Towards the Unmanned Platform

Crude Oil Quality Measurement.

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Summary

Reduction in manning requires the simplification of the measurement of product quality by reducing the need to operate and maintain complex sampling systems. At this point, concerns over the bias and repeatability of a Water Content Analyser (WCA) has prevented their universal acceptance. By deploying on-line density and a WCA in conjunction with a spot sampling technique will enable calibration of these on-line devices and confidence, ultimately, in their use as the primary measurement devices; thus allowing simplification to the design and operation of sampling systems.

Introduction

Traditionally (Fig. 1) the chain of uncertainty in quality measurement comprised:
- a sample probe within the pipeline,
- a sampler controller and
- a sample receiver
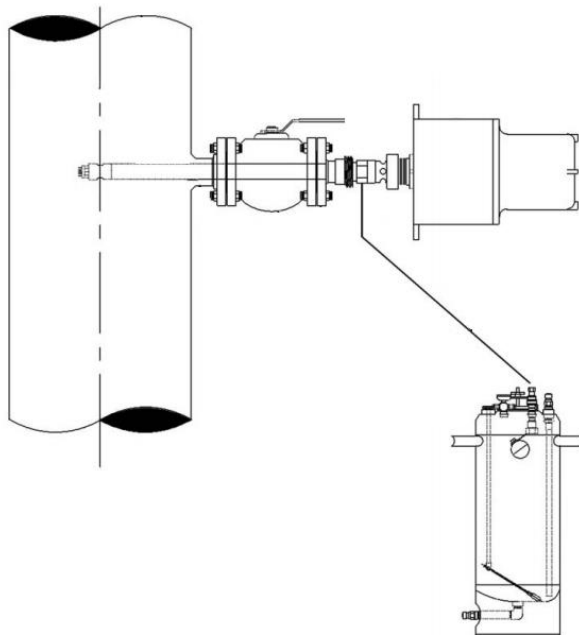
There was no focus on ensuring that the hydrocarbon/water was adequately dispersed at the sample point, nor indeed towards how the sample container was remixed in the field or laboratory to render the analysis aliquot representative of the whole, which in those days was normally determined by centrifuge or in some cases distillation.

Rising commodity prices from the early 1970's oil shocks stimulated the desire to minimise measurement uncertainty. Given that crude oil usage is currently near to 100 million bbls per day, small fractions in measurement accuracy either in physical volume or quality (useable product) represent huge sums of money. Meeting the required uncertainties and performance can be a complex endeavour. (Fig 2, 3.)

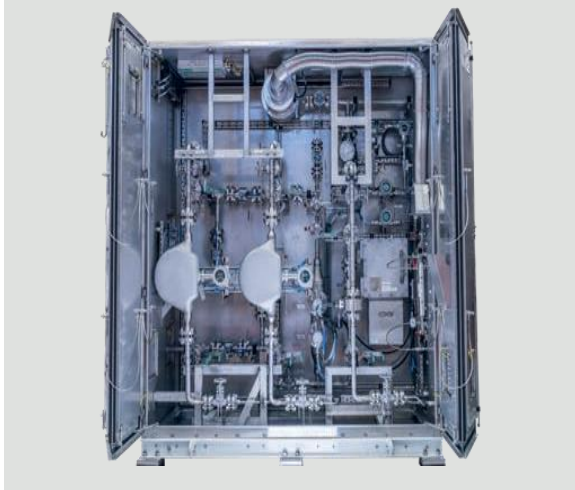*Figure 1- Traditional (simple) Sampling System*

Figure 2 - Analyser Housing - Density, WCA, Flow, Manual Sampling, Pressure and Temperature

Figure 3 - Sampler Housing – Samplers and sample collection vessels (High Pressure)

Water can come from a number of sources including from water flood or ingress to the storage or processing systems, but the majority of water found in crude oil originates primarily during genesis. This wet, organic material became buried in silt below a marine environment. During recovery, this saline material becomes emulsified as the oil-water mixture passes through items such as choke-valves on its way to the surface. In this phase secondary water can be accreted, sometimes deliberately. This composite water-in-oil emulsion is inherently unstable and settling begins immediately and some becomes manifest as free-water in the bottom of tankers and storage vessels. This poses a significant challenge if an accurate determination needs to be made on the 'true' water content of a consignment of crude.

In any measurement, there is uncertainty within the various processes and measurements within the system which ultimately contribute to its overall accuracy and uncertainty. This is often referred to as the chain of uncertainty. The more factors involved will ultimately result is higher uncertainties; it is therefore of value to minimise the number of steps in this "chain of uncertainty".

