Advanced Pyrolysis Data and Interpretation Methods to Identify Unconventional Reservoir Sweet Spots in Fluid Phase Saturation and Fluid Properties (API Gravity) From Drill Cuttings and Cores*

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Abstract

Understanding the EUR and producibility of unconventional reservoirs depends on, among other factors: 1) distinguishing hydrocarbons present as a producible fluid phase saturation from those in the sorbed state that are not producible; and 2) reservoir fluid properties such as API gravity. We present geochemical techniques that address both issues. Analysis was performed on cores from the Marcellus and Burkett Formations of USA together with cores from Mexico's Pimienta Formation, using the HAWK pyrolysis instrument's Petroleum Assessment Method (HAWK-PAM) and advanced pyrolysis plots that model sorbed versus total oil yields. For HAWK-PAM, a ramp rate of 25°C/min is utilized to generate 5 petroleum peaks; 4 on Oil Fractions and 1 on kerogen. Each isotherm has its Tmax temperature. The related peaks correspond to saturates, aromatics, resins, and asphaltenes (SARA) categories; C1-C5, C6-C7, C8-C14, C15-C40, and Kerogen (plus any C40+). 12 Marcellus cores had an average oil fraction yield of 8 mgHC/g at a kerogen Tmax (a proxy for maturity) of 462°C and 4 Burkett cores averaged 7 mgHC/g at a maturity of 466°C. 3 Pimienta cores had 2 to 6 mgHC/g at a maturity of 448 to 455°C. We used HAWK-PAM to evaluate the samples oil content, SARA composition, and to predict its API gravity. Current results indicate that oil fractions sum of at least 3 mgHC/g rock is a necessary - but not sufficient - condition for a formation to be an unconventional liquids reservoir with significant fluid phase saturation ("mobile oil"). HAWK-PAM enables prediction of API gravity from cuttings and cores using a linear correlation of API gravity to a derivative of HAWK peaks with R2 = 0.91. Pimienta cores calculate 35, 28, and 33°API. In order to separate the oil in the rock samples into sorbed versus producible fluid phase states, we then analyzed the HAWK results using t!Ps' advanced pyrolysis plots that model sorbed versus total oil yields. The saturation log and Caterpillar' plots for the Marcellus well highlight zones of fluid phase saturation that are potential targets for liquids production along with the Marcellus gas stream. The combination of HAWK-PAM and t!Ps' interpretation plots can identify storage and producibility sweet spots in unconventional reservoirs, quantifying the presence and composition (API) of liquid hydrocarbons, providing an accurate Tmax maturity proxy and distinguishing zones of fluid phase saturation "mobile oil" from sorbed oil in cuttings and cores.

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Advanced pyrolysis data and interpretation methods to identify unconventional reservoir sweet spots in fluid phase saturation and fluid properties (API gravity) from drill cuttings and cores

AAPG 2017 Annual Convention & Exhibition, Houston, Texas, April 2nd - 5th

Albert Maende[1], Andy Pepper[2], Dan Jarvie[3] & David Weldon[1]

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Outline

HAWK Petroleum Assessment Method (HAWK-PAM)

- Splits the volatile petroleum (former 'S1') peak into 4 separate Yields to provide compositional information on the volatile hydrocarbons
- Yield 4 separates the petroleum 'shoulder' from the petroleum potential (former 'S2') peak to allow more reliable Tmax measurement
- HAWK-PAM pyrograms reflect organic matter maturity and hydrocarbon composition

Prediction of API gravity from drill cuttings and cores

- HAWK-PAM on solvent extracts

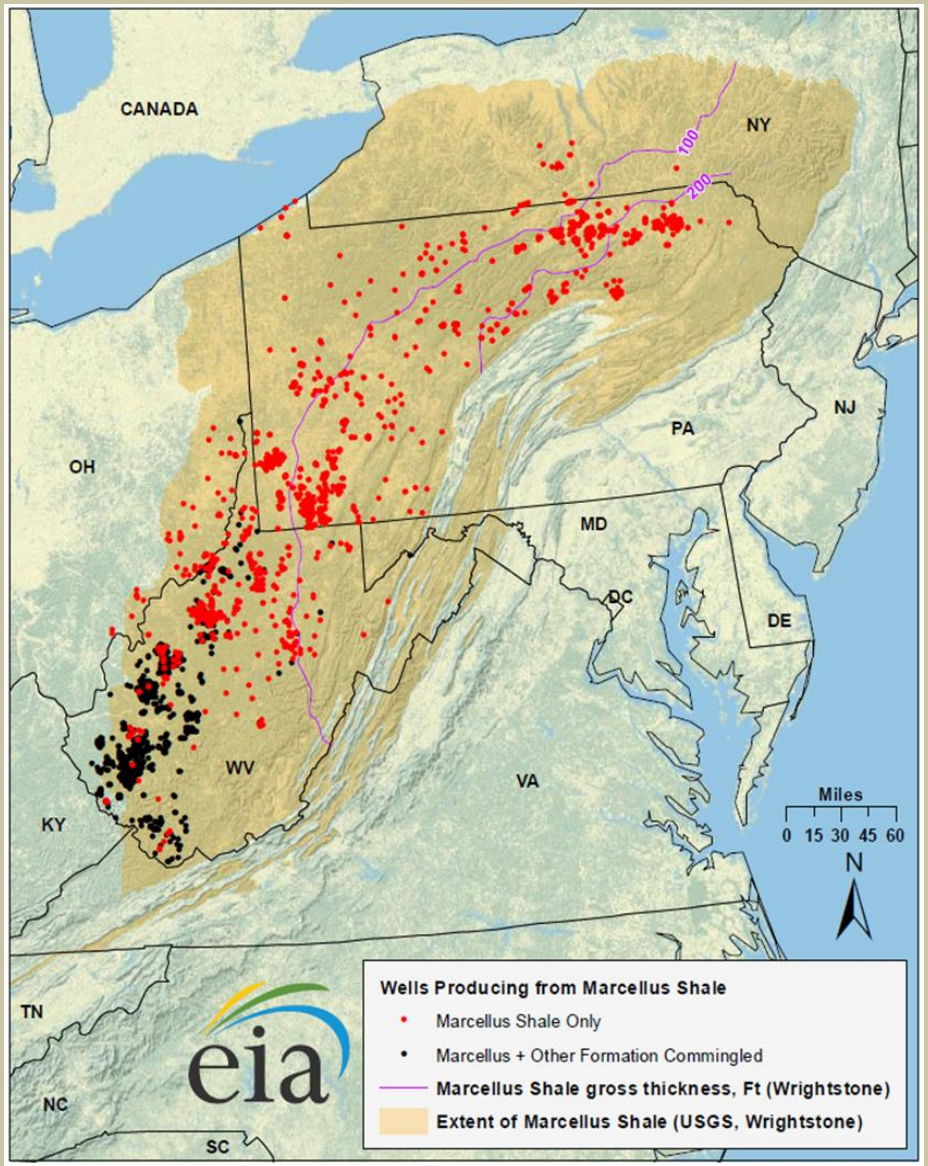
Saturation calculation

- Method to distinguish the mobile from sorbed (immobile) phase and predict 'live' fluid saturation in organic-rich fine-grained rocks
- Identify fluid saturation sweetspots

