
Copyright 2003, Brazilian Petroleum and Gas Institute - IBP

This paper was prepared for presentation at the *Rio Pipeline Conference & Exposition 2003*, held in October, 22-24, Brazil, Rio de Janeiro.

This paper was selected for presentation by the Event Technical Committee following review of information contained in an abstract submitted by the author(s). Contents of the paper, as presented, have not been reviewed by the IBP. *Organizers will neither translate nor correct texts received.* The material, as presented, does not necessarily reflect any position of the Brazilian Petroleum and Gas Institute, its officers, or members. It's Author's knowledge and approval that this Technical Paper will be published in the *Rio Pipeline Conference & Exposition 2003* "brouchure"

Abstract

Measurement of the quantity, density, average temperature and water percentage in petroleum pipelines has been an issue of prime importance. The methods of measurement have been investigated and have seen continued improvement over the years. Issues of pipeline integrity, product loss and production balances are placing further demands on the issues of accurate measurement. Water percentage measurement, often called water cut, is one area that has not received the attention necessary to understand the uncertainty of measurement. Work done with three major oil companies on pipeline measurement problems will be discussed. Spot sampling comparisons over a two-year period will be shown and uncertainty analysis for this data will be presented. Composite sampling versus on line water cut analyzer results will be described.

Introduction

Composite samplers have been used as the standard by which water content is determined in pipelines. Originally pipelines only shipped products with a narrow range of densities. Today pipelines ship products with extremely large variation in density and makeup. Samplers are typically proved on one type of product with the assumption that it is valid for all densities and types. Results are only available after a batch of product is shipped and there is no recourse if something goes wrong with the sampling system during the batch. The exposure of personnel to hazardous liquids and the errors associated with processing the samples are additional issues.

On line water cut has been attempted using various technologies with disappointing results in the past. Problems with these attempts included equipment that was not capable of the required reproducibility, comparison methods inconsistent with the accuracy trying to be proven and lack of knowledge by the on line water cut analyzer users and vendors. The use of on line water cut measurement would help to reduce

exposure to hazardous products and may improve the uncertainty while providing real time data. On line water cut analyzers will not replace composite samplers anytime in the near future because the samplers have been so well established as a standard. There will also be the requirement to measure the sediment that cannot be performed on line.

Until recently there has not been a good comparison of on line water cut analyzers to composite samplers. Several tests were begun in the first months of 2003, which are producing independent data for comparison. Many tests of water cut analyzers using spot sampling has been done but the real proof must be done against the accepted standard using composite samplers.

Work done with three major oil companies on pipeline measurement problems will be discussed. Spot sampling comparisons over a two-year period will be shown and uncertainty analysis for this data will be presented. Composite sampling versus on line water cut analyzer results will be described.

1 – Uncertainty

The petroleum industry generates and uses volumes of data used to buy, sell and balance production. Unfortunately, the documentation with this data typically does not contain statements of uncertainty. Decisions about expectations and corrective actions cannot be made without a statement of uncertainty typically expressed as a standard deviation from a mean value. Two lines of thinking about measurement uncertainty assessment procedures exist. One organization proposing these procedures is the ISO (International Organization for Standardization) and the other is ASME (American Society of Mechanical Engineers).

The ISO approach classifies two error sources as Type A or Type B. Type A is a method of evaluation of uncertainty by the statistical analysis of a series of observations while Type B is using a means other than the statistical analysis of such a series of data. Type A means it is possible to calculate a mean and standard deviation from data obtained. Type B must have the magnitudes of the mean and standard deviation estimated in other ways such as previous data, manufacturer's specifications, calibration data or data from reference books on a process. Another method to estimate Type B is to obtain the maximum and minimum limits that would contain 100% of all possible values and then estimate the standard deviation from this data. One measurement can have both Type A & B evaluations, then the resultant uncertainty is the square root of the sum of the variances of each type.