The chain of uncertainty in today's measurement systems (see Fig. 4) recognises all the steps involved in the generation of the "number" being used to value the quality of the product, including the handling and analysis of the sample itself. Unfortunately, different standards refer to the sampling and sample handling API MPMS Chapter 8.2, 8.3, and (typically) 10.9, so the overall uncertainty is a combination of the performance rendered by each of these standards. Within the ISO standard 3171, the allowance on PAT is +/- 0.05% from 0-1% total water and +/- 0.05% per 1% above that limit and over time most systems tested have been able to meet these constraints. The API MPMS Chapter 8.2 widened these boundaries somewhat from about 1994 onwards but demanded that two sequential tests met the requirements to prevent the tests being repeated until a single run met the lower uncertainty values. Many tests are now performed that capture the tighter requirements of the ISO with the two sequential test regimens demanded by API.
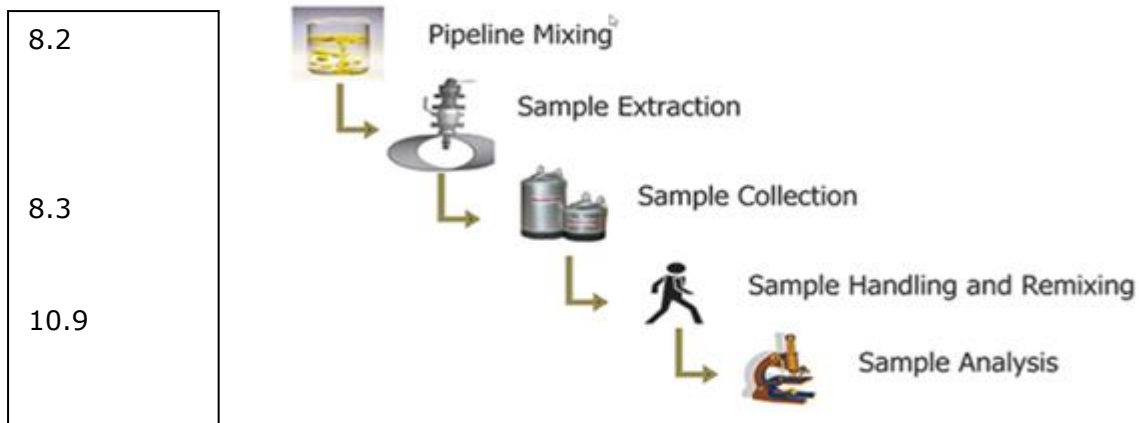
8.2	
	Pipeline Mixing
	Sample Extraction
	Sample Collection
8.3	Sample Handling and Remixing
10.9	Sample Analysis

Figure 4 - "Chain of Uncertainty" [3]

An ideal measurement system would be able to place an on-line quality measurement device directly into the flowing stream and render a fiscally representative result. While it is possible to have a full-bore device, these tend to be intrusive, expensive and hard to handle in the event of any required maintenance. In addition, pipeline mixing will be required to prevent them being subject to a stratified flow regime.

If we could assure the accuracy of on-line measurement, we could eliminate the uncertainties associated with the extraction, collection, handling, subsampling, laboratory handing, aliquoting and analysis steps! (The last three steps shown in the above graphic plus those associated with the analytical method, typically Coulometric Karl Fischer titration.)

Measurement engineers and accountants ignore any steps in the measurement chain at their peril!
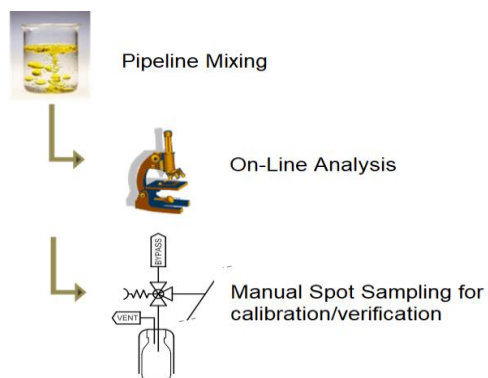

Figure 5 - Simplified Chain of Uncertainty

As the industry moves forwards, both the capital and the operational costs of deriving measurement data come under increasing scrutiny. Labour costs (particularly offshore) are often the largest contributor to the cost of measurement. Sampling is still a fundamentally mechanical process with significant operator input both in maintaining the equipment and in handling and processing the samples derived, with associated health and safety concerns. Reducing these costs and risk by using on-line measurement is a key target. (See Fig. 5)

We should take as a lesson, the application of on-line density measurement. The practice of installing oscillating tube density meters to enable conversion of volume to mass metering (and vice versa) started in the 1970's (See Fig. 6) and there was much pre-occupation with how these devices were to be calibrated. The practice developed that two density meters would be installed in parallel with a pycnometer to allow calibration samples to be taken, the second density meter being a spare. Practice changed quickly due to challenges of calibration "in situ" and soon most installations used one density meter for "pay" and the other for "check" with regular removal and "onshoring" for calibration checks/recalibration.
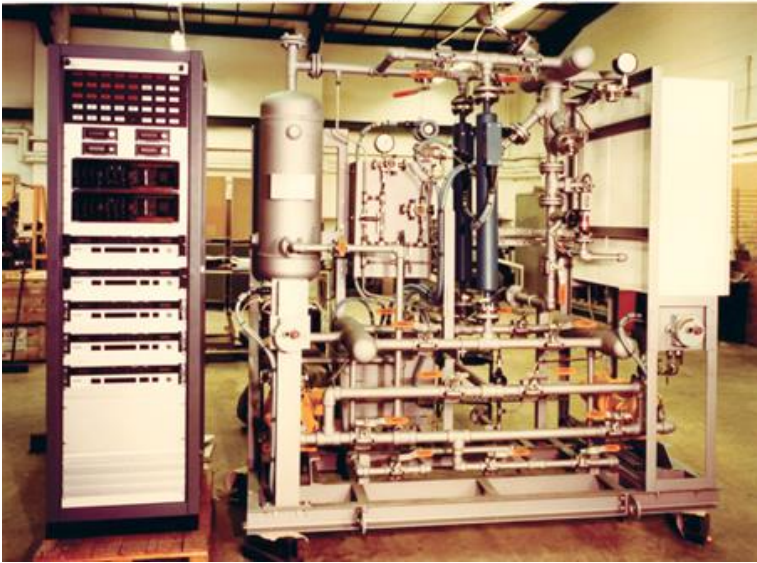
Figure 6 - Early Density Metering system with Pyknometer Ref 5.

