

# LESSONS LEARNED IN PERMIAN CORE ANALYSIS COMPARISON BETWEEN RETORT, GRI, AND ROUTINE METHODOLOGIES

Aidan Blount, Tyler Croft, Brian Driskill, Brian Tepper (Shell Exploration and Production Company)

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## ABSTRACT

In today's competitive cost environment, core acquisition and analysis is too often dismissed as unaffordable. This forces the petrophysicists to make every dollar count in core evaluation. Tough choices, then, have to be made – many people chase the lowest bid, cheapest methodologies, reduced oversight, and less sampling. In this paper, insights will be shared from a comprehensive round-robin study directly comparing the results of the most common techniques (GRI/Retort/RCA) utilized by major vendors. Understanding differences in technique early in an evaluation process can help efficiently direct technical spend.

As with many comparison studies, this project started with the reconciliation of analysis sourced from different laboratories using different methodologies.

There was a significant business driver to this work as we noticed differences in porosity and fluid saturations which contribute to (~25%) difference in hydrocarbon pore volume among vendors using alternative techniques. These differences directly impact log calibration objectives as well as estimations of hydrocarbons in place.

We began to ask simple questions -- should we use crushed samples or routine core plugs? What is the impact of analytical technique on the results? What role does lithology and organic content play in the results from different analytical techniques? What is the role of sample size? What is the variability between vendors for identical procedures? If there is variability, what is the apparent cause?

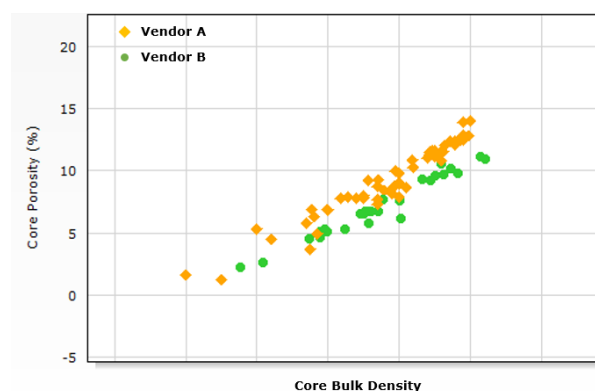
Ten twin Permian samples from the Delaware Basin will be discussed in-depth using a plethora of available information including X-Ray Diffraction (XRD), Total Organic Carbon (TOC)/RockEval, Retort, and Dean-Stark/Gas Research Institute (GRI) protocol analysis

from two labs and RCA from one lab. These 10 samples were picked to represent varying lithofacies with a range of organic, mineralogical, and water/oil content. The level of oversight at each data source was also tracked.

Through detailed analysis of the raw data from these measurements, we address the questions above. With these results, we hope to 1) maximize every dollar spent in core analysis, 2) focus oversight where it is truly required, and 3) accurately and consistently evaluate the core analysis in the Permian play for fast and value-driven business decisions.

## INTRODUCTION

Core data is commonly held as the “ground truth” when completing petrophysical interpretations and generating predictive models. Through the process of petrophysical model development for the Bone Spring formation, we began to notice systematic shifts between various sets of core data, introducing another unwanted uncertainty into the process. More importantly, though, was the severity of these shifts. As illustrated in Figure 1 below, the shift in total porosity was between 2 to 3 porosity units (pu) at the most porous end of the trend – or, generally, between a 20 to 30% porosity difference.



**Fig.1** Core porosity vs. core bulk density: an example of systematic shifts between two vendors in trend space

An implied uncertainty of 20 to 30% in in-place volumes based on vendor choice is difficult to accept,

and so we set out to reconcile the differences and improve our understanding of the reasons for those differences. We designed a robust comparison study between two vendors to analyze sample preparation, analytical technique, assumptions, and – ultimately – results.

## CORE SAMPLING AND METHODOLOGY

The handling and preservation of samples plays a critical role in obtaining high quality data. We started with a list of desired analyses to define the sampling requirements and help ensure each vendor could start with essentially identical samples. We elected to test ten samples using a variety of techniques – shown in Figure 2 below – to assess the variability from two vendors: Vendor A and Vendor B.

Vendor A	Vendor B
Dean-Stark	Dean-Stark
Retort	Retort
RCA	TOC
<i>All analyses using crushed &amp; sieved material except for RCA. XRD was performed at a 3<sup>rd</sup> vendor.</i>	

**Fig.2** Summary of analyses performed at Vendor A and Vendor B

Fresh, wax-preserved core was used for all testing. Sampling was conducted at Vendor A under Shell supervision. After extruding the core from the wax, a single, large puck was taken from the 10 sample locations chosen. An additional full 1” plug was taken for the RCA measurement. Sample locations were designed to represent a variety of lithofacies and mineralogy to help identify any facies effect on testing. An as-received bulk density measurement was completed on the large puck (and, separately, the RCA plug) as the starting point for both laboratories.

