Recommended Practice for Field Analysis of Crude Oil Samples Containing from Two to Fifty Percent Water by Volume

API RECOMMENDED PRACTICE 87
FIRST EDITION, AUGUST 2007

EFFECTIVE DATE: FEBRUARY 1, 2008

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Upstream Segment

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Introduction

This Recommended Practice addresses analytical methods for determining water content in crude oil streams for production allocation measurement applications, where the relative water fraction is higher than those normally encountered in custody transfer measurement applications. Generally, the measurements in these applications are made on the liquid outlet of two-phase (i.e. gas and liquid) separators. However, they may also be made on the oil outlet of three-phase (i.e. gas/oil/water) separators which also may experience high water contents in the oil outlet. In all cases the water content amounts encountered are generally much higher than the water content amounts in custody transfer measurement situations.

Other than the API *Manual of Petroleum Measurement Standards* (*MPMS*), Chapter 20.1, measurement standards have focused on sampling and analysis for custody transfer applications with relatively low water content (0 % to 2 % by volume). Likewise, ASTM sediment and water (S&W) analysis procedures have specifically targeted low water content applications (less than 2 % by volume) since this has been considered to cover most fiscal measurement situations.

However, with the higher financial risks and construction costs associated with offshore deep water production installations or production fields in late-life, most facilities, at some point in the life of the field incur fiscal allocation situations whereby the streams are commingled prior to final oil/water separation. In order to minimize costs, these installations are forced to install fiscal allocation metering and sampling at non-ideal locations. Consequently, fiscal allocation measurements are often made on crude oil streams with water content levels up to 50 %. For this reason the API Upstream Allocation Task Group instituted a project to conduct tests and make the recommendations contained herein.

Summary of Project

In order to facilitate these recommendations the API Upstream Allocation Task Group undertook a project to research the subject and perform tests under controlled laboratory conditions. Following is a summary of the project:

Phase I—Research

The primary outcome of this phase was the review of a published report [*Hi Water 2: The Measurement of Hi Water Content Oil/Water Mixtures by Electronic Methods* from the National Engineering Laboratory (NEL)]. This report was used as a guide for sampling in the intended water content range.

Phase II—Testing

A limited amount of laboratory testing under controlled conditions was conducted on two crude oil types in order to establish analytical methods and application criteria. The two crude oil types were only categorized as a “light” and “heavy” crude oil respectively (see Table 6 in Annex A). Furthermore, only one laboratory and one operator conducted the tests.

For these reasons, the testing results should not be considered as providing a basis of precision and bias evaluation. These data are intended only as guidance in an area that has not been specifically addressed by any other recognized measurement standard. Furthermore, no widely-published industry tests (i.e. data) on stream mixing for water content applications above 2 % exist. Therefore, a procedure documenting the requirements for extracting a representative sample from the flowing stream does not exist. Excerpts from the final project report are included in Annex A.

Recommended Practice for Field Analysis of Crude Oil Samples Containing from Two to Fifty Percent Water by Volume

1 Scope

The purpose of this document is to provide the user with recommended ‘field’ methods of sampling, sample handling and analysis for high water content streams up to 50 % water on a volumetric basis. In particular, this RP was developed giving consideration to offshore installations (both floating and fixed platforms). These installations are generally subject to motion and vibrations, have minimal laboratory equipment, and perform S&W analysis with multi-skilled operations personnel as opposed to laboratory chemists. The techniques described, however, are also applicable to onshore locations.

This document provides design and operating guidelines for sampling, sample handling and sample analysis of high water content streams, up to 50 % water by volume. As a guide, this RP targets a relative accuracy of 5 % of reading up to a maximum of 50 % water content as a qualifier for the various methods described herein. For example, the corresponding absolute accuracy for a 10 % water content stream is ± 0.5 % and for 20 % water content is ± 1.0 %.

This recommended practice may involve hazardous materials, operations, and equipment. This RP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this RP to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

The laboratory testing contained within this RP (see Annex A) is based on a single laboratory—single operator set of results. As with other API standards for field S&W determination methods, no precision and bias calculation was performed and therefore, no inter-laboratory or round robin style testing was performed. The results of the testing of the various methods are primarily intended to provide a general comparison between different methods to facilitate operational choices.

2 References

2.1 Normative

API *MPMS* Chapter 8.2 (ASTM D 4177), “Automatic Sampling of Petroleum and Petroleum Products”

API *MPMS* Chapter 10.2 (ASTM D 4006), “Determination of Water in Crude Oil by Distillation”

API *MPMS* Chapter 10.3 (ASTM D 4007), “Standard Test Method for Water and Sediment in Crude Oil by the Centrifuge Method (Laboratory Procedure)”

API *MPMS* Chapter 10.7 (ASTM D 4377), “Standard Test Method for Water in Crude Oils by Potentiometric Karl Fischer Titration”

API *MPMS* Chapter 20.1, “Allocation Measurement”

ASTM D 95[1], *Standard Test Method for Water in Petroleum Products and Bituminous Materials by Distillation*

2.2 Informative

a) *API High Water Content Project—Phase II Analytical Test Methods—Final Report*, May 5, 2005.

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[1] ASTM, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428-2959, www.astm.org

b) National Engineering Laboratory (NEL) Joint Industry Project Final Report: *The Measurement of High Water Content Oil/Water Mixtures by Electronic Methods* (published in 1998).

c) Taylor, B. N., *Guide for the Use of the International System of Units (SI)*, NIST Special Publication 811, 1995 Edition.

d) Taylor, B. N., *The International System of Units (SI)*, NIST Special Publication 330, 2001 Edition.