Compositional prediction

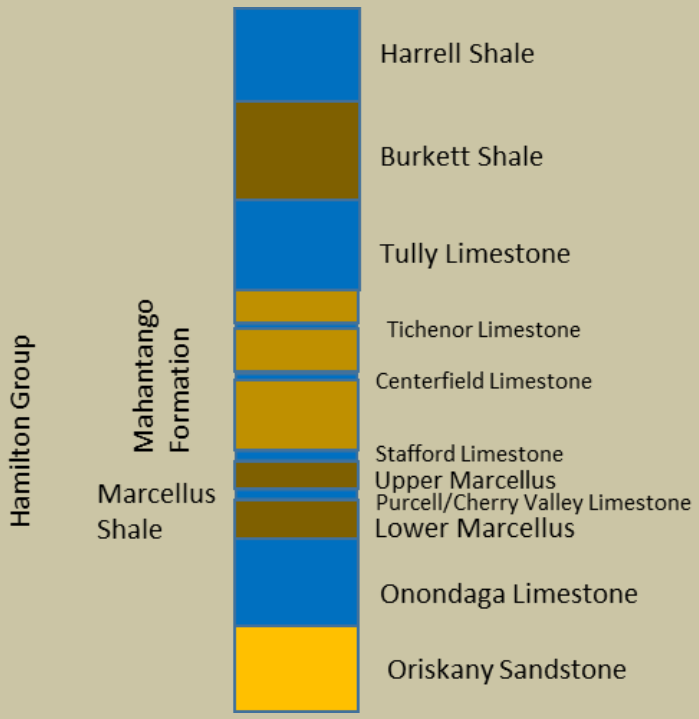
- Method to use the 4 Yields to predict PVT properties - API, GOR - of the mobile phase
- Identify fluid property sweetspots

Location of Study



Source: US Energy Information Administration based on data from WVGES, PA DCNR, OH DGS, NY DEC, VA DMME, USGS, Wrightstone (2009). Only wells completed after 1-1-2003 are shown. Updated June 1, 2011

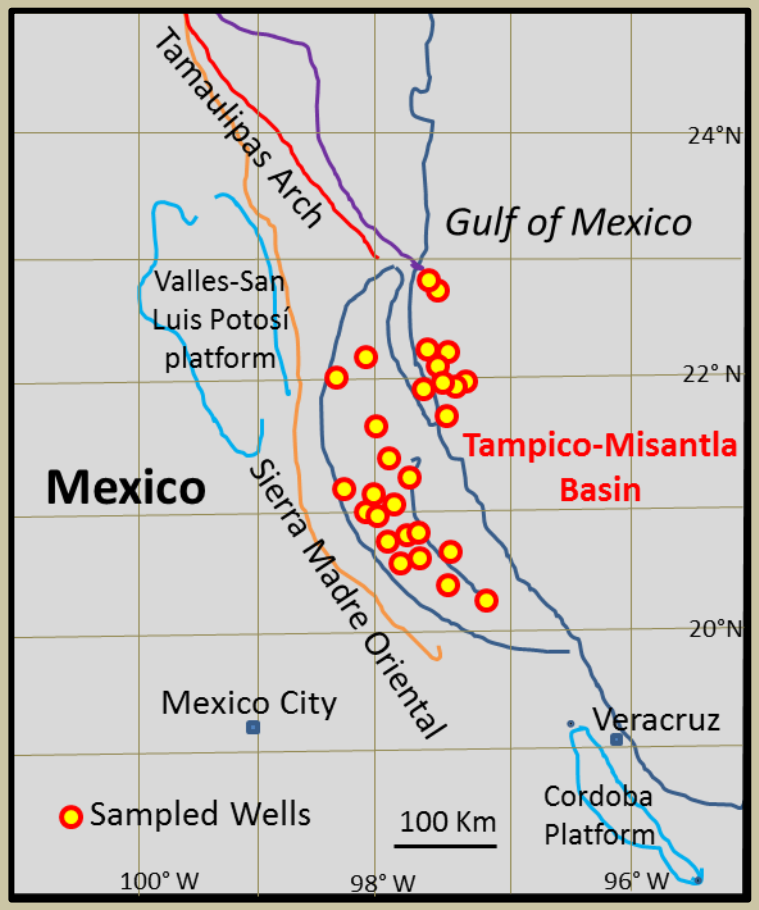
Marcellus and Burkett Formation cores were retrieved from a single vertical well that was drilled in Western Pennsylvania/West Virginia through Devonian age Burkett, Tully Limestone, Hamilton and Marcellus as well as the top portion of the Onondaga (Comet et. al., 2015).



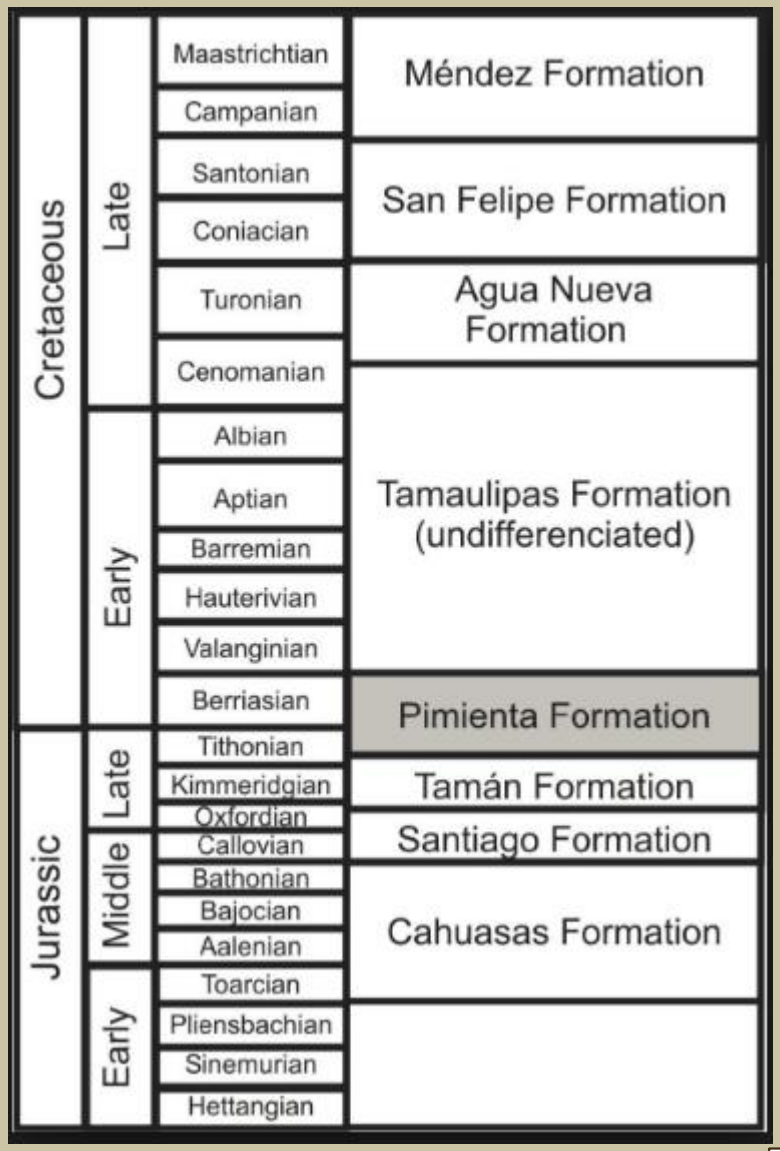
(Wrightstone, 2009)

Location of Study

Pimienta Formation was cored from Mexico's Tampico-Misantla Basin (Wilson and Jordan)



(Jarvie and Maende, 2016)



HAWK Petroleum Assessment Method (HAWK-PAM)

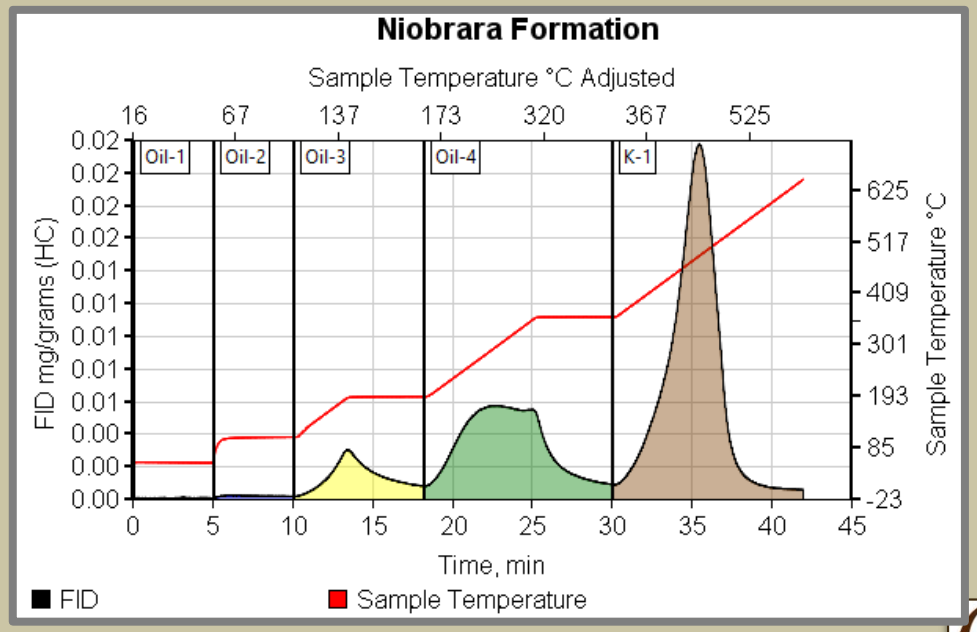
HAWK-PAM utilizes five zones using a multiple ramp and isotherm program.

