



*Technology for Precision Measurements*

## Sampling and Analysis of Crude Oils for Water Content

One fundamental purpose of sampling is to verify online WIC analyzers (Water-In-Crude analyzers or Water-In-Condensate analyzers) are providing accurate indications of water content. The method to determine water content must be carefully considered by observing the types of crude oil present, the installation of the equipment (both sampling and electronic measurement installations) and the temperature, pressure, and level of water present.

**Obtaining a good sample:** Since oil and water do not mix, the temperature, density of the oil, natural properties of the oil, salinity of the water, viscosity of the mixture, the presence or absence of emulsion breakers, velocity at the sample port, and the physical pipe layout will affect obtaining a good sample.

**EMULSION TYPE:** An oil and water emulsion can be one or a mix of several emulsion phases which are called oil continuous emulsions (oil surrounding water), water continuous emulsions (water surrounding oil). The type of emulsion will create different challenges in the attempt to extract a representative sample. The natural emulsifiers in the oil, the temperature, the shear that the liquids have seen, and the salinity of the water all play a part in determining which emulsion phase exists and when the emulsions will change to a different phase. The oil continuous phase at high water percentages before inversion occurs becomes a very high viscosity liquid. Viscosity is a physical property and is analogous to the “stickiness” of the liquid.

A. Oil continuous emulsions: These can range from 0% water up to 85% water in the oil continuous phase. The light oil and NGL and condensates do not have the emulsifiers in the liquid and therefore the water is typically in a free state and will separate out very rapidly. In low flow conditions, this causes severe problems in sampling. The stream must be very well mixed with a good sample probe to extract the sample. With heavier crude oils the natural surfactants will allow the water to be suspended in the emulsion and in some cases it is very difficult to break the emulsion. It is easy for the analyzer to obtain good results in this case. If the natural emulsifiers are present and shear is generated from a pump or high velocity creating a turbulent flow condition, the tighter emulsion called a “rag layer” can be created. This is a very high viscosity liquid which can exist up to 90% water content. Other cases with heavy oils the water can exist in streamers as the continuous (water) phase along with the oil continuous emulsion. This causes sampling problems due to the non homogeneous mixture which can also flow at a different rate than the imbedded water phase. At higher temperatures, some heavy oils are denser than water and the process will invert with water on top of the oil.

B. Water Continuous emulsions: In very light oils like West Texas 40-50 API (less than 800 kg/m<sup>3</sup>) oil, NGL's and condensate, the range where oil-in-water emulsions can exist could begin at 50% water or even lower depending upon the flow rate. Since these liquids have very little or no natural surfactants, the water will immediately drop out if the flow rate decreases. With low flow, the water will flow along the bottom of the pipe with the light oil on top. The higher the water cut the more difficult it is to pull a representative sample unless the flow is high velocity and the sample port is a pitot tube.

**FLOW Rates:** Flow rates will impact the sample quality. Low flow allows the lighter liquid to favor the bottom of the process pipe. Higher flow rates begin to mix the liquids as the turbulent flow regime is entered. If the sample port is too close to an elbow in the pipe, the centrifugal force will tend to separate the heavier product and send it to the outside of the elbow. Mixing due to a static mixer or a centrifugal pump will aid in the dispersion of one phase in the other. Mixers will not help in low flow cases or in cases outside of the mixer's narrow design range. The issue for static mixers is in large pipelines or where a



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small sample is to be extracted from a larger pipeline. Pipelines generally operate in known velocity ranges and therefore a design can be made to accommodate this.

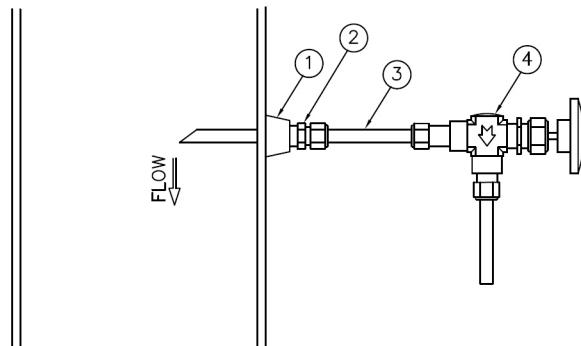
Suggested flow rates for the various analyzers to achieve a suggested minimum velocity of 2 ft/second are given below.