3 Terms and Definitions

The majority of terms used in this RP are defined within API *MPMS* Chapter 20.1 or other related chapters and are therefore not defined here. Following are the terms that are specific to this RP:

3.1
aliquot
A small portion of a larger sample which is analyzed in a laboratory and assumed to represent to whole sample.

3.2
bubble point (in non-stabilized hydrocarbon liquids)
The lowest pressure at which the liquid remains fully in the liquid state (see also gas break-out).

3.3
gas break-out (in non-stabilized hydrocarbon liquids)
The act of dissolved gas coming out of liquid solution and residing as free gas within the predominately liquid flow (see also bubble point).

3.4
jet mixer
A system of pump(s) and nozzle(s) where a small portion of a stream is extracted and pumped and then re-injected through a nozzle back into the stream in order to provide turbulence within the stream and mix free water and oil such that a representative sample may be extracted at a point downstream.

3.5
lab mixing system
A system similar to an automatic sampler circulating mixing system but located in a laboratory where it is used to re-mix a large sample for aliquot delivery.

3.6
slip stream (in single phase liquid flows)
A stream or bypass line of approximately the same velocity as the main stream utilized for extracting representative proportional-to-flow samples (sometimes referred to as fast loop).

3.7
static mixer
A series of internal obstructions designed to use the flowing velocity force of the stream to mix and evenly distribute water throughout the pipe cross-section.

4 Symbols and Abbreviated Terms

4.1 Symbols and Nomenclature

±	plus or minus
ρ	“rho” stands for density

°C	degrees Celsius
°F	degrees Fahrenheit
°API	degrees API gravity
[abs.]	absolute; meaning absolute error
cP	centipoises
ft/s	feet per second
g	grams
mL	milliliter
m/s	meter/second
psi	pounds per square inch (pressure)
[rel.]	relative; meaning relative error
RPM	revolution per minute
S&W	sediment and water
V	volume

4.2 Abbreviated Terms

API	American Petroleum Institute
ASTM	American Society for Testing and Materials
MPMS	*Manual of Petroleum Measurement Standards*
NEL	National Engineering Laboratory

5 Sampling and Stream Mixing

As mentioned above, there has been no widely-published industry testing conducted for sampling of high water content streams. Research on sampling conducted by API which eventually became the basis for the development of API *MPMS* Chapter 8.2 was limited to testing of streams with a maximum of about 2 % water content. Higher water content streams may act differently for various reasons such as the presence of a water-continuous phase or simply the relatively higher mass of the water in proportion to the total stream.

The most widely published high water content stream controlled test was the Joint Industry Project (JIP) identified as *Hi Water-2: The Measurement of High Water Content Oil/Water Mixtures by Electronic Methods* conducted at National Engineering Laboratory (NEL) in East Kilbride, Scotland (final report published in 1998). Although the primary test objective was the testing of electronic on-line analyzers, fast loop or bypass sampler systems were also included in the test. The range of the NEL test with regard to water fraction was from 10 % through 90 % by weight or about 8 % through 80 % by volume at pipeline velocities of 3 ft/s to 10 ft/s (1 m/s to 3 m/s) in a 4-in. (10-cm) pipe size. Therefore, the results of these tests were used in making the recommendations regarding sampling and mixing contained herein. More information on the NEL testing results are listed in Annex B.

5.1 Automatic Sampler and Stream Mixing Recommendations

Since no specific testing has been conducted for this recommended practice, a conservative installation design approach should be taken. Furthermore, lighter crude oil or condensate presents the greatest difficulty in acquiring representative samples. This is due to phase separation which depends on the density difference between water and crude oil and a relatively lower emulsion viscosity. Higher viscosity emulsions tend to suspend water better than lower viscosity emulsions. Therefore, light crude oil applications should be considered to be more difficult than heavier, more viscous crude oils. Following are the recommendations for stream mixing and automatic sampling systems:

1) The design of the automatic sampling system, inclusive of the probe, extraction tubing, receiver, and sampler circulating/mixing system should be in accordance with API *MPMS* Chapter 8.2. Additionally, in-line mixer systems should be employed on all high water content situations regardless of the stream velocity. API *MPMS* Chapter 8.2 provides that in-line mixers are not needed if the velocities are sufficiently high. However, this only applies to low water content situations.

2) The recommended installation includes a properly designed static mixer or a jet mixer. The orientation should be in a vertical down flow pipe. The sample probe (for automatic or spot samples) should be within two to three pipe diameters from the exit of the mixer.

3) If vertical down flow is not a viable option, a vertical up flow orientation is also adequate provided a mixer is installed upstream and that the stream velocity is sufficient so that water droplets will not ‘back flow’.

4) If a vertical orientation is not possible the sample probe may be installed in horizontal pipe, provided a mixing device is installed upstream. The sample probe should be located immediately downstream of the mixer since higher water content streams tend to separate into a layered oil/water flow very quickly.

5) All in-line mixing will likely cause gas break-out in non-stabilized crude oil streams. Therefore all mixing and sampling devices must be located downstream of any associated metering equipment.

5.1.1 Water Injection Tests

Regardless of the installation, it is recommended that a water injection verification test be conducted in accordance with API *MPMS* Chapter 8.2. Furthermore, it is recommended that the entire sampler system (in-line mixer, sample probe, receiver plus mixing system) be included in the testing.

