

# **PS Modified Method and Interpretation of Source Rock Pyrolysis for an Unconventional World\***

**Robert R. King<sup>1</sup>**

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<sup>1</sup>Advanced Geosciences, ALS Empirica, Denver, CO, USA ([ryan.king@alsglobal.com](mailto:ryan.king@alsglobal.com))

## **Abstract**

Our understanding of unconventional reservoirs is evolving daily and never at a greater rate than the past 15 years. However, programmed pyrolysis methods developed in the 1970s are still used today to assess the present day organic matter quality and quantity of potential source rocks. More importantly, the interpretive guidelines for unconventional reservoirs developed for the Barnett Shale in the 80s and 90s are still being used to characterize organic matter quality and maturity of nearly all prospective unconventional plays new and old. Recent advancements in pyrolysis technology, manufacturing, training and communications have paved the way for organic screening via pyrolysis on larger numbers of samples with faster turnaround times. The results are now available for critical time sensitive decisions such as where to land a lateral and how to apply customized completions, but also feed development of more models and trend mapping. Investigation of pyrograms, which now span a much larger range of organic matter types and maturities, has exposed multiple caveats in the traditional pyrolysis method and the interpretive guidelines being applied to liquids rich source rocks. The most problematic of which are attributed to heavy hydrocarbon carryover from S1 to S2 which can complicate kerogen quality assessment, maturity determination and production quantity/quality estimate resulting in potential inconsistencies between maps/models and production. Pyrograms and comparative results from parallel samples run through different pyrolysis methods will be presented for discussion. Modified initial isotherm temperatures designed to volatilize a larger range of hydrocarbon without cracking kerogen provide a possible solution to the heavy hydrocarbon carryover issues. Pyrograms generated from both a traditional temperature ramp and more rapid pyrolysis temperature ramps are presented to investigate the effects on the S2 peak geometry/quantification as well as Tmax assessment. Furthermore, we attempt to properly address maturity as a function of kerogen quality with several new concepts better using the raw data generated from our modified source rock pyrolysis method.

## Abstract

Surprisingly, traditional programmed pyrolysis methods developed in the 1970s and interpretive guidelines developed for the Barnett in the 90s are still routinely used to assess the present day organic matter quality and quantity of potential source rocks/unconventional reservoirs. Recent advancements in pyrolysis technology and manufacturing have paved the way for organic screening via pyrolysis on larger numbers of samples with faster turnaround times. The results are now available for critical time sensitive drilling and completions decisions, but also provide a main input to the development of petrophysical models and geochemical trend maps. Investigation of huge numbers of pyrograms with ranges in organic matter type and maturity has exposed multiple caveats in the traditional pyrolysis method and those interpretive guidelines being applied particularly in regards to liquids rich source rocks. The most problematic of which is heavy hydrocarbon carryover from S1 to S2 also known as low temperature S2 shoulder (Fig 1) complicating kerogen quality assessment, maturity determination and production quantity/quality estimates.