Analyzer Diameter (inches)	Minimum Flow Rate bbls/day (m <sup>3</sup> /day)	Maximum Flow Rate bbls/day (m <sup>3</sup> /day)
1	170 (27)	1258 (200)
2	685 (109)	4800 (763)
3	1510 (240)	10,000 (1800)
4	2642 (420)	20,127 (3200)

The maximum flow rate is where the velocity exceeds 15 ft/second (~3 meters/second). This high flow rate presents difficulties in sampling and can be a problem due to erosion of the components in the process stream at high velocities. Higher velocities can bias the sample due to the change in velocity at the point where the sample is being pulled.

**SAMPLE PORT DESIGN:** The key points are to have a design that will remove the sample in a representative cross section of the main line at the same velocity as the main line. The best will sample across the area of the main line.

Too large of sample port sizing will create several problems. A large sample port will force the operator to pinch down on the valve so that the oil will not spray. Gate valves do not open gracefully and will pop open and flood the operator's collection bucket. Ball valves are much better and 5 turn valves allow the operator to control the flow easily. If the stub between the liquids in the main line is large, the pipe between the liquids and the valve becomes a "dead leg" where water may start to accumulate when pulling the sample. One recommended sample port is a 1/2" tubing with a through swage fitting in a weld-o-let in the main pipe that will be sampled.



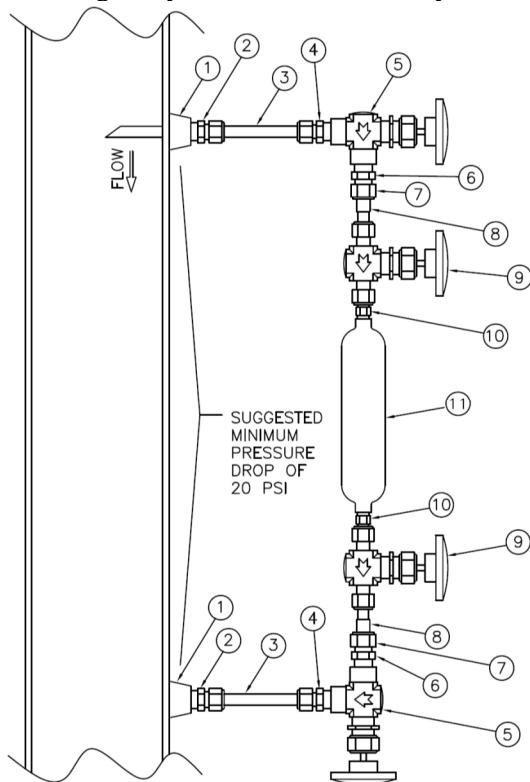
**Sample Port Example.**

Phase Dynamics' drawing below gives an example of a cylinder type of system using a 45 degree cut on the tubing in the middle of the stream. A mark is made on the tubing on the front side of the 45 degree cut so that after it is inserted the technician can make certain that it is facing upstream. The pressure drop will determine the actual fluid velocity when the ports are open. This system was originally designed for very high temperature liquids. The upstream and down stream valves would be fully opened while obtaining



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the sample and the process will flow through the entire system. Once the water is read from that analyzer and is steady the valve downstream on the cylinder should be closed first and then the upstream. Then both end valves should be closed for the sample to cool. The VCO fittings provide for ease of removal of the cylinder from the line after it has cooled. Loosening these fittings will cause any pressure to be released in the tubing safely before removal of the cylinder.



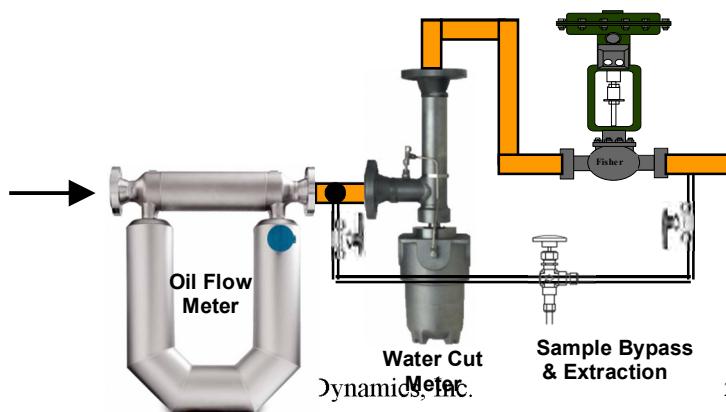
1. 5-3 X 3/4 3000# THREADELET
2. SS-810-1-12BT SWAGELOK MALE CONNECTOR (2 EA)
3. 1/2 INCH OD X 0.035 WALL SEAMLESS 316 STAINLESS STEEL TUBING
4. SS-810-1-8 SWAGELOK MALE CONNECTOR (2 EA)
5. SS-18VF8-A WHITEY NEEDLE VALVE (2 EA)
6. SS-8-VCO-1-8 MALE CONNECTOR (2 EA)
7. SS-8-VCO-4 FEMALE NUT (2 EA)
8. SS-8-VCO-3-8TA SWAGELOK TUBE ADAPTER GLAND (2 EA)
9. SS-18VS8 WHITEY NEEDLE VALVE (2 EA)
10. SS-8-TA-1-4 SWAGELOK TUBE ADAPTER (2 EA)
11. 316L-HDF4-300-T WHITEY SAMPLE CYLINDER (300 CC)