The optimal time (possibly the only time) to conduct this type of test is early in the life of the field before the wells begin to produce significant fractions of water at the sampling point. Thus, the baseline stream water content will (hopefully) be low (e.g. less than 5 %), which will enhance the accuracy of the test. Sea water or production water may be used since the densities are similar. The water injection point should be sufficiently far enough up stream of the mixer and sample probe in order to minimize any test-induced effect on the flow pattern. Since the water fraction is relatively large, both the water and oil meter should have an accuracy of ± 1 % or better.

Automatic sampler container and circulating/mixing systems should also be tested in accordance with API *MPMS* Chapter 8.2. The container/spray bar/mixing system test may be conducted as part of the water injection test or it may be tested separately. If testing the container/mixer system separately, a sample of ‘dry’ oil should be obtained from the sales point, a baseline water content of the sales oil established by analysis and then mixed with incremental amounts of water with tests covering the normal expected range of water content. This test will not only confirm the mixing capability of the system but also provide guidelines for mixing times under normal use.

The acceptance tolerances for water injection testing per API *MPMS* Chapter 8.2 were developed for low water content streams. Thus, for high water content streams, these acceptance tolerances should be increased accordingly and should be a function of the uncertainty of the metering equipment and the analysis. As a guide, the acceptance tolerances should be ± 5 % [rel.] of the actual test point. Following is an example of the recommended tolerances:

Table 1—Water Injection Testing Tolerances

Water Content	Tolerance [abs.]
2 %	± 0.1 %
10 %	± 0.5 %
20 %	± 1.0 %
50 %	± 2.5 %

5.1.2 Stream Mixer Placement

Typically, crude oil flowing from a separator is at or near bubble point pressure. A static mixer may create a pressure drop of up to 15 psi (100 kPa), which causes a gas break-out immediately downstream of the mixer and consequently upstream of the sample probe creating a two-phase flow at the sample probe. There are no definitive control test results of the effects of two-phase flow on sampler performance. Therefore, for the purpose of this RP it is assumed that:

1) The effect of two-phase flow (assumed to be no greater than 5 % gas by volume) does not prevent the sample probe from extracting a representative sample, and;

2) For most relevant applications (i.e. separator liquid outflows) a static mixer will induce 5 % or less gas by volume in the stream.

However, if it is known that more free gas will be present at the sample probe, this RP may not be applicable. Furthermore, no meter types currently in use for separator liquid outflow measurement are capable of tolerating large amounts of free gas (i.e. two-phase gas/liquid flow regimes). Gas breakout upstream of and at liquid meters is a significant contributor to measurement error. Therefore, the mixer and sampler should always be located downstream of the meter, but upstream of a back-pressure control valve. This configuration minimizes metering errors while achieving near single-phase liquid conditions at the sample extraction point.

5.2 Sample Acquisition

5.2.1 Sample Acquisition from Automatic Sampler Systems

Each aliquot should only be taken directly into the laboratory glassware for analysis while circulating within the sample container mixing system. Sample container mixing systems can over-mix the oil/water mixture resulting in a tight oil/water emulsion. Therefore, tests should be conducted to determine optimal mixing times for analysis.

5.2.2 Acquiring Spot Samples

Spot sampling for water content is typically employed for well test applications and may be used in other allocation measurement situations. When taking spot samples and especially for well tests, there should be a sufficient number of representative samples taken for average water content to be determined. For well tests it is preferable to take samples every two (2) hours or frequently enough to represent the flows over any cyclical flow pattern. Non-representative samples should not be used in determining average water fraction. Spot samples taken downstream of a separator dump valve where the water fraction may vary from 100 % water to 100 % crude may seriously bias results. Similarly, for high water content streams, changes between the oil-continuous and water continuous phase may bias results. Spot samples should be taken only after adequately purging the sample probe and any attached sample line.

5.2.3 Spot Sample Extraction Apparatus

It is primarily recommended that the sample probe location within the pipe cross-section and the inlet configuration be in accordance the provisions of API *MPMS* Chapter 8.2. Furthermore, due to the high level of water content and the gravitational effects which cause in-pipe separation, it is recommended that the probe be located in vertical pipe section within two or three pipe diameters downstream of a static mixer.

Alternatively, for spot sampling locations in horizontal pipes or where no specific mixing elements are used, it is recommended that these locations be confirmed as providing adequate results during the water injection tests as described in 5.1.1.

As an exception to the provisions above, well test or other related spot samples taken directly from a test well riser or other piping located directly downstream of a choke are typically well mixed (without a mixer) and should also be representative, provided a probe is installed and that, in the case of a test separator, the test separator is operated in two-phase mode. However, for cases of three-phase test separators, it is normally better to meter the water outflow and sample/analyze the oil outflow in order to determine the total produced water of the well.

A full open ball valve should be installed with $^1/_4$ in. to $^3/_8$ in. (6 mm to 10 mm) tubing which should be continually sloped and without kinks, loops, high or low spots or fittings where water could accumulate. Spot samples shall be taken only after entire sample tubing has been purged at least once.

6 Sample Handling and Mixing

6.1 Sample Handling

Unless an aliquot is delivered directly into the analytical glassware such as from the sample container mixing system or a spot sample probe, the entire sample must be analyzed in order to obtain accurate (unbiased) water content. This is because the water portion of the sample will separate in the capture/transfer container very quickly. The result is a disproportionate amount of the water at the bottom of the sample container which precludes the sub-sampling operation.

If samples must be taken using containers too large to analyze in their entirety (for example, for transportation to shore based or offshore/field laboratories), a circulating laboratory mixing system is required. When the sample arrives at the laboratory and has separated into two phases (oil and water) the entire sample must be re-mixed and a sub-sample analysis may be performed.

