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## Manual of Petroleum Measurement Standards (MPMS), Chapter 8.3

# Standard Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products<sup>1</sup>

This standard is issued under the fixed designation D5854; 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 handling, mixing, and conditioning procedures that are required to ensure that a representative sample of the liquid petroleum or petroleum product is delivered from the primary sample container or container or both into the analytical apparatus or into intermediate containers.

1.2 **Appendix X1** details the background information on the development of Table 1 used in performance testing. **Appendix X2** provides guidance in the acceptance testing for water in crude oil. **Appendix X3** provides a guide for materials of sample containers. **Appendix X4** provides a summary of recommended mixing procedures. **Appendix X5** provides a flow chart for sample container/mixing system acceptance test.

1.3 For sampling procedures, refer to Practices **D4057** (API *MPMS* Chapter 8.1) and **D4177** (API *MPMS* Chapter 8.2). Practice **D5842** (API *MPMS* Chapter 8.4) covers sampling and handling of light fuels for volatility measurement, and **D8009** (API *MPMS* Chapter 8.5).

1.4 It is recommended that the users of this practice perform the tests in Practice **D4177** (API *MPMS* Chapter 8.2) before performing the test in this practice.

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, health, and environmental 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.*

### 2. Referenced Documents

#### 2.1 ASTM Standards:<sup>2</sup>

**D3700** Practice for Obtaining LPG Samples Using a Floating Piston Cylinder

**D4057** Practice for Manual Sampling of Petroleum and Petroleum Products

**D4177** Practice for Automatic Sampling of Petroleum and Petroleum Products

**D4306** Practice for Aviation Fuel Sample Containers for Tests Affected by Trace Contamination

**D5842** Practice for Sampling and Handling of Fuels for Volatility Measurement

**D8009** Practice for Manual Piston Cylinder Sampling for Volatile Crude Oils, Condensates, and Liquid Petroleum Products

#### 2.2 API Documents:<sup>3</sup>

**Manual of Petroleum Measurement Standards, Chapter 10, Sediment and Water (all sections)**

**Publication 2003, Protection Against Ignitions Arising Out of Static, Lighting, and Stray Currents**

**Publication 2026, Safe Descent onto Floating Roofs of Storage Tanks in Petroleum Service**

**Publication 2217, Guideline for Confined Space Work in the Petroleum Industry**

#### 2.3 Department of Transportation:<sup>4</sup>

**Code of Federal Regulations, Title 49, Section 173**

**2.4 Occupational Safety and Health Standards:<sup>4</sup>**

**29 Code of Federal Regulations, Subpart Z, “Toxic and Hazardous Substances,” Part 1910.1000 and following**

<sup>1</sup> This practice is under the jurisdiction of ASTM Committee **D02** on Petroleum Products, Liquid Fuels, and Lubricants and the API Committee on Petroleum Measurement, and is the direct responsibility of Subcommittee **D02.02** the joint ASTM-API committee on Hydrocarbon Measurement for Custody Transfer (Joint ASTM-API). This practice has been approved by the sponsoring committees and accepted by the Cooperating Societies in accordance with established procedures.

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<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard’s Document Summary page on the ASTM website.

<sup>3</sup> Available from American Petroleum Institute (API), 1220 L. St., NW, Washington, DC 20005-4070, <http://www.api.org>.

<sup>4</sup> Available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402.

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

### 3. Terminology

#### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *aliquot, n*—a small portion of a larger sample that is analyzed and assumed to represent the whole sample.

3.1.2 *composite sample, n*—a sample prepared by combining a number of samples and treated as a single sample; also refer to tank composite sample, volumetric composite sample, deck composite sample, and multiple tank composite sample.

3.1.3 *crude petroleum sampling, n*—sampling of unrefined crude oil.

3.1.4 *liquid petroleum sampling, n*—sampling of refined or unrefined hydrocarbon liquids.

3.1.5 *intermediate sample receiver/container, n*—a sample container into which all or part of the sample from a primary sample receiver/container is transferred for transport, storage, or ease of handling.

3.1.6 *petroleum, n*—a substance, generally liquid, occurring naturally in the earth and composed mainly of mixtures of chemical compounds of carbon and hydrogen with or without other nonmetallic elements such as sulfur, oxygen, and nitrogen; the compounds that compose petroleum may be in the gaseous, liquids, or solid state, depending on their nature and on the existent conditions of temperature and pressure.

3.1.7 *primary sample container, n*—a container in which a sample is initially collected, such as a glass or plastic bottle, a can, a core-type thief, a high-pressure cylinder, a floating piston cylinder, or a sample container in an automatic sampling system.

3.1.8 *retain sample, n*—a sample that is stored for future use.

3.1.9 *sample container, n*—receptacle used for storage and transport of the sample.

3.1.10 *sample handling and mixing, n*—the conditioning, transferring, and transporting of a sample in a manner that does not compromise the integrity of the sample.

3.1.11 *sampling, n*—all the steps required to obtain a sample that is representative of the contents of any pipe, tank, or other vessel, and to place that sample in a container from which a representative test specimen can be taken for analysis.

3.1.12 *test specimen, n*—a representative sub-sample taken from the primary or intermediate sample container for analysis.

### 4. Significance and Use

4.1 Representative samples of petroleum and petroleum products are required for the determination of chemical and physical properties used to establish standard volumes, prices, and compliance with commercial and regulatory specifications. The handling of samples from the time of collection until they are analyzed requires care and effort to maintain their compositional integrity. Samples of high RVP (unstabilized) hydrocarbons are required at many measurement points, for example offshore production, at the outlets of test separators or to allow calibration of a flowmeter. This practice also describes requirements associated with handling and mixing samples held within pressurized cylinders.