To maintain consistency between laboratories, the large puck was crushed, sieved to 12/20 mesh, and run through a sample splitter multiple times for homogenization. The homogenized material was then

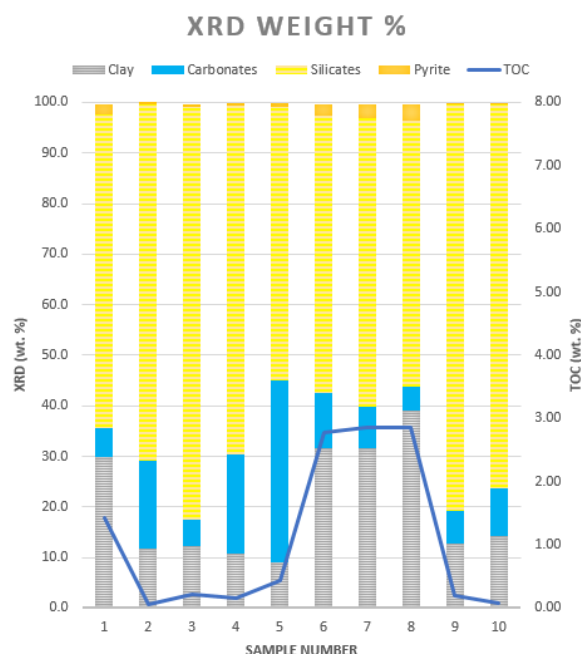
split and double-bagged for each vendor. Vendor B’s split was designed to be same-day shipped in chilled packaging, while Vendor A’s material was held in chilled storage until Vendor B received their samples. This allowed testing to commence at the same time.

*Note: The material sent to Vendor B was not chilled during shipping due to a mishap in the shipping department. However, samples were weighed upon receipt to confirm lack of mass loss and validity for continuing the experiment.*

Separate splits (from the material that did not sieve to 12/20) were used for both TOC (performed at Vendor B only) and XRD (performed at a 3<sup>rd</sup> vendor and provided to Vendor A and Vendor B for reference). The purpose of the TOC and XRD measurements was to ascertain mineralogy and organic richness for correlation with the other analytical measurements.

## SAMPLE MINERALOGY AND TESTING PROCEDURES

As noted earlier, the ten samples represented a range of lithofacies to help span the heterogeneity within the target formation. A summary of the sample mineralogy is shown below in Figure 3.



**Fig.3** Mineralogy and measured TOC distribution in ten selected samples

As expected, the XRD and TOC measurements confirmed a good distribution of mineralogy and organic richness. The Bone Spring is made up of various lean, quartz-rich silt packages with interbedded organic-rich mudstones. In addition, there are calcite-rich and dolomitic streaks that add to the heterogeneity.

A general testing procedure was provided to both laboratories to ensure the same steps, weight/volume measurements, and retort temperature steps were utilized. The procedure provided to each vendor – for each analysis performed – is detailed below.

**Retort:** each laboratory to confirm bag weights prior to commencing procedure. An as-received grain volume measurement is to be made using helium. Each laboratory to retort each sample to the 1<sup>st</sup> temperature step of 105C, following their own vendor-specific protocol for temperature ramping, holding time, and sample size used. Weights and volumetrics to be recorded. Following this, each sample to be retorted to 300C, again using vendor-specific protocol as in the first temperature step. Weights and volumetrics to be recorded. Complete a post-retort dry grain volume measurement using helium. Complete solvent extraction using chloroform/methanol azeotrope, dry samples and weigh. Complete post-extraction dry grain volume measurement using helium.

**Dean-Stark extraction using GRI protocol (Luffel, 1992):** each laboratory to confirm bag weights prior to commencing procedure. An as-received grain volume measurement is to be made using helium. Solvent extract each sample using toluene, followed by chloroform/methanol azeotrope. Extract with methanol, and dry to weight stability. Weigh samples. Complete post-extraction dry grain volume measurement using helium.

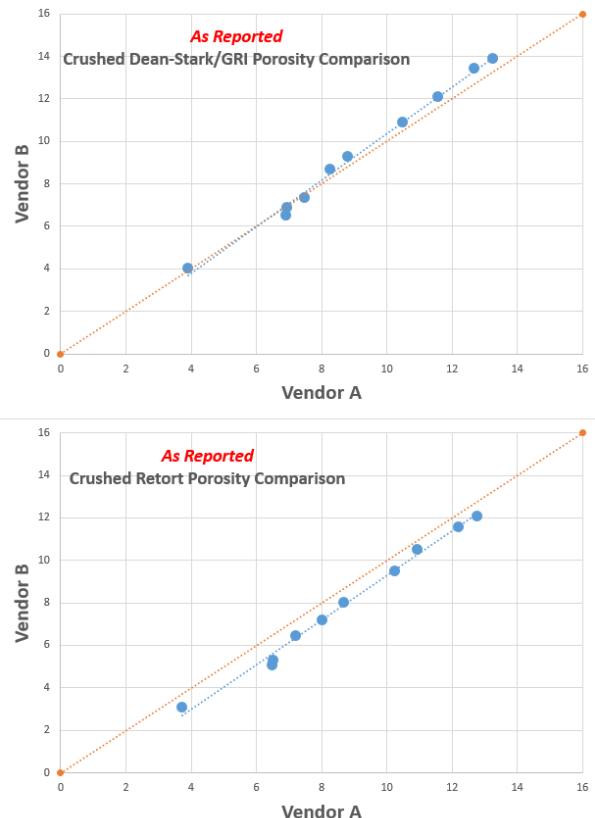
**Dean-Stark extraction on plug samples:** Compare weights against plugged/chilled weights. Extract each sample using toluene, followed by chloroform. Extract with methanol. Dry to a stable weight and weigh samples. Determine ambient net-confining stress (NCS) post-extraction dry grain volume using helium, and determine ambient NCS dry bulk volumes using mercury immersion.