#### OTHER PARTS NOT SHOWN:

- A. SS-8-VCO-1-BL SWAGELOK BLIND BODY (2 EA)
- B. AS-568-111 VITON "O" RING (2 EA)
- C. MS-STR-8 SWAGELOK TAPE THREAD SEALANT

#### Flow Through Method to Pull Samples:

In well testing it is difficult to pull an acceptable sample at high water percentages. One way to assist in this is to have a flow through sample tubing from near the on-line analyzer to downstream of a valve or other pressure drop to achieve flow through the 0.5" tubing. Upstream and downstream ball valves are used to close off the tubing when not in use for sampling. A "T" with a 5 turn valve with a open tube to gather the sample is placed at a convenient place in the line where the analyzer screen can be viewed. When a steady water percentage is seen a sample can be pulled. This method solves many of the issues with sampling.





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The amount of sample pulled should be just enough to process using the analysis method of choice. In the case of centrifuge, this should not be more than 100 to 200 ml otherwise the water will end up in the bottom of the sample jar and not processed in the lab. The entire sample should be centrifuged using the ASTM API method called out in IP359. Emulsion breaker specific to the crude oil type should be used.

**Sample Handling:** Emulsions will “age” as they cool down and time has passed from its removal from the line. This “aging” makes it more difficult to process in the lab especially for the centrifuge method. The sample should be processed soon after obtaining it.

**Laboratory Methods:** Most preferred is the distillation procedure although it is the most difficult and time consuming. Centrifuge is the typical method for well testing applications (0-100% water cuts) but, it is often used for 0-5% water in oil. ASTM/ API Chapter 10.4 (field method) and IP359/82 (Laboratory Method) are standard test methods for centrifuge outlines the technique to obtain reasonable results. Please notice that there are no numbers for Reproducibility and Repeatability for the Field Centrifuge method because the results are highly uncertain and operator dependent. It is important to use water saturated toluene as a solvent. This is of particular importance when the water cut is lower than 0.5%. Kerosene and Soddard solvent do not suffer from absorption of water. Several of the centrifuge vendors sell tubes that do not have any graduations between major marks and therefore are not appropriate for use in low water cases. The procedure does not mention using the complete sample but, many instances this is the only way to achieve reasonable results. In this case multiple tubes are filled and all of the numbers are added together to obtain the average results. For 0-1% water cut the repeatability is 0.12% and the reproducibility is 0.28% for laboratory centrifuge. These numbers are between the same sample and not between separate samples pulled at the same time.

Method	Valid Water Ranges	ASTM Standard	Sample Size	Reproducibility	Repeatability
Distillation	Less Than 1%	D4006	200 ml Min	0.11%	0.08%
Titration	Less Than 2%	D4377	2-5 grams	0.10%	0.04%
Laboratory Centrifuge	Less Than 1%	D4007	100 ml	0.28%	0.12%
Field Centrifuge	Less Than 1%	D4007	100 ml	None	None

**Data Bookkeeping:** Data should be placed in a table similar to that in Figure 1. Be certain that the data from the WIC analyzer is read at the same time when the sample is being pulled. Differences in DCS or PLC timing of data collection usually means that writing down the time of day and then looking up the analyzer reading at that time does not give useful information. This can be due to different clock settings or the time between polling for the DCS data collection. A scatter plot of the data for a given pipeline or well vs time will help in observing the probable error in sampling and method. Fitting a best fit line through the data will show the offset from the analyzer to the laboratory methods. After obtaining sufficient data points the data should be uniformly distributed about the 45 degree line and have correlation between the data from the laboratory within the stated laboratory method’s reproducibility times 1.5 as a guideline. During the period where a sufficient number of data points is obtained no adjustments should be made on the analyzer. Any changes to the Calibration of the WIC should be noted on the record. Constantly changing the offset in the analyzer is not productive as it only adds to the confusion and often the offset will return to the original values with time. Once the data shows a clear offset this should be entered once and more data



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collected. If records are kept and each change is noted the performance of the WIC and sampling vs time can be easily analyzed in a spreadsheet.