We often use density meters to compensate volumetric meters to normalised conditions, but it is worth noting that of itself the "dry oil" density does not typically vary very much within a batch. (see Fig. 7.)
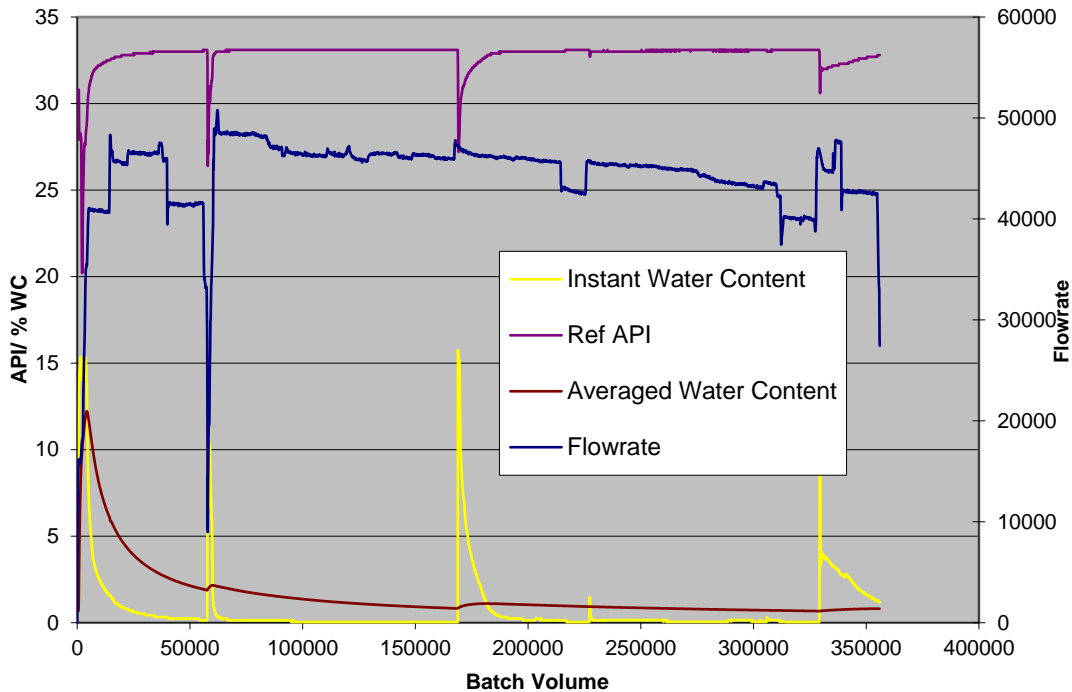

Figure 7 - Ship Unloading [1]

But what of viscosity, water content "Water cut" or other properties such as sediment or sulphur?

Viscosity is not used in valuation of crude oil transfers (provided it meets its overall specifications); on-line viscosity is implicitly a challenge not only in measurement at process conditions, but in converting the process values to Standard Temperature and Pressure (STP) since viscosity/temperature relationships are implicitly non-linear.

Other properties tend to vary less through the duration of a batching process and may as easily served by a manual or "spot" sample.

Samples can be large, with 4 to 10 litres being typical and up to 7O litres being extreme. The reason that we collect a large sample volume for determining water content is that this property changes markedly through batching operations (temporal fluctuation) and renders a property of, in general, negative value as it costs money to process and dispose of water. We typically take a large number of small samples flow proportionally throughout the batch. Beyond pipeline mixing (dispersion quality at the sample extraction position), the second largest contributor to the uncertainty is the grab count. Also, since water settles out from oil in static conditions or at low velocities, it develops both layered and slug flow regimes that can prove impossible to sample representatively using "spot" sampling techniques.

For other properties: density, sulphur etc. not subject to the sample slugging or layering regimes, spot or manual samples are most likely adequate.

We accept the measurement of density to fiscal accuracy "on-line" and we have worked for many years with devices that seek to measure water content. Devices, often very simple gauges of capacitance were developed, and are very useful to indicate trend and switch production streams if the water concentration is too high. The accuracy of these devices was far from suitable for replacing that of a physical, flow proportional, sample; later analysed in the laboratory.

Technology has progressed; microwave and optical methods are now widely in use. Norway was the first country to develop a document focussed on oil-line measurement of water content, the "Handbook of water fraction measurement" (2004). The API worked on a draft standard for "On-Line Water Determination" (OWD) which failed ballot over concerns that the technology was not mature enough to be trusted for fiscal application, it was issued as a technical report as API (TR 2570), and as a guide under the EI (HM 56).