## REPORTED RESULTS

Each laboratory was asked to report results in their typical fashion. Additionally, the raw data was requested so that recovered volumes and mass changes could be

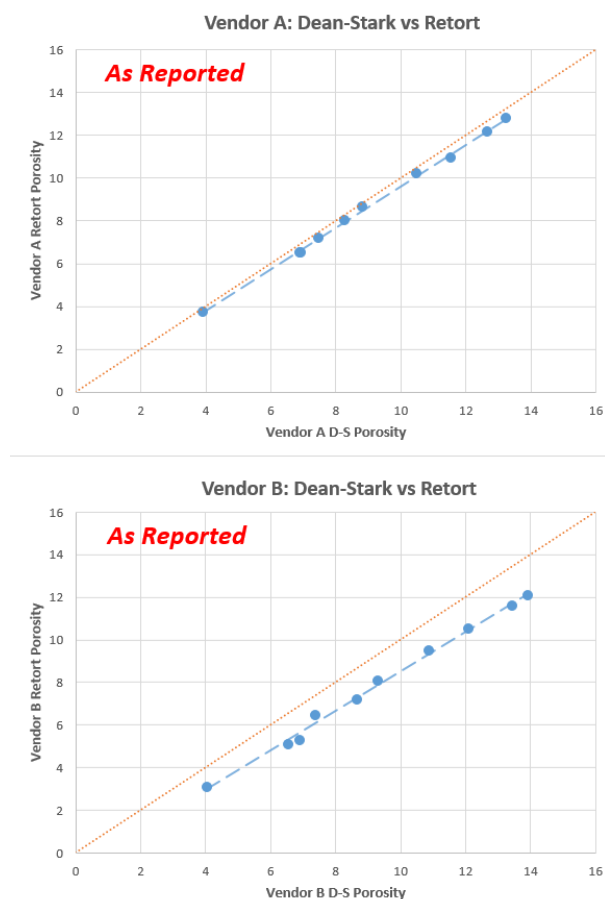
directly compared. This allows the end-user – the operator assessing resource volumes – to see the corrections and assumptions made from raw data to reported data.

First, we can compare reported total porosity values between the two major analytical techniques – retort and Dean-Stark/GRI protocol. This is shown in Figure 4, below. Both labs are relatively close on Dean-Stark, with around a 0.5pu offset at the higher end. The reported retort results, though, show a much bigger difference – a systematic shift of around 1pu.



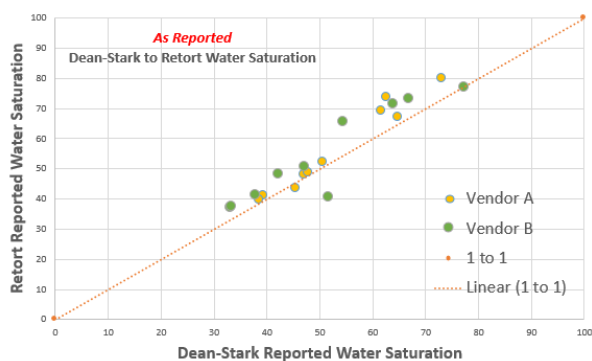
**Fig.4** Dean-Stark and retort porosity comparison

When comparing the *reported* GRI to *reported* retort directly (Figure 5, below), we see a significant difference between the two vendors. Vendor A shows very close agreement between the two methods, whereas Vendor B shows a significant shift – at the higher porosity end of the trend, the Dean-Stark porosities are approximately 2pu greater than the corresponding retort porosity.



**Fig.5** Direct comparison of Dean-Stark/GRI vs. retort

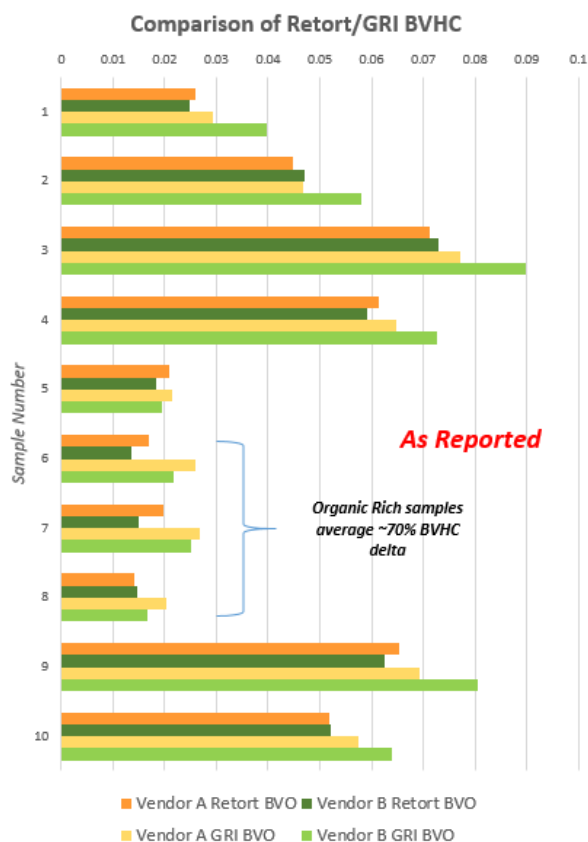
In this set of reported data, however, the water saturations measured via retort – from both vendors – were generally higher than as measured in the Dean-Stark extraction, as shown in Figure 6, below.