Peak (Zone) Name	Oil-1	Oil-2	Oil-3	Oil-4	K-1
Temperature Range (°C) within which Tmax is designated	~50 °C to ~100 °C, hold for 5 minutes	100 °C, hold for 5 minutes	Ramp 100 °C to 180 °C at 25 °C per minute. Hold for 5 minutes	Ramp 180 °C to 350 °C at 25 °C per minute. Hold for 5 minutes	Ramp 350 °C to 650 °C at 25 °C per minute. Hold for 5 minutes
Petroleum fraction	C4-C5	C6-C10	C11-C19	C20-C36	Kerogen (plus any C37+)
SARA disposition	Saturates and Aromatics			Polars	n/a

Approximation of carbon number ranges and SARA fraction disposition utilized in HAWK- PAM.

A ramp rate of 25°C is utilized to generate five petroleum peaks – four on oil fractions and one on kerogen.

(Maende, 2016).



A typical pyrogram generated using HAWK-PAM

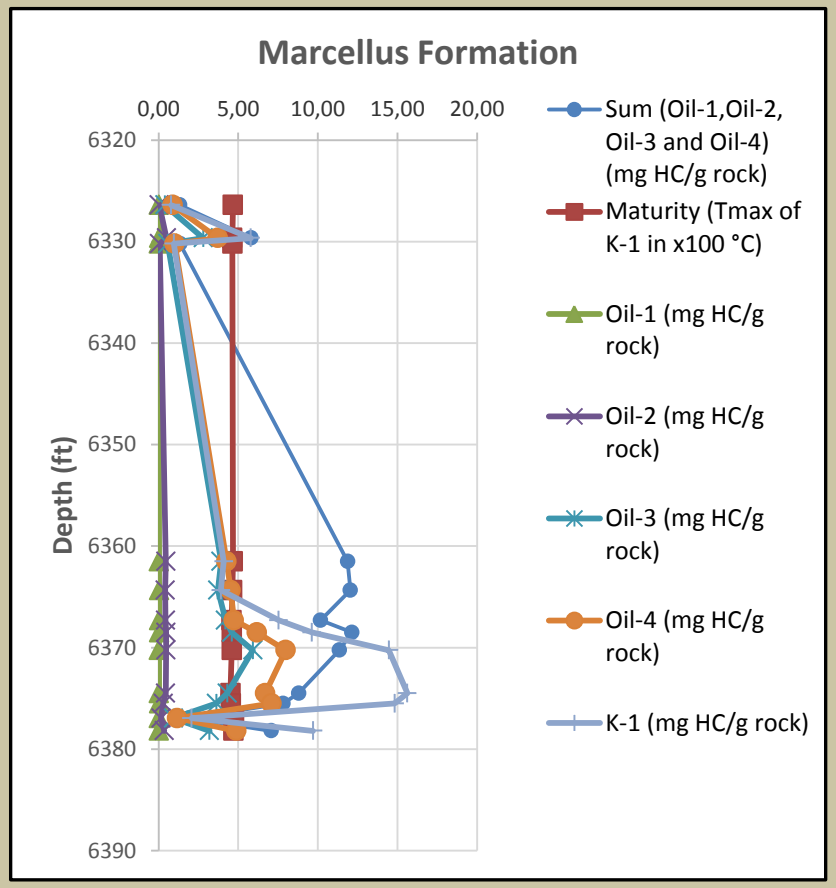
N-Alkane and SARA fractions that were analyzed on HAWK-PAM

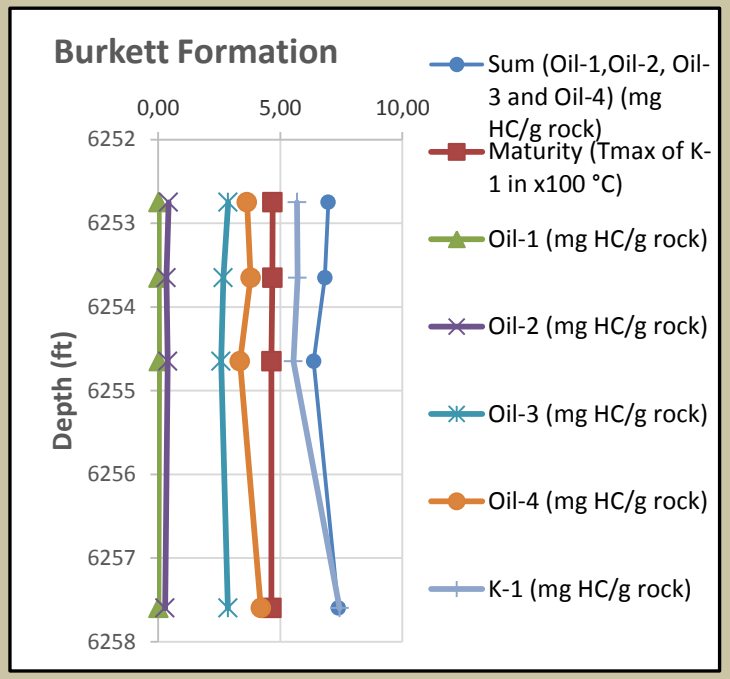
n-Alkane and SARA fractions that were analyzed on HAWK-PAM	Carbon No.	Oil fraction and K-1 fraction designation
6 NSO samples		K-1
4 Aromatics samples		Oil-4 and K-1
2 Saturates samples		Oil-3
3 Kerogen samples		K-1
3 Hexacosane samples	26	Oil-4
3 Decane samples	10	Oil-2
3 Tetradecane samples	14	Oil-3
3 Eicosane samples	20	Oil-4
3 Triatriacontane samples	33	Oil-4
3 Tetratetracontane samples	44	K-1
2 Pentane samples	5	Oil-1
3 Toluene samples	7	Oil-2

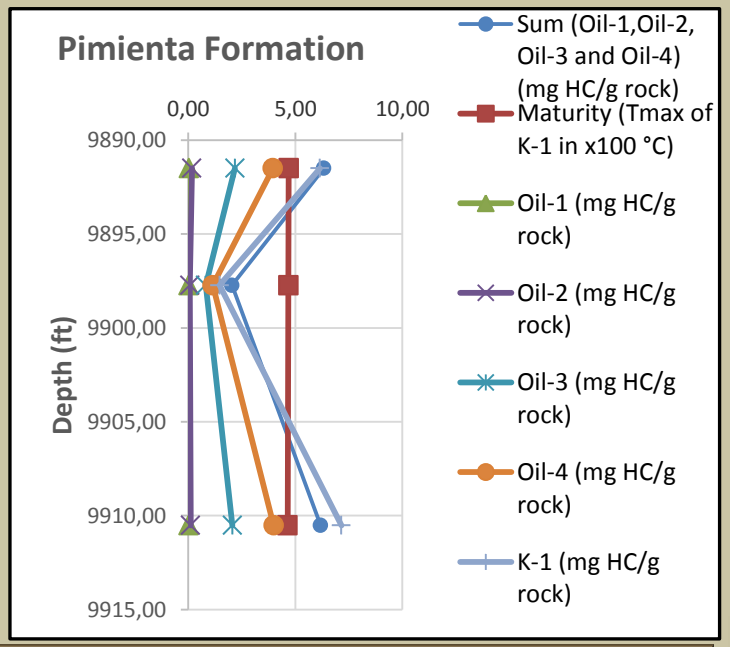
HAWK-PAM Results for Core Samples from Marcellus , Burkett and Pimienta Formations