The AMSE approach defines two error sources as systematic and random uncertainties. Random error sources create data scatter and this can be improved by taking more data points. Systematic uncertainty requires the source of the errors to be defined before corrective action can be taken. NIST (National Institute of Standards and Technology) cautions on the use of random and systematic saying that these can depend on how you define the variables.

The difference between “error” and “uncertainty” is in the fact that error is the difference between a known standard and the measurement value while uncertainty is a statistical statement about a band in which the true value lies. Systematic error sources create offsets with all of the data by the same amount from the “true value.” A new design of the measurement or improvement in the calibration will reduce the effect of systematic sources. It is possible to have the result after correction of a measurement to have a small error although the uncertainty may be large. Accuracy is a qualitative concept and should not be used quantitatively (use numbers to describe it). NIST recommends that the word “precision” be used carefully. ISO

views that it encompasses both repeatability and reproducibility since it defines these respectively as “precision under repeatability/reproducibility conditions”.

A single measurement may have multiple uncertainty components. Measuring the physical dimension of an “End Gauge” would have the following uncertainty components: calibration of the “standard” end gauge, random and systematic effects of the comparator, thermal expansion of standard gauge, mean temperature of test bed, variation in room temperature. Standard industry literature would identify some of these uncertainties which would be classified as Type B. In the petroleum industry the measurement of water cut using centrifuge could have the following uncertainty components (not all inclusive): sample probe location in the main pipeline (center 1/3, wall, top, bottom), sample probe size, valve type and size, upstream conditioning (mixer, elbow, two elbows), flow rate in main line, flow rate in sample probe, difference in pressure between line and atmosphere, temperature differences between ambient and liquid, sample container material, size and type of seal for lid, volume of sample, time before processing sample, mixing of sample before extraction to centrifuge tube, solvent type used, de-emulsifier type, temperature of centrifuge, oil type and viscosity, type of centrifuge tube, operator reading the meniscus, solids content, and clarity of the water.

2 – Pipeline Measurement

Pipeline balance and custody transfer measurement has become a problem with the great variety of crude oil types, viscosity and densities that are being delivered through pipelines today. The API (American Petroleum Institute) Chapter 8.2 described composite sampler accuracy for densities from 855 to 892.7 kg/m³ and viscosity from 6 to 25 cSt at 40°C while many pipelines