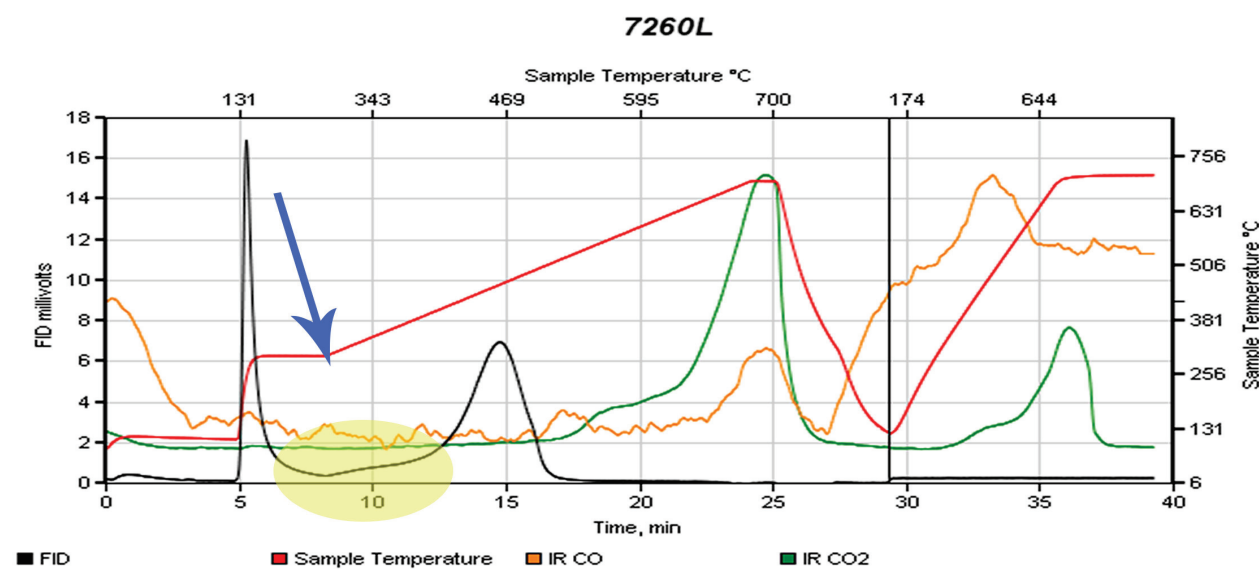


Fig. 1 – Example of Low Temperature S2 shoulder (highlighted in blue/yellow) due to carryover of heavy end S1 hydrocarbons into S2

We utilize the HAWK pyrolysis instrument to generate pyrograms and compare traditional pyrolysis results of samples from multiple wells across the basin to results obtained from modified pyrolysis methods and results obtained after organic solvent extraction on parallel samples. Modified initial isotherm temperatures designed to volatize a larger range of hydrocarbons without cracking kerogen directly address the S1 carryover providing a more reliable assessment of the cumulative oil (S1 peak) and “clean” S2 peak for more accurate kerogen and thermal maturity assessment. Additionally, pyrograms generated from both traditional temperature ramping and a more rapid pyrolysis temperature ramping are presented to fully investigate any effects on the S2 peak geometry/quantification and Tmax determination.

## The PROBLEM with Traditional Pyrolysis Methods

Problems with the established pyrolysis method of the 1970s (Espitalie et al 1977), in particularly the 300°C initial isotherm temperature, were quickly identified. “Under pyrolysis, migrated oil or bitumen in the rock gives a major response near 250-300°C on the pyrogram (S1 – Espitalie et al 1977). However, solid bitumen and the ‘heavy end’ fraction of petroleum produce a measureable response (S2 – Espitalie et al 1977) in the 350-450°C range as well as in the same region kerogen conversion to hydrocarbons occurs.” (Clementz, 1982). Or in other words, a heavy component of liquid bitumen requires temperatures higher than 300°C for volatilization resulting in some “S1” hydrocarbons carrying over to the low temperature side of the S2 peak. Peters (1986) confirms this carryover and Tmax suppression but proposes the possibility of re-worked kerogen as a contributing factor. And further studies (Snowden, 1995) attempt to quantify the effects of this Tmax suppression reported differences as large as 8°C in some low maturity source rock samples from The Second Whit Speckled Shale in Alberta Basin. Recent work in kinetics clearly identifies the issues with overlap of heavy bitumen and solid kerogen. Kinetic data acquired from whole and extracted rock as well as whole and extracted kerogen indicate that extracted rock and kerogen samples yield comparable kinetic parameters, whereas whole rock does not. The reason for this discrepancy is the volatilization of extractable organic matter, which behaves as a zero order reaction rather than the presumed first order reaction (Jarvie and Lundell, 2001).

Utilizing our traditional pyrolysis method in liquids rich source rocks typically will result in: (1) a reduced S1 or completely unreliable S1 when traditionally defined; (2) an artificially elevated S2 peak containing more than just the products of kerogen cracking; (3) a potentially suppressed Tmax value resulting in improper maturation assessment and mapping; (4) Unreliable Hydrogen Index (HI) values which is a primary tool for typing present day kerogen and evaluating conversion. All caveats which must be addressed.

As our appetite for producing liquids rich source rocks has grown, so has our wealth of pyrolysis data on such source rocks. And unfortunately so has our uncertainty in the maps and models based on these potentially unreliable pyrolysis inputs. This carryover of a heavy S1 component to S2 become a serious issue with interpretations on a sample by sample basis. Recent studies (Devine, 2014; Thul, 2012 and Sanei et al, 2015 have investigated alternate approaches for a SINGLE analytical procedure providing (A) hydrocarbon saturation information or S1 equivalent and (B) source rock characterization or S2 and HI equivalent. Our study continues the search for a rapid and repeatable pyrolysis method for attaining (A) and (B) in one analytical procedure.

