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Standard Guide for Sediment and Water Determination in Crude Oil¹

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1. Scope

1.1 This guide covers a summary of the water and sediment determination methods from the API MPMS Chapter 10 for crude oils. The purpose of this guide is to provide a quick reference to these methodologies such that the reader can make the appropriate decision regarding which method to use based on the associated benefits, uses, drawbacks and limitations.

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

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.4 *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

D473 Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method (API MPMS Chapter 10.1)

D4006 Test Method for Water in Crude Oil by Distillation (API MPMS Chapter 10.2)

D4007 Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure) (API MPMS Chapter 10.3)

D4057 Practice for Manual Sampling of Petroleum and Petroleum Products (API MPMS Chapter 8.1)

D4177 Practice for Automatic Sampling of Petroleum and Petroleum Products (API MPMS Chapter 8.2)

D4377 Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration

D4807 Test Method for Sediment in Crude Oil by Membrane Filtration

D4928 Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration

D5854 Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products (API MPMS Chapter 8.3)

2.2 API Standards:³

API MPMS Chapter 8.1 Standard Practice for Manual Sampling of Petroleum and Petroleum Products (ASTM D4057)

API MPMS Chapter 8.2 Standard Practice for Automatic Sampling of Petroleum and Petroleum Products (ASTM D4177)

API MPMS Chapter 8.3 Standard Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products (ASTM D5854)

MPMS Chapter 10.1 Standard Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method (ASTM D473)

MPMS Chapter 10.2 Standard Test Method for Water in Crude Oil by Distillation (ASTM D4006)

MPMS Chapter 10.3 Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure) (ASTM D4007)

MPMS Chapter 10.4 Determination of Water and/or Sediment in Crude Oil by the Centrifuge Method (Field Procedure)

MPMS Chapter 10.7 Standard Test Method for Water in

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

Crude Oils by Potentiometric Karl Fischer Titration (D4377)

MPMS Chapter 10.8 Standard Test Method for Sediment in Crude Oil by Membrane Filtration (D4807)

MPMS Chapter 10.9 Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration (D4928)

3. Significance and Use

3.1 Theoretically, all of the sediment and water determination methods are valid for crude oils containing from 0 % to 100 % by volume sediment and water; the range of application is specified within the scope of each method. The round robins for all methods were conducted on relatively dry oil. All precision and bias statements included in the methods are based upon the round robin data. Analysis becomes more challenging with crude oils containing higher water contents due to the difficulty in obtaining a representative sample, and maintaining the sample quality until analysis begins.

3.2 Currently, Karl Fischer is generally used for dry crude oils containing less than 5 % water. Distillation is most commonly used for dry and wet crude oils and where separate sediment analysis is available or in situations where the sediment result is not significant. The laboratory centrifuge methods allow for determination of total sediment and water in a single analysis. The field centrifuge method is used when access to controlled laboratory conditions are not available.

3.3 In the event of a dispute with regard to sediment and water content, contracting parties may refer to the technical specifications table to determine the most appropriate referee method based upon knowledge of and experience with the crude oil or product stream.

4. Procedure

4.1 To obtain the total sediment and water results when the two are determined by separate methods: First, add the raw, unrounded results together, and then round the sum to the correct significant figure.

4.2 It is critically important that the analytical samples are collected and handled with careful regard to ensure that they are representative of the entire parcel. The crude oil or product stream should be homogenous at the sampling point, and the sample properly mixed prior to analysis. Sub-samples should not be allowed to settle prior to transfer into an analytical device such as a centrifuge tube, distillation apparatus, or extraction thimble. Refer to API MPMS Chapter 8.1 (ASTM D4057) Standard Practice for Manual Sampling of Petroleum and Petroleum Products, API MPMS Chapter 8.2 (ASTM D4177) Standard Practice for Automatic Sampling of Petroleum and Petroleum Products, API MPMS, and Chapter 8.3 (ASTM D5854) Standard Practice for Mixing and Handling of Liquid Samples of Petroleum and Petroleum Products for appropriate sample collection and mixing.

4.3 It is imperative that every sample is mixed sufficiently to ensure that it is homogeneous. However, with prolonged mixing the temperature of the sample will increase. This will decrease the representative nature of the sample due to evaporative losses. The mixing system must be evaluated to

determine that the mixing time is sufficient without undue temperature increases.