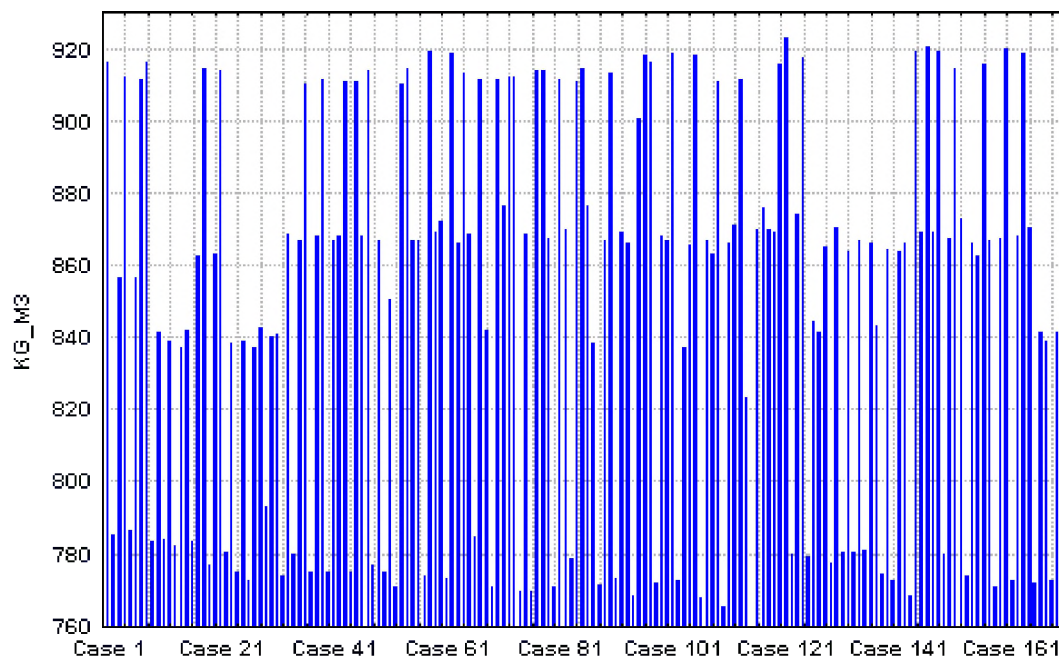


Figure 1. Density Variations USA Pipeline

are now carrying products from 750 to 987 kg/m³ with wide variations in viscosity. Figure 1 shows one pipeline with a density variation from 765 to 925 kg/m³. This increase in the variety of products has been met with difficulty in both physical plant and measurement issues.

Previously methods, procedures and equipment were proven to provide acceptable measurement uncertainty because pipelines worked across narrow crude types. With the changes in the industry new demands are now being made on the performance of equipment and methods for which no standards completely cover today. The following sections will first look at spot sampling and then compare composite sampler results with on line analyzer results.

2 – Spot Sampling Results

The issues about spot samples are better understood when it is clear that each sample is an independent entity. The API guidelines talk about precision with respect to repeatability and reproducibility while discussing a single sample but nothing is stated about sample to sample differences. The data in this section will address sample to sample issues. The results of one analysis method with respect to another can be compared if we take the differences between the two methods and then apply statistics to determine the uncertainty. Some of the systematic uncertainties included in this analysis are; bias of the sample port, operator's methods i.e. obtaining the sample, laboratory's processing of the sample. If there are more personnel involved in each step then the systematic errors may also become correlated and dependent upon the operators as individuals. When the operators change shift the systematic error looks random. Another systematic uncertainty may include the fact that each sample may be a different crude type therefore biasing the water cut value. This bias is not completely removed even when the two methods for comparison are subtracted leaving only the error between methods. One method may still have residual bias from the crude properties.

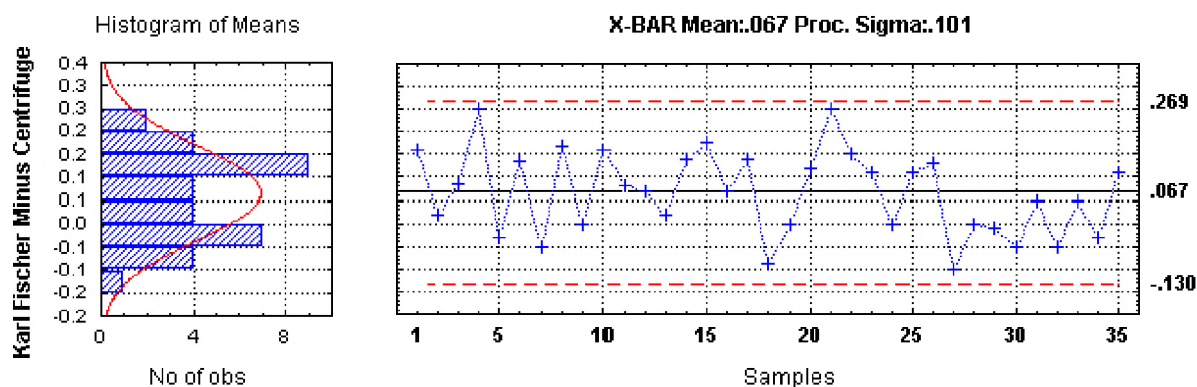


Figure 2. Karl Fischer Titration Minus Centrifuge - First 35 Points
Standard Deviation = 0.101 $2\sigma = 0.202$ X-Bar Mean = +0.067

The data from the pipeline in Figure 2 is for the same single spot sample taken from the pipeline and then processed in the laboratory using Karl Fischer Titration (KF) and centrifuge. Spot samples are useful to establish a water cut analyzer's initial offset value. The first 35 points have a respectable uncertainty of $\pm 0.202\%$ water (2 standard deviations giving a 95% confidence interval) for all data points.