Sample ID	Date/Time	Operator	Flowing Density kg/m3	Fluid Temp Deg F	WIC Cal. Adjust	Analyzer W/C%	Lab W/C %	Analyzer – Lab = Error%
1	2/21/2019 08:20	jws	826	126	0.00	0.16	0.16	0
2	2/22/2019 11:40	jws	826	125	0.00	0.22	0.18	0.04
3	2/23/2019 09:13	stm	826	126	0.00	0.28	0.25	0.03
4	2/23/2019 3:15	stm	826	124	0.00	0.17	0.18	-0.01
5	2/24/2013 10:20	jws	826	123	0.00	0.26	0.20	0.06
6	2/24/2013 9:55	jws	826	125	0.00	0.24	0.21	0.03
7	2/25/2013 16:40	stm	826	125	0.00	0.28	0.26	0.02
							Average	0.024

**Figure 1. Example of data**

In the example the average error would be the sum of the errors which equals 0.17% divided by 7 samples equals 0.024%. Since this is well within the expected uncertainty of the laboratory method nothing should be done to the Oil Adjust value. If it was consistently different in either direction then the average difference should be added or subtracted to the WIC Calibration Adjust.

## **WIC Spot Verification Procedure**

The purpose of this procedure is to verify a (WIC) (Water-In-Crude analyzer) for use in a pipeline crude oil application. It is assumed that proper sampling, laboratory and handling procedures have been implemented.

### **1. Obtain a Sample:**

1.1. Prepare 3 clean sample receivers not larger than 100 ml. Assure that the selected laboratory method is available and appropriate for the water cut to be seen.

1.2 Upon arrival at site of sampling, verify that the WIC is seeing relatively constant water cut so that sampling will be over very small changes in water. Assure line flow rate is appropriate for pulling samples. The more steady a reading is the more likely a good sample can be obtained. If the WIC display is not close to the sample point, have another technician observe the reading while the sample is being pulled.



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1.3. Using a waste bucket, purge the sample port line of existing liquids and then grab a sample into the container without shutting off the flow in the sample line until an appropriate amount of liquid has been accumulated.

1.4. Write down the information in the attached form for the conditions at sampling. This is data for water cut, temperature, WIC Calibration Adjust and known density of the crude. Keeping track of the adjustments in the WIC is important. If the analyzer reads 0.00% water cut at any point in the data collections, an adjustment to the WIC Calibration Adjust should be made to always see a small positive number on the display. If this is not done the calculated number could be negative as this would not be displayed on the WIC.

1.5. Pull two additional samples and label them accordingly. Assure that the water cut is not changing quickly and therefore the sample will not represent the WIC reading.

## 2. Process the Samples:

2.1. Using the ASTM recommended procedures for centrifuge, KF or distillation process the sample noting the results on the line with respect to the sample number. Process the samples taken within ½ hour of the collection if possible.

2.2. If an on line densitometer is not available, laboratory density can be obtained by having another sample pulled at the same time which will be large enough to use a hydrometer. Keep that sample separate from the water cut sample. Recognize that this density will be different from the flowing density obtained by an on line densitometer unless it has been corrected to standard temperature.

## 3. Process the Data:

3.1. Calculate the Error column on the data sheet by taking the Laboratory water cut and subtracting the observed water cut on the analyzer.

3.2. Determine the Average Error for the three samples. At the bottom of the Error column calculate the Average Error by summing all of the numbers in the Error column and dividing by the number of samples.



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- 3.3. Accept the results if the average error is within that expected for the API method used (reproducibility) and the water cut is not significantly different between the three samples.
- 3.4. If the difference between the samples and the WIC are consistently different in either direction then the average difference should be added or subtracted to the Calibration on the WIC.
- 3.5. Maintain a log of all results as shown in Table 2.

### Example WIC Spot Sample Verification DATA SHEET

Sample ID	Date/Time	Operator	WIC Cal Factor		WIC Water %		Lab W/C%		Error
1									
2									
3									
Summary results				` WIC Average		Lab Average		Average Error	
1									
2									
3									
Summary results				` WIC Average		Lab Average		Average Error	
1									
2									
3									
Summary results				` WIC Average		Lab Average		Average Error	
1									
2									
3									
Summary results				` WIC Average		Lab Average		Average Error	
1									
2									
3									

Table 2. Spot Sampling Statistics



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## **WIC Performance Comparison to Composite Sampler Procedure**

Automatic sampling is typically conducted through the use of proportional samplers. If automatic sampling procedures are used, a manual procedure should also be in place for use when the automatic system is out of service or for intermittent verification of the automatic system reading. For more information, API MPMS, chapter 8.2, sections 7 to 15, provide further details on flow conditioning, probe location, and sampling frequency.

