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Standard Practice for Ampulization and Storage of Gasoline and Related Hydrocarbon Materials[1]

This standard is issued under the fixed designation D6596; 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 general guide for the ampulization and storage of gasoline and related hydrocarbon mixtures that are to be used as calibration standards or reference materials. This practice addresses materials, solutions, or mixtures, which may contain volatile components. This practice is not intended to address the ampulization of highly viscous liquids, materials that are solid at room temperature, or materials that have high percentages of dissolved gases that cannot be handled under reasonable cooling temperatures and at normal atmospheric pressure without losses of these volatile components.

1.2 This practice is applicable to automated ampule filling and sealing machines as well as to manual ampule filling devices, such as pipettes and hand-operated liquid dispensers.

1.3 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

D6362 Practice for Certificates of Reference Materials for Water Analysis

E826 Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectrometry

2.2 *ISO Standards:*[3]

ISO Guide 30 Terms and Definitions Used in Connection with Reference Materials

ISO Guide 31 Contents of Certificates of Reference Materials

ISO Guide 35 Certification of Reference Materials – General and Statistical Principles

ISO/REMCO N280 Homogeneity Testing Procedure for the Evaluation of Interlaboratory Test Samples

2.3 *Government Standard:*[4]

29 CFR 1910.1200 Hazard Communication

3. Terminology

3.1 *Definitions:*

3.1.1 *accepted reference value (ARV)*—a value that serves as an agreed-upon reference for comparison and that is derived as: *(1)* a theoretical or established value, based on scientific principles; *(2)* an assigned value, based on experimental work of some national or international organization, such as the National Institute of Standards and Technology (NIST); or *(3)* a consensus value, based on collaborative experimental work under the auspices of a scientific or engineering group.

3.1.2 *ampule*—a glass vessel for the storage of liquid materials, possessing a long narrow neck for the purpose of providing a flame-sealed closure.

3.1.3 *headspace*—the unfilled capacity of an ampule that allows for physical expansion due to temperature and pressure changes of the filled material while maintaining the integrity of the package.

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

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[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.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[4] Available from U.S. Government Printing Office Superintendent of Documents, 732 N. Capitol St., NW, Mail Stop: SDE, Washington, DC 20401, http://www.access.gpo.gov.

3.1.4 *homogeneity*—the uniformity of the characteristics of the packaged material across the entire packaging run determined for the purpose of demonstrating the suitability of the batch for its intended purpose.

3.1.4.1 *Discussion*—There are two homogeneity testing cases; one in which the material is ampulized as a reference material at the time of ampulization, and one in which the material is not.

(1) reference material at time of ampulization—The material to be ampulized is a reference material that has accepted true or consensus values. Ampulization of a reference material would require homogeneity testing in order to assess the variability caused by the ampulization process on the true or consensus values for the reference material.

(2) not a reference material at time of ampulization—The material to be ampulized is *not* a reference material at the time of ampulization but is intended to have characterization and assignment of true or consensus values at some future date. Rigid homogeneity testing is not required on such a material at the time of ampulization since the true or consensus values have not yet been determined. However, ampules must be retained at the beginning, middle, and end of the ampulization process. It is recommended that qualitative testing be done on at least one sample from each of the beginning, middle, and end of the ampulization process. The remaining ampules should then be retained for future homogeneity testing to determine quantitative or consensus values.

3.1.5 *reference material (RM)*—a material or substance of which one or more properties are sufficiently well established to enable the material to be used for the calibration of an apparatus, the assessment of a method, or the assignment of values to similar materials.

3.1.6 *shelf life*—the period of time, under specified storage conditions, for which the RM will possess the same properties or true values, within established acceptance limits.

3.1.7 *stability testing*—tests required to demonstrate the chemical stability of the ampulized RM for the purpose of determining the shelf life of the RM.

4. Summary of Practice

4.1 The physical and chemical characteristics (for example, volatility, reactivity, flammability, and so forth) of a gasoline or related hydrocarbon mixture is first assessed to determine the appropriate procedures for sample handling, sample transfer, and ampulization. Then a uniform quantity of gasoline or hydrocarbon mixture is dispensed into suitably sized glass ampules (purged with an inert gas), and the ampules are flame-sealed with a torch. A number of ampules from throughout the filling and sealing process are selected and tested by appropriate test methods to determine homogeneity across the lot. Additional ampules are retained for later testing to determine stability and shelf life.