**Fig.6** Dean-Stark and retort water saturation comparison

At first glance, the reason for this is not obvious. As the maximum retort temperature used is 300C, structural water should not be liberated from the samples. This suggests there may be another reason to be found.

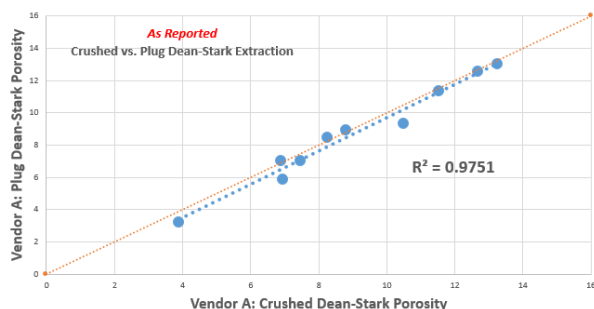
In bulk volume hydrocarbon (BVHC) space – defined as  $(1-S_w) \cdot \Phi$  – the difference in the methods and vendors becomes even more significant. In the cleaner, siltstone samples (3, 4, 9, and 10), the BVHC changes 20 to 30% depending on analytical technique and vendor. In the lower porosity, organic-rich mudstones (predominantly samples 6, 7, and 8), the BVHC averages a 70% difference between the high and low cases. This is highlighted in Figure 7.



**Fig.7** Bulk volume hydrocarbon comparison

Another set of data not touched on so far is the routine core analysis (RCA) data. Full-plug RCA analysis is often dismissed in tight, sub-microDarcy permeability rocks, but we see very good agreement in the RCA and crushed D-S extraction porosities. A capital constrained analysis plan could utilize RCA to significantly reduce cost while obtaining highly comparable results, even in clay-rich mudstone samples with porosity values ranging

from 4 to 10%. Figure 8 illustrates this comparison.



**Fig.8** RCA vs. GRI/Crushed Dean-Stark extraction

## RECONCILIATION USING RAW DATA

As mentioned earlier, the raw data – which often is not provided except upon request – was also obtained for these datasets. Diving into the raw data revealed several key insights. These learnings are vital for a practicing petrophysicist to understand and interpret the data they have available.

Our first critical learning is around the significant differences in porosity and saturation determination based on the raw data acquired. The onus is on the operator to request, audit, and understand any data corrections made in the process of converting raw weights and volumes into porosities and saturations for quantitative petrophysical evaluation.

As part of the retort process, both water and oil fluid volumes are considered to be recovered and can be measured volumetrically. Additionally, this fluid recovery can also be measured in weight. A key point is that the fluid summation for processing raw data into porosity can be completed using *either* weight or volume. Some vendors use weight as a standard process, whereas others use volume. As will be shown, the two do not easily reconcile.

While volume is a more direct measurement, there is an implicit assumption that **1) all fluid is recovered** and that **2) the volumes can be measured accurately with low uncertainty**.

The first of these two assumptions will be likely dependent upon vendor and equipment setup – setting up a perfect retort apparatus is not trivial. However, studies (notably Rathmell, 1967 and API RP 40) have shown

that significant volumes of oil could be missed. The noted corrections suggest up to 40% of the oil may not be recovered.

To the second assumption, this is again dependent upon equipment setup. There are modern – yet cost prohibitive – methods of measuring even miniscule volumes at extremely high accuracy, such as high-definition photography and lasers. However, these are not commonly deployed in commercial laboratories for lack of practicality. The volume readings completed in commercial laboratories are regularly done manually, and the extremely low fluid volumes – often less than 0.1cc – consequently carry what we consider to be a significant uncertainty.

Completing the calculations using weights is the alternative, which also carries its own set of assumptions and limitations. The first assumption here is that the weight deltas can be measured accurately. The weight delta is the difference between the before extraction (or retort) sample weight and the sample weight after the extraction (or retort). We believe that the accuracy of a laboratory weight measurement carries a significantly lower uncertainty than the corresponding volume measurement. The weight delta can be used to determine if the loss of weight is consistent with the amount of fluid (either volume or mass) that was recovered. If the weight delta is greater than the amount recovered, the implication is that some fluid was lost in the process and needs to be accounted for.

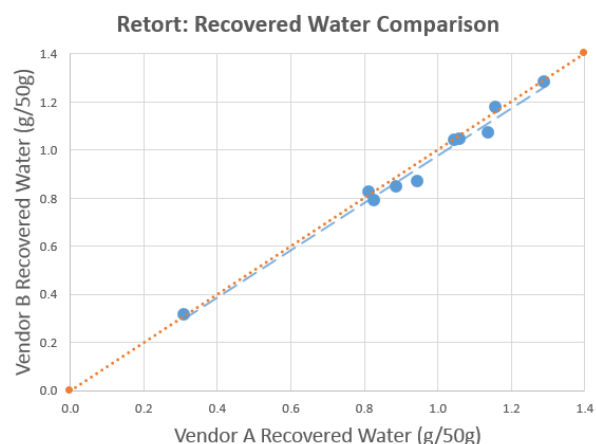
There are other assumptions that must be used to invert the weight deltas into volume space – most notably fluid densities (brine and oil). Another learning – although it has a relatively minor effect on the end result – is that different vendors will typically use different values for fluid densities and distilled water to brine volume (VbVw) corrections.

