



Designation: D4307 – 17

Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards¹

This standard is issued under the fixed designation D4307; 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 practice covers a laboratory procedure for the preparation of small volumes of multicomponent liquid blends for use as analytical standards.

1.2 This practice is applicable to components that are normally liquids at ambient temperature and pressure, or solids that will form a solution when blended with liquids. Butanes can be included if precaution is used in blending them.

1.3 This practice is limited to those components that fulfill the following conditions:

1.3.1 They are completely soluble in the final blend.

1.3.2 They are not reactive with other blend components or with blend containers.

1.3.3 The combined vapor pressure of the blended components is such that there is no selective evaporation of any of the components.

1.3.3.1 The butane content of the blend is not to exceed 10 %. (**Warning**—Extremely flammable liquefied gas under pressure. Vapor reduces oxygen available for breathing.) Components with a vapor pressure higher than butanes are not to be blended.

1.4 The values stated in SI units are to be regarded as the standard.

1.5 *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.*

1.6 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

¹ This practice is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.04.0A on Preparation of Standard Hydrocarbon Blends.

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2. Referenced Documents

2.1 *ASTM Standards*:²

D1364 Test Method for Water in Volatile Solvents (Karl Fischer Reagent Titration Method)

3. Summary of Practice

3.1 The individual blend components are precisely weighed and combined in an inert, tight-sealing glass vial or similar container. When volatility is a consideration, the components of lowest vapor pressure (least volatile) are added first and the highest (most volatile) last. Mass (weight) percent composition of the final blend is calculated from the mass and purities of the pure components. Volume percent composition can be calculated using the density of each component.

4. Significance and Use

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

5. Apparatus

5.1 *Containers*:

5.1.1 *Vial*, glass, threaded neck, approximately 22 mL capacity, short style. Vials of other capacities may be substituted as required. When blending light-sensitive components, use amber glass vials or wrap clear glass vials with black tape.

5.1.2 *Bottle Cap*, molded plastic with TFE-fluorocarbon, polypropylene, or polyethylene conical liner.

5.1.3 *Bottle Cap*, molded plastic with aluminum foil liner. Aluminum foil liners are preferred to other metal liners because they seal better.

5.1.4 *Mininert Valve*, screw cap, 20 mm or appropriate size to match vial size used. These caps are especially valuable for preparing blends that contain volatile components.

NOTE 1—The use of Mininert valves is recommended when components lighter than hexane are contained in the liquid blends.

² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

5.2 *Balance*, capable of weighing to 0.1 mg.

5.3 *Pipet*, dropping, medicine dropper.

5.4 *Spatula*, semi-micro, scoop style.

6. Reagents and Materials

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

6.1.1 To verify the purity of blend components, analyze each compound by the same technique for which the blend is intended or by another suitable technique. Check for other impurities such as water, if necessary. Water cannot be determined with sufficient accuracy by most GC methods and must be measured by other procedures such as Test Method **D1364**, or equivalent, and the result used to normalize the chromatographic value. If any of the impurities found are other components of the blend, determine their concentrations and make appropriate corrections.

7. Procedure

7.1 Examine the vial and cap to verify that a leak-free closure is obtained. The rim at the top of the vial should be smooth and flat and the cap should fit snugly.

7.1.1 Glass vials are inert to most compounds and are the usual choice. Plastic containers shall never be used since specific compounds can preferentially diffuse through them.

7.1.2 Plastic caps with aluminum foil liners provide a good seal unless blend components react with the aluminum. Polyethylene or polypropylene-lined caps usually provide a good closure but are not to be used for aromatic hydrocarbons and similar compounds since these materials will, with time, diffuse through the liner.

7.2 Weigh the vial and cap to the nearest 0.1 mg. Remove the cap and add the first component to the vial, being careful not to allow the component to contact the rim of the vial, which could produce losses. Liquids may be added by either pipet or medicine dropper while solids are usually added with a small spatula. Place the cap on the vial and reweigh to the nearest 0.1 mg, recording the mass. Repeat this procedure with each additional component, always being careful not to allow the contents of the vial to contact the cap. After all components have been added and the final weighing completed, thoroughly shake the vial to mix the solution.

7.2.1 When volatile components are being combined, the lowest vapor pressure (least volatile) compound is added first and the highest (most volatile) last.

NOTE 2—Exercise care when adding additional components since the resulting agitation can lead to excessive loss of headspace and acts to amplify the preferential removal of more volatile components from the blend. This condition is further amplified by the fact that each time the vial cap is removed, the equilibrium of the headspace will be altered. Since liquid films form spontaneously on the vial caps from super-saturated headspaces and from equilibrium processes of evaporation and condensation (especially if the vial is cooled), all of the blend components should be added to the blend in as short a time as is reasonable.