Over the last few years, the field has been revisited and this technology is now identified by the initialism "WCA" (Water Content Analyser). The API/EI are working together towards developing a new standard, API MPMS Chapter 10.10, which hopefully will go to ballot later this year.

Driven by the cost of sample handling and laboratory processing of the physical samples collected from sampling systems, there has been a focus in industry, supported by the ASTM, to develop methodologies for reducing the volume of sample taken from field locations and avoid the additional uncertainties as samples are remixed and processed in the laboratory for water determination using conventional Karl Fischer titration.

Currently, crude oil samples collected in the field via the various homogenization procedures can be analysed for water by several methods. The use of an immediately available field centrifuge is common where an aliquot is heated with toluene and centrifuged, and water and sediment results can be available in about 20 minutes. Though convenient, this method is labour intensive, inaccurate and imprecise.

Other methods involve transporting a field sample to a laboratory for testing, usually by techniques involving Karl Fischer titration. The inherent delay between sample collection and analysis means that a secondary homogenization and potentially a tertiary homogenisation must be applied before a sample aliquot is drawn for testing. This has been a consistent source of error as the optimal conditions for homogenization are dependent on the density, viscosity and water content of the crude. The mixing energy and methodology used also varies according to the geometry and size of the container in which the sample is provided. In addition, the containers must be cleaned, and the excess oil disposed of. Any actions that can reduce the handling, processing and reprocessing of samples will therefore improve the uncertainty of the measurement, reduce costs and provide environmental gains.

Development of API MPMS 10.10

In developing a new draft standard, API MPMS Chapter 10.10, the API is seeking not only to provide guidance but to standardise the use of WCA. The scope requires that WCA must be used in conjunction with "proven" sampling systems. "Proven" being where a Performance Acceptance Test (PAT) has been performed by injecting water into the process stream and validating that the injected water is retrieved within the physical (composite) sample. Unfortunately, PAT processes are close to impossible to perform in many offshore production situations.

Within the development of this standard there has been a significant focus towards ensuring the validation and ongoing verification of the WCA performance, this includes the requirement to compare the Flow Weight Averaged (FWA) results of the WCA to the results from the proven composite sampling system and also proposes the use of manual, "spot" samples for calibration.

It is intended that this new standard encourages the long-term collection and blinded exchange of data so that confidence can be developed in this technology to enable, by itself, such measurements to be used for custody transfer; at which point an update to this standard will be released. (Potentially removing the above condition)

The nature of an on-line measurement of this sort is that it is essentially continuous, whereas the "composite" sample comprises perhaps 10,000 individual aliquots taken at repeatable volume intervals to ensure flow proportionality. To compare these two results, and indeed to use a WCA (beyond trend or limit) it is necessary to take the instantaneous value and average it flow proportionally across the batch being measured ("Flow weight averaging" or FWA).

Other challenges are "excursions" beyond the calibrated ranges of the devices (for example, what happens if it is scaled for 0-5% and there are short term transients that exceed 15%), but these are not to be discussed here.

Calibrating an FWA result from a WCA makes sense, but in the longer term it would be useful to develop methodologies that enable instant calibration/diagnostic measures; for these "spot" or manual samples. But where can these be drawn to assure representivity at that instant that the measure is being taken/recorded?

Some WCA, like sample extractors, density meters, viscometers etc. are "in-line" devices i.e. they are inserted into the main pipeline, others are "flow through" devices like the density meters described earlier and so require installation in a sample/analyser loop. This raises the question as to where the manual sample point should be installed and how can it be validated? For WCA and sample extractors installed "in-line" the manual sample point must be installed either "in", or "on", the main process pipeline, but so doing may present its own challenges in attaining representivity.

Where a WCA is installed in a sample loop, the installation of a manual sample point is significantly simplified as the design of the loop assures homogeneity of the flow through the loop itself. A manual sample point on a properly designed sample loop is analogous to the manual sample point on a laboratory mixer (or indeed that on a fixed receiver installation). In all cases this manual sample point should be verified (proven) against the extreme limits of the process (typically lowest viscosity, lightest/lowest density/API). The draft API standard proposes processes to achieve these goals.
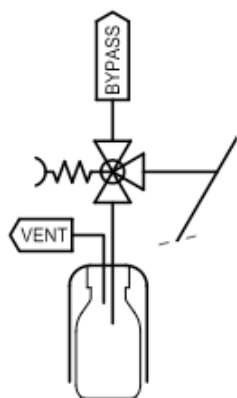
Opportunity

Coupling the developments in WCA technology, automated "spot" sampling and the evaporative KF development by industry renders the opportunity to reduce the complexity of the sampling technology and operations used in field locations.

In the simplest form, the driver to automate their laboratory analytical process could eliminate the need to transport large volumes of sample to the laboratory for remixing and automate the (aliquot) sample handling.

Figure 8 – Spot Sample to Ampoule

The use of spot sampling also enables the validation, and correction, of any bias that may be evident within a WCA system.