4.2 Practice **D4057** (API *MPMS* Chapter 8.1), Practice **D4177** (API *MPMS* Chapter 8.2), Practice **D5854** (API *MPMS* Chapter 8.3), Practice **D5842** (API *MPMS* Chapter 8.4), and Practice **D8009** (API *MPMS* Chapter 8.5). The primary purpose of this suite of standards, is to ensure proper sampling and handling for custody transfer applications. There are a significant number of test methods that may be used to analyze the samples taken by techniques described in API *MPMS* Chapter 8.1 and 8.2. For samples that are taken for test methods outside the general scope of custody transfer covered by this practice, the personnel assigned to take the sample are responsible to refer to the test methods for additional critical information that may impact the sampling process, that is, specific container selection, transport methods, storage times, etc. Those requirements should be found in the appropriate test method.

### 5. Safety and Health Precautions

5.1 Potential health and safety hazards may be associated with the handling and mixing of petroleum samples.

5.2 All sample handling and mixing equipment should be approved by the parties involved. All equipment should be installed, operated, and maintained in a manner to minimize potential health and safety hazards.

### 6. Sample Containers

6.1 No single container type will meet requirements of all petroleum sampling operations. The following are general design and construction considerations for sample containers.

6.2 *Container Configuration*—Containers may be disposable or recyclable. Due care should be taken to ensure that samples extracted are representative before a subsample is removed or that the entirety of the sample may be removed for further processing.

6.2.1 If a container is to be reused, it should drain continuously toward the outlet to ensure liquid withdrawal or incorporate a sump and dip tube to ensure complete evacuation of the composite sample.

6.2.2 Cylindrical containers are better suited for samples that are to be tested for free water or sediment and water.

6.2.3 Containers should not have internal pockets or dead spots that can create a bias to the overall result. (For example, give due consideration to sight glasses or float indicator mechanics that can retain sample that is not then mixed.)

6.2.4 Internal surfaces of containers should minimize corrosion, incrustation, water, adsorption of elements of interest, or clingage.

6.2.5 Container configuration should allow for the transfer of samples from one container to another or to the analytical apparatus while maintaining the integrity of the sample's composition. It may be desirable to reduce or increase the temperature of the sample prior to transfer (that is, reducing temperature to minimize the loss of light ends).

6.2.6 Containers should have an inspection cover/closure/cap of sufficient size to facilitate filling, inspection, and cleaning. Where a sample represents a high value transaction, a means of installing security seals to prevent tampering should be provided.

6.2.7 If the sample is likely to separate because it contains immiscible fluids (for example, water or sediment in oil), the containers should be designed to allow for homogenization while preventing the loss of any constituents that affect the representativeness of the sample and the accuracy of the analytical tests.

6.2.8 Containers should be made so as to avoid contamination from external foreign material (for example, the ingress of water or other contaminants). When the sample contains immiscible fluids, care shall be taken to adequately homogenize the content so that any extracted sample is within the allowed repeatability of the bulk value of that property. Note that in the case of hydrocarbon and water, adequate mixing to determine water content is likely to irreversibly damage other properties of interest such as density.

6.2.9 Containers used with closed loop mixers may need a pressure/vacuum relief valve set so as not to exceed the design pressure of the container. A pressure gauge may also be incorporated.

6.2.10 Containers used with closed loop mixers for non-homogeneous fluids shall have a suction port at or near the bottom.

6.2.11 Constant pressure cylinders are referred to in Practice **D3700**, Practice **D4057** (API *MPMS* Chapter 8.1), Practice **D4177** (API *MPMS* Chapter 8.2), and Practice **D8009** (API *MPMS* Chapter 8.5) discusses the merits of the constant pressure cylinder for the sampling of rail cars and the like. These cylinders are designed to allow spot or composite samples to be taken from a pressurized tank or pipeline at full line conditions and maintain the sample at those conditions until analyzed.

6.2.12 The laboratory container shall be selected such that its construction material does not affect sample compositional integrity and its volume and its dimensions are sufficient to allow for adequate mixing. In selecting the laboratory test container, take particular care in respect of the following:

6.2.12.1 Liquids containing volatile materials, as loss by evaporation can occur;

6.2.12.2 Liquids suspected to contain sediment and/or water, as separation can occur;

6.2.12.3 Samples with potential wax deposition, as separation can occur if a sufficient temperature is not maintained;

6.2.12.4 Samples of high viscosity and/or density, as both temperature and mixer placement may be affected to obtain the required homogenization; and

6.2.12.5 Make sure constituents are compatible with the container material (that is, mercury readily forms an amalgam with aluminum).

### 6.3 Container Volume:

6.3.1 A general rule is that both primary and intermediate containers should be large enough to hold the required sample size within 60 % to 80 % of the total capacity. This provides for thermal expansion.

6.3.2 The size of primary containers is determined from the sampling operation as described in Practices **D4057** (API *MPMS* Chapter 8.1) and **D4177** (API *MPMS* Chapter 8.2).

6.3.3 The size of intermediate containers should be as large as practical to minimize surface tension effects with due

consideration given to storage space requirements, shipping rules and regulations, availability, and other practicalities.

6.3.4 Refer to API 8.2 for composite sample volume and the number of samples when using automatic sampling systems.

### 6.4 Container Material:

6.4.1 Sample containers are normally made of glass, metal, or plastic. Exercise care in the selection of container material as it could affect the test results obtained from the sample. Containers acceptable for samples to be tested immediately may not be acceptable for storage of sample.

6.4.2 Glass containers are suitable for many sample test and storage requirements. Clear glass bottles may be examined visually for cleanliness and allow for visual inspection of the sample for free water or solid impurities. Some petroleum samples are affected by exposure to sunlight or fluorescent lamp UV emissions if clear glass is used. In these cases, brown glass bottles may afford the necessary protection. Care should be taken to ensure the necessary protection is provided when selecting a container.