Other requirements for automatic sampling:

- Containers made of suitable material for handling and storage of the sample must be used. Container lids must be vapor tight.
- All sample containers must be cleaned and dried prior to collection of the next sample.
- Sample containers must allow adequate room for expansion and content mixing, taking into consideration the temperature of the liquid at the time of filling.
- The sample containers must be housed in a secured enclosure to prevent any tampering with the sample.
- Sample lines must be as short as practical and sloped downward to reduce the possibility of plugging up the sample line.

Use Flow Weighted Average calculations for the WIC based on the same timing as used for the composite sampler pacing. Be certain that all totals for the WIC are also zeroed at the beginning of a batch. Provide software which can display at the site DCS the results of the Flow Weighted WIC at the end of a batch.

Once the batch has ended and results obtained for both the Composite Sample and the WIC a comparison table should be maintained versus time and batches similar to that in Figure 3. Since the WIC data is at process temperature and pressure no corrections should be made for the comparison unless it is done in real time and applied to the WIC Flow Weighted Average.

### **Process the Data:**

The data in Figure 3 should be processed using a Control Chart where the data is shown on a chart along with the standard deviation (2 or 3 sigma) and the data centered on the mean value. With this chart and sufficient batches an expectation of performance for the WIC Flow Weighted Average results across time compared to the Composite Sampler results can be determined. This would

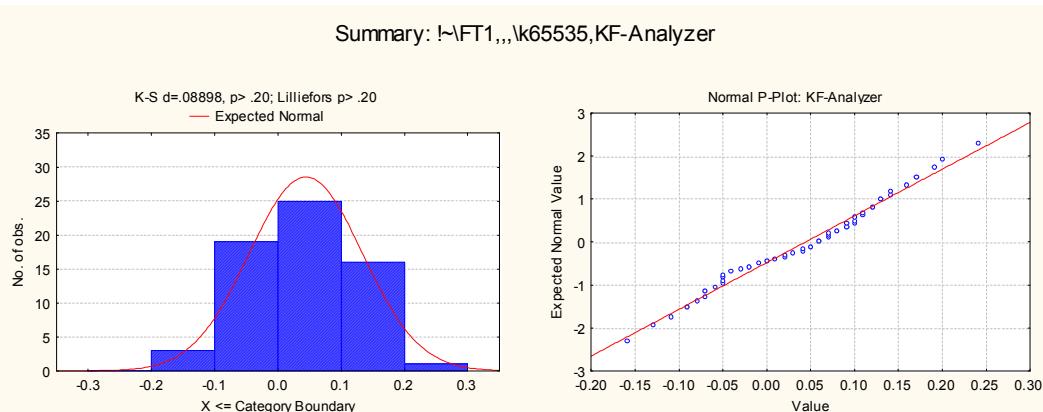


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be useful if something happens to the Composite Sampler the WIC results might be accepted in place of the missing results.

## Example WIC & Composite Performance Results DATA SHEET

**Table 3. Composite & WIC Statistics**



Summary Statistics: !~\FT1,,,\k65535,KF-Analyzer  
Valid N=64  
Mean= 0.044063  
Minimum= -0.160000  
Maximum= 0.240000  
Std.Dev.= 0.089384



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## **Example WIC Flow Weighted Average Single Batch Comparison to Composite Sampler DATA SHEET**

**BATCH ID:** \_\_\_\_\_

**BEGINNING DATE/TIME** \_\_\_\_\_

**ENDING DATE/ TIME** \_\_\_\_\_

**TOTAL BATCH SIZE** \_\_\_\_\_ BBLS

**AVERAGE FLUID TEMPERATURE** \_\_\_\_\_ DEGREES F

**AVERAGE FLUID DENSITY** \_\_\_\_\_ API OR KG/M3

**WATER CUT ANALYZER (WIC) FLOW WEIGHTED AVERAGE** \_\_\_\_\_ %

**COMPOSITE SAMPLE #1** \_\_\_\_\_ % WATER

**COMPOSITE SAMPLE #2** \_\_\_\_\_ % WATER

**COMPOSITE SAMPLE #3** \_\_\_\_\_ % WATER

**CALCULATE AVERAGE SAMPLER WATER %** \_\_\_\_\_