



## Standard Practice for Preparation of Low-Pressure Gas Blends<sup>1</sup>

This standard is issued under the fixed designation D 4051; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

### 1. Scope

1.1 This practice describes a laboratory procedure for the preparation of low-pressure multicomponent gas blends. The technique is applicable to the blending of components at percent levels and can be extended to lower concentrations by performing dilutions of a previously prepared base blend. The maximum blend pressure obtainable is dependent upon the range of the manometer used, but ordinarily is about 101 kPa (760 mm Hg). Components must not be condensable at the maximum blend pressure.

1.2 The possible presence of small leaks in the manifold blending system will preclude applicability of the method to blends containing part per million concentrations of oxygen or nitrogen.

1.3 This practice is restricted to those compounds that do not react with each other, the manifold, or the blend cylinder.

1.4 *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 hazard statement, see Note 3.

### 2. Summary of Practice

2.1 Through the use of a blending manifold, the blend components are combined based upon partial pressure. Components are added in order of ascending vapor pressure; that is, components of lowest vapor pressure are added first, with the exception that components at concentrations of 5 % or less would usually be added first. Compressibility factors are applied to the component partial pressures to convert them from ideal to real gas. The real partial pressures, which are proportional to gas volumes, are normalized to give mol percent composition of the blend.

### 3. Significance and Use

3.1 The laboratory preparation of gas blends of known composition is required to provide primary standards for the calibration of chromatographic and other types of analytical instrumentation.

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analyses.

Current edition approved Apr. 10, 1999. Published June 1999. Originally published as D 4051 – 81. Last previous edition D 4051 – 89 (1993) <sup>$\epsilon$ 1</sup>.

### 4. Apparatus

4.1 *Blending Manifold*—Construct manifold as shown in Fig. 1. Details of construction are not critical; that is, glass, pipe, or tubing with welded or compression fittings may be used. The manifold must be leak free and arranged for convenience of operation. More than one feedstock connection point may be included if desired. Connections to the pump and manometer shall follow accepted vacuum practice. Valves shall have large enough apertures to permit adequate pumping in a reasonable length of time.

4.1.1 The finished manifold shall have a leak rate no greater than 1 mm Hg/h (0.133 kPa/h).

4.2 *Gage*, open manometer, vacuum, or pressure, consisting of a full-length U-tube mounted on a vertically adjustable meter scale.

NOTE 1—A well-type manometer such as the Miriam Model 30EB25 may be used in place of the U-tube manometer.

NOTE 2—A high-vacuum gage of the McLeod Manostat type pressure transducer or a 0 to 2 bar (absolute) may be included in the manifold system to determine how well the system has been evacuated.

4.2.1 Alternatively, an electronic pressure gage may be used in place of a mercury manometer.

4.3 *Pump*, high-vacuum, two-stage, capable of pumping down to a pressure of  $1.33 \times 10^{-4}$  kPa (0.1  $\mu$ m).

### 5. Reagents and Materials

5.1 *Blend Components* high-purity, as required depending on the composition of the proposed blend.

5.2 *Mercury* reagent grade, triple distilled.

NOTE 3—**Warning:** Mercury may be harmful if inhaled or swallowed.

5.3 *Nitrogen*, high purity, as required, for purging and for balance gas, where applicable.

### 6. Procedure

6.1 Connect the blend cylinder to the manifold at position A (see Fig. 1 for valve and position designations). Open valves 1, 2, 3, and 6 and evacuate the manifold system thoroughly. Valves 4 and 5 are closed.

NOTE 4—A McLeod gage may be used at various times during the procedure to determine how well the system has been evacuated and to indicate if there are leaks present. Otherwise, a steady state condition of the mercury in the manometer can be taken as an indication that an acceptable vacuum has been attained.