For the purpose of this study, both weights and volumes were measured by both vendors as requested by the operator. This may not typically be the case. Having both weight and volume data allows the operator to take another critical step: **the reconciliation of weight and volume**. Using the same set of assumptions, it is possible to compare volume recoveries and see if they are in line with the weight deltas. **We noticed a significant amount of “missing weight” in the retort data**, giving substantial importance to the difference in the calculation process; generating porosity from the volumes will give a lower result than the corresponding porosity generated using weight, *if the missing weight is*



*not accounted for.* Referring back to Figure 4, we see that Vendor A reported the raw porosity using a weight calculation whereas Vendor B used volume for the calculations. Our belief is that the missing weights were handled differently by the vendors in this case.

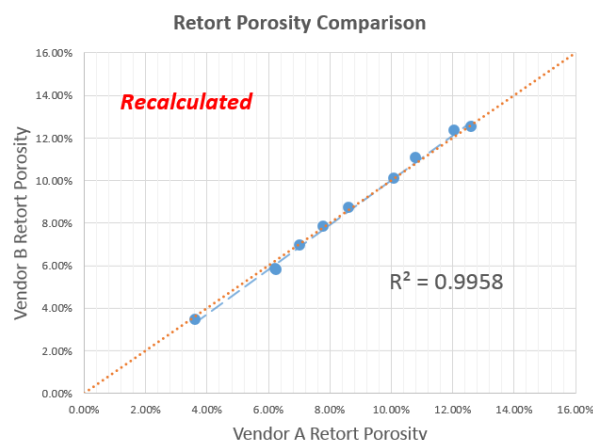
We decided to re-calculate the retort porosities using a constant set of assumptions to see if this would help reconcile the differences between Vendor A and Vendor B; it did. The first check was on the recovered water volume, to see if we were on the right track. Figure 9, below, shows a comparison of the recovered water normalized for sample size (grams of recovered water to 50 grams of rock). Both vendors were very close on a 1 to 1 trend. Note that this comparison is done in weight, not volume. *Note: any “missing weight” – weight delta that is greater than the comparative volume recovered – is considered to be water for the purposes of this process. In reality, this could be – and likely is -- a mixture of both water and oil. As water is the denser fluid, this gives the low-case porosity.*



**Fig.9** Recovered retort water Comparison

The recovered water weights (including “missing weight”) and recovered oil weights were then calculated into porosity space using a single set of assumptions. Oil density was fixed to 0.8 g/cc for both retort and, further below, the Dean-Stark re-calculations. Brine density was based on an acquired water sample, giving ~1.03g/cc density. The VbVw correction was made based on McPhee, 2015, for the sake of using a published correction. Another note here is that each commercial laboratory typically has their own VbVw correction, which is another (minor) source of difference in the reported results. No corrections were made to the recovered oil volumes, although this is not uncommon within industry. After re-calculation, the retort porosities

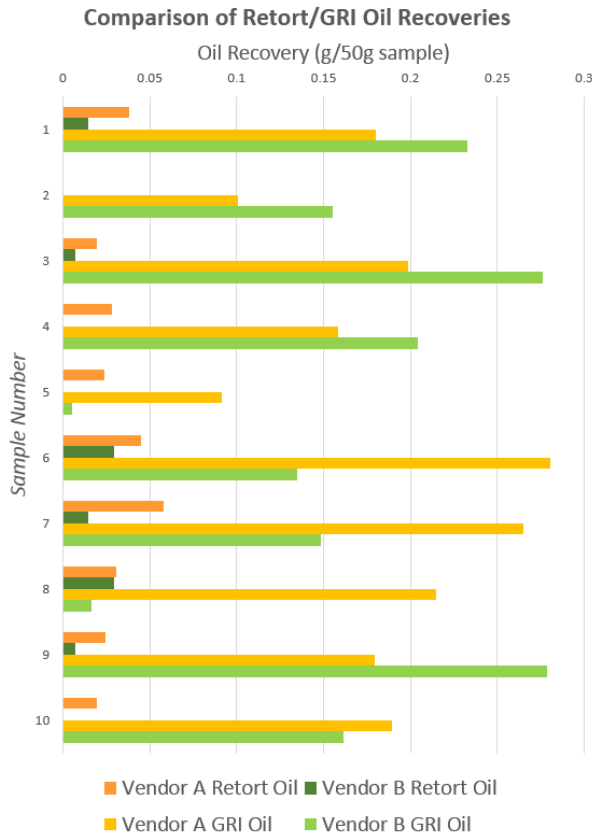
from Vendor A and Vendor B line up very closely on a 1:1 trend, as shown in Figure 10. This is in contrast to the reported data shown in Figure 4, where we saw a ~1pu difference.