4.2 This practice addresses the common difficulties associated with the ampulization and storage of gasoline and similar liquid hydrocarbon materials, which may contain volatile components. The process of ampulization, whether performed using manual or automated equipment, involves the same fundamental issues, namely, assessment of the characteristics of the material to be ampulized, sources of contamination, sampling of the bulk container, volume dispensing accuracy, inert atmosphere blanketing, flame sealing, sequential ampule labeling, packaging homogeneity sampling, and homogeneity testing. Failure to adequately consider any of the above issues may negatively impact the quality, consistency, and value of the ampulized material as an RM.

4.3 Confidence in the homogeneity of the ampulized product can only be established through homogeneity testing, which involves the sampling, analysis, and statistical treatment of data from randomly selected ampules obtained from the beginning, middle, and end of the ampulized lot. Determination of ampulization homogeneity requires that the order in which the ampules have been filled and sealed be maintained. Homogeneity testing reveals the variability of the product introduced during the ampulization process. Homogeneity results must be within acceptable limits of the ARV or consensus value for the RM.

4.4 Ampulization does not necessarily guarantee sample stability or indefinite shelf life of the RM. Initial homogeneity data establish reference values for future tests of sample stability and determination of shelf life.

5. Significance and Use

5.1 Ampulization is desirable in order to minimize variability and maximize the integrity of calibration standards or RMs, or both, being used in calibration of analytical instruments and in validation of analytical test methods in round-robin or interlaboratory cross-check programs. This practice is intended to be used when the highest degree of confidence in integrity of a material is desired.

5.2 This practice is intended to be used when it is desirable to maintain the long term storage of gasoline and related liquid hydrocarbon RMs, controls, or calibration standards for retain or repository purposes.

5.3 This practice may not be applicable to materials that contain high percentages of dissolved gases, or to highly viscous materials, due to the difficulty involved in transferring such materials without encountering losses of components or ensuring sample homogeneity.

6. Procedure

6.1 *Manual Ampule Filling and Sealing:*

6.1.1 *Apparatus*—Devices used for manual filling of ampules include glass pipettes as well as other types of commercially available hand-operated, mechanical, liquid-dispensing devices.

6.1.2 *Storage of Bulk Material*—Bulk gasoline and similar liquid hydrocarbon materials must be adequately sealed and stored to prevent loss of volatile components prior to ampulization. Refrigerated storage in sealed metal drums, barrels, or amber glass containers is recommended.

6.1.3 *Compatibility of Materials/Sources of Contamination:*

6.1.3.1 Materials that come in contact with the bulk RM and its vapors during dispensing must be compatible with the gasoline or hydrocarbon material. Glass pipettes are recommended. Plastic or rubber materials containing phthalates or other types of plasticizers must be avoided.

6.1.3.2 Any part of the dispensing device that comes in contact with the material, including glass pipettes, hand dispensers, and any necessary connection hardware, must be cleaned prior to packaging a different material. Recommended cleaning procedures involve soaking parts in soapy water, rinsing with clean water, followed by methanol or other suitable solvent, followed by drying under a stream of clean nitrogen.

6.1.4 *Assessment of Material to Be Ampulized:*

6.1.4.1 *Volatility*—Prior to packaging, materials containing highly volatile components must be cooled sufficiently to minimize volatile losses during ampulization. Failure to sufficiently cool the material also may result in difficulty in obtaining effective ampule sealing. The material must not be cooled to temperatures below which the composition of the RM would be affected (for example, producing precipitation or solidification). Gasoline may be cooled to –20 °C without incurring compositional changes. The bulk material must be kept cold during the filling process.

6.1.4.2 *Reactivity*—Consideration should be given to the chemical reactivity of the RM being packaged. Gasoline samples containing olefins and diolefins should be packaged under an inert atmosphere blanket of nitrogen, argon, or other suitable gas. Ampules should be flushed with inert gas immediately prior to dispensing of the gasoline. Use of amber glass ampules will minimize photo-oxidation.

6.1.4.3 *Odors*—Odorous materials such as gasoline should be packaged in a well-ventilated area. The bulk material should be kept adequately sealed during the ampulization process to minimize loss of volatiles.

6.1.4.4 *Flammability*—Ampule sealing requires use of a flame hot enough to melt glass. Care must be taken in ampulization of highly flammable materials since ampule contents could ignite. Ampules must be kept cold through the sealing step. However, care should be taken to avoid, as much as possible, condensation of water inside the ampule. Ampulization is best carried out when the room humidity is low.