6.1.1 When a good vacuum less than 0.01 kPa (0.1 mm Hg)

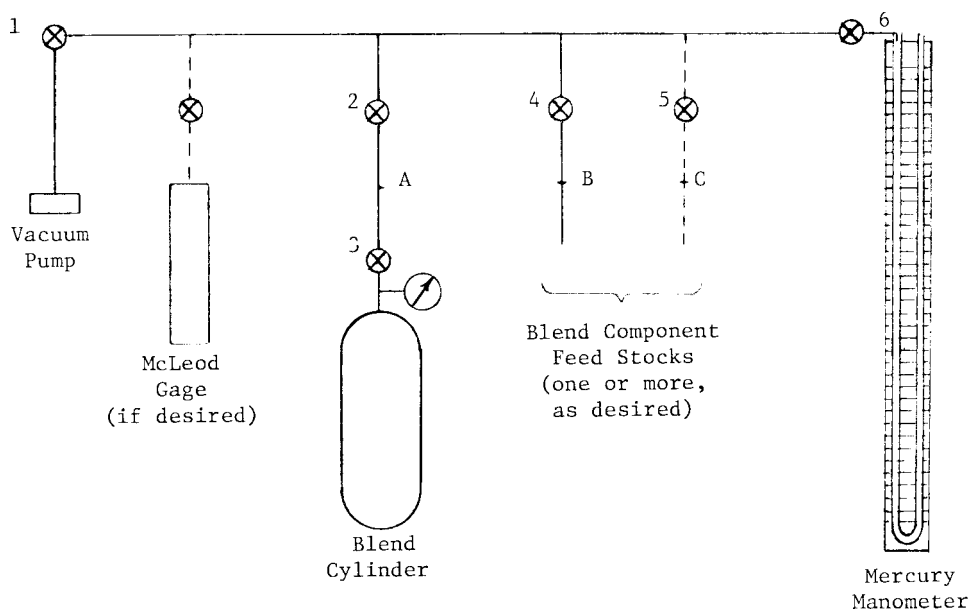


FIG. 1 Manifold System

is reached, connect one or more blend component cylinders to the manifold at positions *B* or *C*, or both. Close valve 2 and open valves 4 and 5, thereby evacuating the connecting lines up to the blend component cylinder valves. When a good vacuum is again reached, close valves 4 and 5 and open the blend component cylinder valves. Ensure that the pressure of any blend component delivered to valves 4 and 5 does not exceed 200 kPa (1500 mm Hg). Record the initial pressure readings from both sides of the manometer.

6.1.2 The first component to be added will either have the lowest vapor pressure or will be present in the final blend at a concentration of 5 % or less. Assume that the first component feedstock is connected to manifold valve 4. Close valve 1 and open valve 2. While carefully watching the mercury level in the manometer, *slowly* open valve 4. Allow the blend gas component to flow into the blend manifold until the desired precalculated manometer reading is reached (see 7.1). Close valve 4 and be sure that the pressure remains constant. Tap the manometer lightly to be certain the correct reading is obtained. Record the reading of both sides of the manometer and then close valve 3. Open valve 1 and wait until the manifold is thoroughly evacuated.

6.1.3 If the manifold includes only one feedstock connection point it will be necessary at this time to remove the first feedstock cylinder, connect the second, and evacuate the line back to the feedstock cylinder valve. Assume this to be the case; valve 4 will, therefore, always be used as the feedstock control valve.

6.1.4 When manifold evacuation is complete, close valve 1 and 4. Open the feedstock cylinder valve and then *slowly* open valve 4, allowing the second blend gas to flow into the manifold. Carefully watch the mercury level of the manometer.

NOTE 5—All additions should be made slowly to avoid temperature changes.

6.1.5 When the pressure in the manifold is several pascals (or millimetres of mercury) higher than the previous reading

and is still slowly rising, slowly begin to open valve 3 so as to admit the component to the sample cylinder. Valve 4 will remain partially open. Continue to open valve 3 while controlling the flow through valve 4 until the next desired pressure level is reached, always maintaining a higher pressure in the manifold than that in the cylinder. Close valve 4, allow the pressure to equilibrate, and record the manometer reading from both sides. Close valve 3. When additional components are to be included in the blend, repeat the procedures outlined above for each component.

6.1.6 When all components have been added, and valve 3 is closed, evacuate the manifold, close valve 2 and disconnect the blend cylinder from the manifold at position *A*. To shut down the apparatus, close the feedstock cylinder valve and open valve 4 to evacuate the connection. Close valve 4, remove the feedstock cylinder, close valve 1 and by using valve 2 or 4 *slowly* admit air into the system until it is at atmospheric pressure.