Alternatively, after measuring the total volume of the entire sample, the free water may be removed from the oil phase and volumetrically measured. Subsequently, the residual oil phase will be remixed, sub-sampled, and analyzed for water content. The water content of the oil-phase and the free water volume will be mathematically combined to determine the overall water content.

Spot samples may be taken directly into the analytical glassware (such as centrifuge tubes or graduated cylinders whereby the entire amount is analyzed). Likewise an aliquot may be taken directly from an automatic sampler mixing system into glassware. In these cases the analysis of the contents of the glassware is generally considered valid for the stream or the entire contents of the automatic sampler.

6.2 Laboratory Sample Mixing Procedure

Based on industry observation, the use of a high speed (13,000 rpm to 22,000 rpm) shearing mixing device inserted into a cylinder or jar is not considered to be an adequate mixing device for high water content samples greater than about one liter. Stirring or agitation of the separated samples will not adequately mix the contents for aliquot sub-sampling. Therefore, it is recommended that a lab mixing system of the following design be used:

- 1 gal to 5 gal (4 L to 20 L) sample container size.
- A variable speed pump (speed based on viscosity/volume/density).
- Circulating tubing of 0.5 in. (12 mm) diameter with a static mixer.

— Tee style sample extraction connection.

The recommended sample mixing procedure consists of:

— Empty the entire sample into the container, or for portable sample containers, attach to the laboratory sample mixing apparatus.

— Mix for the proper amount of time.

— Remove aliquots for analysis.

7 Test Apparatus Measurement Integrity

7.1 Glassware Verification Requirements

Regardless of the analytical method used, the glassware must be accurate throughout the entire range of use. Centrifuge tubes, even those certified with an ASTM stamp may only be verified in the conical section of the tubes. Graduated cylinders are not typically used for precision measurements and therefore should be verified or calibrated prior to use.

The glassware may either be verified and/or calibrated by the vendor or by an onshore qualified laboratory. All glassware should be etched with a serial number for audit trail so that corrections, if required, may be correlated with printed tables.

7.2 Test Equipment Verification Procedure

Glassware verifications and or calibrations may be conducted by adding distilled water measured with a gravimetrically (by weigh system) calibrated burette or by gravimetric methods only.

For water density purposes, the laboratory density meter should have the following specifications:

Table 2—Density Meter Specifications

Parameter	Item	Specification
Density	Range	0 g/cm^3 to 3 g/cm^3
	Accuracy	± 1 g/cm^3 $\times$ 10^{-4} g/cm^3
Temperature	Range	± 10 °C to + 70 °C
	Accuracy	± 0.1 °C

Weigh scale devices utilized for weighing the filled glassware should be of an appropriate range. They should only be used in the upper portion of the calibrated range where the resolution is best. The laboratory weigh scales should be calibrated before and after service with no zero reading error in excess of the tolerance given in the following table over the above calibrated range after service.

Table 3—Weigh Scale Resolution

Calibrated Range	Reading Resolution	Zero Tolerance
0.5 g to 150 g	0.1 g	0.1 g
10 g to 5000 g	1 g	1 g
100 g to 10000 g	10 g	10 g

Graduated cylinders should be calibrated throughout their scale. For example, in a 1000 mL cylinder the top portion (700 mL to 1000 mL) is critical for the total oil/water mixture volume and the lower portion (100 mL to 500 mL) is critical for the oil/water interface or water volume portion. Therefore, the entire scale needs to be calibrated.

Centrifuge tubes that are to be filled to the 50 mL graduation (adding 50 mL of solvent) need only to be calibrated from about 1 mL to the 50 mL graduation. The reading of the meniscus (top or bottom) should be stated within the calibration table. The calibration points for standard 8 in. (203 mm), 100 mL conical centrifuge tubes should be at every mL graduation for 1 mL to 6 mL, 8 mL, 10 mL and at each 5 mL increment graduation up to 50 mL.

An example of the recommended calibration table for 8 in. (203 mm), 100 mL centrifuge tubes for high water content applications is provided in Table 4.

Table 4—Centrifuge Tube Calibration Table Example

Tube Marking (mL)	Actual Volume (mL)
1	1.2
2	2.3
3	3.2
4	4.1
5	5.0
6	6.0
8	8.0
10	10.0
15	15.0
20	20.0
25	25.0
30	30.5
35	35.0
40	41.0
45	46.0
50	51.0

Similar calibration tables should be generated for graduated cylinders.

8 Analytical Methods

This RP is intended for field use, with an emphasis on offshore (floating and fixed platforms) facilities that have inherent motion and vibration. Typically, the tests are conducted with limited laboratory equipment by multi-skilled operators (i.e. not specifically skilled lab technicians or chemists). Therefore, the methods considered were primarily those that are readily deployed consistent with this type of work environment.

8.1 Overview of Methods Considered

8.1.1 Test Methods Considered Viable for Offshore Use

The following analytical test methods were determined to be viable for offshore and remote field use and are described in detail below.

a) Centrifuge method;

b) Graduated cylinder method;

c) API *MPMS* Chapter 10.2 / ASTM D 4006 distillation (reduced sample size).

NOTE This method is deemed as a referee method to be performed on shore or in an established (not a field) laboratory.