Ampoule sampling and analysis

The design of an ampoule-based Karl Fischer analyzer, and an associated ampoule are shown in Figure 9.
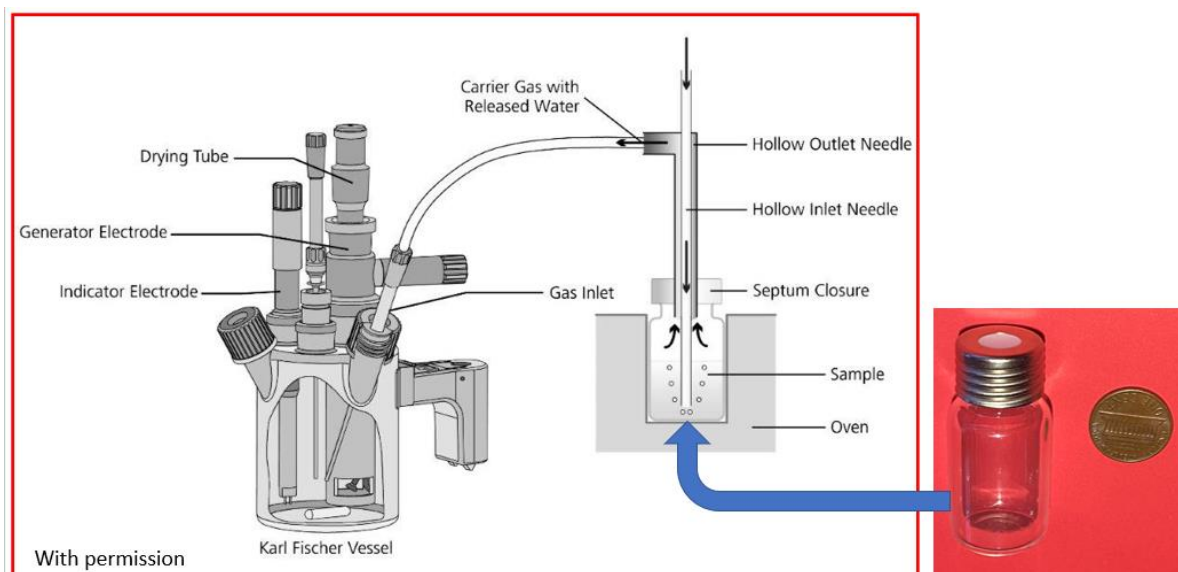

Figure 9 - Ampoule Based Sample Analysis

In the current context a sample for analysis can be drawn from the homogenized oil in the flow loop associated with a fixed sample receiver at the sampling locations described above and deposited into the ampoule which has been weighed and identified before filling and sealed. Note that the ampoule has a septum to allow automated handling.

The current practice is for the ampoule to be filled, weighed and loaded into a laboratory autosampler (not to be confused with the initial autosampler from which this sample was derived) which is designed to transfer the ampoules sequentially to an oven. When in place, a sheathed needle is passed through the sealing septum on the ampoule cap, the oven is heated to around 150°C and hot, dry nitrogen is passed over the sample. This causes quantitative water evaporation and partial oil evaporation and the transfer of these vapors into the Karl Fischer titrator, where they condense into the titrating solution. The

titration then proceeds according the well-established coulometric method and the results automatically communicated to the user.

A critical point is that the water content of the oil in the ampoule is measured in its entirety, and it is irrelevant whether water settling has occurred in the ampoule. Thus, any issues related to settling and secondary non-homogenization are circumvented.

Another important benefit of this procedure is that the non-volatile components in the crude (asphaltenes, inorganic salts, minerals etc.) are not transferred to the titration cell. The absence of these materials allows many more samples to be processed before it is necessary to bring the system off-line for cleaning and the replacement of titration cell chemicals.

In its currently available form this technology is only partially automated. Ampoule filling, sample weighing, sealing and loading into the autosampler are manual operations but with a moderate investment can be upgraded to robotic status.

As this procedure is not yet accepted by API and ASTM, several programs have been completed to demonstrate its's applicability.

One involved collecting about one gallon of eleven crude oils with API gravity values between 17 and 41º and water contents from about 0.03 and 5%. They were homogenized and distributed into 4 250mL bottles. These bottles were re-homogenized and an aliquot immediately drawn and placed into ampoules similar to the ones shown in the figure. The ampoules were then submitted to the oil companies' laboratory and analyzed using the evaporative method described above.