7.2.2 For blending very volatile components, it is advisable to reduce the volatility when the vial is uncapped by cooling the vial to about 4 °C between weighings. When this technique is utilized, the volatile component is added, and the vial is

closed and weighed. The vial and contents then are chilled thoroughly before the vial is opened to allow addition of the next component. The next component is added quickly, the vial closed, and the vial and contents brought to ambient temperature before the mass is obtained. Exercise care to ensure that moisture condensed on the exterior of the vial is removed before weighing. After weighing, the vial and contents are re-chilled before the vial is opened to permit addition of the next component.

7.3 To prepare a blend containing components at low concentration, for example, mg/kg, where the weighed quantities would be too small for sufficient accuracy, it is necessary to make an initial blend of those components at higher concentrations. Successive dilutions are then made until the final desired concentration is reached. For example, if a blend is desired that contains 56 mg/kg (mass-ppm) *n*-heptane in cyclohexane, weigh together 2 mL of *n*-heptane and 20 mL of cyclohexane. Make certain that between all weighings the unmixed liquid does not contact the container cap, which could cause preferential losses. After both components have been added, thoroughly mix this blend by shaking. Make three successive dilutions, with careful weighings, of one part (2 mL) of blend with ten parts (20 mL) of cyclohexane. Shake thoroughly between each dilution. Each blend should have a finished volume of 22 mL so that quantities are large enough to weigh accurately. The mass-ppm of *n*-heptane in the final blend is calculated from the recorded weights.

8. Preblending Calculations

8.1 In order to make blends of components at specific levels, it is necessary to calculate beforehand the mass of each component required to achieve these levels. Calculate these masses as follows:

$$W_N = \frac{AT}{100} \quad (1)$$

where:

W_N = mass of component *N* to be added, g,

A = desired mass percentage in the final blend, and

T = desired mass of the total final blend, g.

9. Calculations

9.1 Calculate the mass percent concentration of each component as follows:

$$N, \text{ mass \%} = \frac{W_N \times 100}{\sum (W_N + W_O + W_P \dots)} \quad (2)$$

where:

W_N, W_O, W_P = mass of components *N, O, P*, etc, g.

9.1.1 When an added component is less than 100 % pure (see 6.1.1), corrections shall be made to the mass of that compound, as well as to other components included in the blend. For example, if the mass of component *N* added to the blend is 3.0 g but previous analysis indicated it to be 95 % component *N*, 3 % component *O*, and 2 % component *P*, then the actual mass of component *N* in the blend would be 2.85 g, and 0.09 g and 0.06 g would need to be added to the masses of components *O* and *P*, respectively.

9.1.1.1 When a standard being prepared contains one or more components being used as an internal standard, Eq 2 shall not include the mass of the internal standard component(s) in the denominator summation when calculating the mass percent of the other components in the blend. The mass of the internal standard component(s) is only included in the denominator summation in Eq 2 when calculating the mass percent of the internal standard component(s) in the blend.

9.1.1.2 *Example Calculations*—The following mixture was prepared (for simplicity, purities were not taken into account for this example).

Component	Mass (g)
Methyl <i>tert</i> -Butyl Ether	15.02
Ethanol	10.05
Methanol	5.02
1-Propanol	3.03
Gasoline	66.88
1,2-Dimethoxyethane	5.25

Calculations:

Sample: 15.02 g + 10.05 g + 5.02 g + 3.03 g + 66.88 g = 100.00 g

MTBE Concentration: 15.02 g/100.00 g = 15.02 % by mass

Ethanol Concentration: 10.05 g/100.00 g = 10.05 % by mass

Methanol Concentration: 5.02 g/100.00 g = 5.02 % by mass

1-Propanol Concentration: 3.03 g/100.00 g = 3.03 % by mass

Internal standard calculation:

1,2-Dimethoxyethane Concentration: 5.25 g/105.25 g = 4.99 % by mass

9.2 Calculate the volume percent concentration of each component as follows:

$$N, \text{ volume } \% = \frac{(W_N/D_N) \times 100}{\sum [(W_N/D_N) + (W_O/D_O) + (W_P/D_P) \dots]} \quad (3)$$

where:

W_N, W_O, W_P = mass of components N, O, P , etc, g, and

D_N, D_O, D_P = density of components N, O, P , etc., all determined at the same temperature.

9.2.1 The final volume of the solution is not necessarily the same as the sum of the volumes of the components due to possible expansion or contraction on mixing.

9.2.1.1 When a standard being prepared contains one or more components being used as an internal standard, Eq 3 shall not include the mass/density ratio of the internal standard component(s) in the denominator summation when calculating the volume percent of the other components in the blend. The mass/density ratio of the internal standard component(s) is only included in the denominator summation of Eq 3 when calculating the volume percent of the internal standard component(s) in the blend.

10. Keywords

10.1 analytical standards; liquid blends

SUMMARY OF CHANGES

Subcommittee D02.04 has identified the location of selected changes to this standard since the last issue (D4307 – 99 (2015)) that may impact the use of this standard. (Approved May 1, 2017.)

(1) Revised several subsections of Section 9.

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