6.4.3 Sample containers coated with tin shall have seams that have been soldered on the exterior surfaces with a flux of rosin cleaned in a suitable solvent. Such a flux is easily removed with gasoline, whereas many others are very difficult to remove. Minute traces of flux may contaminate the sample so that results obtained on tests such as dielectric strength, oxidation resistance, and sludge formation may be erroneous. Exercise care also to ensure that samples containing free or entrained water are not corrosive to the metal. Internally epoxy-lined tin cans may have residual contamination and precaution should be taken to ensure its removal.

6.4.4 Sample containers made of stainless steel with welded seams are suitable for many sampling operations. Other than ensuring the cleanliness, use of these containers presents no unusual concerns.

6.4.5 Plastic bottles shall be of a material that is impervious to attack from the sample. This is especially a consideration when using plastic for long term storage of certain petroleum products. Clear plastic bottles are unsuitable for samples sensitive to light.

6.4.6 When sampling aviation fuels, Practice **D4306** should be consulted for guidance on container selection. This practice gives information on the types of containers that have been found satisfactory for tests to determine water separation, copper corrosion, electrical conductivity, thermal stability, lubricity, and trace metal content.

6.4.7 **Appendix X3** is a guide for selecting the material of which sample containers may be made. It is impossible to cover all petroleum sampling container requirements; therefore, when questions arise as to a container's suitability for a given application, experience and testing should be relied upon.

### 6.5 Container Closures:

6.5.1 Stoppers made of a material that will not deteriorate or contaminate the sample may be used. Care should be used when using cork stoppers. Situations where corks should not be used include liquids where loss of light ends may affect the

test's results and liquids that are hygroscopic or that have a low water content specification. Rubber stoppers should never be used.

6.5.2 Screw caps for containers used to store or transport samples should be protected by a disk faced with a material that will not deteriorate or contaminate the sample. Consideration of closure type is important for samples where vapor loss will affect the test results. Other containers should be closed with screw caps. Caps should provide a vapor tight seal.

6.5.3 *Federal Container Requirements*—In addition to the requirements listed above, any sample container that contains hazardous materials or the residue of hazardous material offered for shipment or transportation by air, public roadway, rail, or water, or any combination thereof, shall meet the requirements set forth in applicable regulations such as DOT regulations in the Code of Federal Regulations, Title 49, Section 173.

6.6 *Container Cleanliness:*

6.6.1 Sample containers shall be clean and free from all substances that might contaminate the material being sampled (such as water, dirt, lint, washing compounds, naphtha and other solvents, soldering fluxes, acids, rust, and oil). Prior to further use, reusable containers such as cans and bottles should be rinsed with a suitable solvent. Use of sludge solvents to remove all traces of sediments and sludge may be necessary. Following the solvent wash, the container should be washed with a strong soap solution, rinsed thoroughly with tap water, and given a final rinse using distilled water. Dry the container either by passing a current of clean warm air through the container or by placing it in a hot dust-free cabinet at 40 °C (104 °F) or higher. When dry, stopper or cap the container immediately. Normally, it is not necessary to wash new containers.

6.6.2 Depending on service, containers used in conjunction with automatic samplers may need to be washed with solvent and dried between uses. In most applications, it is not desirable or practical to wash these receivers using soap and water as outlined above for cans and bottles. The cleanliness and integrity of all sample containers/receivers shall be verified prior to use.

6.6.3 When sampling aviation fuel, Practice D4306 should be consulted for recommended cleaning procedures for containers that are to be used in tests for determination of water separation, copper corrosion, electrical conductivity, thermal stability, lubricity, and trace metal content.

6.6.4 When sampling from rail cars, Practice D8009 (API MPMS Chapter 8.5), should be consulted for specific application recommendations.

7. Labeling

7.1 Each sample container shall have a label attached to it that meets the requirements of the parties involved.

7.2 Fig. 1 is an example of a label that shows the typical information needed to properly identify the sample. In addition to this basic information, certain governmental agencies such as DOT and OSHA have additional labeling requirements with which personnel involved in the handling and shipping of samples should be familiar.

8. Transport

8.1 *Sample Transportation and Handling*—From time-to-time, a sample needs to be sent off-site for analysis. This may be a part of normal operations, due to lack of onsite lab, or because the sample needs to undergo a special analysis. Regardless, there are several aspects that should be considered prior to transportation:

Sample Identification Number:	
Product Name / Grade:	
Terminal Station or Lease:	
Sample Date / Time:	
Gauger/Sampler:	
Sample Origin: (tank, grab, composite, all-level among others) as agreed to by both parties.	
Sample Source: (such as ship, railcar, barge, pipeline, tank)	
Laboratory / Job reference:	
Date and Time in Laboratory:	
Laboratory Technician:	

FIG. 1 Example Sample Label

8.1.1 *Local Hazardous Goods Regulations*—Most jurisdictions have limits on what can be transported on public roads and allow for exemptions for small hydrocarbon samples.

8.1.2 *The Container Selected*—It is crucial that the container selected complies with local transportation regulations and does not affect the results of the pending analysis. Additionally, consider using a protective case for the sample container to avoid damage during transportation. Section 6 contains advice related to container material, maximum fill, size, and so forth.

8.1.3 *Container Labeling*—If applicable, consult the local transportation company to determine what is required on the container’s label especially related to hazardous goods. Other labeling advice is found in Section 7.

8.1.4 *Sub-sampling*—It is likely that the primary sample will need to be subsampled into a secondary container. If so, proper mixing of the primary sample may be crucial. See Section 9 for more details.

8.1.5 *Container Sealing*—There may be a requirement to seal the container against potential tampering. If they exist, these requirements are likely to be found in commercial agreements or regulatory guidelines.

8.2 *Shipping Enclosures*—Many sample containers require special shipping enclosures before they can be transported from the point of collection. Regulations covering the transport of samples should be consulted. (for example, Code of Federal Regulations, Title 49, section 173).