4.4 Sampling error can be a source of bias in analytical methods. This is reflected in the precision and bias statement for each method, but it should be considered when evaluating methods. A larger sample size will increase the probability that a sample is representative of the entire parcel and can minimize the potential bias arising from a less homogenous sample stream. Measuring sample size by weight using an analytical balance is not subject to human error; measuring sample size by volume using analytical glassware is a source of human error.

4.5 When sample size is determined by weight, consider the type of analytical balance used to weigh the sample. Ensure that the resolution is appropriate, having sufficient significant figures, for the analysis.

5. Report

Water Only Determination Methods

5.1 *MPMS Chapter 10.4, Determination of Water and/or Sediment in Crude Oil by the Centrifuge Method (Field Procedure):*

NOTE 1—ASTM Test Methods D96 for Water and Sediment in Crude Oil By Centrifuge (Field Procedure), the technically equivalent ASTM standard was withdrawn without replacement in 2000.

5.1.1 Range of Application:

5.1.1.1 There is no approved precision and bias statement for this method.

5.1.1.2 The practical minimum detection limit is 0.025 % v/v water. Lower concentrations of water should be reported as less than 0.025 % v/v or 0 % v/v.

5.1.1.3 This scope of the method indicates that it applies to crude oil, there is no water content specified in the scope.

5.1.2 Interferences, Biases, and Limitations:

5.1.2.1 The round robin for this method was conducted for combined sediment and water, not the sediment or water fractions separately. Therefore the precision and bias statements do not apply to analysis of water only.

5.1.2.2 This method will typically quantify light alcohols such as, (but not limited to), methanol and ethanol in the water fraction, biasing the water result high.

5.1.2.3 Centrifuge tubes may be filled directly from a sample tap and analyzed minimizing sample handling. Minimizing sample handling helps to maintain the representative nature of a sample.

5.1.2.4 A 50 mL sample is used for analysis as measured in the centrifuge tube.

5.1.2.5 The variety of acceptable solvents allows the user to match the best solvent to the crude type. This can minimize bias resulting from precipitated material (asphaltenes or paraffins) being measured as sediment.

5.1.2.6 This method will not measure dissolved water, thus the results may be biased low in crudes with dissolved water. In addition, depending upon the efficiency of the emulsion breaker used, some highly stable emulsions may not fully break down which will bias the results low.

5.1.2.7 The sensitivity of this method is limited to the divisions marked on centrifuge tubes. The intervals range from 0.025 % to 12.5 % by volume of sediment and water.

5.1.2.8 The method is not highly prescriptive, and lack of consistency may be a source of variability in the results.

5.1.2.9 Because the user reads the result directly off the glassware, result interpretation is susceptible to human error.

5.1.2.10 Because this method is often performed in an uncontrolled environment, maintaining “stoppered” tubes throughout the entire analytical process may help maintain the representative nature of the sample.

5.2 *MPMS Chapter 10.2 (ASTM D4006, IP 358/82), Standard Test Method for Water in Crude Oil by Distillation:*

5.2.1 *Range of Application:*

5.2.1.1 The scope of this test method does not indicate a range of water content. The round robin, upon which the precision and bias statement was developed, ranged from 0.1 % to 1 % water by volume.

5.2.1.2 The practical minimum detection limit is 0.025 % by volume. Lower concentrations of sediment and water should be reported as less than 0.025 % v/v or 0 % v/v.

5.2.2 *Interferences, Biases, and Limitations:*

5.2.2.1 This test method will typically quantify light alcohols such as, but not limited to, methanol and ethanol in the water fraction, biasing the water result high.

5.2.2.2 Volumetric glassware may be filled directly from a sample tap. The volumetric glassware is rinsed with multiple portions of solvent to ensure full transference of sample into the distillation apparatus. This helps ensure that sample did not settle prior to collection of analytical portions. If the sample is allowed to settle, the representative nature may be in question.

5.2.2.3 Samples used for analysis range from 5 g to 200 g or mL, with the smaller sample used for crude oils containing a higher water content.

5.2.2.4 The sensitivity of this test method is limited to the divisions marked on the distillation trap. The intervals range from 0.125 % to 0.5 % water by volume. The intervals increase as the water content of the crude oil increases.

5.2.2.5 The repeatability for this test method ranges from 0.017 for 0.005 volume % of water to 0.08 for 0.130 volume % of water.