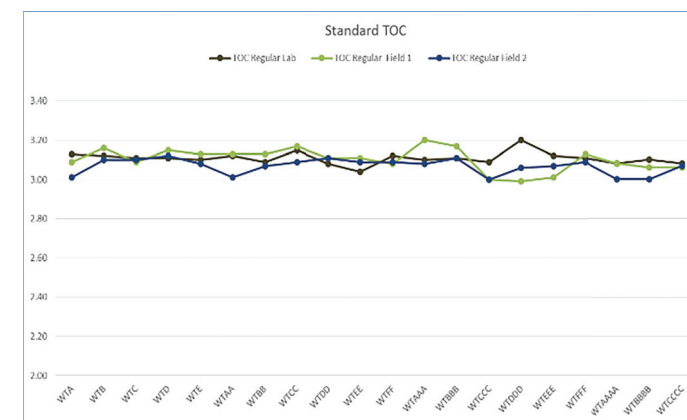


Fig 2 – Multiple Standards with TOC values +/- 0.20% of True value (3.11%)

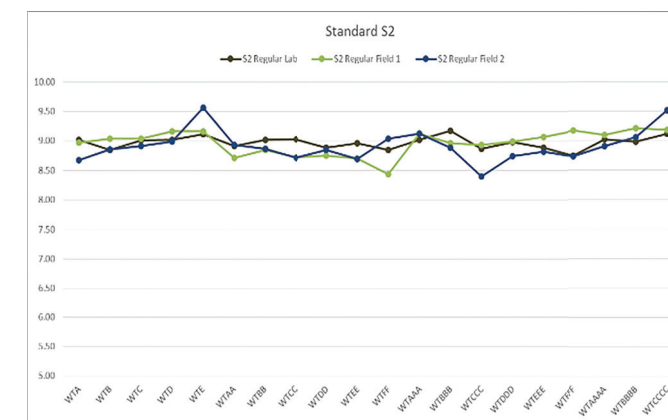


Fig 3 – Multiple standards with S2 values +/- 0.5 mg/g of True value (9.00 mg/g)

## Instrument Accuracy

ISO 5725 recently defined accuracy as the combination of a measurement’s trueness and precision. An instrument’s trueness would be the measurement of systematic error OR the nearness of the produced values to known values of a given material. Alternately precision is the measurement of random error OR the reproducibility/repeatability of the instrument results generated. A measurement of instrument is only considered accurate or valid with high levels of both trueness and precision.

A comparison of nineteen Rock-Eval 2 instruments in 1992 showed the accuracy of such results (D. Jarvie, 1992, unpublished data). When calibrated with the same standard (IFP #37133) under the same conditions and then analyzing the standard as an unknown, the results showed excellent accuracy and reproducibility. These data showed a standard deviation of 1.7°C for Tmax, whereas S1, S2, and S3, and TOC were within 11, 6, 12, and 5 % of each other. However, when five different unknowns were analyzed the variability increased dramatically to over 50°C for Tmax, upwards of 50% for S1, 18% for S2, 60% for S3, and 8% for TOC. While there are numerous causes for these variations, the key factor was the absolute or true temperature of the Rock-Eval instruments. At a programmed temperature of 300°C, Rock-Eval 2 instruments had a spread upwards of 50°C. Obviously this resulted in very large differences in S1 and S3 as they are the most temperature sensitive measurements. This is truly the difference between nominal temperatures (what the microprocessor in the instrument read) versus the true temperature of the oven and sample. The HAWK instrument has addressed the operating temperature variable with all instruments operate within +/- 1°C of true value.

Building on technological developments of the past the HAWK pyrolysis instrument delivers the most accurate results available today. The degree of trueness is most easily visualized in the comparisons of our routine standard collected over all analytical runs (Figs 2, 3 and 4). The precision of the instrument and results is demonstrated in those same simple comparisons highlighting very minimal variation across multiple runs on multiple instruments. Additionally a host of additional validation data is available through the [www.wildcattechnologies.com](http://www.wildcattechnologies.com) website.

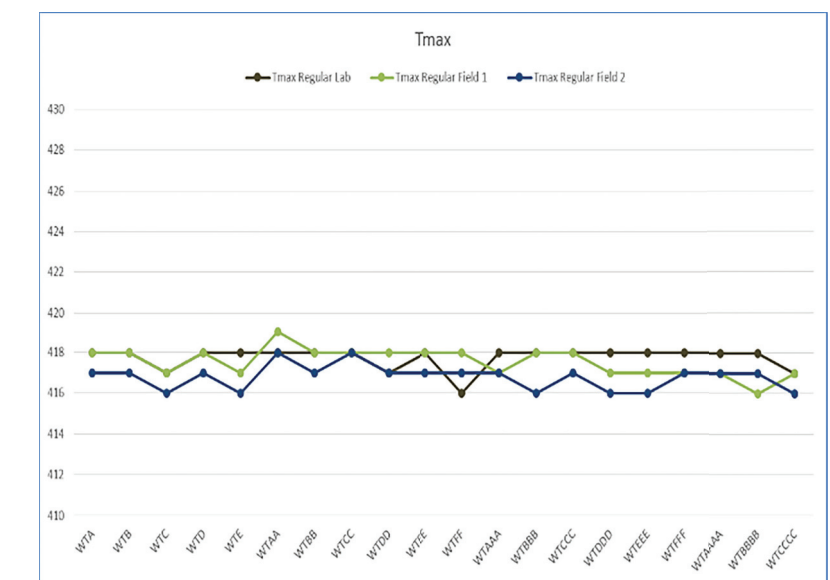


Fig 4 – Multiple Standards with Tmax values +/- 1°C of True value (417°C)