The next 65 data points in Figure 3 show a different story about uncertainty between the KF and centrifuge data for spot samples. The standard deviation went from 0.101% to 0.292% for no apparent reason. After this was brought to the measurement technician's attention the chemicals in the KF system were changed out. A thorough cleaning and replacement of the chemicals returned the uncertainty back to previous levels.

From the above analysis carried over 6 months the centrifuge was more consistent than the Karl Fischer titration at this location. This was because the KF system maintenance was not consistent. Without the centrifuge and data comparison it was not known when the KF was providing data that was unacceptable.

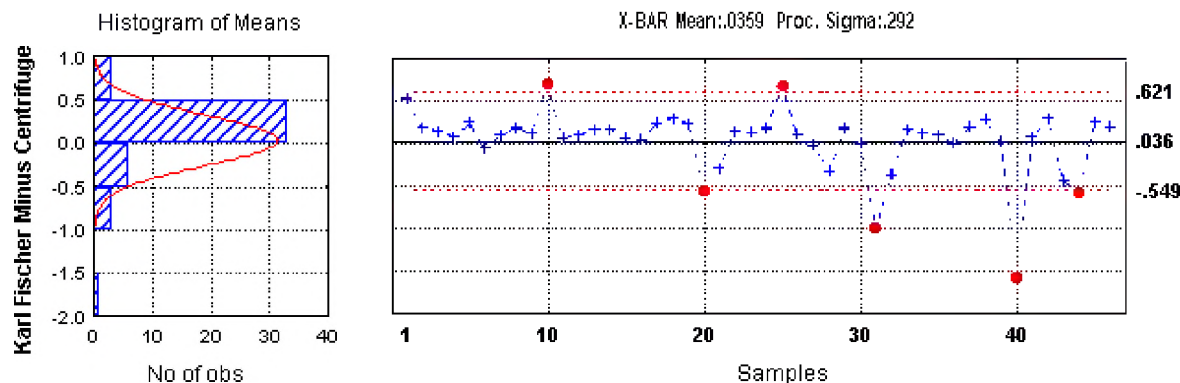


Figure 3. Karl Fischer Titration Minus Centrifuge
Standard Deviation = 0.292 $2\sigma = 0.584$ X-Bar Mean = +0.036 Samples 35 to 100

A water cut analyzer was installed during this same period and comparison samples for KF, centrifuge, water cut analyzer and density using on line and laboratory data were taken. The water cut analyzer gave the uncertainty shown in Figure 4 after 90 data points were taken when compared to the centrifuge. The statistics again was performed on the difference between the two results. The standard deviation was 0.092 with the 95% confidence level then becoming $\pm 0.184\%$ with a mean of -0.069.

