Determining Moisture Content in Crude Oil: Karl Fischer vs. Distillation vs. Centrifuge

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The determination of the amount of water in crude oil and petroleum products has always been important. Rather than paying crude oil prices for water, contracts have been based on "net dry oil." This is calculated by reducing the total gross standard volume (GSV) by the amount of water and sediment present as determined by analyzing a sample of the oil. Accurate analysis for the water content is usually more difficult than the determination of gross volume, temperature, and gravity of the oil.

In production areas as well as pipeline, custody transfer is based on "net dry oil." Marine facilities must determine the water content of the oil to verify the Bill of Lading figures in addition to determining the quantities received in their shore tanks. In the refinery, maintaining low water content is important to the operation of the crude unit, and it is a major part of quality control in the production of products like lubricating oils and transformer oils.

The water content of an oil can be determined either by static or dynamic methods. The static methods require that a sample of the oil be removed from the pipeline or tank; then it is analyzed. Dynamic methods determine the water content as the oil flows through, or past, an instrument located in the pipe. The following will focus on the determination of water content in the static state.

There are three different static methods for determining the water content of crude oil and petroleum products. The oldest and most widely used method is the centrifuge test, in which equal volumes of oil and solvent are placed in a graduated centrifuge tube. After centrifugation, the volume of the higher gravity water and sediment layer at the bottom of the tube is read. This test is detailed in several API/ASTM Standard Methods, including ASTM D-4007 (laboratory procedure) and D-96 (field procedure). Even if these methods are followed in detail (heated centrifuge, water saturated solvent, etc.), the total water content will be understated for most types of oil. At some locations unheated centrifuges, non-standard tubes (i.e., pear shaped), and improper solvents are still being used. Each departure from the standard increases the uncertainty of the test and usually tends to understate the water content even further.

During the past few years the water by distillation test (also called the Dean and Stark test), ASTM D-4006 has been used more frequently since it is more accurate and is the accepted referee method when parties cannot agree on centrifuge results. In the test, a sample of the oil is heated under reflux conditions with a water immiscible solvent, which co-distills with the water in the sample. The water and condensed solvent are continuously separated in a trap with the water settling in the graduated section of the trap while the solvent returns to the distillation flask. This method is very time consuming and can only be conducted in a laboratory.

The third method for water determination is based on the titration of the sample with Karl Fischer reagent, ASTM D-4928 (API Chapter 10.9). This method has been used for many years to determine water in liquid petroleum products, but it has not been used for crude oil until the past few years. In 1985 the API Sediment and Water Sub-Committee started evaluating the Karl Fischer test method for the determination of water in crude oils. The preliminary studies of the Karl Fisher test method conducted by the API S &W work group showed promising results, which paved the way for a round robin. The API, ASTM, and IP joined forces and coordinated a round robin to establish a precision statement for the Karl Fischer test method.

Table 1 lists the accuracy (reproducibility) that can be expected from each of these different methods for crude oil samples containing 0.1 and 0.5 volume percent water, as stated in the appropriate API/ASTM Standards. It can be seen that for 0.1% water/Coulometric Karl Fischer is ten times more accurate than the centrifuge, and five times more accurate than distillation. At 0.5% water, Coulometric Karl Fischer is four times more accurate than centrifuge and about two times more accurate than distillation.

The Karl Fischer method has several advantages over the other water determination methods. The most important of which is increased accuracy. Also, samples can be analyzed in less than five minutes, as opposed to at least thirty minutes for the centrifuge test and several hours for the distillation test. The Coulometric Karl Fischer can be utilized in the back of a pick-up truck for field use, on an off-shore platform for production use, in a pipeline station for custody transfer use, and in a laboratory for quality control and other uses.

The laboratory procedure for Coulometric Karl Fischer requires that the oil sample be taken with a syringe, accurately weighed on a scale, and injected into the titration cell; then the syringe is weighed again to determine the net weight of the sample. After the titration is completed, the meter will indicate the number of micrograms of water that were in the sample. Dividing this by the weight of the sample will give the mass percentage of water in the sample (or ppm of water depending on the multiplier).

In the field method a precision micro-syringe is used to inject an exact volume of sample into the titration cell. After the titration is complete, the instrument will display the volume percentage of the water. For use in the field, a volume percentage of water is of much greater value than a mass percentage. The water content is multiplied by the volume of oil to determine the volume of water to be deducted from the total measured volume of oil. If a mass percentage (or ppm) is desired then the resulting micrograms can be divided by the specific gravity of the oil and the injected sample volume.

The portable Coulometric Karl Fischer moisture meter and the field test method have many applications in the oil industry. Upon agreement by both parties, this method can be used to accurately determine the water content of oil for pipeline custody transfer purposes. At most custody transfer locations, an automatic inline sampler is used to collect a representative sample of the oil being transferred. Most samplers have a pump on the bottom of the receiver that circulates the oil through a static mixer and back into the receiver. The oil is mixed for a period of time before a sample is taken for analysis (there is usually uncertainty as to the optimum mixing time required: too little and the water is understated, too much and light ends are lost and the gravity is overstated). If this system is slightly modified by installing a tee with a valve and septum just down the stream of the static mixer, a sample can be withdrawn directly from the line with a syringe. This sample can then be analyzed in the moisture meter. Multiple samples can be analyzed to determine the optimum mixing time for particular oils, and various water contents. Also, this procedure reduces the problem of obtaining a reliable sample during inclement weather. The Coulometric Karl Fischer is the fastest and the most accurate method of determining water in crude oil and petroleum products today.

Regardless of the method used to determine the water content, the result cannot be any better than the quality of the sample analyzed. The sample must be truly representative of the total volume of oil. If the sample to be analyzed is obtained from tank sampling, the proper procedures must be followed to assure a representative sample (API Standard, Chapter 8.1). If the sample is obtained from a continuous, automatic, on-line sampler, the system must be operated and maintained in accordance with the API Standard (Chapter 8.2). After the sample has been obtained in a sample bottle, it must be completely homogenized to assure that the portion actually analyzed is completely representative of the total volume. High-speed, no-aerating, sheer mixers are recommended in the API chapter 10-9 and ASTM D-4928 standards to assure complete homogeneity of the sample before analysis.

Regardless of the water determination methodology employed, several basic points need be followed. The application should be studied to determine the specific need for water determination and whether they can best be met by static methods or dynamic methods. Then, which specific method will provide

the most desirable result. Then the best equipment/instruments should be selected to meet the requirements of the application. The equipment should meet all of the appropriate standards; such as, API, ASTM, US Coast Guard, Bureau of Land Management, Minerals Management Service, etc. The manufacturer's instruction should be followed in operating and maintaining the equipment. For Static methods, the appropriate analytical procedures must be properly followed. One should remember that the determination of the water content of the oil directly affects the revenue received for the oil.

TABLE 1

REPRODUCIBILITY OF STANDARD TEST METHODS FOR WATER DETERMINATION

	WATER VOL %	
TEST METHOD	**0.1%**	**0.5%**
Centrifuge (D-4007)	0.20	0.28
Water by Distillation (D-4006)	0.11	0.11
Karl Fischer Titration Weight Injection (D-4928)	0.02	0.06
Karl Fischer Titration Volume Injection (D-4928)	0.02	0.07

REFERENCES

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