5.2.2.6 This test method is more time consuming than the centrifuge or Karl Fischer methods.

5.2.2.7 This test method requires a laboratory environment to set up and operate.

5.2.2.8 Because the user reads the result directly off the glassware, result interpretation is susceptible to human error.

5.3 *MPMS Chapter 10.7 (ASTM D4377-00, IP 356/99), Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration:*

5.3.1 *Range of Application:*

5.3.1.1 The scope of this test method applies to crude oils containing 0.02 to 2 mass or volume % of water.

5.3.1.2 The average practical minimum detection limit for this method is 0.08 mass %. This is based upon oil with a relative density of 0.850 and a water equivalence of 4 for the titration.

5.3.2 *Interferences, Biases, and Limitations:*

5.3.2.1 This test method may be appropriate for crude oils and products which contain light alcohols such as, but not limited to, methanol and ethanol. However, no samples containing alcohols were used in the round robin study; consequently the precision and bias statements in the test method do not apply.

5.3.2.2 Mercaptans in crude oils will bias the results high. This interference is limited with the use of pyridine free reagents. The titration speed and sensitivity settings on Karl Fischer units may also mitigate the interference. Refer to the method for information about mercaptan bias.

5.3.2.3 This test method allows the user flexibility with implementation, the lack of consistency may be a source of variability in the results.

5.3.2.4 Syringes of sample may be drawn directly from the sample vessel or they may be drawn from a subsample container. The syringe contents are then transferred to the titration vessel. The use of a subsample container and the syringe are a source of error.

5.3.2.5 The analytical sample size is 1 g to 5 g of crude oil.

5.3.2.6 The resolution for this test method is in the nearest hundredth 0.08 mass % for relatively dry crude up to the nearest 0.4 mass % for wetter crude oils.

5.3.2.7 This repeatability for this test method ranges from 0.012 for 0.05 mass % of water to 0.040 mass % for 2.0 mass % of water.

5.3.2.8 Due to the non-prescriptive flexibility in selection of solvents and titration parameters, the potentiometric Karl Fischer method may have greater interference from mercaptans than the coulometric method.

5.3.2.9 Samples and aliquots in secondary containers, which includes syringes, may stratify over time and bias the results.

5.3.2.10 This test method requires weighing the sample, but does not include a balance as required equipment.

5.3.2.11 This test method allows manual titration using Karl-Fischer reagent. Because the user reads the result directly off the glassware, result interpretation is susceptible to human error.

5.3.2.12 Top loading balances must be calibrated and certified regularly.

5.4 *MPMS Chapter 10.9 (ASTM D4928-00, IP 386/99), Standard Test Method for Water in Crude Oils by Coulometric Karl Fischer Titration:*

5.4.1 *Range of Application:*

5.4.1.1 This procedure is applicable to the determination of water in crude oils containing from 0.02 % to 5 % water.

5.4.1.2 The practical minimum detection limit is 0.005 %. Lower concentrations of sediment and water should be reported as less than 0.005 % v/v or 0 % v/v.

5.4.2 *Interferences, Biases, and Limitations:*

5.4.2.1 This test method may be appropriate for crude oils and products which contain light alcohols such as, but not limited to, methanol and ethanol. However, no samples containing alcohols were used in the round robin study; consequently the precision and bias statements in the method do not apply.

5.4.2.2 The precision and bias statement was developed over the range of 0.02 % to 5 %. Due to reagent consumption, it is generally less practical than other methods for very wet crudes.

5.4.2.3 Syringes of sample may be drawn directly from the sample vessel or they may be drawn from a subsample container. The syringe contents are then transferred to the titration vessel. The use of a subsample container and the syringe are a source of error.

5.4.2.4 The sample size for this test method is 0.25 g to 1.0 g or 0.25 mL to 1.0 mL.

5.4.2.5 Resolution is 0.01 mass % or 0.01 volume %.

5.4.2.6 The repeatability ranges from 0.003 for 0.01 volume % of water to 0.16 for 5.0 volume % of water.

5.4.2.7 Mercaptans in crude oils will bias the results high, however this interference is limited when pyridine free reagents are used. The titration speed and sensitivity settings on coulometric Karl Fischer units may also mitigate the interference. Refer to the method for information about mercaptan bias.

5.4.2.8 Samples and aliquots in secondary containers, which include syringes, may stratify over time and bias the results.