## Modified Pyrolysis Methods – Lab vs “Field”

No surprise in our world of instant gratification that the 49 minute analysis time associated with traditional Pyrolysis + Oxidation (TOC) is simply too long. Experimentation with faster pyrolysis rates developed alongside the drive for wellsite analysis (Toby et al, 2005). Faster analytical times equates to higher resolution in sampling and/or additional wellbore section analyzed on projects requiring rapid results turnaround. The original temperature ramping rate of 25°C/min was increased to 75°C/min and oxidation times slightly reduced resulting in a 26 minute Pyrolysis + Oxidation (TOC) analysis time.

The reduction in analysis time is beneficial only if there is no compromise in data quality or results. A battle fought valiantly by top level geochemists (Laughrey 2009 – Present). So we begin our study with a comparison of the two methods and RESULTS attained from properly calibrating each method individually to known standard. Figure 5 is an overlay of the pyrogram for our routine standard through traditional “Lab” method with the pyrogram of that same standard run through the “Field” Method. Aside from the difference in temperature profile (blue arrow to Field Temp Profile and Green Arrow to Lab Method Profile), the geometry of the S2 peak is the most notably different feature between the two runs. As we would expect the faster temperature ramp produces a sharper peak with higher intensity compared to the lower and broader peak generated from the lab method. At first glance this change in geometry is concerning. However, proper calibration of the field method to the known values of the standard will provide raw values very comparable to the lab method and negligible interpretation differences (Fig 6 – 9).