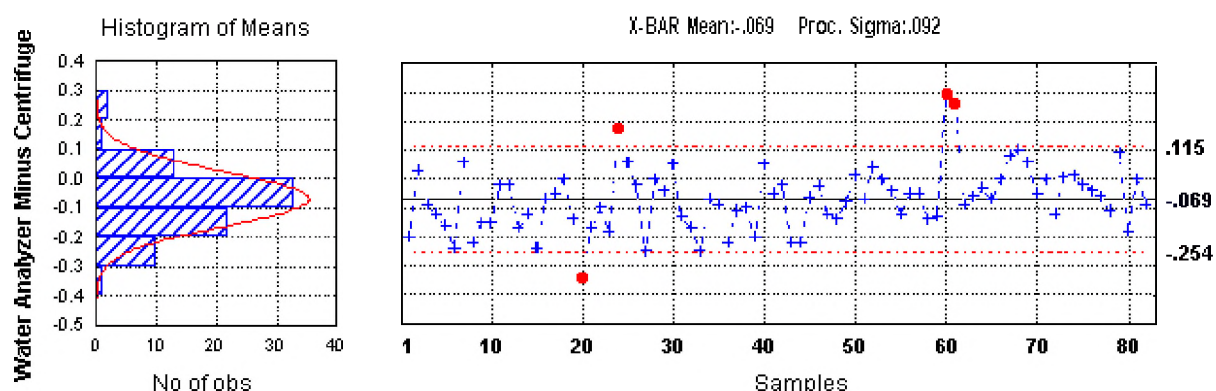


Figure 4. Water Analyzer Minus Centrifuge – 85 Samples
Standard Deviation = 0.092 $2\sigma = 0.184$ X-Bar Mean = -0.069

The use of a two-sigma or 95% confidence interval instead of a single (68.5%) or three-sigma (99.5%) interval is due to review of actual oilfield data and procedures. Real data in the field always have outliers that are generated by operator error or sample handling. Most operators of pipelines will not accept a one-sigma level of confidence because this means that 1 out of 3 samples lie within the confidence interval. They will typically accept 1 out of 20 as reasonable. If a three-sigma (99.5%) is selected the outliers are less than 1 out of 100 which is a goal that is not achievable in the oilfield due to the opportunity for many errors. These errors are a part of

the procedure and methods and are difficult to remove. If three-sigma numbers are stated the confidence interval is large (3 times the standard deviation) and managers of the pipeline will not accept statements of such large uncertainty. There were several data points where very large discrepancies existed between the data collected for the above analysis. These were determined to be “outliers” and therefore, were removed from the data before the analysis. These were usually very large and were obvious to everyone that something went wrong. This could be simply not reading or writing down the correct numbers or reading the screen showing the water cut and pulling a sample during rapidly changing water periods. If the data is reviewed immediately after analysis and a large discrepancy is seen then another sample should be obtained and the analysis confirmed. This is not the typical way things are done in actual practice.

3 – Composite Sampler Results

The standard of the pipeline industry for water is the composite sampler. The results described below were obtained with a water cut analyzer down stream from the composite sampler probe. The data from the water cut analyzer was corrected for density and crude type and is a flow weighted average paced with the composite probe sample.

API Chapter 8.2 covers the design, installation, testing and operation of composite sampler systems. Discussions on the requirement for proper location, mixing, extraction, flow rates and use are all pertinent to the use of a water cut analyzer in line with the sampler. The analyzer must see the same cross section sample as the composite probe or the data comparing the two will not be valid. The analyzer further complicates the issues by measuring a larger cross sectional area than the probe. This creates an increased assurance of good mixing of the product in the pipeline.

Density of the product is important for pipeline operation and for correction of the water cut analyzer. Today many products are blended and therefore changes of density for the same crude type has larger variations than in the past when blending was not an issue. Measurements of density and the corrections for temperature are very important to have good water cut measurement. Issues of density correction for the analyzer and crude type variations will not be covered in this paper in order to concentrate on data a comparison and issues other than specific analyzer requirements.

Figure 5 shows the results for a composite sampling system where each batch composite sample was used to obtain both centrifuge and Karl Fischer results. The comparison of one standard