8.1.2 Test Methods Considered but Rejected for Offshore Use

a) Reduced volume (10 mL), API *MPMS* Chapter 10.2 / ASTM D 4006 distillation method, was considered for offshore use but eliminated due to the need to gravimetrically measure the sample to a high level of precision. While equipment may improve in the future, it is inferred herein that precision weigh scales required for this method can not be effectively used on offshore facilities. However, as stated above, this method has been designated as the onshore referee method.

b) Distillation method (ASTM D 95) with standard, 200 mL crude oil sample and 20 mL trap with pet cock drain. The tests conducted as a basis for this RP demonstrated that large amounts of water in the sample caused violent boiling problems with subsequent condenser eruption.

c) Pre-separation graduated cylinder method of determining water content of the remaining oil phase by distillation (API *MPMS* 10.2 / ASTM D 4006) or Karl Fischer titration. This method was abandoned due to inherent problems in obtaining a representative aliquot sample from the larger oil phase sample.

d) Reduced sample size centrifuge tests (API *MPMS* 10.3 / ASTM D 4007) with the intent to increase the resolution through readability of scale (oil/water interface readings in the conical section for better resolution). This method was abandoned since results were better using the volume specified in the standard centrifuge test method.

e) The Karl Fischer (KF) titration method is considered to very precise and may be applicable for high water content samples. However, in this method as the water content increases the injected KF sample volume must be reduced because of reagent dilution. Therefore, precision weigh scales are required, which do not function well, or at all, when they can not be positioned on a motionless foundation such as is typical on offshore facilities.

8.2 Centrifuge Method

The centrifuge method (API *MPMS* Chapter 10.3 / ASTM D 4007) is the most widely accepted laboratory (and field) analytical method in fiscal applications for several reasons:

- industry test results are well documented;
- good precision with minimal bias;
- inclusion of sediment;
- applicable for a wide range of crude oil types (insensitive to color, density, viscosity, sand, composition and salinity);
- ease of use;
- speed of results; and,
- relatively low-cost apparatus.

However, the design of the standard tubes and associated apparatus of the centrifuge method (i.e. graduations and shape of tubes, heat blocks and centrifuge) are intended to primarily address water fractions only up to 2 %.

In the laboratory testing for this RP, the centrifuge method which is a modified test method based on API *MPMS* Chapter 10.3 / ASTM D 4007, yielded acceptable results over a range of 2 % to 50 % water content (see Annex A). Results obtained from control tests on both light and heavy crude oil samples were typically within ± 1 % [abs.] of the reference. However, since the centrifuge tube is primarily designed for accuracy at low water contents, there are additional critical steps and procedures that must be followed.

8.2.1 Centrifuge Method Procedures

a) Refer to API *MPMS* Chapter 10.3 / ASTM D 4007 regarding laboratory procedures, and requirements for solvents, demulsifiers, and centrifuge equipment.

b) Centrifuge tubes should be standard 8-in. (203-mm), 200 mL conical shaped tubes with graduations not to exceed 1 mL increments, as prescribed in API *MPMS* Chapter 20.1, Section 1.7.3.5.

c) Centrifuge tubes should be calibrated and verification numbers etched in accordance with 7.1. Corrections to readings should be applied where applicable.

d) Samples should be taken directly into the centrifuge tubes if they can be filled exactly to the 50 mL graduation (i.e. no volume reduction due to foam). It is critical that the total volume be measured precisely for samples with high water content. (For example, at the 50 % water content level a 1 mL reading error in total volume results in a 1 % error in net oil content.)

e) If foaming prohibits filling tubes to exactly 50 mL, an alternate method may be used. This method allows:

1) Filling tubes to approximately 50 mL (without being exactly at 50 mL).

2) Summing the total sample volumes from two or four tubes.

3) Dividing the sum of the water volumes by the sum of the total volumes. Regardless of the actual total volume amount (i.e. not exactly 50 mL), Equation 1 still applies.

8.2.2 Automatic Sampler Centrifuge Analysis Procedure

a) Run sample receiver circulating pump/mixer for appropriate time to insure homogeneous mixture and representative aliquot samples.

b) While circulating pump is running, fill two or four centrifuge tubes to exactly 50 mL graduation after the sample has settled from foaming.

c) Add 2 to 3 drops of demulsifier per API *MPMS* Chapter 10.2 / ASTM D 4006 to ensure a definite, clear interface without emulsion layer.

d) Add 50 mL of water saturated solvent per API *MPMS* Chapter 10.2 / ASTM D 4006.

e) Stopper, mix by inverting ten times, heat to 140 °F (60 °C) and centrifuge per API *MPMS* Chapter 10.2 / ASTM D 4006.

f) Place tubes in a rack to ensure vertical orientation.

g) Read the interface volume.

h) Add the volume for two tubes or sum the volume of four tubes and divide by two.

If an emulsion layer is present after the initial spin, add additional two to three drops of demulsifier, mix by inversion, heat to 140 °F (60 °C) and spin again. For heavier, viscous oils laden with sand, this process may require repeat centrifuge of two to three times with possibly longer spin times until no emulsion layer is detected. Do not attempt to estimate the water fraction of the emulsion layer.

8.2.3 Transfer Container used for Sample Handling

If circumstances do not allow for samples to be taken directly into the centrifuge tubes (i.e. spot samples for well tests) and a transfer container must be used, the total sample must be analyzed as follows:

a) Extract a 200 mL sample directly into a 'collection' graduated cylinder so that the total volume may be estimated. An appropriately sized graduated cylinder should be used (e.g. no greater than 1000 mL total volume).

b) Fill four centrifuge tubes to the 50 mL graduation. If there is insufficient sample to supply exactly 200 mL, fill three tubes to the 50 mL graduation and add the remainder to the fourth tube, draining the entire amount of the graduated cylinder.

c) Read and record the total volume of all four tubes.

d) Use solvent to rinse residue oil from transfer graduated cylinder into the last centrifuge.

e) Centrifuge and calculate the S&W % as below.