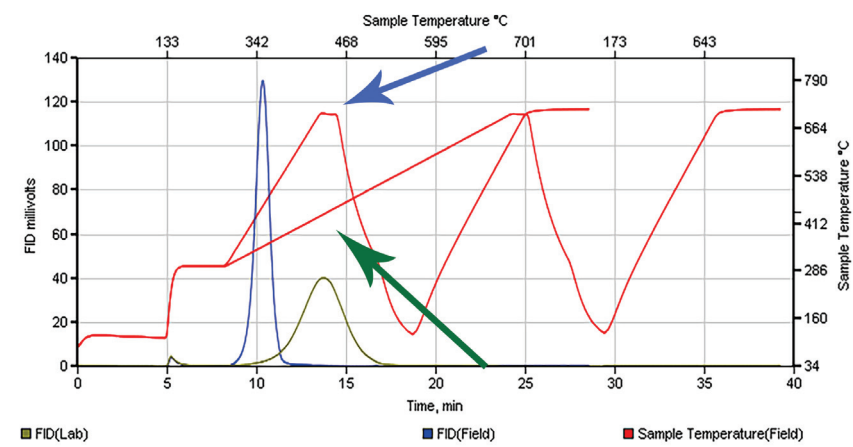


Fig 5 – Overlay of Field and Lab method pyrograms on parallel sample splits

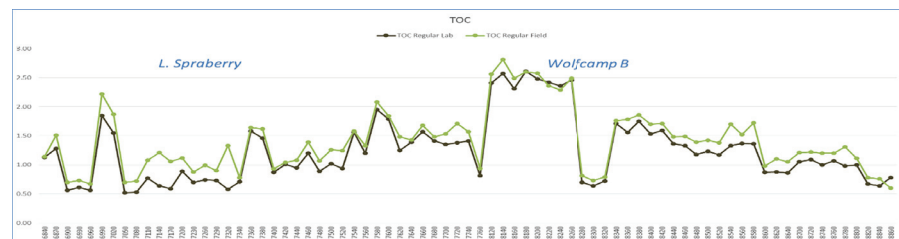


Fig 6 – TOC Values for Lab Method vs Field Method on our showcase sample set

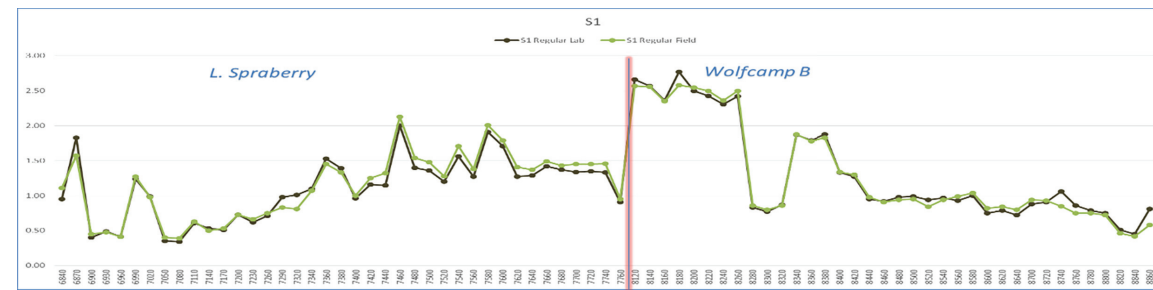


Fig 7 – S1 Values for Lab Method vs Field Method on our showcase sample set

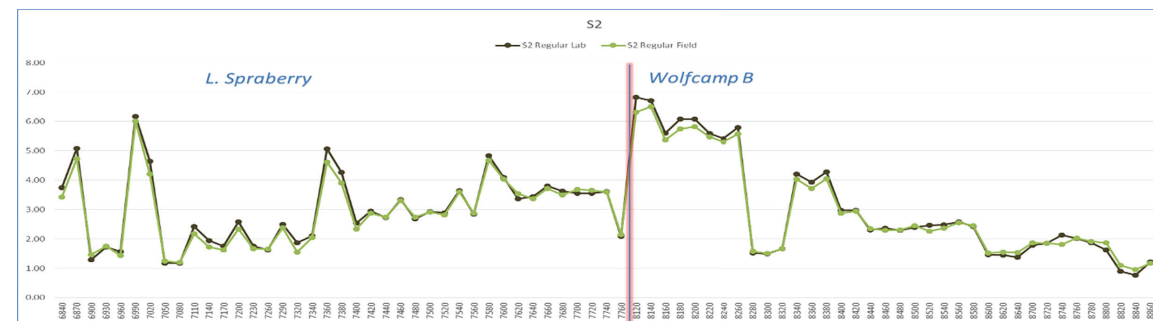


Fig 8 – S2 Values for Lab Method vs Field Method on our showcase sample set

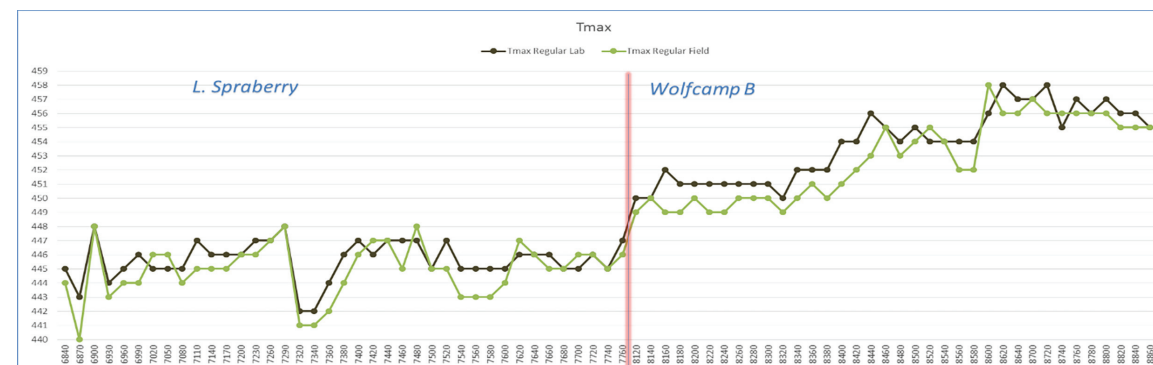


Fig 9 – Tmax Values for Lab Method vs Field Method on our showcase sample set

## As-Received vs Solvent Extracted – Investigating the Extent of S1 to S2 Carry-Over

Kerogen by definition is the portion of organic matter in the rock that is insoluble in organic solvent. Earlier studies (Peters 1986, Snowden 1994, Jarvie 1998 and others) validated the use of organic solvents to remove liquid bitumen from a source rock sample leaving the solid kerogen behind for evaluation.

We performed solvent extraction on a large split of the water-based mud samples in our showcase sample set. S1 values below 1 mg of HC/g of rock, reduction in S2 and increase in Tmax values are all encountered and are all indicative of thorough solvent extraction of the bitumen component. A pyrogram for the extracted sample split is overlaid on the as-received pyrogram to highlight the differences in peak geometry (Fig 10).