6.1.5 *Sampling of the Bulk Container:*

6.1.5.1 After bringing the bulk container temperature down to the working temperature, withdraw a minimum of three samples from each bulk container, using clean manual pipettes. Immediately dispense the material into crimp top chromatography vials, seal, and label. These samples will be designated as representative of the bulk material and will be used to establish reference values for the homogeneity testing.

6.1.5.2 Some vial closures are not suitable for hydrocarbon analyses, such as uncoated silicone rubber. Only TFE-fluorocarbon-coated closures should be used. In addition, the vials should be analyzed as soon as is practical, since no crimped vial is completely leak free.

6.1.6 *Adjusting Dispensing Volume:*

6.1.6.1 Typically, it is more important to provide a minimum dispensed volume in the ampule rather than to provide an accurately determined volume of RM. The minimum dispensing volume for packaging the RM must be known ahead of time.

6.1.6.2 Introduce an inert atmosphere into the ampule by purging the ampule for a few seconds with nitrogen or other inert gas immediately prior to filling. A disposable glass dropper connected to a gas source using rubber tubing provides a convenient way of purging the ampule.

6.1.6.3 If using graduated pipettes, introduce a sufficient volume of material to the ampule to meet the minimum dispensing volume requirements for packaging the RM. Note that the final dispensed volume at room temperature will be affected by the bulk material temperature at the time of dispensing. Therefore, for consistent volume dispensing, the temperature of the bulk material must be known and must be kept constant during the entire dispensing process.

6.1.6.4 If other types of nongraduated, manual, filling devices are being used, they must be calibrated. Using Class A glassware or pipettes, measure into an ampule a volume of room temperature water equal to the volume of RM to be dispensed. Mark the level on the ampule.

6.1.6.5 Make adjustments to the manual dispensing device until 50 consecutive ampules are consistently filled to the predetermined mark on the ampule.

6.1.6.6 Once volume dispensing adjustments have been completed, begin filling ampules from the bulk supply, keeping the filled ampules cold by placing them immediately into a container that is at a temperature of approximately –20 °C. This may be achieved by using crushed dry ice.

6.1.6.7 The ampules should be sealed as soon as possible after filling to avoid loss of volatile components. If ampules are being manually sealed, a two person operation, in which one person dispenses the material and a second person seals the ampules, is suggested.

6.1.6.8 Periodically inspect filled and sealed ampules to ensure that the fill volume is maintained throughout the packaging run.

6.1.7 *Ampule Sealing:*

6.1.7.1 Ampules may be flame-sealed by hand, using a suitable torch. The flame used must be hot enough to quickly soften the neck of the ampule. Propane/air or natural gas/air flames are sufficient for most applications. Hydrogen/oxygen flames may be required for sealing large, thick-walled glass ampules.

6.1.7.2 The ampule should be kept cold through the sealing process.

6.1.7.3 To facilitate sealing, the torch should be mounted on a stand on a bench top such that both hands can be free to perform the actual sealing process.

6.1.7.4 Wearing gloves, hold the ampule by the bottom in one hand and by the neck tip in the other. Alternatively, large tongs may be used to hold the neck in order to minimize the risk. The ampule neck is placed into the flame, constantly rotating to ensure uniform heating of the glass. Focus the flame midway between the open end and the breakmark on the ampule. The flame should never contact the contents of the ampule or the direct open end of the ampule. (**Warning—**For safety reasons, if the material being ampulized is flammable, it is recommended that the volume being ampulized be minimized.)

6.1.7.5 After several seconds of exposure to the flame, the glass should begin to soften. Once the glass is softened, the neck may be pulled away from the ampule while still in the flame, until the glass draws down and forms a seal. The top of the ampule should be polished by rotating it in the flame until a smooth seal is obtained.

6.1.7.6 The seal should be inspected and should be smooth and free of any carbon deposits. The thickness of the seal should be comparable to the thickness of the ampule wall. If the RM contains volatile materials, sealing may be difficult if the material is not sufficiently cooled. Some problems encountered include thin seals or bubbles, formed due to pressure from volatile components, and carbon formation at the seal. These problems usually can be eliminated by further cooling of the ampules. For gasoline, a temperature of –20 °C usually is sufficient to avoid such difficulties.