6.2 The blend *must* be mixed before it is used. This can be accomplished in several ways, one of which is to cause convection currents to occur within the cylinder. This may conveniently be done by heating one end of the cylinder with either a hot air gun or by running hot water over one end of it for about an hour. Never use a flame to heat the cylinder. Blends containing hydrogen or helium are very difficult to mix. Therefore, it is necessary to periodically alternate heating of first one end of the cylinder and then the other for several hours.

6.3 To prepare a blend containing components at the parts per million level, it is necessary to make an initial blend of those components at higher concentrations and then to make successive dilutions until the final desired concentration level is reached. For example, if a blend is desired that contains 64 ppm, butane in nitrogen, the initial blend would be made to contain 4 % butane in nitrogen. After mixing, a second blend is prepared by combining 4 % of the initial blend and 96 %

nitrogen. After mixing this blend, the final blend is prepared by combining 4 % of the second blend and 96 % nitrogen. This procedure will provide manometer readings that are large enough to be accurately read.

## 7. Preblending Calculations

7.1 In order to make blends of components at specific levels, it is necessary to calculate before hand the desired manometer readings required to achieve these levels. Calculate these partial pressures as follows:

$$L_N = L_E - \frac{N\%}{100} \times P_T \quad (1)$$

where:

- $L_N$  = desired manometer reading on the side connected to the manifold for component N, kPa (mm Hg),
- $L_E$  = expected manometer reading on the same side before component N is added, kPa (mm Hg),
- $N\%$  = desired percentage of component N, and
- $P_T$  = expected total absolute pressure of blend, 202 kPa (1520 mm Hg)

For the first component to be added,  $L_E$  is equal to the initial manometer reading of the side connected to the manifold. For each component thereafter,  $L_E$  is equal to the calculated  $L_N$  of the component to be added just previous to it.

NOTE 6—Compressibility factors may be included in preblending calculations but their usage will not significantly change the calculated values. Compressibility factors are, however, utilized in the final-blend calculations.

## 8. Blend Cylinder Preparation

8.1 It is advisable to equip the cylinder with a compound gage capable of indicating pressures from vacuum up to a gage pressure of 200 kPa (15 psi). The volume of the blend cylinder is not critical; however, a size of 1½ to 2 L, or larger, is satisfactory.

8.2 The interior of the cylinder must be dry and free of volatile substances. Thorough cleaning of the interior may be required if the cylinder had previously been used to contain gas mixtures having heavier components or components that would have absorbed on the walls.

8.3 Purge the cylinder several times with air from a low-pressure source and then pull a partial vacuum on it for at least 15 min. Close the cylinder valve while the cylinder is still under vacuum.

## 9. Calculation

9.1 Calculate the partial pressure of each component as follows:

$$P_N = (L_B - L_A) + (R_A - R_B) \quad (2)$$

where:

- $P_N$  = partial pressure of component N, kPa (mm Hg),
- $L_B$  = manometer reading on the side connected to the manifold, before component addition, kPa (mm Hg),
- $L_A$  = manometer reading on the side connected to the manifold, after component addition, kPa (mm Hg),

$R_A$  = manometer reading on the side not connected to the manifold, after component addition, kPa (mm Hg), and

$R_B$  = manometer reading on the side not connected to the manifold, before component addition, kPa (mm Hg).

For the first component added,  $L_B$  and  $R_B$  are equal to the initial readings taken. For each component added thereafter,  $L_B$  and  $R_B$  are equal to  $L_A$  and  $R_A$  of the component just previously added.

NOTE 7—If a well-type manometer is used, calculations will be different from those shown above since only one manometer reading is taken with the addition of each compound.

9.2 Calculate the mol percent composition as follows:

$$\begin{aligned} \text{Mol \% of component } N &= \frac{(P_N/F_N) \times 100}{\Sigma[(P_N/F_N) + (P_O/F_O) + (P_Q/F_Q)]} \dots \quad (3) \end{aligned}$$

where:

- $P_N, P_O, P_Q$  = partial pressure of components N, O, Q, etc., kPa, (mm Hg) as calculated above and
- $F_N, F_O, F_Q$  = compressibility factor of each compound.