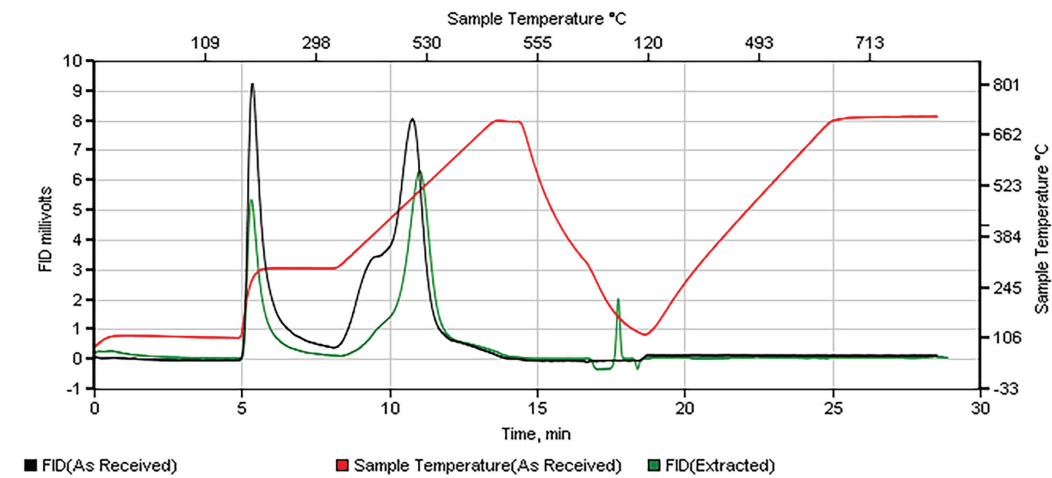


Fig 10 – As-Received vs Extracted on parallel sample splits

Note the large low temperature shoulder of the S2 peak in the As-Received pyrogram and the absence/significant reduction of that shoulder after extraction. Results for the entire showcase sample set (As-Received vs Extracted) demonstrate both the prevalence and magnitude of the carry-over caveats across a range of maturation values (Fig 11 and 12). As expected the less mature Lower Spraberry samples are more susceptible due to an inherently heavier hydrocarbon saturation than the deeper, more mature Wolfcamp B samples when kerogen quality is consistent.

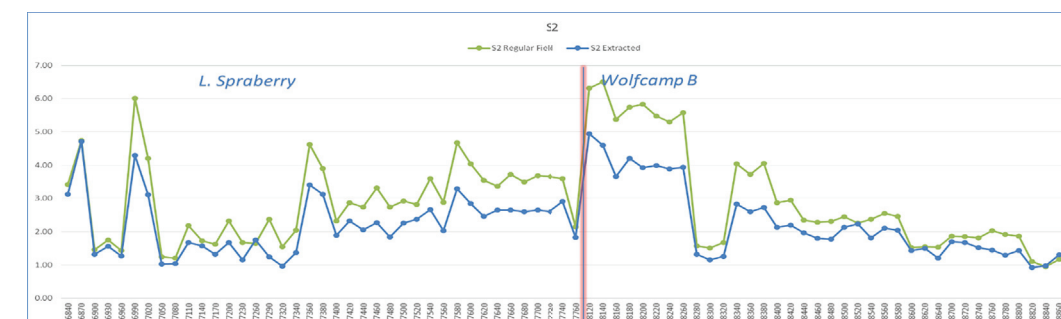


Fig 11 – S2 Values for As-Received vs Extracted on our showcase sample set

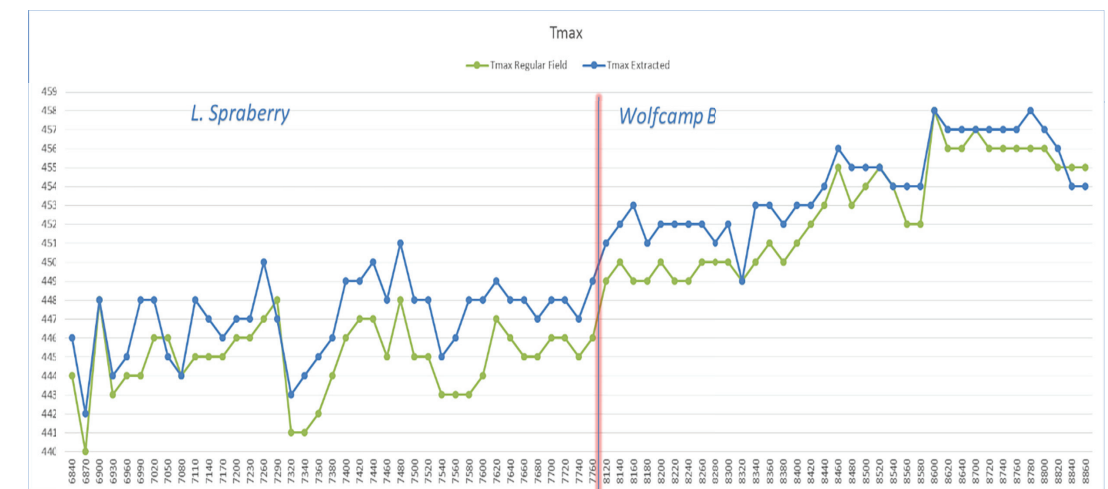


Fig 12 – Tmax Values for As-Received vs Extracted on our showcase sample set

The resulting S2, Tmax and HI values (B) from the extracted samples will serve as our indication of trueness when evaluating modified methods. However, since solvent extraction will eliminate our S1 peak and part of our S2 peak (A) is still the missing variable and the focus of future experimentation.