8.2.4 Centrifuge Method Calculation of S&W %

The sediment and water fraction is determined by the following formula:

$$\text{S\&W \%} = \frac{\sum \text{Volume}_{\text{S\&W}}}{\sum \text{Volume}_{\text{Total}}} \times 100 \tag{1}$$

Regardless of sampling method or analytical procedure, the water content fraction must be reported at metered conditions. For high water content applications corrections for the difference in thermal expansion factors of water and oil should be applied in accordance with API *MPMS* Chapter 20.1, Section 1.9.6.

8.3 Graduated Cylinder Method

There are no published API or ASTM standards for the graduated cylinder test method. Because of its simplicity, the method is used for allocation measurements and is applicable for some high water content situations. The graduated cylinder method is applicable for relatively light crude oils with a low viscosity. Heavier crude oils with higher viscosity may take 24 hours or longer to produce a clean phase break even if placed in a heated bath. Therefore, the graduated cylinder method is not recommended for heavy crude oils. However, it is best suited for light crude oils or condensates less than 850 kg/m^3 (> 35° API Gravity) with low viscosity (< 10 cP @ 100 °F) and relatively high water content (> 10 % water content).

The graduated cylinder test is very simple and consists of taking a sample directly into a verified or calibrated 500 mL or 1000 mL cylinder, adding demulsifier, placing it in a water bath for a period of time until a clean oil/water interface break is demonstrated. The water fraction is calculated simply by dividing the water volume by the total volume.

Due to inherent sample handling and transfer problems, the graduated cylinder method may be ideal when (spot) samples cannot be taken directly into centrifuge tubes. The major disadvantage of the graduated cylinder method is that due to the lack of any externally imparted force (i.e. centrifuge), the separation time may be up to 12 hours or more depending on the viscosity of the crude oil emulsion. Conversely, an advantage of the method is that a water bath temperature equal to the metered stream temperature avoids any independent thermal expansion corrections.

Graduated cylinders may be made of glass or plastic. Standard 1000 mL graduated cylinders with 10 mL graduations are typically used. Before using the cylinders, they must be verified or gravimetrically calibrated throughout the range using distilled water and precision weigh systems.

8.3.1 Graduated Cylinder Procedure

a) Using sampling procedures included above, samples are taken directly into the graduated cylinder so that it is approximately 80 % full (e.g. 800 mL in a 1000 mL cylinder). Note the stream temperature.

b) Add six drops of demulsifier to a 1000 mL cylinder (proportionally less or more for different sizes).

c) Place the cylinder in a temperature bath ± 5 °F (3 °C) of the stream temperature. Continue controlling the temperature bath until a clear or definite oil/water interface is visibly apparent.

d) Read the total volume, water volume and the emulsion volumes. Readings should be from the bottom of the meniscus on total volume readings and at the indicated interface for others. All measurements should be recorded to nearest mL by estimating between graduations.

e) If a sufficiently large enough emulsion layer persists, remove 100 mL of the emulsion using the calibrated burette filler draw method. Two methods are available for analyzing the emulsion layer:

1) Place 50 mL in two 8-in. (203-mm), 100 mL centrifuge tubes and follow the centrifuge procedures as described in 8.2 to determine S&W (%).

2) Extract a sub-sample with appropriate apparatus and perform a Karl Fischer Titration Test.

f) If temperature is not controlled at the stream temperature or varies by more than ± 5 °F (3 °C) of stream temperature, independent volume correction factors for water and oil shall be applied in accordance with API *MPMS* Chapter 20.1, Section 1.9.6.

8.3.2 Graduated Cylinder Calculations

Referring to Figure 1, Graduated Cylinder, the water content is calculated as follows:

$$\text{S\&W (\%)} = \frac{[V_w + (V_e \times \text{S\&W}_E)]}{V_T} \times 100 \qquad (2)$$

where

V_T is the total volume of the sample in the graduated cylinder;

V_E is the volume of the emulsion layer ($V_E = V_T - V_W$);

V_W is the volume of the free water in the graduated cylinder;

$\text{S\&W}_E$ is the water content of the emulsion layer as % by volume.

NOTE In the graduated cylinder method, the oil phase above the emulsion layer is assumed to be free of water.

8.4 Reduced Volume Distillation Method (Laboratory Referee Method)

The reduced volume distillation method follows API *MPMS* Chapter 10.2 / ASTM D 4006 standard. This method uses a 10 mL gravimetrically measured sample size (called “reduced sample”). In the laboratory testing it was found to be the most repeatable and controllable (see Annex A). This method yielded accurate results without bias from crude oil

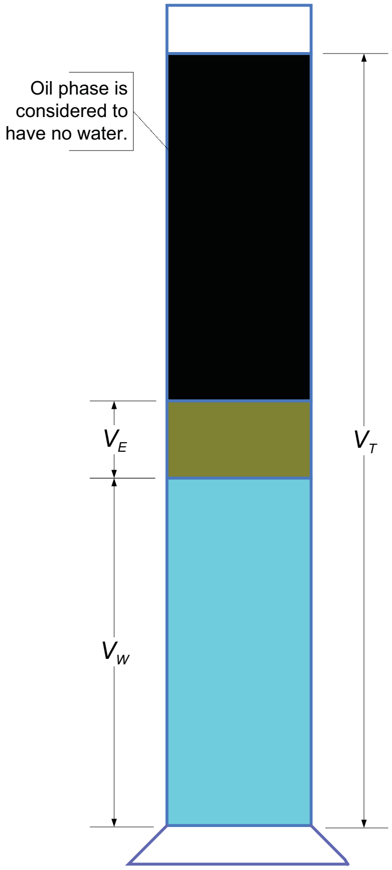

Figure 1—Graduated Cylinder

type. Therefore, the reduced volume distillation method (API *MPMS* Chapter 10.2 / ASTM D 4006) is considered to be the 'referee' laboratory method for high water content samples up to 50 % water content by volume.