Formation	Depth (ft)	Tmax K-1 (°C)	Sum (Oil-1,Oil-2, Oil-3 and Oil-4) (mg HC/g rock)
Average (Range) for Marcellus Formation (12 core samples)	6326.4 – 6378.2	462 (451 – 475)	7.64 (1.33 – 12.14)
Average (Range) for Burkett Formation (4 core samples)	6252.75 – 6257.6	462 (451 – 475)	6.89 (6.37 – 7.38)
Average (Range) for Pimienta Formation (3 core samples)	9891.5 – 9910.52	467 (464 – 469)	4.85 (2.04 – 6.33)

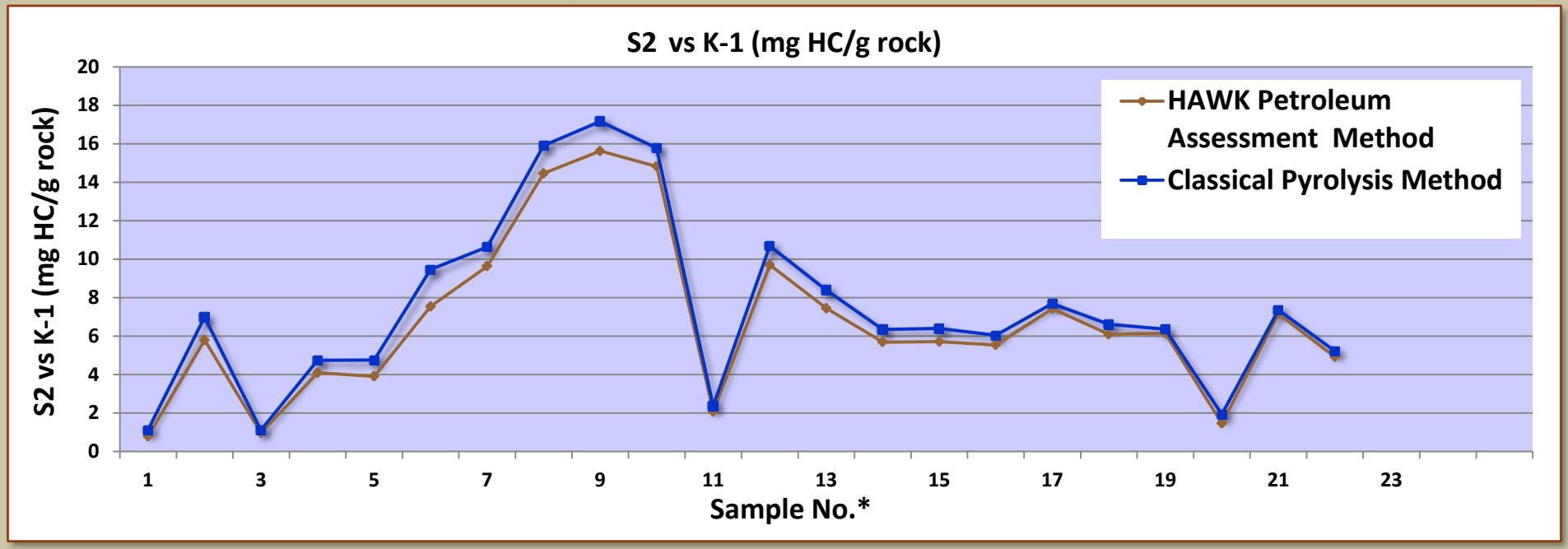
HAWK-PAM Results for Core Samples from Marcellus, Burkett and Pimienta Formations







Comparison of HAWK-PAM and Classical Pyrolysis Results for Core Samples from Marcellus, Burkett and Pimienta Formations

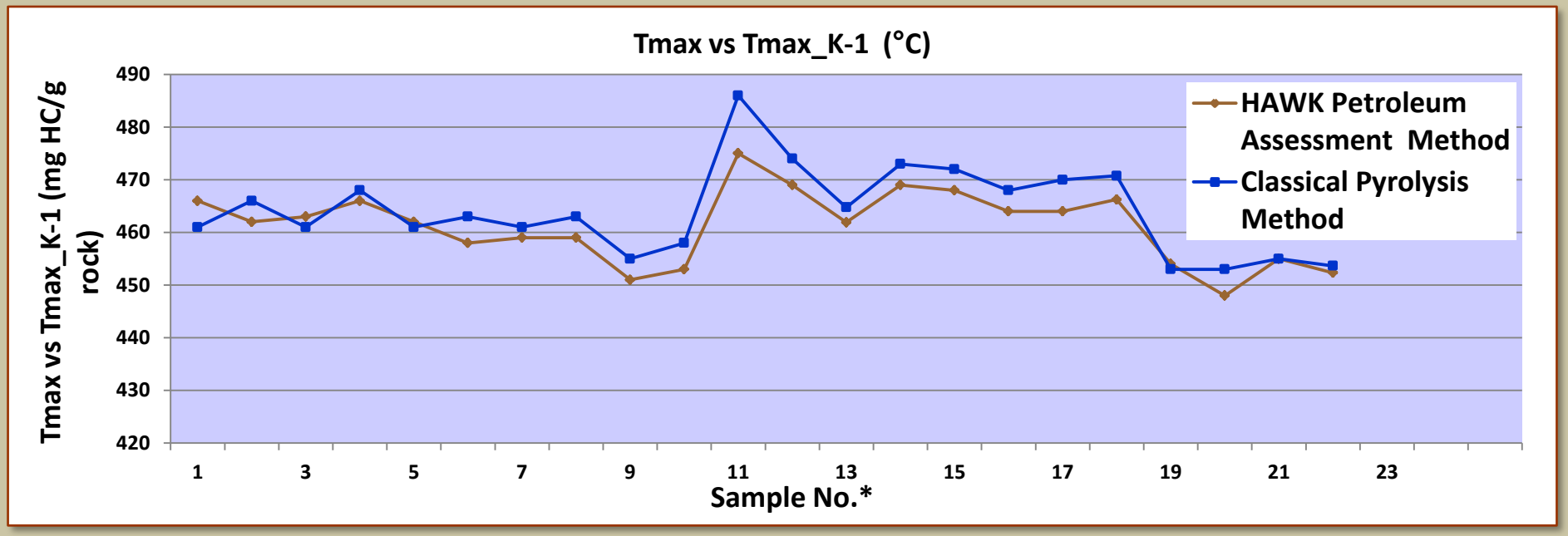


Note:

Sample No.*	Formation
1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12	Marcellus
13	Marcellus Average
14, 15, 16 and 17	Burkett
18	Burkett Average
19, 20 and 21	Pimienta
22	Pimienta Average

* K-1 is typically less than S2

Comparison of HAWK-PAM and Classical Pyrolysis Results for Core Samples from Marcellus, Burkett and Pimienta Formations