The test data were then analyzed using procedures prescribed in ASTM D6300, to generate a precision statement for method repeatability. This equation is plotted against the existing repeatability statement for Method ASTM D4928, in Figure 10.
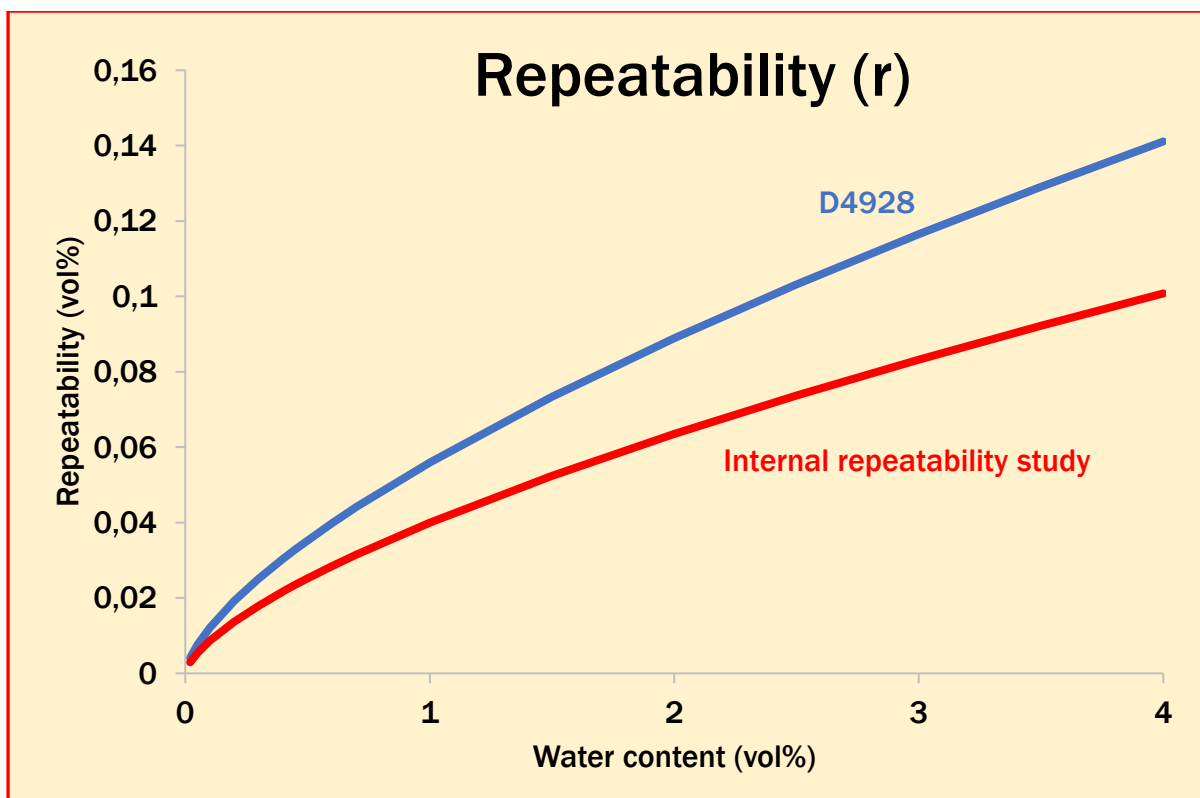
Figure 10 - Repeatability Study

As can be seen the repeatability of the procedure was better in the case of the evaporative procedure. In addition, it can be noted that the range of crude oil API Gravity was 17-41º in the current study, compared to about 35-42º in the D4928 study.

The procedure described, includes an extra step compared to what is foreseen on an automated platform where homogenized samples are transferred directly from the crude oil stream to the ampoules, so a further improvement can be expected.

Removing the requirement to collect the field samples into a large container that must then be transported to the laboratory removes significant handling steps and uncertainties. Other properties of interest are not subject to these sample handling and stratification uncertainties (or temporal fluctuations).

While this work indicates the potential for significant improvements in uncertainty and cost from the field through the laboratory handling process, the real prize is the use of an WCA and density meter in the field and the reduction in the capital expense and operating expense in using an automatic sampling system by eliminating those steps of the process.

Spot sampling to validate WCA
In using microwave or capacitance based WCA for the evaluation of water concentration is largely dependent upon ensuring that the zero offset is correct for the batch.

Extensive testing of the leading vendors technology has indicated that with the correct offset (bias correction), these devices appear capable of fiscal accuracy. The fundamental theory behind most technologies currently available is to measure the dielectric value of the oil/water mix and use the knowledge of the dielectric of the water component and the oil component to determine the ratio between those fractions.

The dielectric value of oil is about 2 and that of pure water around 80, measuring the overall dielectric value enables determination of the water concentration, provided of

course you know the dry oil dielectric value and an appropriate value for the water being measured.

There is a broad correlation between the dry-oil dielectric and the dry oil density and this certainly can improve their performance, but even then, there is a degree of inconsistency that undermines confidence in this approach.
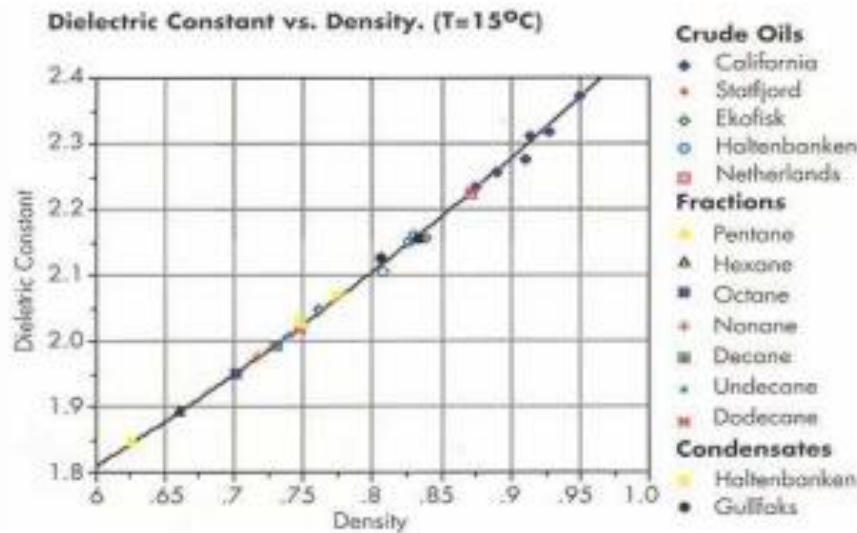