Table 1 lists compressibility factors for a number of commonly occurring compounds from ASTM DS 4A.<sup>2</sup>

NOTE 8—This calculation is not rigorous in that the calculation of compressibility does not allow for binary interactions. The errors however are small by comparison with those associated with the pressure measurements.

## 10. Precision and Bias

10.1 Precision and bias for preparation of gas blends cannot be determined since the result merely states whether there is conformance to the criteria for success specified in the procedure.

10.2 The maximum systematic error introduced by use of this procedure is dependent largely upon the precision of the equipment used and the care exercised in its use. This error can be estimated by taking into account such error sources as the readability and accuracy of the pressure measuring device, temperature variations during blend preparation, and whether compressibility factors are known for all blend components. For example: a component having a partial pressure in the blend of 1.07 kPa (8 mm Hg) whose compressibility factor is unknown, measured by means of a manometer readable to 0.07 kPa ( $\pm 0.5$  mm Hg) could be subject to an error of as much as  $\pm 12\%$  relative at constant temperature, in the worst case.

$$\left( (0.5/8) + \frac{[(8/0.95) - (8/1)]}{8} \right) \times 100 = 12\% \quad (4)$$

As component concentration increases, the error becomes smaller.

## 11. Keywords

11.1 analytical standard; low-pressure gas blends

<sup>2</sup> Available from ASTM Headquarters.

**TABLE 1 Compressibility Factor of the Real Gas at 15.6°C (60°F) and 1 Atm  $Z = PV/RT$  (Data from ASTM DS 4A Except as Noted)**

NOTE 1—Values in parentheses are estimated.

Compound	Z	Compound	Z
Methane	0.9981	Propadiene (allene)	0.9828
Ethane	0.9916	1,2-Butadiene	(0.969)
Propane	0.9820	1,3-Butadiene	(0.965)
<i>n</i> -Butane	0.9667	1,2-Pentadiene	(0.963)
2-Methylpropane (isobutane)	0.9696	1, <i>cis</i> -3-Pentadiene	(0.963)
<i>n</i> -Pentane	0.9549	1, <i>trans</i> -3-Pentadiene	(0.962)
2-Methylbutane (isopentane)	0.9544	1,4-Pentadiene	(0.956)
2,2-Dimethylpropane (neopentane)	0.9510	2,3-Pentadiene	(0.963)
Cyclopropane	0.9823	2-Methyl-1,2-butadiene	(0.963)
Cyclobutane	(0.97)	2-Methyl-1,3-butadiene (isoprene)	(0.962)
Cyclopentane	0.9657	Ethyne (acetylene)	0.9925
Ethene	0.9983	Propyne (methylacetylene)	0.9835
Propene	0.9844	1-Butyne	0.9650
1-Butene	0.9704	2-Butyne	(0.965)
<i>cis</i> -2-Butene	0.9661	1-Pentyne	(0.959)
<i>trans</i> -2-Butene	0.9662	2-Pentyne	(0.964)
2-Methylpropene (isobutylene)	0.9689	3-Methyl-1-butyne	(0.951)
1-Pentene	0.9550	Air	0.9999 <sup>A</sup>
<i>cis</i> -2-Pentene	(0.959)	Argon	0.9993 <sup>A</sup>
<i>trans</i> -2-Pentene	(0.959)	Carbon dioxide	0.9996 <sup>A</sup>
2-Methyl-1-butene	0.9551	Carbon monoxide	0.9995 <sup>A</sup>
3-Methyl-1-butene	(0.958)	Hydrogen	1.0006 <sup>A</sup>
2-Methyl-2-butene	0.9554	Nitrogen	0.9996 <sup>A</sup>
Cyclopentene	(0.964)	Oxygen	0.9992 <sup>A</sup>

<sup>A</sup>Values from *Chemical Engineers Handbook*, 5th Ed, 1973 McGraw-Hill Book Co.

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