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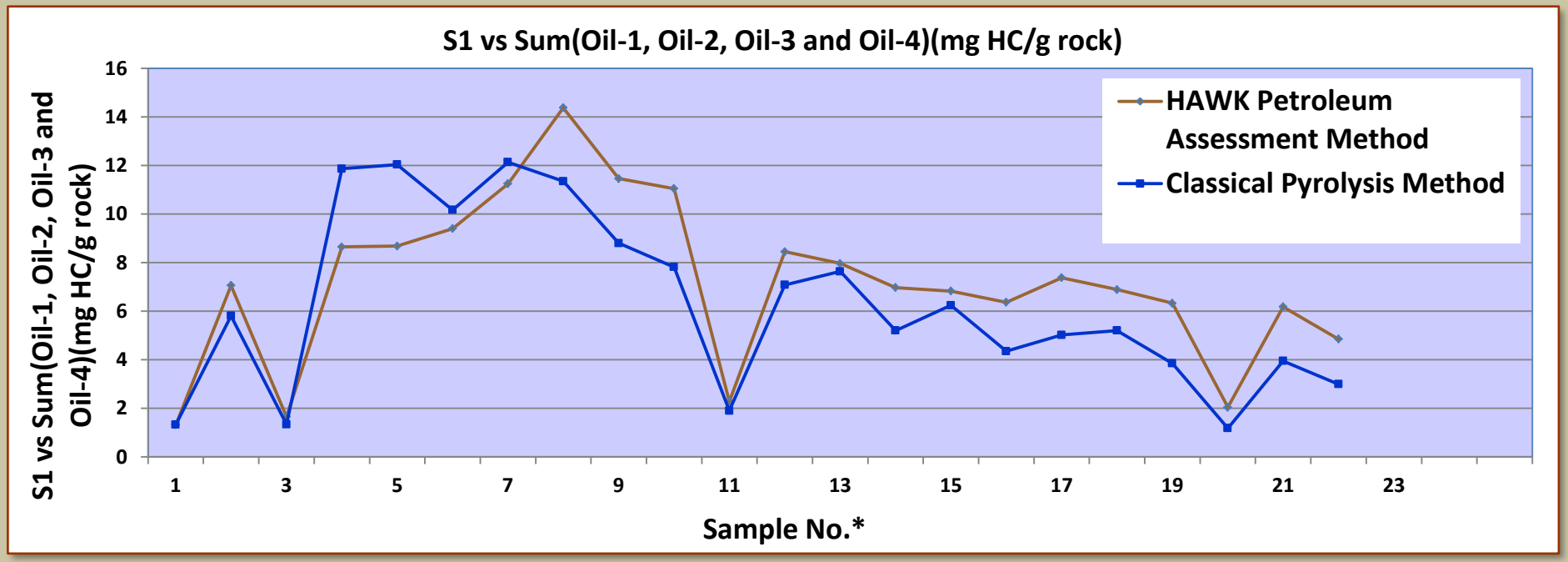
14, 15, 16 and 17	Burkett
18	Burkett Average
19, 20 and 21	Pimienta
22	Pimienta Average

* Tmax_K-1 is a proxy for maturity measurement and is more accurate than the S2 derived Tmax because Tmax_K-1 has no interference from the S2 shoulder.

Comparison of HAWK-PAM and Classical Pyrolysis Results for Core Samples from Marcellus, Burkett and Pimienta Formations



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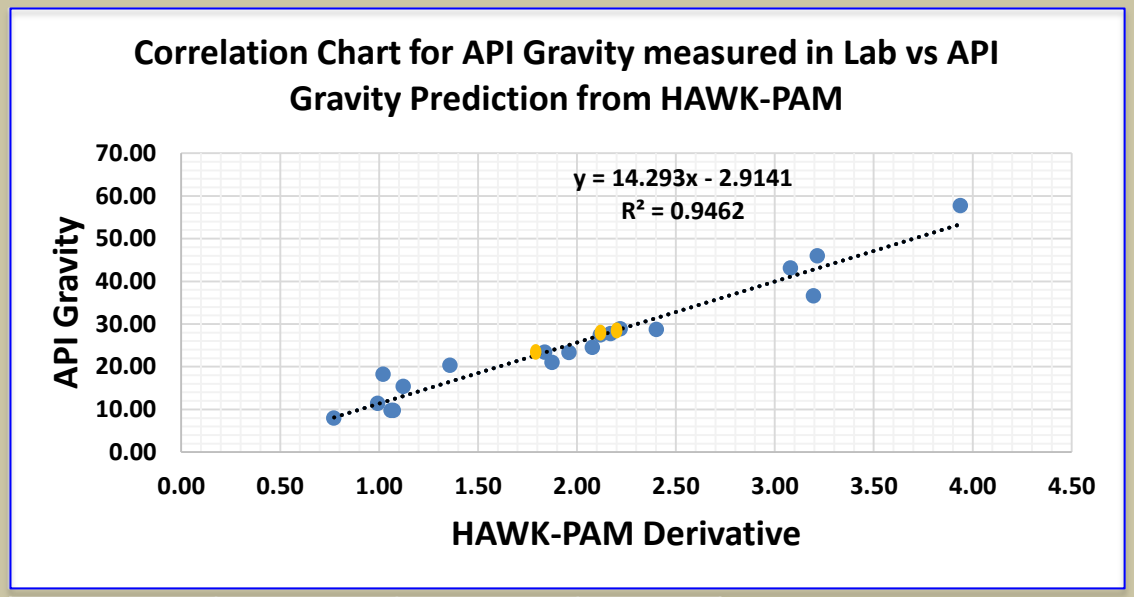
1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12	Marcellus
13	Marcellus Average
14, 15, 16 and 17	Burkett
18	Burkett Average
19, 20 and 21	Pimienta
22	Pimienta Average

* The sum of oil-1, oil-2, oil-3 and oil-4 is typically higher than S1 and provides a more accurate estimate of barrels of oil-in-place than the latter.

API Gravity Prediction from HAWK-PAM

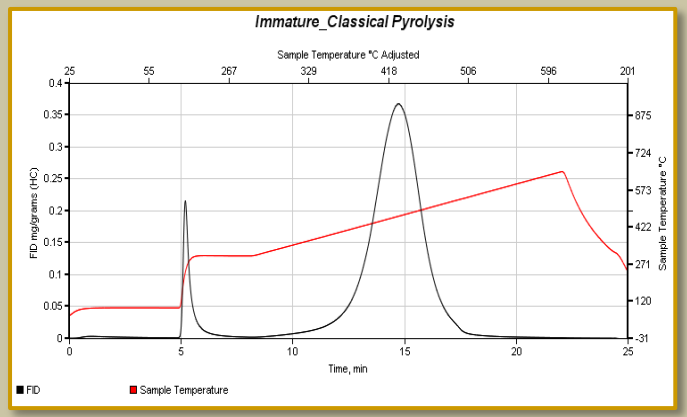


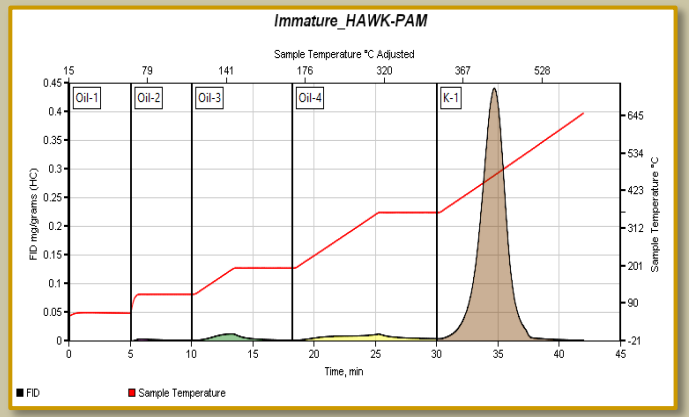
Sample Description	API Gravity measured in Laboratory (Hydrometer method)	API Gravity Prediction from HAWK-PAM	Color of Symbol
Black oil	15.31	13.14	
Black oil	18.16	11.67	
Core extract*		28.81	
Core extract*		23.36	
Core extract*		27.38	

HAWK-PAM API Gravity prediction on the Pimienta Formation's core extracts* utilized 30 microliters and so did the prediction on the oils