## Modified Pyrolysis Methods – Alternate Initial Isotherm Temperatures (350°C and 375°C)

A simple (and admittedly naïve) possible solution to our carry-over issue would be to increase the initial isotherm temperature in an effort to capture the entire range of liquid hydrocarbons potentially present without cracking the solid kerogen present in the rock.

Building on the recent wealth of kinetics data, we modified the existing Field Method by increasing the initial isotherm temperature to 350°C for Modified Method 1 and then 375°C for Modified Method 2. Fig 13 is an overlay of the as-received, extracted and modified pyrograms on parallel splits of the same sample along with the full suite of results from our showcase sample set (Fig 14 and 15) indicate a shift towards our extracted S2 and Tmax values plotting in between the As-Received and Extracted results. However, the separation of liquid bitumen from solid kerogen is obviously not complete; therefore the trueness of the results are not acceptable for characterizing either (A) or (B) in the same method.

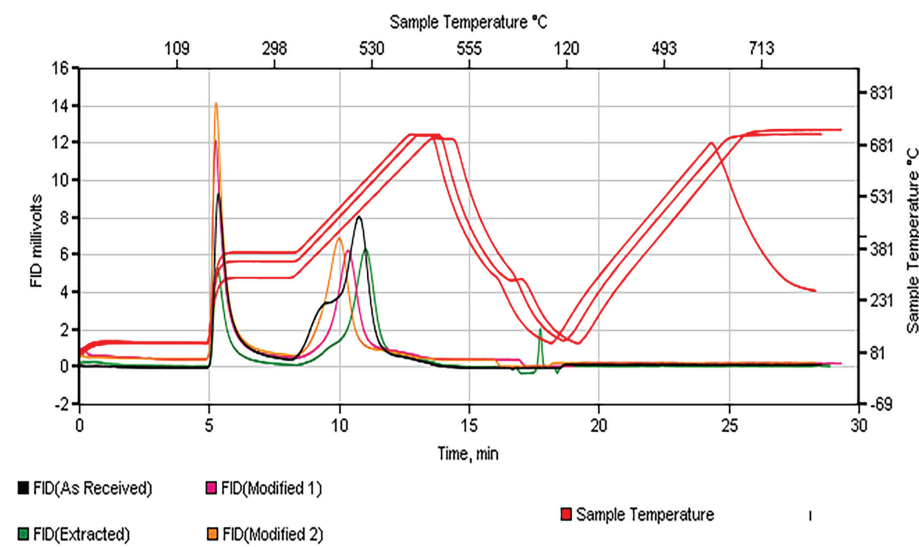


Fig 13 – Overlay of As-Received, Extracted, Modified Method 1 and Modified Method 2 pyrograms on parallel sample splits

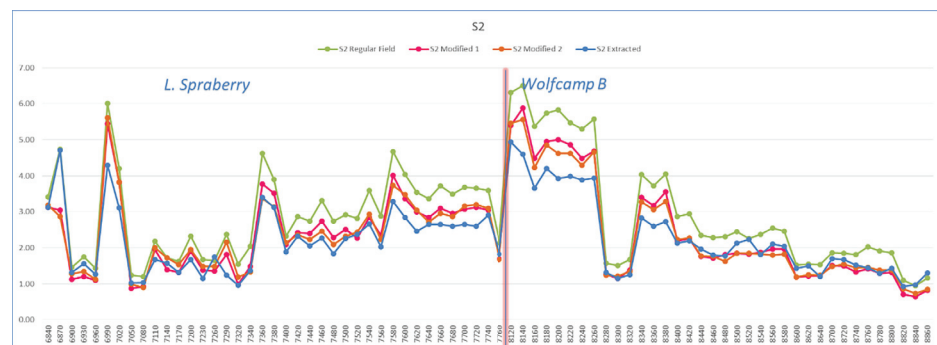


Fig 14 – S2 Values for As-Received vs Extracted vs Modified Methods 1 and 2 on our showcase sample set

