C 57.104 Guide for the Interpretation of Gases Generated in Oil-Immersed Transformers⁵

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 Gases⁶

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 10⁶ 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 Annual Book of ASTM Standards, Vol 14.02.

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

⁶ Available from IEC.

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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 Apparatus⁷ 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

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.

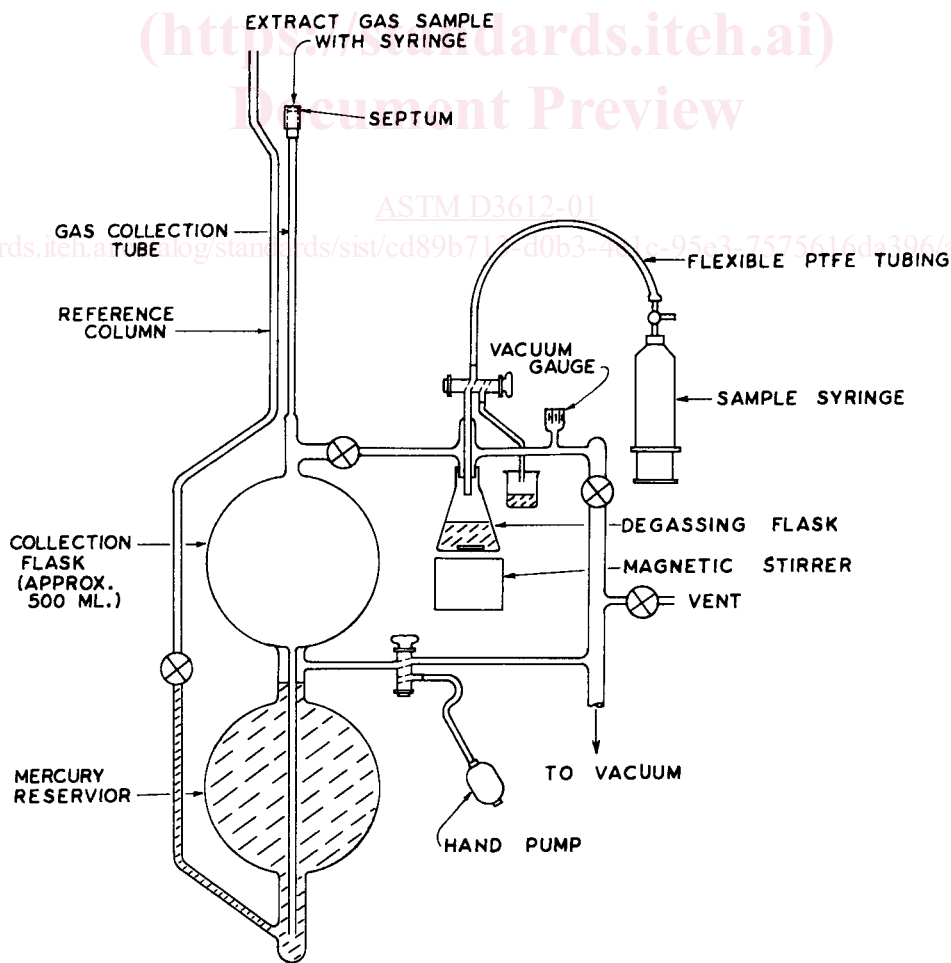


FIG. 1 Extraction of Gas from Insulating Oil

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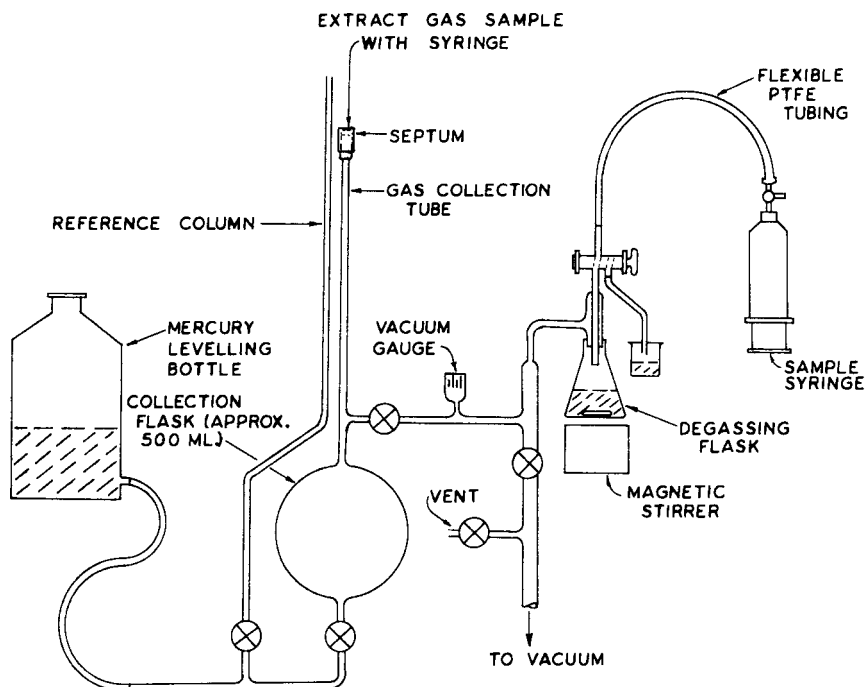


FIG. 2 Extraction of Gas from Insulating Oil

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.