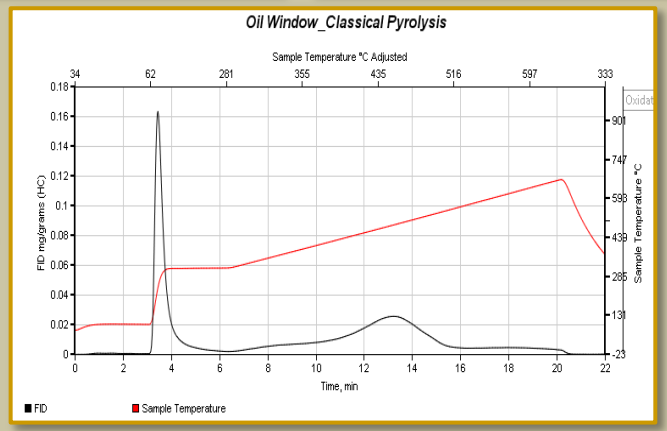
Sample Description	API Gravity measured in Laboratory (Hydrometer method)	API Gravity Prediction from HAWK-PAM	Color of Symbol
Condensate	57.70	53.39	
Black oil	9.72	12.26	
Black oil	20.30	16.51	
Black oil	28.70	31.42	
Black oil	43.05	41.09	
Black oil	45.96	43.05	
Light-brown oil	36.57	42.77	
Black oil	23.30	25.12	
Black oil	24.50	26.79	
Black oil	21.00	23.89	
Black oil	27.70	28.12	
Black oil	11.41	11.28	
Black oil	9.72	12.41	
Black oil	7.91	8.12	

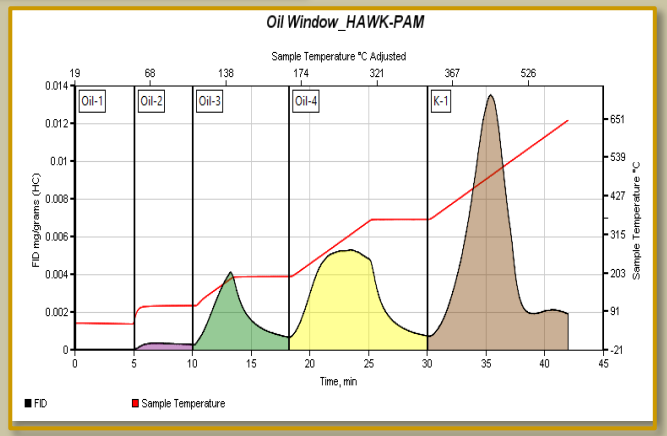
Maturity characteristic HAWK-PAM Pyrograms compared with those of Classical Pyrolysis

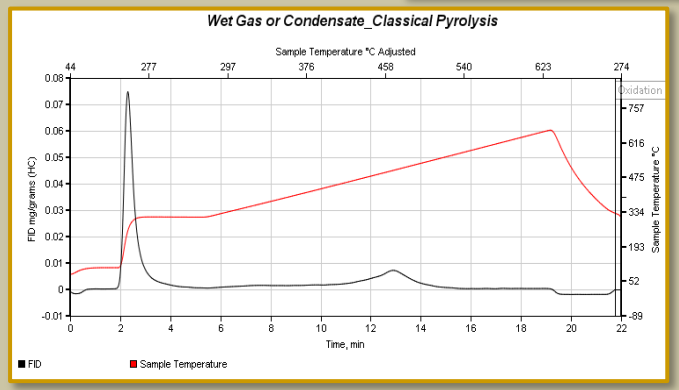


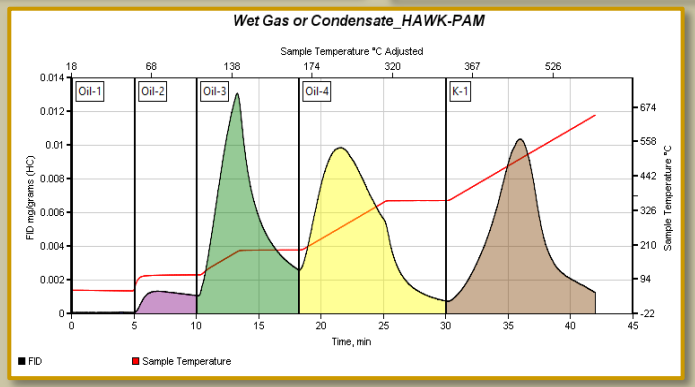


Classical Pyrolysis "S2 shoulder" is resolved on HAWK-PAM









SATURATION CALCULATION: NEW TOOLS

‘t!PsSAT2016’

A tool to distinguish fluid phase from sorbed phase liquids and to estimate original reservoir fluid phase saturation in organic-rich “shale” reservoirs

‘t!PsSAT2017’

An augmentation to estimate both original reservoir fluid phase saturation *and composition* using HAWK-PAM™ pyrolysis splits

t!PsSAT2016 & 2017

- Organic-rich 'Shale' reservoir rocks present a problem in laboratory core and petrophysical analysis
- Need to separate liquid yields in a mobile fluid phase from immobile sorbed phase
- 't!PsSAT2017' expands the capabilities of tiPsSAT2016 by **using advanced compositional pyrolysis data from HAWK-PAM™**
- Independent method complements and informs petrophysical saturation estimates

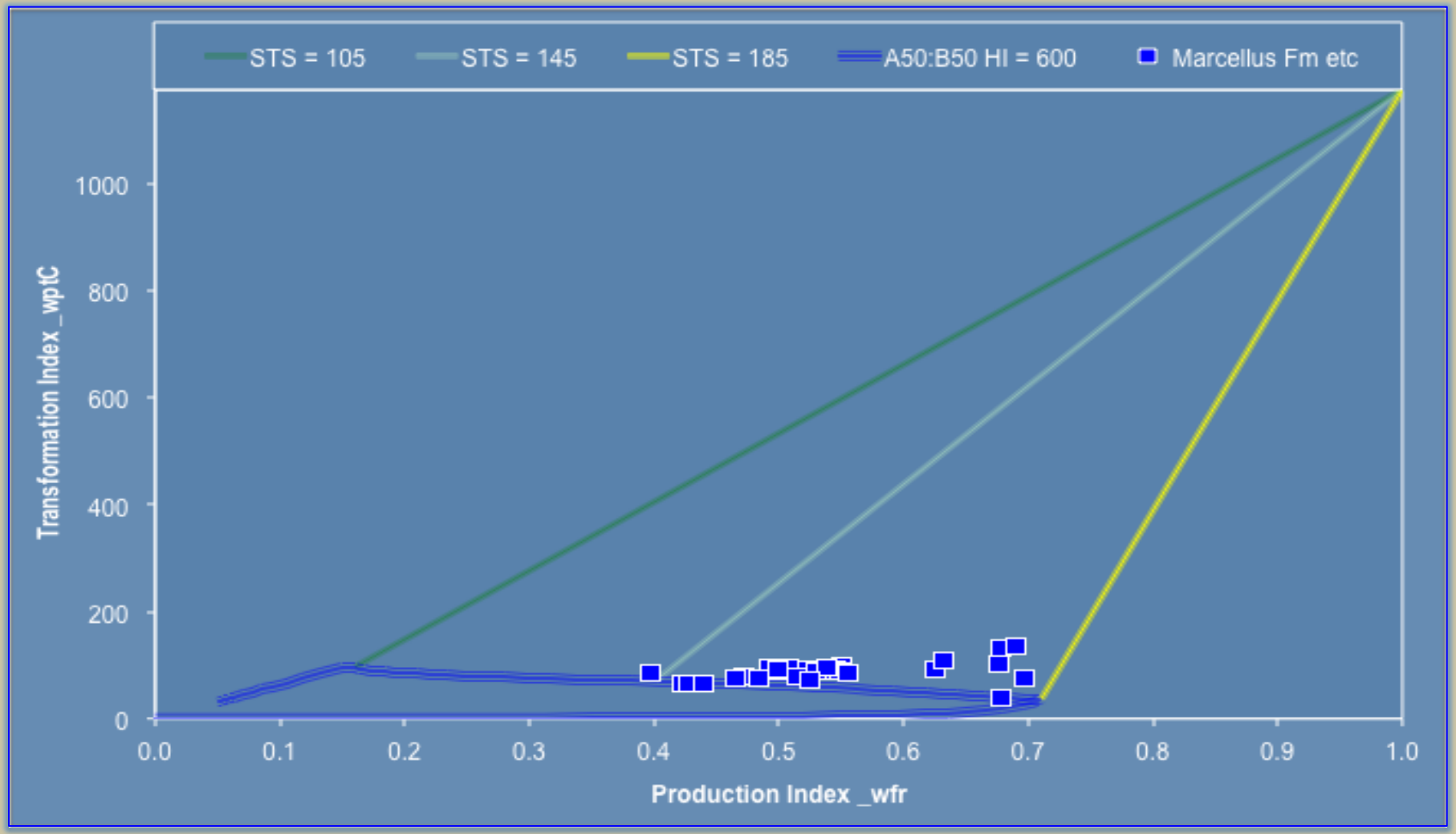
Inputs

- Organic carbon and pyrolysis yields on (preferably freshly cut) rock samples, un-extracted / un-cleaned (using Rock Eval or Hawk)
- Porosity: to estimate volumetric saturation
- GOR, P & T: to convert to 'live' reservoir fluid saturations