**Fig.10** Recalculated retort porosity comparison

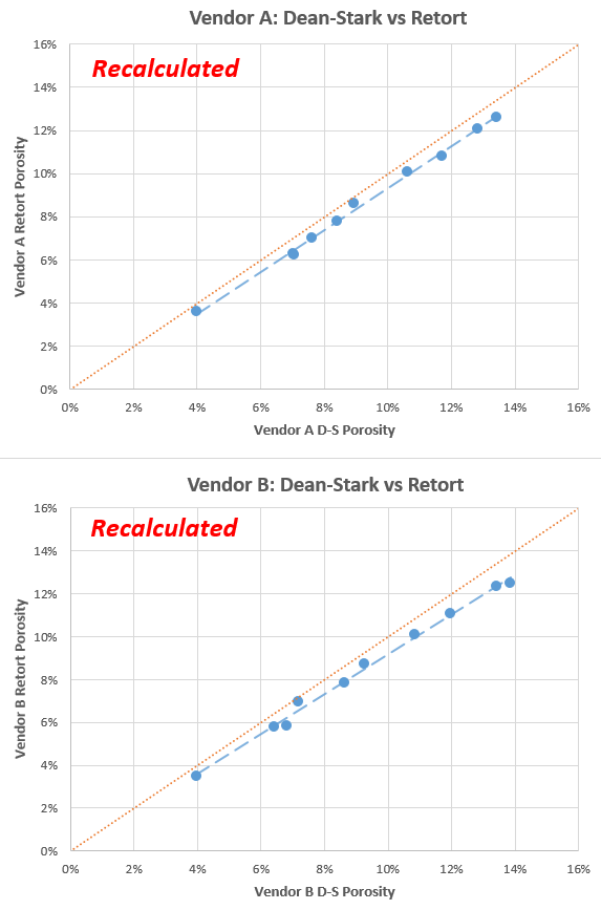
We also decided to go through a similar process on the Dean-Stark results, where another key learning transpired. As there is also water recovery as part of a Dean-Stark apparatus, the water can (similar to retort) be measured in volume and weight. The typical process is to measure the weight of the recovered water. The weight of the recovered water is then subtracted from the weight delta of the sample – this difference is assumed to be the oil weight.

**This is a key fundamental difference between a typical retort calculation and typical Dean-Stark calculation.** As mentioned earlier, it is assumed in retort that all of the oil is recovered, except for the possibility of residual oil being left in the sample (Rathmell, 1967 and API RP 40). Therefore, all of the “missing weight” is assumed to be water. In a typical Dean-Stark calculation, it is assumed that we are recovering all of the water. The missing weight is consequently placed into the oil bucket. These are two extremes that we find unlikely to be true. The truth is likely somewhere in the middle, where some of the missing weight in a Dean-Stark apparatus could be water that is somehow lost or hung up in the equipment, and some of the missing weight in a retort apparatus could be oil that is similarly not recovered. The difference in the computed oil recovery is shown in Figure 11, below, where the stark difference between these two extremes is very evident.



**Fig.11** Comparison of oil recoveries by method and vendor

The Dean-Stark/GRI method consistently shows substantially higher oil recovery than the retort methods, which show minimal oil recovery. We believe this lends credence to the belief that not all moveable hydrocarbon is recovered as part of the retort process, and also re-emphasizes our belief that measuring in volume carries a significant error; almost all oil recoveries are less than 0.05cc. Additionally, this demonstrates the significant difference in calculation process between Dean-Stark and retort. Figure 12, below, illustrates this key point; **when both methods are re-calculated using the same set of base assumptions and no corrections are applied, the difference in result is not clearly related to vendor.** Note: as discussed at length previously, the missing weight in Dean-Stark is still assumed to be oil, whereas the missing weight in retort is assumed to be water.



**Fig.12** Direct comparison of Dean-Stark/GRI vs. retort after porosity is recalculated

Both vendors show a very similar trend after re-calculation, with the Dean-Stark porosity trending higher than the retort from both vendors. Typically, this might be seen in rocks that have a not insignificant amount of bitumen. The Dean-Stark extraction would remove the bitumen, adding to the measured pore space, whereas the retort methodology (at the temperature steps described) would not remove the bitumen component. However, the delta between Dean-Stark and retort is significant even in the lean (<0.5 weight percent TOC), quartz-rich siltstones, suggesting that the difference is not primarily attributed to bitumen effect.

This effect has been observed before multiple times, notably by Handwerger et al., 2011. One possibility is that the Dean-Stark cleaning process strips excess, structural water that should not be considered a part of the saturating fluid inside the pore space; however, we believe this possibility has been dismissed.

There are two other possible contributors to this delta that have been discussed earlier in the paper: 1) the bucketing of the “missing weight” and 2) not recovering all oil during the retort process. The first of these would slightly lower the Dean-Stark porosities (due to possibly low average fluid density by assuming all weight delta is oil), bringing the trend closer to the 1:1 line. The second – not recovering all oil – would *increase* the retort porosities, again shifting the trend closer to the 1:1 line. Our belief is that the combination of these two assumptions is the primary driver in the apparent differences between the two methodologies.

Finally, we can look at the re-calculated bulk volume hydrocarbon to compare to Figure 7. The results still show significant uncertainty, which is in many cases even more significant than the original data. This again reinforces the importance of understanding vendor assumptions and corrections, going through the process of looking at the raw data, and choosing an appropriate method that values the goals you may have as an operator or core interpretation practitioner. The results are shown in Figure 13, below.