## 9. Mixing

### 9.1 *General Considerations:*

9.1.1 It is essential to ensure that any mixer or mixing method applied to the sample does not materially change the properties of interest. Ullage space available in the sample container and type of mixing employed can affect the properties of interest for the sample in question. Mixing may affect changes in temperature and pressure, which might influence the properties for which the sample is being analyzed.

9.1.2 Some samples may not require mixing, however in the majority of instances some degree of mixing may be required to ensure that the aliquot removed for analysis is representative of the bulk properties of the sample.

9.1.3 Sample mixing is typically required to obtain a test portion representative of the bulk sample to be tested. Precautions shall be taken to maintain the integrity of the sample during this operation. If a sample is transferred from one container to another, a homogeneous mix shall be created and maintained throughout the transfer. To preserve the integrity of the sample, the number of transfers of the sample, before analysis, should be minimized to reduce the chances of: (a) loss of key properties such as light hydrocarbons in handling; (b) in some cases, “loss” of components elements of the sample for example, through clingage, adsorption or loss in dead pockets and, (c) interference from external sources including the local environment to which that sample may be exposed during any transfer processes.

9.1.4 Transferring a sample between containers (the number of transfers between the primary container and the final analytical equipment) should be minimized. Each transfer, and

particularly those that may expose the sample to air may influence the representivity of the final result.

9.1.5 The ideal method would be to withdraw the sample from the primary container directly into the analytical glassware. However, it is recognized that not all sampling methods or operational constraints permit this, nor do the requirements to transport, store and distribute the same sample to various interested parties.

9.1.6 Where a number of containers (or samples, for example running samples, spot samples) are to be mixed prior to extraction of samples for analysis that is, a composite, be aware that these samples may not proportionately represent the overall bulk that they are intended to represent.

9.1.7 This section refers to all sample containers and all processes where a sample is handled prior to representative extraction of the aliquot that is utilized for the analytical measurement and therefore includes any intermediate containers between the field and the laboratory analysis equipment.

9.1.8 Each sample container and mixing/transfer system shall be tested and verified independently as suited to provide the required uncertainty for the properties of interest.

9.1.9 Nothing in this practice should preclude the use of technologies that can be proven within the required uncertainties of the analytical methods used.

### 9.2 *Sample Container Types:*

9.2.1 Sample containers of any style may be stationary (for example, fixed in place on a metering skid or lease automatic custody transfer (LACT) unit), or they may be portable (for example, taken to an offsite laboratory for mixing and analysis). Other examples of portable sample containers would be samples obtained from marine or shore tanks by “running,” “all-levels,” and spot “core thief” samples or the containers used within the laboratory (typically glassware/plastic/plated metals) or for sample retention.

9.2.2 Sample containers may also be designed to retain samples at elevated pressures, including full process pressure. These can be fixed volume (such as a spun cylinder) or constant pressure with a moveable partition, typically a piston or bladder.

9.2.3 Sample containers may be for one-time use, or reusable. In either case the materials used for construction should not materially affect the sample properties, for example through adsorption, clingage or perhaps light for the period of use for that they are intended.

9.2.4 In the case of multiple stationary containers on a common skid with either a separate pump/motor circulating system for each container, or a single pump/motor circulating system for all containers, each container pump/motor circulation system configuration to be utilized should be tested independently. In the case of portable containers of the same design with a common mixing system in a laboratory, only one container shall be tested with the common mixing system. However, if a container of a different design is brought to the laboratory, it shall be tested independently.

### 9.3 *Sample Mixing Methods:*

9.3.1 Sample mixing methods can be divided into three general categories that should be used as appropriate to the initial homogeneity and properties of interest.

9.3.1.1 No mixing.

9.3.1.2 Shaking (by hand or with a shaking device).

9.3.1.3 Power mixing/mechanical.

9.3.2 These categories vary greatly in energy addition depending on the type of analytical test to be conducted and the characteristics of the sample. **Appendix X2** describes an acceptance testing method for mixing systems used for determining water in crude oil. Methods for determination of other properties will follow a similar format.

9.3.3 The addition of energy during the mixing process (particularly using power mixers/mechanical) may result in temperature and potentially pressure rise. Many standards define limitations on acceptable changes, for example for mixing water into crude oil a limit of 10 °C is allowed. If the temperature rise exceeds the allowed limits, some method will be required to prevent this.

9.3.4 The following is a brief discussion of each category:

9.3.4.1 *None (no mixing if not required)*—If a sample is known to be homogeneous regarding the property of interest, no mixing is required. Samples should not be mixed where the analytical tests to be conducted may be affected by induction of air or a secondary phase found within the sample container of mixing system or where a property could materially be affected by excess mixing (for example RVP).

9.3.4.2 *Shaking:*

(1) Shaking involves manually or mechanically shaking the sample container to eliminate stratification. It is generally difficult to manually agitate laboratory samples of dense or heavy petroleum liquids sufficiently to disperse contaminants, such as sediment and water, homogeneously throughout the liquid. Mechanical or hydraulic mixing will be necessary to ensure an even distribution.

(2) *Internal Mechanical Mixers*—Some mixing devices use baffles, agitators or balls inside the container that can be moved by hand. Such designs provide a variety of levels of energy dissipation as appropriate to the fluids contained and the

analytical methods used. Where the fluid to be mixed comprises insoluble elements (such as water/sediment in oil), hand shaking is generally considered unsuitable but may be proven to meet the test criteria as defined in **Table 1**.

(3) Hand shaking is typically used on samples that are essentially homogenous in regard to the property of interest.

(4) In some cases, magnetic stirrers or paddles may be permanently installed in the sample container.

9.3.4.3 *Power Mixing:*

(1) Power mixers currently fall into two general groups: insertion or closed loop. Single sample container/mixer systems do not have to be tested individually if they are of the same mechanical design and operate within the demonstrated service range (for example, in the determination of crude oil properties, water concentration, density, viscosity of product, RVP, product purity, contaminant detection and sample volume).