Outputs

- 'Caterpillar' screening cross-plot – quick look using bulk pyrolysis-derived ratios
- Depth logs of sorbed vs. fluid phase quantities
- 2017 version: **compositions** of the total, sorbed and fluid phases, related to PVT fluid properties

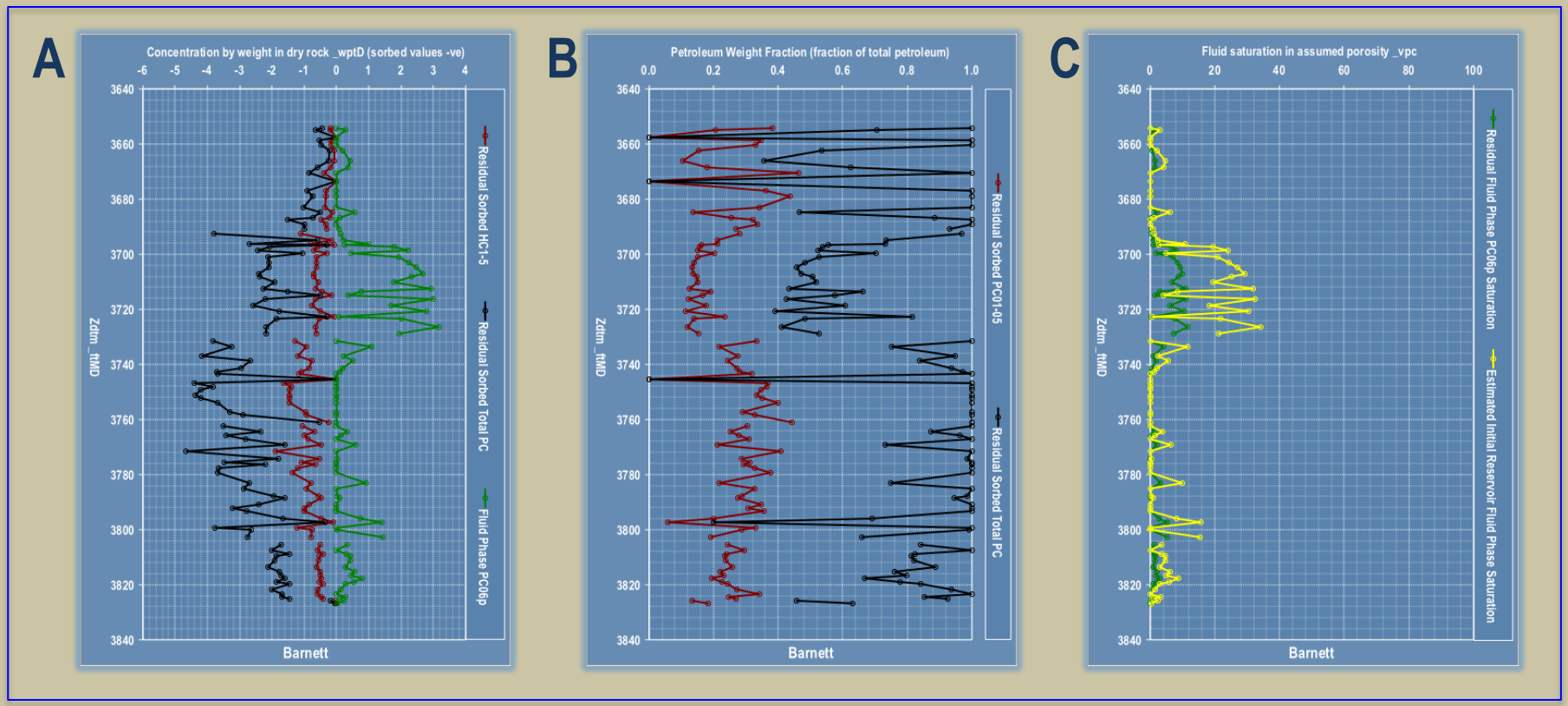
‘Caterpillar’ Screening Plot



Appalachian Basin well interval: Burkett to Onondaga

Samples with fluid phase storage appear above the sorption limit ‘caterpillar track’

t!PsSAT2016 tool output logs



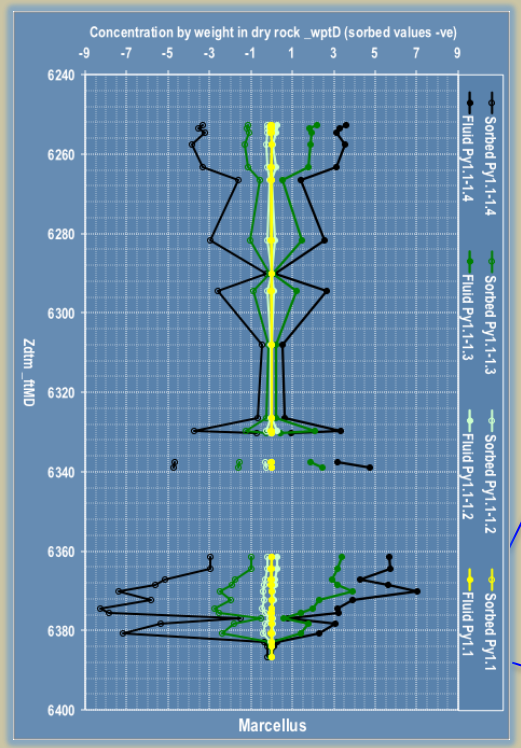
Well log plots for saturation estimation (non-productive Barnett well)

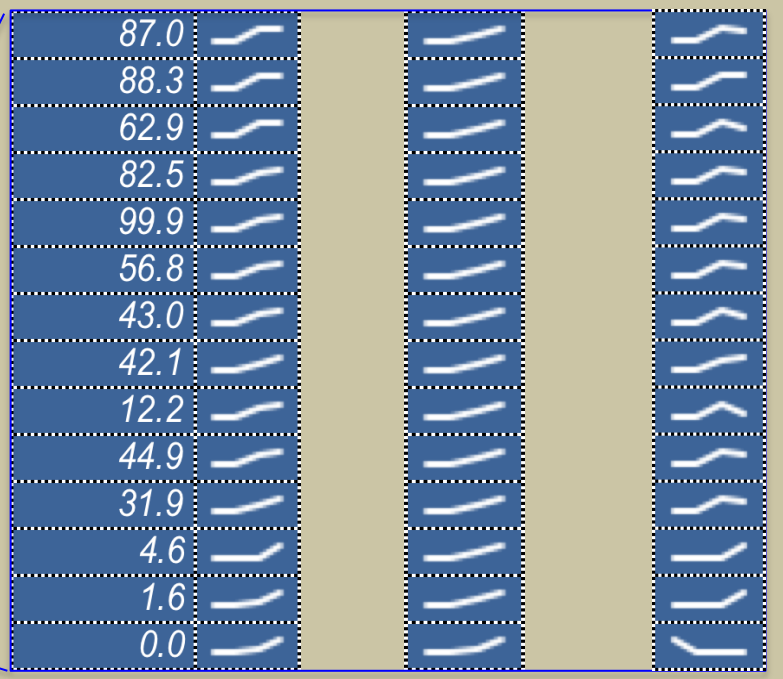
A: sorbed vs. fluid phase yields by weight of rock