API *MPMS* Chapter 10.2, Section 10.2.7.2.1 / ASTM D 4006, Section 7.1.2.1 suggests the use of a 10 mL sample size for water content between 25 and 50 % by weight. This method is ideally suited for the 5 mL trap and will provide accurate results (within ± 2 % [abs.]) provided the weigh scale is precise and API/ASTM sample handling procedures are adhered to. However, the distillation method is not commonly used in the field since it requires greater time, delicate glassware and constant attention by the technician. Two very important criteria must be met to achieve the expected precision:

a) The 10 mL sample volume tolerance (uncertainty) should be no greater than ± 0.05 mL.

b) The 10 mL aliquot sample must be obtained directly from a circulating system such as the mixer described in 6.2.

8.4.1 Reduced Volume Distillation Method Procedures

The recommendation for this method is to follow the procedures as prescribed by API *MPMS* Chapter 10.2, Section 10.2.7.2.1 / ASTM D 4006, Section 7.1.2.1, which describes the distillation method using a reduced sample. Furthermore, the 10 mL sample size and the 5 mL trap size are optimal for the range of water contents and uncertainty targets of this RP.

Annex A

Laboratory Testing Results

This annex documents the test results for various analytical methods performed under the direction of the API Upstream Allocation Task Group in 2005 under laboratory controlled conditions. The complete report is entitled, *API High Water Content Project—Phase II Analytical Test Methods—Final Report*, May 5, 2005.

A.1 Summary of Testing

Following is a summary of the various tests conducted as well as test methods considered but not attempted.

1) Graduated cylinder method using standard 500 mL and 1000 mL cylinders depending on sample size.

2) Centrifuge method (API *MPMS* Chapter 10.3 / ASTM D 4007) using standard 100 mL crude samples and calibrated, 8-in. (203-mm) conical shaped tubes (with 1 % minimum increment);

3) Distillation method (API *MPMS* Chapter 10.2 / ASTM D 4006) using reduced sample size (gravimetrically measured, 10 mL approximate).

The following tests were attempted but not included in the RP due to analytical problems:

4) Pre-separation graduated cylinder method which consists of draining free water from the 1000 mL graduated cylinder with pet cock and determining water content of the remaining oil phase. The water content of the residue or oil phase is determined by distillation, centrifuge or Karl Fischer titration (API *MPMS* Chapter 10.7 / ASTM D 4377) methods and added to the free water.

5) Heavy oil tests with the graduated cylinder method was suspended for highest water content samples due to separation time requirements.

6) Centrifuge tests with reduced sample size in order to increase resolution through readability of scale (interface readings in conical section) was abandoned due to the inability to obtain more accurate results than with the standard centrifuge test method volume.

7) Distillation method (ASTM D 95) with standard, 200 mL crude oil sample and 20 mL trap with pet cock drain. The increased amount of water in the sample causes violent boiling problems with subsequent condenser blow out.

In order to eliminate the possibility of skewed results, the reference blend water content was not determined until the test result was recorded. All of the above test measurements except for the reduced volume distillation method were intended for field use. The reduced volume distillation method is intended to be used as a referee/onshore laboratory method utilizing weigh systems.

A.2 Reference Water Content Determination

All of the reference blends were determined gravimetrically using calibrated weigh scales and a laboratory densitometer. The laboratory density meter had the following specifications:

Range: 0 g/cm^3 to 3 g/cm^3

Accuracy: ± 1 g/cm^3 $\times 10^{-4}$ g/cm^3

Temperature Range: – 10 °C to + 70 °C with accuracy of ± 0.1 °C

The weigh scales used for determining the mass of each component and glassware used are as follows:

Table 5—Weigh Scale Devices

Model	Calibrated Range	Reading/Resolution
A	0.5 g to 150 g	0.1 g
B	10 g to 5,000 g	1 g
C	100 g to10,000 g	10 g

The above weigh scales were all calibrated within three months prior to the tests with no error correction required over the above calibrated range after service. In order to minimize uncertainty, the most appropriate/accurate weigh scale was used for each blend component. Based on the above, the estimated uncertainty of the water content in the reference blends was typically between ± 0.1 % and 0.2 %.

Reference Blending Procedure and Calculations

The procedure for preparing each test point blend was as follows:

1) Clean and weigh the glassware to be used.

2) Pre-wet the oil transfer glassware (typically one quart jars) to minimize any non-representative adherence to the glassware.

3) Heat the transfer glassware to 140 °F (60 °C).

4) Heat oil and water samples to 140 °F (60 °C).

5) Combine and homogenize the blend.

The reference blend calculations are based on gravimetric measurements of oil and water and converted to volume by dividing by the respective density at 140 °F (60 °C). Following are the associated equations:

$$\text{Ref. Water Content (Vol/Vol \%)} = \frac{\text{Volume}_{\text{Water (60°C)}}}{\text{Volume}_{\text{Water (60°C)}} + \text{Volume}_{\text{Oil (60°C)}}} \times 100$$

$$\text{Volume}_{\text{Water (60°C)}} = \frac{\text{Mass}_{\text{Water}}}{\rho_{\text{Water (60°C)}}}$$

$$\text{Volume}_{\text{Oil (60°C)}} = \frac{\text{Mass}_{\text{Oil}}}{\rho_{\text{Oil (60°C)}}}$$

The final reference water content is adjusted by adding the baseline water content for the respective test method, if appropriate.