(2) Over-mixing with power mixers on non-homogeneous fluids (for example, oil and water) may create an emulsion that will affect the accuracy of certain analytical tests. Refer to API MPMS 10.9.

(3) Power mixers may entrain air or gases into the sample that could affect certain analytical tests. Loss of vapor normally associated with rise in temperature as the sample is transferred from mixer loop may also occur, which could affect tests results for example for water, RVP, and density. Temperature rise during mixing may impact the measurement because of potential condensation in cold spots. Over-mixing may compromise the analysis method, for example, oil and water mixtures, if over-mixed will destroy the density and RVP values as well as provide erroneous water content values. Generally, the amount of energy that is required to be dissipated will depend on the fluid properties and volume, therefore any method used to verify mixing must recognize that either extended testing must be performed or a clear physical understanding of the process must be applied.

**TABLE 1 Maximum Permissible Difference between Test Specimens and Maximum Permissible Difference between the Average of All Test Specimens and Total Water Concentration (Based upon Three Test Specimens)**

NOTE 1—Values in Column A are calculated from the larger of 0.05 % or  $2.92 \times 0.064 \times (\text{Wk } \%)^{0.5}$ .

NOTE 2—Values in Column B are calculated from the larger of 0.05 % or  $1.96 \times 0.064 \times ((\text{Wk } \%)^{0.5})/(\sqrt{3})$ .

NOTE 3—Values in Wk not shown in the table may be obtained by interpolation.

Wk	Column A Repeatability Check		Column B Bias Check
	Total Water Concentration Based upon the Average of Three (3) Test Specimens	Maximum Permissible Difference Between Three (3) Consecutive Test Specimens	Maximum Permissible Difference Between Average of All Test Specimens and Total Water Concentration
0.00 %		0.05 %	0.05 %
0.05 %		0.05 %	0.05 %
0.10 %		0.06 %	0.05 %
0.15 %		0.07 %	0.05 %
0.20 %		0.08 %	0.05 %
0.25 %		0.09 %	0.05 %
0.50 %		0.13 %	0.05 %
1.00 %		0.19 %	0.07 %
1.50 %		0.23 %	0.09 %
2.00 %		0.26 %	0.10 %
2.50 %		0.30 %	0.11 %
3.00 %		0.32 %	0.13 %
3.50 %		0.35 %	0.14 %
4.00 %		0.37 %	0.14 %
4.50 %		0.40 %	0.15 %
5.00 %		0.42 %	0.16 %

(4) *Insertion Mixers*—These mixers are stand-alone devices that are not an integral part of a given sampling or mixing system. These mixers can be used on a variety of different types and sizes of sample containers. Non-aerating or high-speed shear mixers are examples of insertion mixers.

(5) In some cases, magnetic stirrers, paddles, or insertion mixing devices may be permanently installed in the sample container.

(6) *Closed Loop Mixers*—These mixers are typically used in conjunction with an automatic pipeline sampling system. The mixer may be an integral part of a stationary sample container or a stand-alone unit used for portable sample containers. Jets are sometimes used within the sample container that may be permanently mounted.

#### 9.3.4.4 *Improper Mixing:*

(1) The following are considerations when using mixers:

(a) Under-mixing may result in a non-representative sample.

(2) If the sampling procedure requires that multiple samples be taken from a single process line, storage tank, or in the case of marine vessels, multiple or single samples from multiple tanks, analytical tests may be performed on each sample or on a composite of the various samples. Note that compositing of samples results in the analysis of one or more aliquots, all of which will, in best circumstances, be an average value of the bulk composite. A composite technique is generally considered inappropriate for properties that vary significantly through the volumes collected if the bulk volume properties are likely to vary significantly unless the composite is created in proportion to the volumes to which each container relates.

(3) When analytical tests are performed on individual samples, which is the recommended procedure (but not always available), the test results are averaged. Depending on the particular application, the results should be averaged arithmetically or on a proportional basis by weight or volume according to the proportion of the total liquid that the sample represents.

#### 9.3.4.5 *Composite Samples:*

(1) A composite sample may be prepared from individual samples taken from the same process line or storage tank, and it shall consist of proportional parts from each zone if it is from a single tank. If the composite is from multiple tanks, it shall consist of proportional parts from each tank sampled.

(2) Composite samples from multiple tanks should be prepared, in the laboratory or other controlled environment, in proportion to the volume in each tank. Samples to be composited should be submitted to the laboratory along with a list of each tank and the volume represented by each sample. The method of compositing should be documented and care taken to preserve the integrity and that the composite sample is representative.

(3) Individual samples that make up the composite sample may be retained separately for retesting, if necessary.

(4) After a composite sample has been mixed, it is important to note that it will likely separate quickly (for example, water in oil). The analysis or transfer should therefore be performed immediately after the mixing has taken place.

#### 9.3.4.6 *Selection of Sample Mixing Method:*

(1) Power mixing, and in some cases, mechanical mixing, is required for all crude oil samples to be tested for sediment and water unless the results would be adversely affected (for example, small sample size), as well as a number of petroleum products being tested for a variety of analytical test procedures. Power mixing is also required when the sample has been transported or stored in either a primary or intermediate container. Note that density results are best determined before full mixing for water.

(2) Mixing is not required if a representative sample is directly transferred from the sample extractor to the analytical test device at the time of extraction.

(3) The mixing method shall be compatible with the type of analysis and the volumes being analyzed.

(4) *Homogenization of Viscous Samples*—If the sample is not sufficiently fluid to withdraw a test portion in a syringe for Karl Fisher analysis at ambient temperatures, utilize a safe external warming method or a constant temperature bath to obtain a temperature approximately 10 °C above the minimum temperature at which it becomes possible to obtain a test portion by syringe, but not exceeding 60 °C. Maintain the samples at this temperature during homogenization.

(5) Certain analytical tests require the sample to be analyzed at temperatures either above or below common ambient conditions, due care should be taken not to transfer samples between containers and/or the analytical equipment in such a way as to compromise the properties of interest.