B: sorbed vs. fluid phase proportions by weight fraction

C: residual liquid ‘dead oil’ and ‘live’ reservoir fluid phase saturations by volume, relative to the input porosity of the sample

‘t!PsSAT2017’ PAM fingerprints

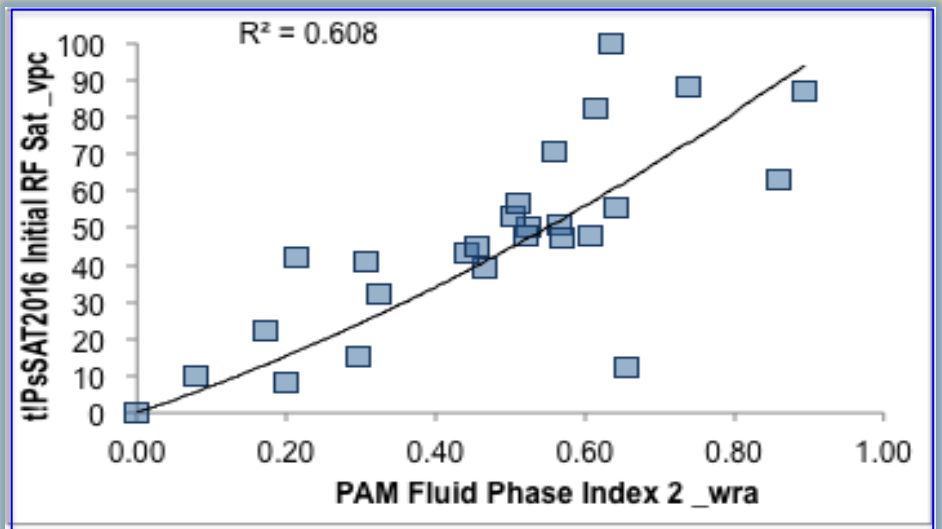


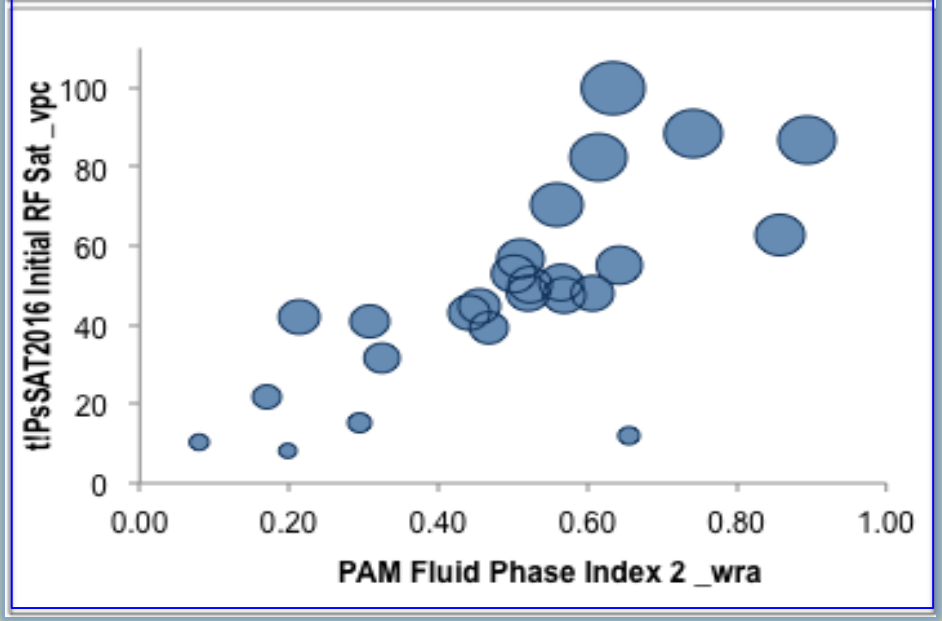


PAM profile contains information about the fluid phase

- Py1.3HC are deficient in samples with only sorbed petroleum; but present in ‘excess’ in samples with high fluid phase saturation based on t!PsSAT2016 (first column)
- Need to link to PVT data to understand full compositional implications of Py1.3HC
- Light end losses in current sample set preclude use of Py1.1 and Py1.2 HC splits

Fluid Phase Saturation vs. PAM profile





Information from the PAM profile

- Parameter 'PAM Fluid Phase Index 2' reflects 'excess' amount of PAM Py1.3HC weight in the sample

Compare with Fluid Saturation

- Saturation calculated using the basic t!PsSAT2016 method - but recalibrated to PAM Py1HC yields (which are larger than RE Py1HC yields)

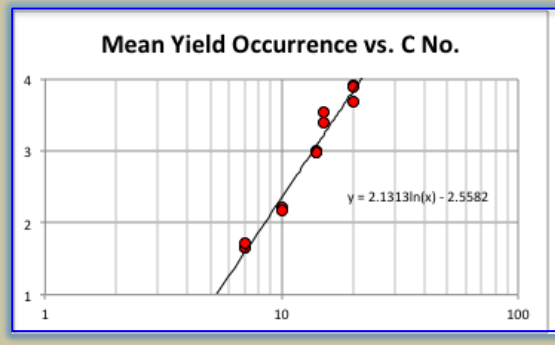
Compare independent methods

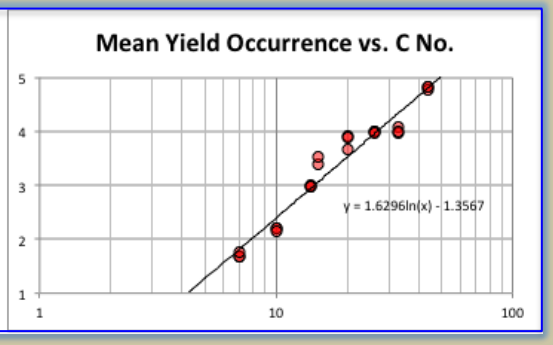
- Good correlation but with scatter at low concentration (upper chart)
- Bubble area shows fluid phase Py1HC yield as signal/noise indicator (lower chart)

Ongoing work: PAM to PVT

Interpolation results for PC No. range for Hawk-PAM splits

Hawk-PAM split	4-split method	5-split method (rock extracts)
Oil 1 / Py1.1HC	05-06	04-05
Oil 2 / Py1.2HC	07-10	06-10
Oil 3 / Py1.3HC	11-17	11-19
Oil 4 / Py1.4	18-43	20-36
K-1 / Py2.0	44+	37+





Calibration vs. known compounds (Carbon No. and SARA) – and with PVT data

- MW ranges of PAM splits firmly established
- PVT database of PAM splits in place: can predict API and broad GOR range
- Thermo-vaporization GCs show losses in PC06+ in legacy cores investigated to date. Currently analyzing fresh core programs to obtain full range datasets of PAM splits 1-4

Conclusions

New HAWK Petroleum Assessment Method (HAWK-PAM)

- New pyrolysis instrument provides data to better characterize volatile hydrocarbon composition as well as yield
- Separates the 'shoulder' from the petroleum potential peak, better determining Tmax

Prediction of API Gravity from Drill Cuttings and Cores

- Predicting API Gravity from drill cuttings and cores using only micro-liter extract quantities as opposed to the milli-liter current lab requirements for hydrometer API Gravity measurements

Saturation calculation

- *t!PsSat2016* method distinguishes the mobile from sorbed (immobile) phase
- Also able to predict 'live' fluid saturation, if porosity known

Compositional prediction

- Capability of PAM 1-4 MW profile to predict PVT properties - API, GOR - of the mobile phase
- Currently generating calibration sets on fresh core (no light end loss) to test *t!PsSAT2017* saturation / composition prediction method

References

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