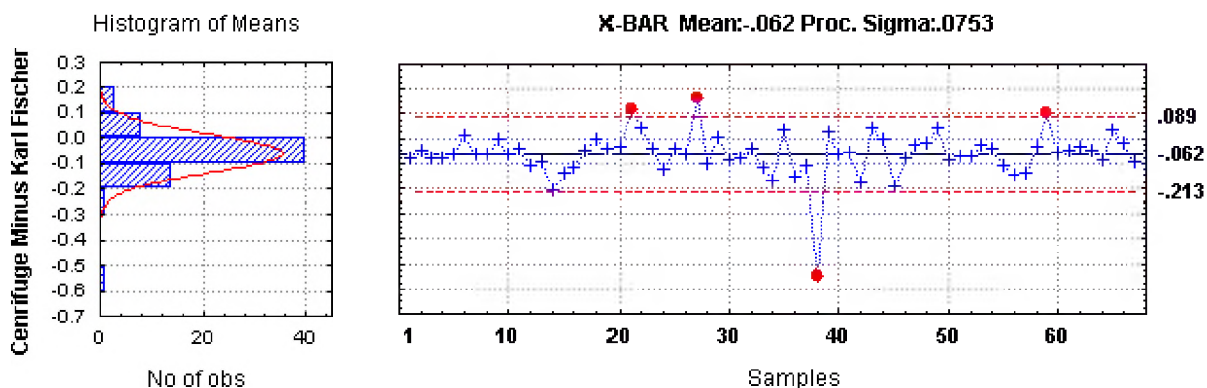


Figure 5. Centrifuge Minus Karl Fischer Composite Sampler Statistics by Sample
Standard Deviation = 0.075 $2\sigma = 0.150$ X-Bar Mean = -0.062

versus another sets a baseline of expectation for this site, operators and equipment. There is one sample that has a difference between centrifuge and KF of 0.55%. This sample was not run a second time to validate which one was wrong and therefore it is included in the above data. Four data points lie outside of the two sigma (95% confidence level) and each should have been run a second time to validate the error. A second sample from the composite sampler may have been necessary to resolve the issue.

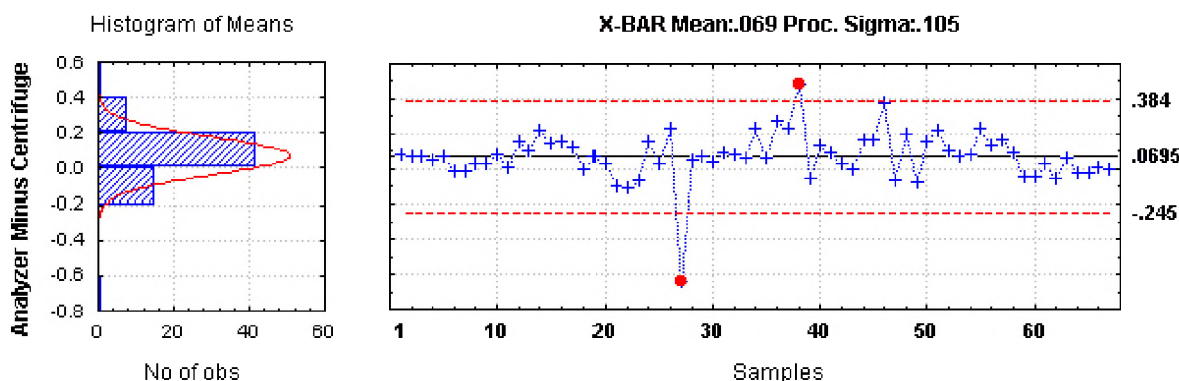


Figure 6. Analyzer Minus Centrifuge Composite Sampler Statistics by Sample
Standard Deviation = 0.105 $2\sigma = 0.210$ X-Bar Mean = 0.069

With a baseline set with a variance between standards of $\pm 0.150\%$ (95% confidence) for the same sample it is appropriate to look at what an on line analyzer may provide. The analyzer data in Figure 6 shows flow weighted average data versus centrifuge and gives a variance in water cut of $\pm 0.210\%$. There is one data point that has a difference of 0.64% (data point 27) which was included in the statistics. Since the total data points are still below a statistical number of points that would consider this anomalous value as part of the noise it does impact the uncertainty.