5.4.2.9 Karl-Fischer coulometric titration may be conducted by weight or by volume. Analytical balances allow for resolution to one ten thousandth of a gram and are an objective measurement of sample size. (Balances with lower resolution may be used as well.) Volumetric measurement is susceptible to human error as the volume is read directly off of the glassware. The volume resolution of syringes allows for measurement to the nearest hundredth of a millilitre. Syringes with lower resolution may be used for sample measurement.

5.4.2.10 Using an uncalibrated syringe, or a syringe without verified volumetric markings may be a source of error. In addition, volume measurement is subjective, which is a potential source of error.

5.4.2.11 It is more difficult to draw higher viscosity crude oils into sample syringes. Volumetric determination of sample size may not be suitable for some highly viscous crudes.

5.4.2.12 Air bubbles in the syringe may be difficult to detect and will bias results low for volumetrically measured samples.

5.4.2.13 Top loading balances used to determine sample weights, must be calibrated and certified regularly.

5.4.2.14 Because the result is a digital readout, result interpretation or water content is objective.

Sediment Only Determination Methods

5.5 *MPMS Chapter 10.4, Determination of Water and/or Sediment in Crude Oil by the Centrifuge Method (Field Procedure):*

NOTE 2—ASTM Test Methods D96 for Water and Sediment in Crude Oil By Centrifuge (Field Procedure), the technically equivalent ASTM standard was withdrawn without replacement in 2000.

5.5.1 Range of Application:

5.5.1.1 No round robin has been approved; there is no precision and bias statement for this method.

5.5.1.2 The method applies to crude oil, no sediment content range is noted in the scope.

5.5.1.3 The practical minimum detection limit is 0.025 % sediment by volume. Lower concentrations of sediment should be reported as less than 0.025 % v/v or 0 % v/v.

5.5.2 Interferences, Biases, and Limitations:

5.5.2.1 The round robin for this method was conducted for combined sediment and water, not the sediment or water fractions separately. Therefore the precision and bias statements do not apply to sediment only analysis.

5.5.2.2 The variety of acceptable solvents allows the user to match the best solvent to the crude type. This can minimize bias resulting from precipitated material being measured as sediment.

5.5.2.3 The method is not highly prescriptive; therefore the results may be less reproducible and repeatable than other Chapter 10 methods. There is no precision and bias data for this method.

5.5.2.4 The sensitivity of this method is limited to the divisions marked on centrifuge tubes. The intervals range from 0.025 % to 12.5 % by volume of sediment and water.

5.5.2.5 Because the user reads the result directly off the glassware, result interpretation is susceptible to human error.

5.5.2.6 Because this method is often performed in an uncontrolled environment, maintaining stoppered tubes throughout the entire analytical process may help maintain the representative nature of the sample.

5.6 *MPMS Chapter 10.1 (ASTM D473-02, IP 53/82), Standard Test Method for Sediment in Crude Oils and Fuel Oils by the Extraction Method:*

5.6.1 Range of Application:

5.6.1.1 The round robin, upon which the precision and bias statement was developed, ranged from 0.01 % to 0.40 % sediment.

5.6.1.2 This test method applies to crude oil and fuel oil containing from 0.01 to 0.40 % sediment by weight.

5.6.1.3 The practical minimum detection limit is 0.01 mass %. Lower concentrations of sediment and water should be reported as less than 0.01 % v/v or 0 % v/v.

5.6.2 Interferences, Biases, and Limitations:

5.6.2.1 Toluene insoluble crude oil components adhering to the thimbles will bias results high.

5.6.2.2 Sample is transferred directly from the sample tap into the thimble minimizing error. More volatile samples are subject to bias as components off-gas prior to determination of sample weight.

5.6.2.3 The sample size is 10 g.

5.6.2.4 The resolution is 0.01 mass %.

5.6.2.5 The repeatability ranges from 0.02 for crude oils containing 0.01 mass % sediment to 13 for crude oils containing 50 % sediment.

5.7 *MPMS Chapter 10.8 (ASTM D4807-05), Standard Test Method for Sediment in Crude Oil by Membrane Filtration:*

5.7.1 Range of Application:

5.7.1.1 The precision and bias statement was developed using crude oils that contained up to 0.15 % sediment.

5.7.1.2 This test method applies to crude oils containing up to 0.15 % sediment by weight.

5.7.1.3 The practical minimum detection limit is: 0.001 mass %.