## 10. **Sample Integrity and Storage, Preservation, and Audit**

10.1 There are many governmental agencies and jurisdictions that have regulations governing the storage and disposal of petroleum samples and containers that can be classified as hazardous materials or hazardous wastes. Those who handle petroleum samples may be familiar with these regulations in addition to their own company policies and procedures. “Retain Samples” shall not be disposed of until the primary sample results are known to all interested parties, and/or as per contractual agreements.

### 10.2 *Sample Integrity and Storage:*

10.2.1 Except when being transferred, samples should be maintained in a closed container in order to prevent loss of light components. Samples should be protected during storage to prevent weathering or degradation from light, heat, or other potential detrimental conditions.

10.2.2 Maintain sample integrity as required by contract.

10.2.3 Maintain control of the sample as required by contract.

10.2.4 If a composite sample is to be transferred from a primary container to a secondary container, then both containers should be under collector control.

10.2.4.1 Consider sealing the sample container that will be transported to the analysis location.

10.2.4.2 Ensure that no external substance can enter a sample container so the sample cannot be contaminated.

### 10.3 *Preservation:*

10.3.1 The sample storage location should:

10.3.1.1 Preserve the integrity of the samples.

10.3.1.2 Allow no direct sunlight on the samples.

10.3.1.3 Be ventilated sufficiently to prevent a hazardous atmosphere.

10.3.2 *Chain of Custody:*

10.3.2.1 The sample records should be kept in a safe location away from the samples.

10.3.2.2 A copy should be sent with the sample if it is transferred.

10.4 *Audit*—If an audit trail is required, these should be kept:

10.4.1 “Sample” records.

10.4.2 “Chain of custody” documents.

10.4.3 Sample storage (retain) records.

10.4.4 Sample results.

## 11. Testing—Acceptance Test for Sample Container/ Mixing Systems for Water in Crude Oil

11.1 *Introduction:*

11.1.1 The acceptance test described is applicable to both fixed sample container/mixing systems and portable sample container/mixing systems. The test criteria is not dependent upon the type or design of the sample container/mixing system.

11.1.2 Before a sample is transferred from one container to another, a homogeneous mixture shall be created and maintained until the transfer is completed. A sample container/mixing system should be tested, using the acceptance criteria shown in **Table 1**. The criteria for acceptance for custody transfer, with an example of test procedures and calculations, are presented below.

11.1.3 The purpose of the test is to determine whether a container/mixing system can produce a representative sample of crude oil with varying amounts of water. The tests also determine the effective mixing times required to produce a representative sample of crude oil and water. It is understood that the proper mixing time is determined by testing. It is possible to overmix as well as under mix in certain circumstances.

11.2 *General Guidelines:*

11.2.1 Each sample container/mixing and water concentration test (that is, water determination by centrifuge or Karl Fischer), whether conducted at a low volume (LV), a normal volume (NV), or a high volume (HV) of sample in the container, will consist of: (a) an analysis for total water in the baseline (BL) oil; (b) an analysis for total water after adding an amount of water to the oil for the lower water (LW) determination; and, (c) an analysis for total water after adding an amount of water for the higher water (HW) determination.

11.2.2 For any given oil sample amount (LV, NV, HV), the MINIMUM levels of water should be as follows:

11.2.2.1 Baseline water concentration (BL) is determined as found.

11.2.2.2 Lower water concentration (LW) is determined for a total water concentration that is:

(1) 0.5 % when the baseline (BL) is less than 0.25 %.

(2) 0.5 % when the baseline (BL) is equal to 0.25 %.

(3) 0.25 % + baseline (BL) when the baseline (BL) is greater than 0.25 %.

11.2.2.3 Higher water concentration (HW) is determined for a total water concentration that is:

(1) 1.0 % when the lower water (LW) is equal to 0.5 %.

(2) 0.5 % + lower water (LW) when the lower water (LW) is greater than 0.5 %.

11.2.2.4 For example, a crude oil with a baseline of 0.3 % should be tested with a minimum lower total water concentration of 0.55 % and a minimum higher total water concentration of 1.05 %. On the other hand, if enough water were added to make the lower total water concentration 0.7 %, then the minimum higher total water concentration should be 1.2 %.

11.2.2.5 Separate complete sets of tests should be considered for crudes exhibiting very different physical properties. For example, consider a set of three (3) crude oils, at sample temperature, in which the one with the highest density is also the one with the highest viscosity, the one with the lowest density is also the one with the lowest viscosity, and the third crude lies somewhere in between for both density and viscosity:

(1) Gravity of 20° API (highest density) and highest viscosity of 25 centipoise (cP).

(2) Gravity of 44° API (in between density) and in between viscosity of 7 centipoise (cP).

(3) Gravity of 48° API (lowest density) and lowest viscosity of 5 centipoise (cP).

11.2.2.6 In the example above, a complete set of tests should be made for both the 20° API crude and the 48° API crude oil. On rare occasions, a third crude oil (for example, one in which the heaviest crude is not necessarily the most viscous or the lightest crude is not necessarily the least viscous) should be considered for tested.

11.2.2.7 If sample volumes in a container are constant in normal operations (for example, 70 % of fill for all batches), the test should be conducted at that single sample volume (for example, 70 % of fill). In cases where the sample volume varies from batch to batch, the test should be conducted at a lower sample volume (for example, 25 % to 30 % of fill) and a higher sample volume (for example, 75 % to 80 % of fill).

11.2.2.8 When transitioning from a lower water concentration to a higher water concentration for any given sample volume being tested, the total higher water concentration is equal to the original baseline volume of water, plus the amount of water added for the lower water concentration, plus the amount of water added for the higher water concentration. Therefore, to account for these volumes of water, any amounts used in purging the withdrawal port (in the case of closed loop mixing) shall be preserved and reintroduced into the container at the time of adding more water into the container.