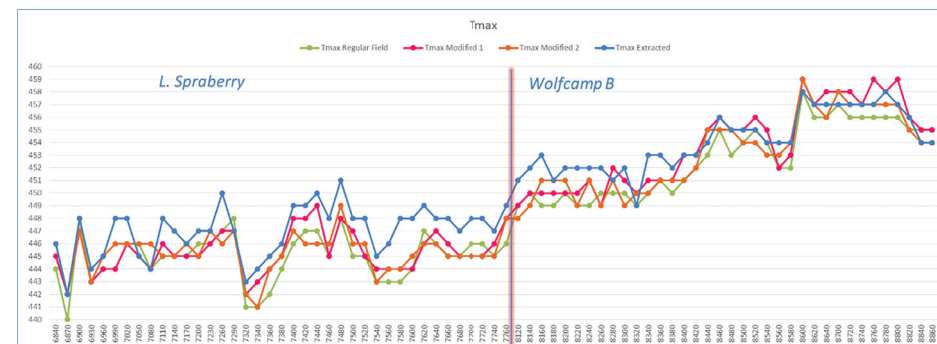


Fig 15 – Tmax Values for As-Received vs Extracted vs Modified Methods 1 and 2 on our showcase sample set

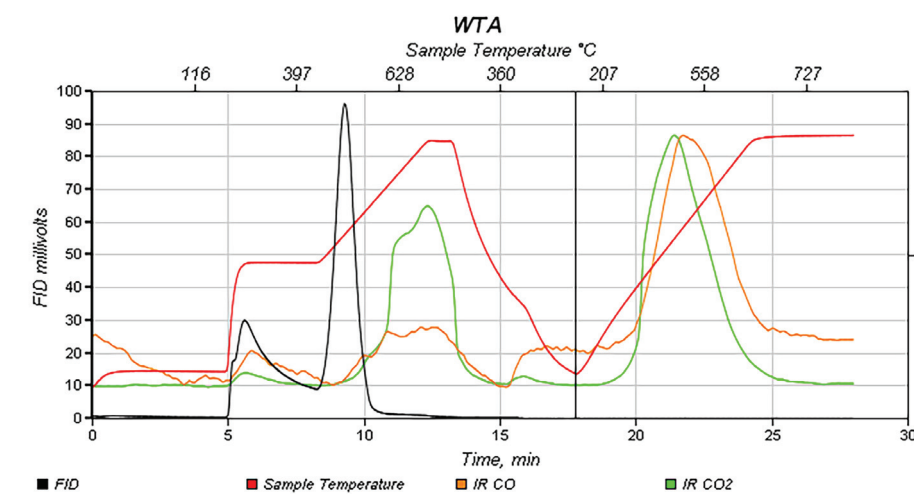


Fig 16 – Standard run at experimental 400°C Initial Isotherm Temperature. Note the incomplete separation of S1 and S2 likely due to some extent of kerogen cracking during the Isotherm

Increasing the initial isotherm temperature to above 375°C results in potential cracking of kerogen. Limited experimentation with a 400°C isotherm (Fig 16) confirmed this and thus was not pursued any further.

## Analytical Conclusions

Evaluating hydrocarbon saturations (‘S1’) and compositions have become almost essential to pyrolysis interpretations. Aside from straight S1 curves; routine calculated values such as Production Index (Espitalie et al, 1977) and Normalized Oil Content (Jarvie and Baker, 1984) rely on accurate S1 values for insight into conversion and identification of hydrocarbon accumulations respectively. Our recommendations above require elimination of the S1 peak prior to analysis thus we must determine an alternative way of reliably and rapidly quantifying (A) to accompany our source rock analysis (B). And to complicate the situation our measurement must be performed on a known weight of sample for integration with S2, S3 and TOC from pyrolysis.

Currently two different methods of attaining our reliable (A) are being tested and will be the focus of future updates to this study.

1. High speed gas chromatography in conjunction with Hawk pyrolysis (HAWK fast GC). Liquid Chromatography on whole rock extracts. Reference Jarvie et al, 2015.
2. Independent hydrocarbon liberation techniques for whole rock in conjunction with high speed gas chromatography.

Please stay tuned for future updates on the feasibility and accuracy of these experimental analytical procedures. A rapid and reliable assessment of (A) is coming very soon. Once that hurdle is cleared and we can rely on our techniques for predicting in-situ hydrocarbon generation we can move to the next and potentially more challenging investigation of migratory contributions. Even in our tight unconventional reservoirs migration is possible. I like Dave Cannon’s independent research conclusions...In order for a hydrocarbon to migrate 20 miles over the course of 30 million years, it must only travel the width of a single human hair each year. Entirely possible and soon to be a complex issue for operators and service companies to address together.

## Special Thank You to:

- David Cannon and Diamondback Energy
- Dan Jarvie at Worldwide Geochem
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