Figure 11 - Dielectric value vs Density [2]

Testing of multiple cargoes grouped by crude type to the same facility show a variance in results. (see Fig. 14)

The challenge is not that WCA are non-linear, but that an accurate understanding of the offset (bias) is required. This can be established by measuring the instantaneous WCA output and comparing it with one or more manual samples taken at specific points of time through a batch.

Manual "Spot" Samples
Spot samples are typically initiated and taken by an operator in the field by taking a sample at the same time point as a reading is taken from the WCA, though there is absolutely no reason why a spot sample could not automatically be removed from the process and placed in an appropriate container. This would still be called a "spot sample". Such a container could be an ampoule (see Fig. 13.) as described above for low pressure systems or a pressurized syringe (see Fig 12) for high RVP systems. The content of the high-pressure syringe could be injected directly to the KF titrator or placed into an ampoule to use the evaporative technique described earlier. In both cases the mass of the empty and full container will be measured and recorded to define the mass of oil being analyzed.

Figure 12 - High Pressure Syringe (Proserv)

Figure 13 - Ampoule (With Septum - low pressure)

The use of high-pressure syringes that allow direct injection to a KF titrator have been used for several years in the North Sea, most recently industry has been developing technology to enable the use of ampoules that best function with evaporative KF techniques.

Either of these spot samples are relatively small in volume/mass and of low risk for transport.

There are a number of vendors who already manufacture manual "spot" samplers with appropriate purging capabilities that could be automated and adapted to this service.

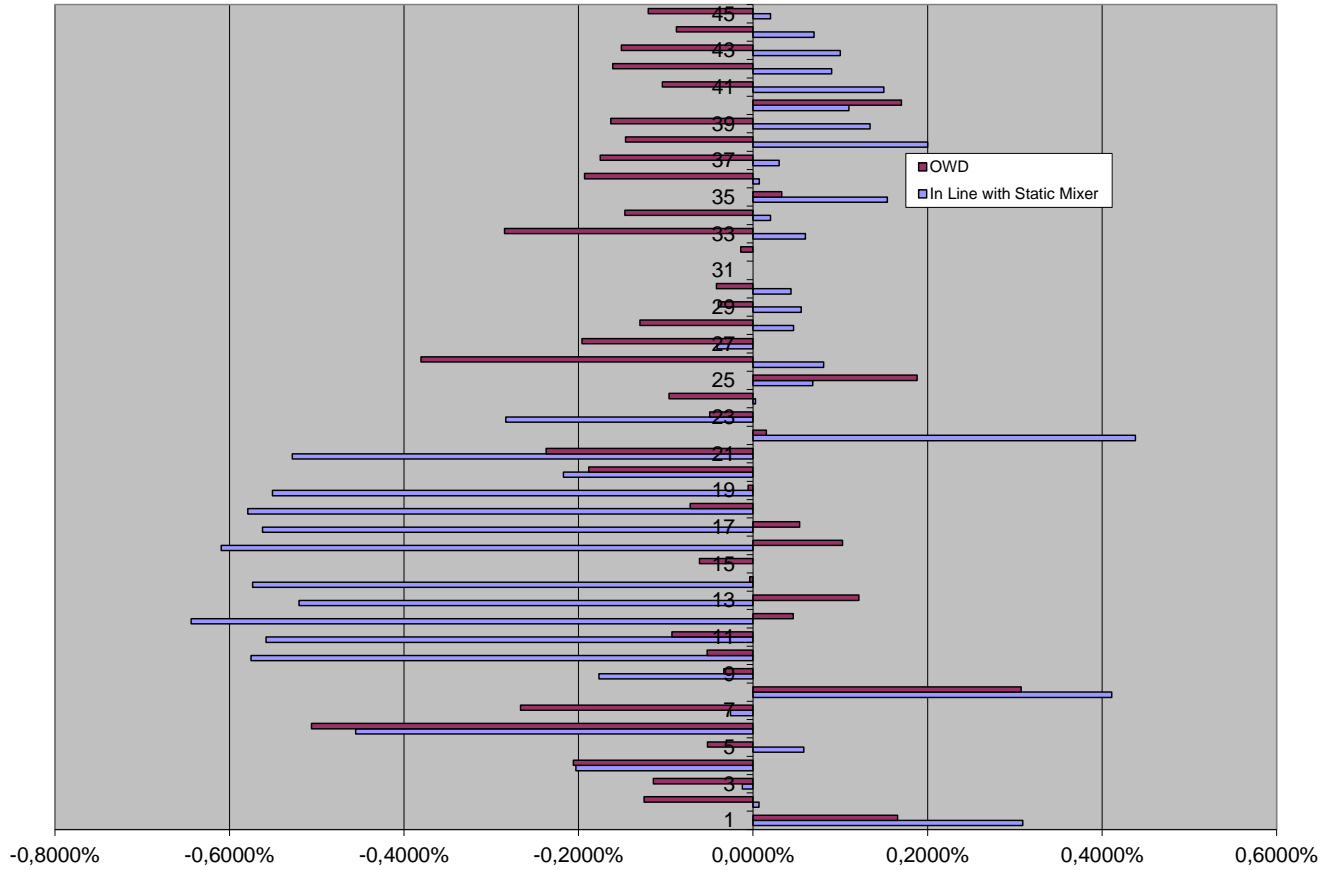**Scatter of results based upon CoJetix as Datum**