11.2.2.9 When transitioning from the lower sample volume (LV) to the higher sample volume (HV), a new baseline value is established by test.

11.2.2.10 The mixing times used in the test, whether for the baseline or for higher concentrations of water, should overlap the normal mixing times as nearly as practical. Thus, for any given water concentration (that is, baseline water (BL) percent, lower water (LW) percent, and higher water (HW) percent):

(1) Mixing Time 1 is slightly less than or equal to the Normal Time (NT).



(2) Mixing Time 2 is approximately equal to the Normal Time (NT).

(3) Mixing Time 3 is slightly greater than or equal to the Normal Time (NT).

11.2.2.11 The three (3) tests shall have a range of repeatability within the limits of Column A in **Table 1** (repeatability check). In the tests with concentrations of water above the baseline, the average of the three (3) tests shall also have a deviation from the known concentration within the limits of Column B in **Table 1** (bias check).

11.2.2.12 If a failure of the repeatability check or bias check at any stage of the process results in a failure, the reason shall be determined and remedied, and that test shall then be started from the beginning. If it is determined that a range of mixing times, different than the currently used mixing times in normal operations is required to achieve a successful test, the new mixing times shall be recommended for use in normal operations.

11.2.2.13 *Scenario 1: Sample Volumes are Normally Constant with a Single Grade of Crude Oil.*

Test Number 1 at NORMAL VOLUME (NV) of a SINGLE GRADE of crude oil  
 NVBL = Test at BASELINE WATER concentration  
 NVLW = Test at LOW WATER concentration  
 NVHW = Test at HIGH WATER concentration

11.2.2.14 *Scenario 2: Sample Volumes Vary from Batch to Batch on a Single Grade of Crude Oil.*

Test Number 1 at LOW VOLUME (LV) of a SINGLE GRADE of crude oil  
 LVBL = Test at BASELINE WATER concentration  
 LVLW = Test at LOW WATER concentration  
 LVHW = Test at HIGH WATER concentration

Test Number 2 at HIGH VOLUME (HV) of a SINGLE GRADE of crude oil  
 HVBL = Test at BASELINE WATER concentration  
 HVLW = Test at LOW WATER concentration  
 HVHW = Test at HIGH WATER concentration

11.2.2.15 *Scenario 3: Sample Volumes Vary from Batch to Batch and there are Multiple Grades of Crude Oil.*

Test Number 1 at LOW VOLUME of the HEAVIEST MOST VISCOUS crude oil  
 LVBL = Test at BASELINE WATER concentration  
 LVLW = Test at LOW WATER concentration  
 LVHW = Test at HIGH WATER concentration

Test Number 2 at HIGH VOLUME of the HEAVIEST MOST VISCOUS crude oil  
 HVBL = Test at BASELINE WATER concentration  
 HVLW = Test at LOW WATER concentration  
 HVHW = Test at HIGH WATER concentration

Test Number 3 at LOW VOLUME of the LIGHTER LESS VISCOUS crude oil  
 LVBL = Test at BASELINE WATER concentration  
 LVLW = Test at LOW WATER concentration  
 LVHW = Test at HIGH WATER concentration

Test Number 4 at HIGH VOLUME of the LIGHTER LESS VISCOUS crude oil  
 HVBL = Test at BASELINE WATER concentration  
 HVLW = Test at LOW WATER concentration  
 HVHW = Test at HIGH WATER concentration

11.3 *Outline of Test*—This acceptance test is a volume-balanced test that is similar to that in API *MPMS* Chapter 8.2 (a test using injected water into a crude oil stream), in the following steps:

11.3.1 Determine the range of crude type(s) normally being sampled.

11.3.2 Determine the range of water concentration(s) normally being sampled.

11.3.3 Determine the total volume of the primary container.

11.3.4 Determine the volume(s) normally received in the primary container.

11.3.5 Determine the mixing time(s) normally used at this site.

11.3.6 Select the test mixing times based upon the times normally used.

11.3.7 Design the test plan according to Scenarios 1, 2, or 3 (see **Appendix X2** for calculation examples).

11.3.8 Fill the container with baseline crude oil to the test volume (that is, low, normal, or high volume).

11.3.9 Mix and determine the percent water in the baseline crude oil.

11.3.10 Evaluate results using **Table 1**, Column A, and if they pass, proceed with test.

11.3.11 Add the volume of water needed for the lower concentration amount.

11.3.12 Mix and determine the percent water in the test samples.

11.3.13 Evaluate the results using **Table 1**, Columns A and B, and if they pass, proceed with test.

11.3.14 Add the volume of water needed for the higher concentration amount.

11.3.15 Mix and determine the percent water in the test samples.

11.3.16 Evaluate the results using **Table 1**, Columns A and B, and if they pass, proceed with test.

11.3.17 Repeat steps 8 through 16 for the higher test volume in the case of multiple volumes.

11.3.18 Repeat steps 8 through 16 for the opposite end of the range of grades of crude oil in the case of multiple grades of crude oil.

11.3.19 See Exercises B.1, B.2, and B.3 for details on Scenarios 1, 2, and 3 in **Appendix X2**.

11.3.20 *Test Example:*

(1) Range of crude oils in degrees API: 41 (single grade).

(2) Range of water concentrations: 0.05 % to 0.10 %.

(3) Total volume of primary container: 5 gal.

(4) Range of sample volumes:

(a) Some batches have: 30 % or 1.5 gal.

(b) Some batches have: 80 % or 4.0 gal.

(5) Normal mixing time used by operator: 10 min (this normal time for example only).

(6) Test mixing times chosen:  $\leq 10$  min, = 10 min, and  $\geq 10$  min.

(7) Design the test plan:

(a) Conduct the tests using 41° API crude oil.

(b) Test at the 30 % (1.5 gal) level at the lower water concentration amount of  $\geq 0.50$  %.