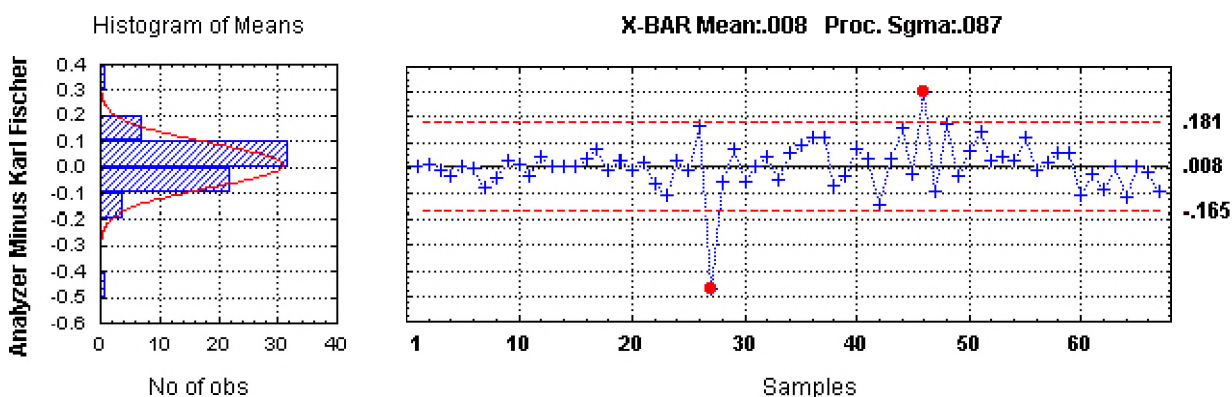


Figure 7. Analyzer Minus Centrifuge Composite Sampler Statistics by Crude
Standard Deviation = 0.087 $2\sigma = 0.174$ X-Bar Mean = 0.008

If Karl Fischer is used for the same composite samples to compare with the on line analyzer the results are better as shown in Figure 7. Now the variance in water cut is ± 0.174 instead of ± 0.210 obtained by centrifuge. The one data point is still very visible in this data set as it was in the centrifuge data. This data point is 1.6% by centrifuge, 1.43% by KF and 0.96% analyzer. The two higher waters from the sample taken from the composite container were both high and therefore another sample from the batch composite should have been taken and processed. This

batch may have been a small one and the amount of liquid in the composite container may have been low due to a small number of sample grabs by the probe. The height of the liquid in the composite sample container is not something that is recorded.

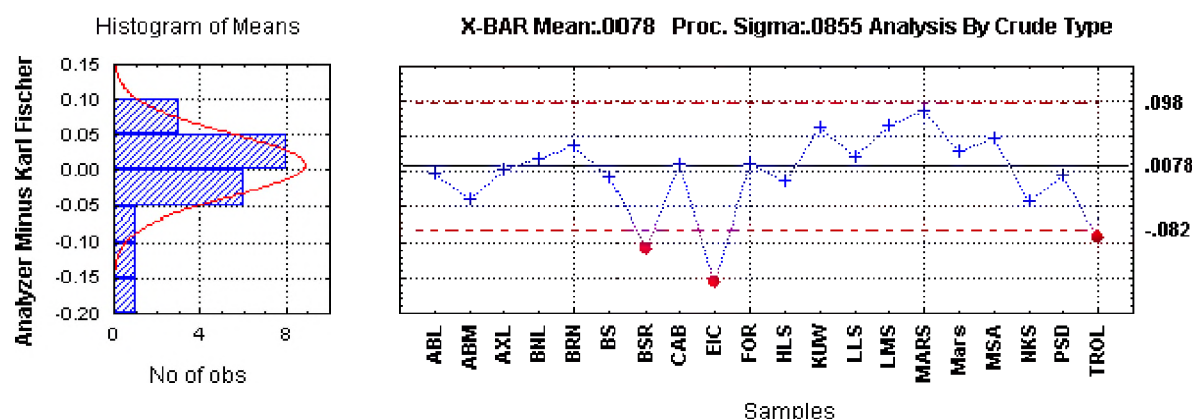


Figure 8. Analyzer Minus Centrifuge Composite Sampler Statistics by Sample
Standard Deviation = 0.086 $2\sigma = 0.171$ X-Bar Mean = 0.008

Another way to process this data is to consider the statistics from a different calculation. Since the data collection has groups of crude oils from the same source, the variance can be calculated considering each population. Samples that have less than 2 batches are considered as a sample of one in the calculation. Figure 8 shows the results when the analyzer minus KF variance is similar to the previous where all of the samples were considered independent but now it is easy to see that there are three crude types that are creating much of the variance; BSR, EIC and TROL. If these crude types which are the ones with the fewest data points (1, 2, 1 respectively) are excluded from the variance the results are greatly different as shown in Figure 9.

