

FIELD AND LABORATORY TESTING OF SEDIMENT AND WATER IN CRUDE OIL

Class # 5160

Jane Williams
President
Oil and Gas Training Corporation
DWG, TX, USA

Introduction

The quantity of sediment and water in crude oil must be accurately established as part of the custody transfer process. Purchasers only pay for the crude oil received, and want to minimize the quantity of sediment and water they must transport and dispose of. Consequently, monitoring of the sediment and water content is performed at the production site to prevent excessive sediment and water from entering the pipeline system. The quantity of sediment and water a pipeline is willing to accept into their system depends on geographic location, market competitiveness and their ability to handle the sediment and water in the system. Each pipeline publishes the quantity of sediment and water it will accept. States also may have sediment and water limits as well.

Field Testing of Sediment and Water

Field testing of sediment and water is used for the determination of the custody transfer quantity for which the producer will be paid. Typically, this measurement is performed at the production facility, utilizing American Petroleum Institute (API) Manual of Petroleum Measurement Standards (MPMS) Chapter 10, Section 4, Determination of Sediment and Water in Crude Oil by the Centrifuge Method (Field Procedure) – 1999, which was revised in 2013..

API MPMS Chapter 10, Section 4 requires that the centrifuge tubes used be either 6 or 8 inch cones. The standard specifies allowable tube dimensions and tolerances. These tubes must be traceable to the NIST.

Field Procedure

1. Fill two centrifuge tubes to the 50 milliliter (ml) or 100 part mark with the homogeneous sample to be tested. Read the top of the meniscus (the curved upper surface of a liquid column). It is important to put the sample in first because it allows for easy addition or removal of sample if the proper amount is not achieved initially. If the solvent is inserted first, no modification can be made properly, so one has to start over. Since the solvent should not impact the sediment and water, it is not critical that exactly 50 ml is inserted in the next step.
2. Fill the two tubes with 50 ml of solvent which brings the total contents of the tubes to the 100 ml or the 200 parts mark. The acceptable solvents are Stoddard, kerosene, toluene, and xylene. Note that toluene and xylene should be water-saturated at test temperature and are the only solvents acceptable if an asphaltenic or waxy crude is being tested. Stopper the centrifuge tubes.
3. Invert the tubes 10 times to mix the sample and solvent. This should be done below eye level for safety, and safety glasses are highly recommended. Solvents can be hazardous and should be handled with caution. Material Safety Data Sheets (MSDS) and handling precautions recommended by the chemical manufacturer should be followed. See additional safety notes listed in the solvents section.
4. Place the tubes in the preheater and heat to 140° F +/- 5° F. If asphaltenic or paraffinic crudes are tested the temperature should be increased to 160° F.
5. Invert the tubes ten times again to mix.
6. Place the tubes on opposite sides of the centrifuge to balance the load. Close the centrifuge lid.
7. Centrifuge for a minimum of 5 minutes at the appropriate rpm in order to obtain a relative centrifugal force of 500.
8. When the centrifuge comes to a stop, test the temperature of the tube contents without disturbing the oil-water interface.
9. If the temperature of the sample is 125° F or above for 140° F test temperature or 145° F or above for

160° F test temperature, read and record the combined sediment and water content at the bottom of each tube. If the temperature is below 125° F (145° F if appropriate), the tubes must be reheated and the test repeated without further agitation until two consecutive consistent readings are obtained.

10. If an emulsion is visible, add a solvent containing a demulsifier to the sample and retest (this is covered in the appendix of the standard). If the demulsifier does not eliminate the emulsion, additional heat may be required to break the emulsion.

11. Compare the readings from the two tubes. If the results vary by more than one subdivision of the centrifuge tube, the sample was not homogeneous. Thus the test should be repeated with two fresh samples. By following the procedure closely, the results obtained will be reliable and accurate. In order for the correct results to be obtained, special attention should be given to obtaining a representative sample. Sampling is covered in API-MPMS Chapter 8, Section 1, for sampling a tank and Chapter 8, Section 2, for locations with a meter.

Sample Size

If the centrifuge tube is filled with any proportion other than 50/50 sample/solvent, the results cannot be read directly from the centrifuge tube. The following equation must be utilized to adjust for the incorrect mixture.

$$\text{Sediment and Water \%} = (S/V) * 100$$

Where: S = Volume of sediment & water found, ml

V = Volume of oil tested, ml

This is why the procedure recommends that the sample be placed in the centrifuge tube initially. If this is done, adjustments to the quantity can be made by either adding more or removing sample until the 50 ml mark is achieved.

Reading the Tubes

The proper reading is the top of the meniscus. If tubes marked with 100 ml at the top are utilized, the actual sediment and water is the sum of the readings from the two tubes. If tubes marked with 200 parts are used, the correct sediment and water result is the average of the two readings to three decimal places.

Solvents

Solvents can be hazardous and consequently should be handled with caution. Some typical common sense precautions include, but are not limited to:

Avoid breathing the vapors and contact with skin or eyes.

- 1 Use only in well ventilated locations.
 - 2 Chemical resistant gloves should be utilized to avoid repeated or prolonged contact with the skin.
- Handling precautions recommended by the manufacturer should be followed.
- 3 These solvents are either flammable or combustible and thus necessary precautions should be observed.
 - 4 Eye protection should be utilized.
 - 5 Mix the liquids below eye level

Stoddard solvents are most commonly used in the field since they are readily available and do not require water saturation. Asphaltenic and paraffinic crudes require the use of either toluene or xylene to obtain the correct results. However, both of these solvents must be water saturated at test temperature (140° F) and maintained at this temperature until used. The proper technique for water saturation is covered in Appendix of API-MPMS, Chapter 10, Section 4. A vendor has started packaging water saturated toluene in glass vials which are easy to use in the field and minimize any exposure to the toluene. The same vendor has a device available to heat the glass vials to 140° F prior to use.