(c) Test at the 30 % (1.5 gal) level at the higher water concentration amount of  $\geq 1.00$  %.

(d) Test at the 80 % (4.0 gal) level at the lower water concentration amount of  $\geq 0.50$  %.

(e) Test at the 80 % (4.0 gal) level at the higher water concentration amount of  $\geq 1.00$  %.

(8) Fill the container with baseline crude oil to the test volume:

(a) Calculated amount: 1.5 gal  $\times$  3785 mL/gal = 5678 mL.

(b) Actual amount: 5700 mL for ease of measurement using graduation marks.

(9) Mix and determine the percent water in the baseline crude oil:

(a) Turn on the mixing system.

(b) At a time of ( $\leq$  Normal Time), purge the withdrawal port, withdraw an aliquot, and analyze.

(c) Repeat procedure at a time of (= Normal Time) and a time of ( $\geq$  Normal Time).

(d) Turn off the mixing system and pour the purged volumes back into the container.

(10) Evaluate results using **Table 1**, Column A, and if they pass, proceed with test:

(a) Test result at a time of ( $\leq$  Normal Time): 0.08 %.

(b) Test result at a time of (= Normal Time): 0.04 %.

(c) Test result at a time of ( $\geq$  Normal Time): 0.06 %.

(d) Average of test results: 0.06 %.

(e) Range test results:

(1) Range % = MAX – MIN.

(2) Range % = 0.08 % to 0.04 %.

(3) Range % = 0.04 % (for use with **Table 1**).

(f) Verify that the results agree within the acceptable range of repeatability.

(g) From **Table 1**, Column A, the acceptable value by interpolation would be 0.05 %.

(h) The test result range value of 0.04 % is less than 0.05 %.

(i) Repeatability check: PASS.

(11) Add the volume of water needed for the LOWER concentration amount:

(a) Calculate the amount of water in the baseline oil.

(b) Baseline %  $\times$  volume = baseline water in mL.

(c) (5700 mL  $\times$  0.06 % mL) = (5700 mL  $\times$  0.0006) = 3.42 mL of baseline water.

(d) Target percent for low concentration = 0.50 %.

(e) Calculate added water by: ((5700 mL  $\times$  0.005) – (3.42 mL)) / (1 – 0.005 %) = 25.21 mL.

(f) Therefore: ((25.21 mL + 3.42 mL) / (5725.42 mL))  $\times$  100 = 0.50 %.

(g) Add 30 mL of water for this test (whole graduation marks are easier to read).

(h) Measured total water in the sample: (3.42 mL + 30 mL) = 33.42 mL.

(i) Measured total water and oil in the sample: 5730 mL.

(j) Known water concentration (Wk): (33.42 mL / 5730 mL)  $\times$  (100) = 0.5832 %.

(12) Mix and determine the percent water in the test samples:

(a) Turn on the mixing system.

(b) At a time of ( $\leq$  Normal Time), purge the withdrawal port, withdraw an aliquot, and analyze.

(c) Repeat procedure at a time of (= Normal Time) and a time of ( $\geq$  Normal Time).

(d) Turn off the mixing system and pour the purged volumes back into the container.

(13) Evaluate the results using **Table 1**, Columns A and B, and if they pass proceed with test:

(a) Test result at a time of ( $\leq$  Normal Time) minutes: 0.57 %.

(b) Test result at a time of (= Normal Time) minutes: 0.51 %.

(c) Test result at a time of ( $\geq$  Normal Time) minutes: 0.54 %.

(d) Average of test results: 0.54 %.

(e) Range of test results: MAX – MIN = Range % = 0.57 % to 0.51 % = 0.06 %.

(f) Verify that the results agree within the acceptable range of repeatability.

(g) From **Table 1**, Column A, and Wk: the acceptable range value would be 0.1427 %.

(h) The test result range value of 0.06 % is less than 0.1427 %.

(i) Repeatability check: PASS.

(j) Test value of total water concentration = 0.54 %.

(k) Test value of concentration – Measured value of concentration = Deviation %.

(l) DEV% = (0.54 % – 0.5832 %) = –0.0432 %.

(m) From **Table 1**, Column B, the acceptable Deviation % is 0.0553.

(n) The absolute value of the deviation of –0.0432 % is less than 0.0553 %.

(o) Bias check: PASS.

(14) Add the volume of water needed for the HIGHER concentration amount:

(a) Volume of water in the container at present: 33.42 mL.

(b) Volume of oil and water in the container: 5730 mL.

(c) Target percent for higher concentration = 1.00 %.

(d) Calculate added water by: ((5730 mL  $\times$  0.01) – (3.42 mL)) / (1 – 0.50 %) = 28.96 mL.

(e) Therefore: (28.96 mL + 33.42 mL) / (5728.96 mL) = 1.00 %.

(f) Add 30 mL of water for this test (whole graduation marks are easier to read).

(g) Measured total water in the sample: (3.42 mL + 30 mL + 30 mL) = 63.42 mL.

(h) Measured total water and oil in the sample: 5760 mL.

(i) Known water concentration (Wk): (63.42 mL / 5760 mL)  $\times$  (100) = 1.1010 %.

(15) Mix and determine the percent water in the test samples:

(a) Turn on the mixing system.

(b) At a time of ( $\leq$  Normal Time), purge the withdrawal port, withdraw an aliquot, and analyze.

(c) Repeat procedure at a time of (= Normal Time) and a time of ( $\geq$  Normal Time).

(d) Turn off the mixing system and pour the purged volumes back into the container.

(16) Evaluate the results using **Table 1**, Columns A and B, and if they pass proceed with test:

(a) Test result at a time of ( $\leq$  Normal Time) minutes: 1.18 %.

(b) Test result at a time of (= Normal Time) minutes: 1.10 %.

(c) Test result at a time of ( $\geq$  Normal Time) minutes: 1.14 %.

(d) Average results of test: 1.14 %.