A.3 Reference Oil Data

Table 6—Reference Oil Data

Crude Type	API Gravity (° API)	Viscosity @ 100 °F (cP)
Light	33.4	7.77
Heavy	22.8	49.7

A.4 Graduated Cylinder Method Test Results

Table 7—Graduated Cylinder Method Results for Light Oil

Reference (%)	Reading (%)	Difference/Error (%)
5.74	5.47	– 0.27
11.63	11.40	– 0.23
19.29	18.80	– 0.49
33.24	32.44	– 0.8
47.4	47.39	– 0.01
Average Error: – 0.36 % [abs.] (without shear mixing) Error Range: – 0.8 % to – 0.01 %		

Table 8—Graduated Cylinder Method Results for Heavy Oil

Reference (%)	Reading (%)	Difference/Error (%)
5.68	5.15	– 0.53
11.66	11.51	– 0.15
Average Error: – 0.34 % [abs.] (after 24 hours)		

A.5 Centrifuge Method Test Results

Table 9—Centrifuge Method Results for Light Oil

Reference (%)	Reading (%)	Difference/Error (%)
2.27	2.10	– 0.17
5.58	5.6	+ 0.02
11.76	12.25	+ 0.49
19.47	20.50	+ 1.03
36.03	35.50	– 0.53
41.03	41.5	+ 0.47
49.51	50.0	+ 0.49
Average Error: + 0.25 % [abs.] Error Range: – 0.53 % to + 1.03 %		

Table 10—Centrifuge Method Results for Heavy Oil

Reference (%)	Reading (%)	Difference/Error (%)
2.35	2.30	– 0.05
5.87	5.60	– 0.27
12.24	12.50	+ 0.26
19.42	19.25	– 0.17
37.83	38.50	+ 0.67
41.25	41.50	+ 0.25
48.98	49.50	+ 0.52
Average Error: + 0.17 % [abs.] Error Range – 0.27 % to + 0.67 %		

A.6 Distillation (API *MPMS* Chapter 10.2 / ASTM D 4006) Method Test Results

Table 11—Distillation Method Results for Light Oil

Reference (%)	Reading (%)	Difference/Error (%)
11.87	11.925	+ 0.055
18.937	19.1	+ 0.163
41.795	40.925	– 0.87
Average Error: – 0.22 % [abs.] Error Range: – 0.87 % to + 0.163 %		

Table 12—Distillation Method Results for Heavy Oil

Reference (%)	Reading (%)	Difference/Error (%)
12.166	12.075	+ 0.091
19.238	19.3	+ 0.062
41.665	39.90	– 1.765
Average Error: – 0.53 % [abs.] Error Range – 1.765 % to +0.091 %		

Annex B

Prior NEL Testing

In the NEL Hi Water JIP tests, the sampling system employed is described as follows:

> A fast loop sampler system which is common in many areas utilizes a steam or bypass line of approximately the same velocity as the main stream (called a “slip stream”). The NEL sample probe has a 90° inlet ‘scoop’ nozzle facing upstream with a 30° chamfer on the inside of the tip. The (external) ‘cell’ sampler grabs a sample from the bypass sample loop.

In the Hi Water JIP at NEL, the sampler was located in a horizontal section of pipe where maximum oil/water separation was expected to occur (i.e. worst case). A jet mixer was installed immediately upstream of the sample inlet probe.

With regard to the sampler results, the NEL Hi Water JIP tests reported that the retrieved sample was typically within ± 1 % [abs.] of indicated (metered) water content when the jet mixer was 100 % operational. However, even when the mixer was at full operation, the sampler did indicate an average negative bias (sampler results less than that based on meters) in the overall results of – 0.37 % [abs.].

The NEL did not cover all applications with regard to high water content stream sampling since the test equipment did not conform to some configurations typically used in offshore operations. For example, in some areas the static mixer is more prevalent than the jet mixer and the insertion probe is installed directly in the main carrier pipe instead of the bypass line. Also the range of oil densities and viscosities in the NEL tests covered a limited range.

For the purposes of this RP, the following conclusions were derived from the NEL report:

1) It is possible to homogenously mix high water content (segregated streams) in horizontal pipes sufficiently to dynamically extract representative samples over a wide range of velocities and water contents.

2) For velocities ranging from 3 ft/s to 10 ft/s (1 m/s to 3 m/s) in horizontal pipe, additional mixing aides (other than inherent mixing from frictional forces related to velocity) must be employed for representative sampling.

3) The minimum velocity guidelines stated in API *MPMS* Chapter 8.2 for horizontal pipe installations without upstream mixing devices are not adequate for all high water content streams. The threshold water content, at which the API *MPMS* Chapter 8.2 minimum guidelines become inadequate was not precisely concluded for the report.

4) For the purpose of this recommended practice, it is also assumed from the NEL report that the isokinetic insertion type sample probe may be used to extract a representative composite or spot sample from a well-mixed high water content stream. It is also assumed that the 45° beveled, fixed probe (bevel facing upstream and tip in the center $^1/_3$ of the pipe) may be used to extract a representative composite or spot sample. However, the stream must be well-mixed and the sample must be taken dynamically after sufficiently purging the entire probe and associated tubing system.

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