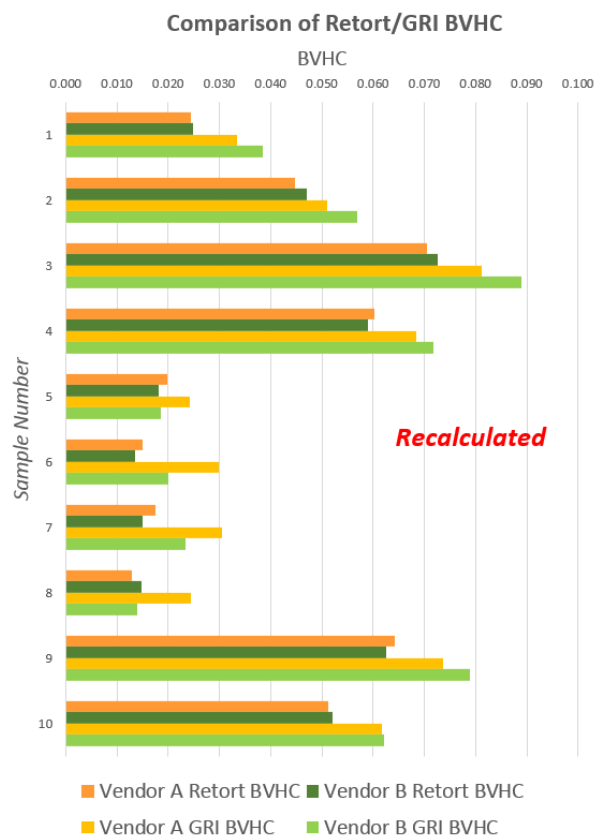


Fig.13 Final re-calculated BVHC

In summary, we have several key questions that we believe a prudent operator should consider when interpreting vendor provided lab data:

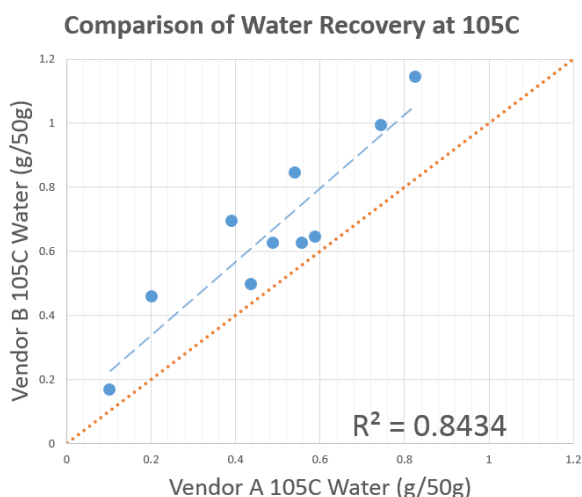
- What assumptions are being made for fluid densities in order to complete the calculations?
- Are my calculations being done using weights or volumes? What is my expected error based on the size of sample I am testing?
- What conversion factor is being used for distilled water into brine volume?
- If my calculations are being done using weights (as we recommend), how is the missing weight being assigned to a fluid? Am I assuming I recover all fluids in my chosen testing method?
- By comparing my volume and weight measurements, do I have a significant “missing weight” issue?
- Do I have a significant bitumen component that may be affecting the results?

## RETORT TEMPERATURE STEPS

A primary driver for using retort instead of a Dean-Stark extraction is the goal of separating out the saturation of the effective pore space from the total porosity. This separation has been sought using multiple temperature steps – in this project, steps of 105C and 300C were used.

However, a cautionary note we want to state is that the temperature steps ideally need to be calibrated to both equipment utilized, lab location, and rock type. We noted in our analysis of the raw data that the water recoveries after the first temperature step (105C) were significantly different – however, the water recoveries are nearly identical by the end of the second temperature step (300C). This suggests that using the same temperature steps at different labs will not give you the same result, and is consequently a poor predictor of clay-bound water unless it is well calibrated. This is illustrated in Figure 14, below.





**Fig.14** Water recoveries at 105C

Thermogravimetric analysis (TGA) – not completed as part of this study – provides a data-driven way to calibrate the temperature steps to the specific equipment setup being used and the rock type. To get reliable temperature steps, the petrophysicist wants to look for temperatures where significant mass loss occurs in the rock, suggesting a critical temperature for a given pore type and saturating fluid.

## PROPOSED ANALYSIS WORKFLOW

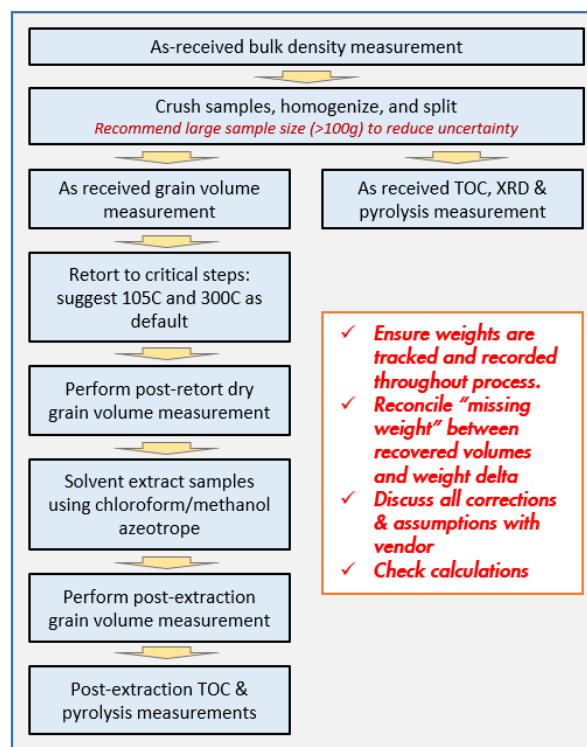
The ultimate goal of this kind of core analysis is to help ascertain in-place volumes, and our study has helped us gain perspective on what we consider to be a recommended “best practice” for the practicing petrophysicist.