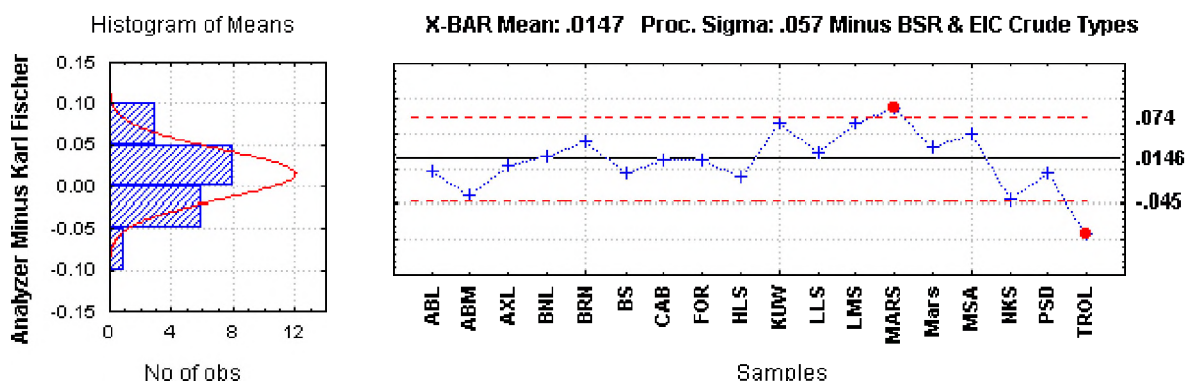


Figure 9. Analyzer Minus Centrifuge Composite Sampler Statistics by Crude Minus Two Types
Standard Deviation = 0.057 $2\sigma = 0.114$ X-Bar Mean = 0.0147

If the variance between two API standards (KF and Centrifuge) is $\pm 0.150\%$ (95% confidence) the larger variance between the analyzer and centrifuge of $\pm 0.210\%$ was expected. The error between the analyzer and KF was smaller and equal to $\pm 0.174\%$. Since the two standards were looking at the same composite sample the question would not have been asked about the bad sample point unless the analyzer was present looking at a different sample in the main pipeline.

4 – Conclusion

The composite sampler under API Chapter 8.2 can only be shown to provide +/- 0.09 to +/- 0.11% allowable deviation at an acceptance test and this is usually done with one density crude oil. As crude types change the flow patterns, rates, water affinities, viscosity and temperatures change. These effects on the sampling system may or may not be known. The acceptance testing for composite samplers typically is not done for all crude products shipped through pipelines in the USA today. Variance in pipeline measurement is a very complex and difficult topic to define and discuss because there are many variables to consider. This paper has only touched on some of the issues that are involved in this discipline.

Although the composite sampler will be around for many more years, the on line real time companion may aid in improving the measurement and provide real time data about when the water came through the line. When differences occur, they can be identified and resolved if the data obtained during routine operation can determine that a question should be asked. The data obtained from composite samplers is not real time and can only provide answers that are obtained by human involvement after the batch has left the station. Analytical measurement coupled with the computing power that is now available will change the way pipeline data on water cut is collected and analyzed. Methods to prove the viability of this approach are just now being tested. Among the remaining things to be understood and defined are how to process the data and how to use it to be more effective operators of pipelines.

5 – Acknowledgements

This paper would not have been possible without many diligent companies looking for answers to problems in their operations. The time to collect and properly analyze samples is time consuming and requires dedicated personnel. The data shown in this paper represents many man years of work. Many thanks are given to each and every person that have assisted in the collection, processing and transfer of the information which led to this paper.