6.2 *Automated Ampule Filling and Sealing:*

6.2.1 *Apparatus*—Various commercial devices are available for automated filling and sealing of ampules. These devices typically consist of a pump, liquid transfer lines, dispensing or dosing needles, sealing torch, and an ampule conveying mechanism.

6.2.2 *Storage of Bulk Material*—Bulk gasoline and similar liquid hydrocarbon materials must be adequately sealed and stored to prevent loss of volatile components prior to ampulization. Refrigerated storage in sealed metal drums, barrels, or amber glass containers is recommended.

6.2.3 *Compatibility of Materials/Sources of Contamination:*

6.2.3.1 Tubing used to transfer the bulk material to automated dispensing devices must be compatible with the gasoline or hydrocarbon material. Plastic or rubber tubing containing phthalates or other types of plasticizers must be avoided. TFE-fluorocarbon tubing is highly recommended. To avoid cross-contamination, the transfer tubing must be replaced after every RM.

6.2.3.2 Any part of the dispensing apparatus that comes in contact with the RM, including pumps, dosing needles, and connection hardware, must be cleaned prior to packaging a different material. Recommended cleaning procedures involve soaking removable parts in soapy water, followed by rinsing with water, followed by methanol or other suitable solvent, followed by drying under a stream of clean nitrogen.

6.2.4 *Assessment of Material to Be Ampulized:*

6.2.4.1 *Volatility*—Prior to packaging, materials containing highly volatile components must be cooled sufficiently to minimize volatile losses during ampulization. Failure to sufficiently cool the material also may result in difficulty in obtaining effective ampule sealing. The material must not be cooled to temperatures below which the composition of the RM would be affected (for example, producing precipitation or solidification). Gasoline may be cooled to –20 °C without incurring compositional changes. The bulk material must be kept cold during the filling process. Provisions should be made to maintain constant temperature throughout the transfer tubing lines. As the bulk container is emptied and the headspace is correspondingly increased, differential vaporization can change the bulk concentration, enriching the high boilers (less volatile components) and depleting the low boilers (more volatile components). Care must therefore be taken to complete the ampulization process as expeditiously as is reasonably possible.

6.2.4.2 *Reactivity*—Consideration should be given to the chemical reactivity of the RM being packaged. Gasoline samples containing olefins and diolefins should be packaged under an inert atmosphere blanket of nitrogen, argon, or other suitable gas. Ampules should be flushed with inert gas immediately prior to dispensing of the gasoline. Use of amber glass ampules will minimize photo-oxidation.

6.2.4.3 *Odors*—Odorous materials such as gasoline should be packaged in a well-ventilated area. The bulk material should be kept adequately sealed during the ampulization process to minimize loss of volatiles.

6.2.4.4 *Flammability*—Ampule sealing requires use of a flame hot enough to melt glass. Care must be taken in ampulization of highly flammable materials or ampule contents could ignite. Dosing needle dripping of flammable materials may result in ignition.

6.2.5 *Sampling of the Bulk Container:*

6.2.5.1 After bringing the bulk container temperature down to the working temperature, withdraw a minimum of three samples from each bulk container, using clean manual pipettes. Immediately dispense the material into crimp top chromatography vials, seal, and label. These samples will be designated as representative of the bulk material and will be used to establish reference values for the homogeneity testing.

6.2.5.2 Place the end of the pump transfer line tubing into the bulk container and secure it. A vent line should be connected to the bulk container to avoid transfer problems due to vacuum buildup during the pumping process and to minimize odors.

6.2.6 *Adjusting Filling/Sealing Parameters:*

6.2.6.1 Automated filling and sealing machines typically have the capability of automatically introducing a purge gas into the ampule prior to filling. Make sure that the appropriate inert gas supply is in place and that a sufficient volume of gas will completely flush the ampule container prior to filling (at least 1.5 ampule volumes).

6.2.6.2 Adjust the dosing needle (fill heads) dispensing height so that filling occurs from the bottom of the ampule up.

6.2.6.3 Set the fill/seal rate at a sufficient speed such that the temperature of the dispensed RM does not increase by more than 5 °C over the bulk temperature during the filling process.

6.2.6.4 Adjust the liquid dispensing volume in accordance with the filling device instruction manual. Typically, it is more important to provide a minimum dispensed volume into the ampule rather than to provide an accurately determined volume of RM. The minimum dispensing volume for packaging the RM must be known ahead of time.

6.2.6.5 Dispensed volume will be affected by the temperature of the bulk material. Therefore, for consistent volume dispensing, the temperature of the bulk material must be