Our recommendation is shown in Figure 15, below. In addition to this protocol, there are other considerations that the practicing petrophysicist should think about to determine applicability for their problem:

- Routine core analysis may be a viable alternative to crushed GRI/retort methods, depending on the type of rock. It is worth trialing this on your samples for possible cost savings – you could use that money for greatly increased sampling!
- For separation of bound and free fluids in a multi-fluid reservoir, we prefer retort analysis, which is the method summarized in Figure 15. However, the GRI method/Dean-Stark extraction is perfectly effective for obtaining total porosity. For example, this may be more

applicable in a dry-gas situation where no water production is seen.

- TGA measurements can be used to help determine the critical temperature steps for your rock and chosen vendor setup.
- We have seen no effect on results due to sieving of the sample, and our testing using XRD shows consistent mineralogy. If anything, we believe the additional step of sieving adds more time for the sample to be exposed to the atmosphere and cause potential fluid loss.
- Discuss fluid density assumptions, distilled water to brine corrections, and retort oil recovery corrections with the vendor. Decide on a consistent set of parameters that you can apply across your field. Our data above suggests a high probability that not all oil is recovered in retort, and we recommend making a correction.
- The core analysis interpreter should hope to see correlations between the recoveries at critical temperature steps and pyrolysis/XRD data – such as clay weight fraction (and certain clay species, if possible) correlating to bound water.



**Fig.15** Recommended core analysis workflow

## SUMMARY

We began this project with a target end-state:

- 1) Maximize every dollar spent in core analysis for fast and value-driven business decisions
- 2) Focus oversight where it is truly required
- 3) Accurately and consistently evaluate the core analysis in the Permian play for fast and value-driven business decisions

Through close cooperation with our vendors, we have been able to take a deep dive into core analysis protocols. During this project, we have made several key findings that we think position an operator for success in core analysis and play evaluation:

- Reported porosities and saturations are often generated with corrections and assumptions you may not agree with; it is worth discussing this with the vendor.
- With corrections applied, Dean-Stark and retort show strong agreement. API RP 40 recommends correcting the retort oil recovery.
- Without corrections for oil recovery, Dean-Stark/GRI method consistently shows higher porosity than retort.
- When data is re-calculated from raw weights with consistent assumptions, both Vendor A and Vendor B show good agreement.
- By default, some vendors calculate in volume and others calculate in weight: it is important to do this consistently across your datasets.
- Reconciling the recovered volumes and weights is critical to understand the effect of “missing weight” – weight delta that is not accounted for in fluid volume.
- The missing weight in Dean-Stark is assumed to be oil, which is very different than retort – in retort, it is assumed that all oil is recovered, and so missing weight is often considered water.
- Routine core analysis may provide a reliable, cost-saving alternative to crushed analysis, depending on the porosity and permeability of the sample – even in our low porosity samples, we saw good agreement overall between plug and crushed data.
- Not all equipment is equal: our two vendors exhibited very different water recoveries at the first temperature step, suggesting this needs to be calibrated to equipment, location, and rock type.
- *Significant* uncertainties in BVHC will be

observed between retort and Dean-Stark/GRI methodologies unless corrections are made to the data for “missing weight” and retort oil recoveries.

Overall, this work allows us to understand the core data we have – from varying vintage and various vendors – in order to accurately calibrate a petrophysical model for the play. This greatly reduces the uncertainty on in-situ calculations, allowing us to more appropriately allocate capital for development and maximize value in our business decisions.

## ACKNOWLEDGEMENTS

We are extremely appreciative of our vendors for both taking part in this study and working with us to discover solutions. Both vendors showed a high level of proficiency and patience, working closely with us throughout the study. We are also grateful for the support of Shell management, specifically Sonja Perry, Nitin Chowdhury, and Brice Peterson for the opportunity to work this study. We would also like to acknowledge our talented geologists – spearheaded by Long Ma – who have worked with us side-by-side in derisking and understanding this basin. Finally, we received significant support and effort from Anton Nikitin, Senior Petrophysicist at Shell.

## REFERENCES

- API RP 40, 1998, Recommended practices for core analysis, second edition. Washington, DC: API
- Handwerger, D.A., Keller, J., and Vaughn, K., 2011, Improved petrophysical core measurements on tight shale reservoirs using retort and crushed samples. Society of Petroleum Engineers, SPE 147456-MS
- Luffel, D.L., and F.K. Guidry, 1992, New core analysis methods for measuring reservoir rock properties of Devonian shale, SPE 20571
- McPhee, C., Reed, J., and Zubizarreta, I., 2015, Core analysis: a best practice guide. Amsterdam: Elsevier
- Rathmell, J.J., 1967, Errors in core oil content data measured by the retort distillation method, SPE 1552