Laboratory Testing of Sediment and Water

Sometimes samples are transported to a laboratory for the determination of sediment and water for custody transfer purposes. In a lab environment, the actual tests performed can be more accurate; however, proper sample handling becomes even more critical. During transportation to the lab, the sample may stratify or

separate into layers. Before the analysis is performed, the sample must be brought back to its original state by mixing. The number of times the sample is transferred also affects the ability to obtain a sample representative of the actual field fluid. Without a representative sample, it is impossible to obtain the correct results.

Representative samples can be analyzed for water content by utilizing API MPMS, Chapter 10, Section 3, "Determination of Water & Sediment in Crude Oil by the Centrifuge Method" (Laboratory Procedure). This method is very similar to the field centrifuge method, except only 8 inch centrifuge tubes and water-saturated toluene are permitted. The water content may also be determined by API MPMS, Chapter 10, Section 2 Standard Test Method for Water in Crude Oil by Distillation or Chapter 10, Section 9, "Determination of Water in Crude Oils by Coulometric Karl Fischer Titration". Since water by distillation is far more time consuming than the Karl Fischer method, it is typically only utilized to resolve conflicts. The Karl Fischer methodology provides accurate results in the 0.02 to 5% water in crude oils. Mercaptan and sulfide in the crude may interfere with the Karl Fischer test, so extra care should be taken if these exist in the crude being tested. The methodology in API MPMS, Chapter 10, Section 9, requires that an aliquot be injected into the titration vessel of a Karl Fischer apparatus. Iodine for the Karl Fischer reaction is coulometrically generated at the anode. Excess iodine is detected by an electrometric end-point detector and the process terminated when all the water has been titrated. One mole of iodine reacts with one mole of water, thus the quantity of water is proportional to the total integrated current according to Faraday's Law.

Proper mixing and a representative sample is critical to this methodology since the largest aliquot injected is only 1 gram (g) maximum. In the higher water content ranges (0.5 – 5.0%), only 0.25 g aliquots are recommended. Thus the ability to get a representative sample is extremely critical. The quality of the reagents and solvents used in this test is also important.

Laboratory Procedure

1. Add fresh solvents to the anode and cathode compartments of the titration vessel and bring the solvent to end-point conditions.
2. Mix the sample so that a representative aliquot can be obtained.
3. Starting with a clean, dry syringe (high quality of suitable capacity), withdraw at least three portions of the sample and discard to waste.
4. Withdraw the aliquot to be tested into the syringe.
5. Clean the needle with a paper tissue.
6. Weigh the syringe and contents to the nearest 0.1 milligram (mg).
7. Insert the needle through the inlet port septum, start the titration and with the tip of the needle just below the liquid surface, inject the sample.
8. Withdraw the syringe.
9. Weigh the syringe to the nearest 0.1 mg.
10. After the end-point is reached, record the titrated water registered on the instrument display.

Calculation

$$\text{Water, mass \%} = W1 / (10,000 * W2)$$

Where: W1 = mass of water titrated, mg

W2 = mass of sample used, g

$$\text{Water, volume \%} = AR$$

Where: A = mass percent of water

R = relative density of crude oil

Additionally, the appendix covers a methodology which utilizes volumetric determination of sample size. Results of round-robin testing indicate that the volumetric methodology can be just as accurate as the methodology described above. The volumetric methodology can be performed in a laboratory environment or in the field. This technique requires high quality syringes (10 micro liter graduated for readings to 0.01 micro liter is preferred, but the resolution must be at least 0.01 ml. The presence of gas bubbles in the syringe is a source of uncertainty, so any gas bubbles should be removed prior to performing the test. The procedure is the same as above except

instead of weighing the sample, note the sample volume.

Volumetric Calculation

$$\text{Water, volume \%} = V1 / (10,000 * V2)$$

Where: V1 = Volume of water titrated, micro liters

V2 = Volume of sample, ml

Water by Distillation is covered in API MPMS, Chapter 10, Section 2, and is considered the most accurate methodology available, but realistically must be performed in a laboratory. However, this technique is very time consuming and thus is rarely performed for normal custody transfers of crude oil. It is the method specified to be used if there is any doubt about the proper water content, as it is considered the referee methodology.

All of the above laboratory methods except the centrifuge method only test for the water content. Thus a second test method must be performed to determine the sediment content. Occasionally, the Coulometric Karl Fischer methodology is utilized to obtain the water content and the sediment content is obtained by centrifuge. Generally, if laboratory tests are performed to obtain the water content, the sediment content is obtained by either sediment by extraction or sediment by filtration. Sediment by extraction is covered in API MPMS, Chapter 10, Section 1. Sediment by filtration is covered in API MPMS, Chapter 10, Section 8. Both of these techniques are strictly laboratory techniques and will not be covered here as they are relatively time consuming.

Summary

Sediment and water content is monitored at the field production site so that excessive sediment and water does not enter the pipeline system. This is accomplished by manual methods, or on-line devices like that utilize capacitance, density, or energy-absorption techniques. These devices are utilized in determining whether or not the oil is measured by LACT unit into the pipeline system. For custody transfer purposes, the sediment and water is determined by actual test following one of the API MPMS, Chapter 10 standards. Typically, this is done in the field by the field centrifuge method, which if performed properly yields very accurate results. Laboratory tests can be performed, but sample handling becomes even more critical. If a dispute over sediment and water content occurs between two parties, it should be resolved by using the referee method which consists of water by distillation and sediment by extraction.