Figure 14- Comparison of Proven Composite (Automatic) Sampler – zero datum - to original Sampler and to FWA WCA values per batch)
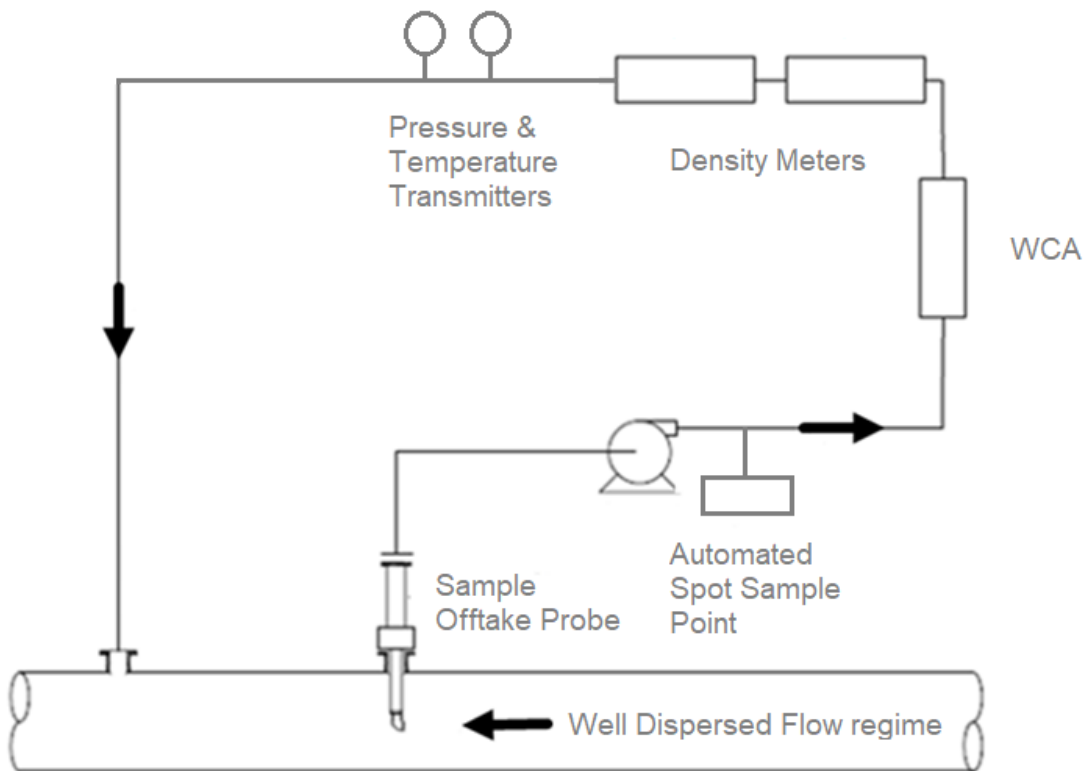
Figure 15 - Schematic of a sampling system comprising pipeline mixing, WCA, spot sample point

Conclusion

Over time it is planned that the industry can gain confidence in the correlation between composite samples, WCA FWA results and between spot samples and instantaneous FWA results.

Establishing confidence in the performance of WCA and using an automated "spot" sampling process, it is easy to see the potential to eliminate the composite sample from the equation.

Spot samples are best delivered at a volume that is simple to transport and does not require secondary mixing, i.e., in an ampoule or high-pressure syringe. Eliminating handling steps always reduces uncertainty in measurement.

A well-designed sample loop (see Fig. 15) with WCA density meters and an automated spot (calibration) sample will remove the requirement for a composite sample which is delivered by a sample extractor and requires the collection, handling processing, analysis, retention and disposal of significant volumes of sample. This would result in simplification of the design of the measurement system, not only in capital but in operating, maintenance costs as well as reducing risk.

References

[1} Jiskoot, M., 2013 – Sampling: What the Standards don't tell you. North Sea Flow Measurement Workshop 22nd – 25th October 2013

[2] Johnsen, J., Martinussen, R., 2007 - Test of a 1 inch Roxar Watercut meter on light condensate with very low water content. North Sea Flow Measurement Workshop 16th – 19th October 2007

[3] Potten, G., Wright, S., 2014 - Methods of Determining and Verifying Fiscal Sampling System Uncertainty by Analysis 25 years of Real Field Proving Data and Laboratory Tests Compared with International Acceptance Criteria. North Sea Flow Measurement Workshop 21-24th October 2014

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