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

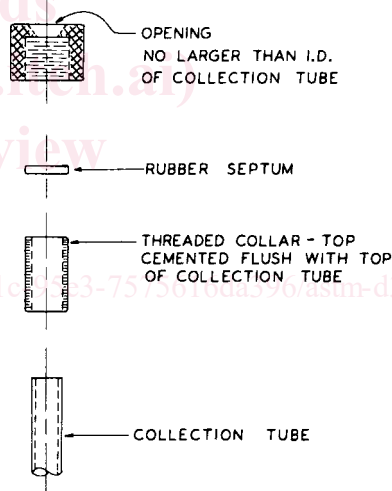


FIG. 3 Retaining Rubber Septum for Gas Collection Tube

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 ^a (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/cm³ used in the original determination. Ostwald coefficients for mineral oils of different density may be calculated as follows:

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

^a “Analysis of Gas Dissolved in Transformer Oils;” Daoust, R., Dind, J. E., Morgan, J., and Regis, J.; Doble Conference, 1971, Sections 6–110.

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 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 $\pm 0.5^\circ\text{C}$.

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 $\pm 1\%$ 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

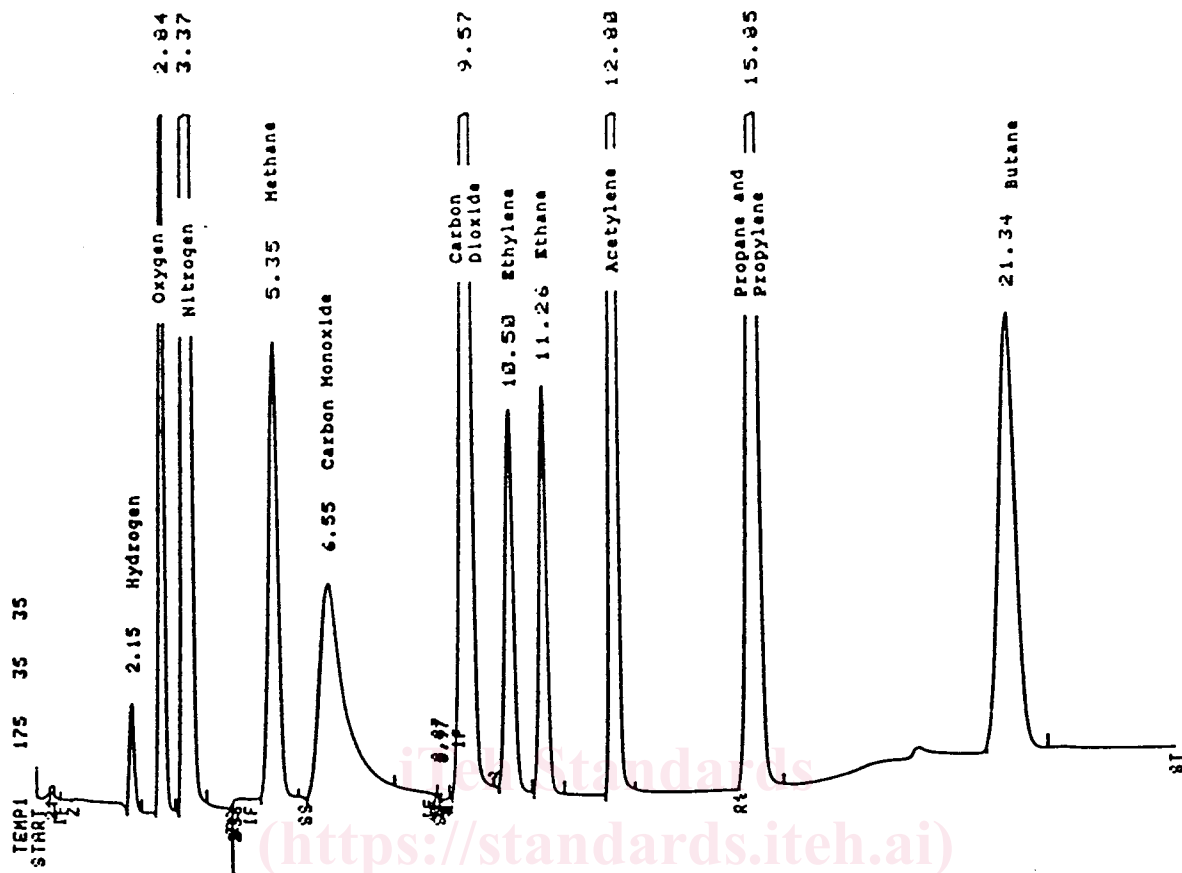
13.1 Prepare the gas chromatograph for use as directed by the manufacturer, and establish a set of operating conditions capable of separation of the indicated component gases.

13.2 Inject a pre-established volume of the reference standard gas mixture into the chromatograph and establish a pattern

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 × 1/8 in.
Molecular sieve, 13X, 40–60 mesh, 3 ft × 1/8 in.

Catalytic converter for detection of CO and CO₂

Detectors: Thermal conductivity: H₂, O₂, N₂
Flame ionization: CH₄, CO, CO₂, C₂H₆, C₂H₄, C₂H₂, C₃H₈, C₃H₆, C₄H₁₀

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

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.