

## Application Note (181003-2)

### HAWK Analysis for Drill Cuttings, Cores, Outcrop and Soil Samples

#### Classical Pyrolysis and HAWK Petroleum Assessment Method™ (HAWK-PAM)

*Albert Maende, Wildcat Technologies, [albertmaende@wildcattechnologies.com](mailto:albertmaende@wildcattechnologies.com)*

#### Pyrolysis in Petroleum Exploration

Pyrolysis has been used to characterize petroleum source rocks for over 40 years now (Barker, 1974; Espitalie et al., 1977). Up to the present date, pyrolysis instrumentation has been utilized to evaluate source rock formations (e.g., Jones, 1984; Peters, 1986; Peters and Caasa, 1994). Jarvie (2012) sought to directly address identification of sweet spots in unconventional reservoir intervals in his promulgation of the pyrolysis interpretation parameter referred to as “Oil Saturation Index” or Normalized Oil Content (Jarvie et al., 2001; Jarvie and Baker, 1985).



**HAWK Pyrolysis, TOC and Carbonate Carbon Instrument**

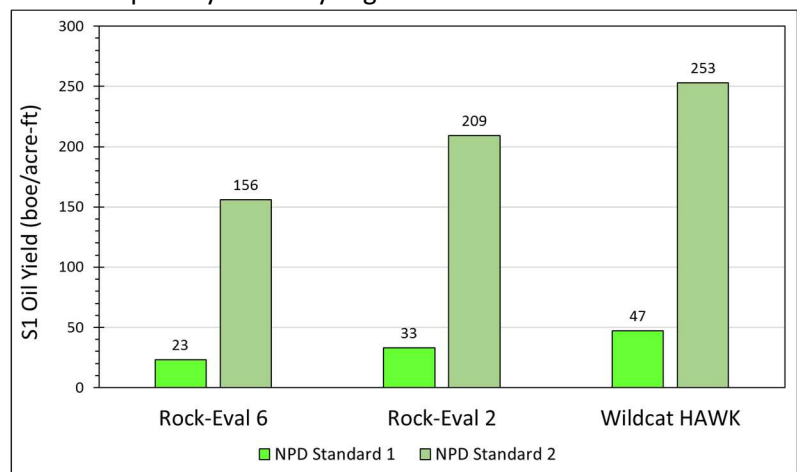
Wildcat Technologies has advanced the capabilities and utility of bulk thermal extraction/pyrolysis instrumentation with its advanced HAWK instrument that provides highly accurate and reliable measure of TOC, oil and kerogen yields as well as thermal maturity. Wildcat Technologies has advanced this technology further by announcing the launch of its recently developed multiramp/multizone pyrolysis method that is now operational on the HAWK Pyrolysis instrument. This HAWK Petroleum Assessment Method (HAWK-PAM), is geared at hydrocarbons assessment in both unconventional and conventional systems (Maende, 2016).

It is useful to note that oil yields can vary according to the instrumentation used. The figure below utilizes standard rock analysis reported by the Norwegian Petroleum Directorate (NPD) showing higher values in Rock-Eval 2 and more recently, by HAWK compared to Rock-Eval 6 (Jarvie, 2014).

## Comparison of oil (S1) yields reported by the Norwegian Petroleum Directorate on their standard rock samples

In summary, the HAWK instrument measures all the classical pyrolysis parameters (S1, S2, S3, S4 and Tmax) together with TOC (Total Organic Carbon) using only about 100 milligrams of 60 mesh size ground rock sample. In addition, the HAWK measures inorganic carbon and therefore provides the carbonate content of the analyzed samples. Acid preparation of samples for TOC analysis on the HAWK is not required. The HAWK is ideal for analysis of not only conventional samples but also unconventional ones for which, the rock formation's potential, sourced and reservoir hydrocarbons (S1<sub>free oil</sub>, S2<sub>kerogen yield</sub>) together with its TOC and Carbonate contents as well as maturity (Tmax), can be measured. This instrument is suitable for analysis of rock, soil and fluid samples both in the laboratory as well as directly at the well-site because of its relatively small size of only 19 inches wide by 20 inches depth and 23 inches height together with the fact that in designing the HAWK, minimal electronic wiring was used. The HAWK's maximum oven temperature is 850 °C, which insures complete pyrolysis of difficult to break-down Type III kerogen. The HAWK also provides capability for analyzing kinetics data and then processing the data using software such as Geolsochem's Kinetics2015. Wildcat Technologies can configure the HAWK's output kinetics data to suite any preferred database.

Whenever desired, analyses on the HAWK can continue overnight with no operator attention because the HAWK has a fully electronic, high precision autoloader with removable and interchangeable trays holding up to 126 samples.



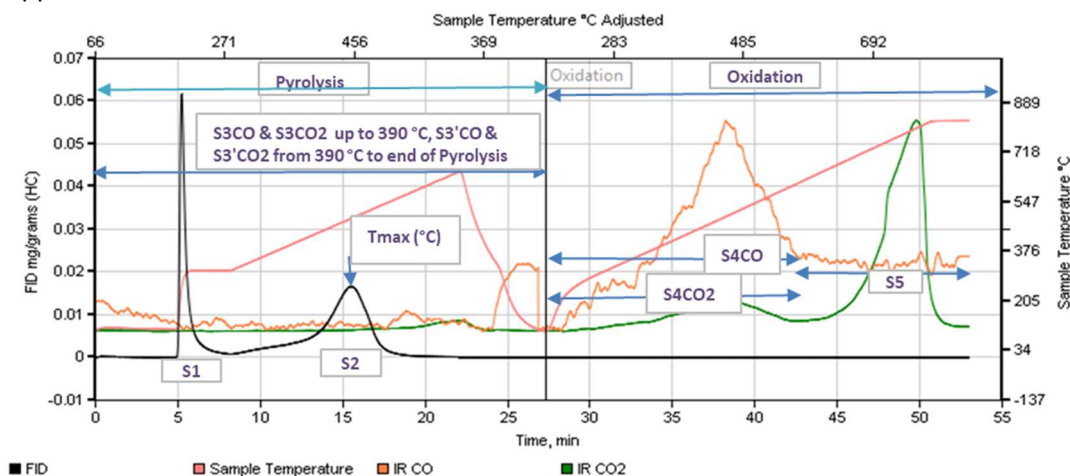
HAWK-Eye software is included with the HAWK instrument and is used for operating the HAWK. The HAWK's data file captures all real-time data associated with individual runs. All the critical parameters including gas flows are stored within the sample file so when you review your data, you can go into the data base and investigate both the instrument and sample run parameters. The software that is in-built in the HAWK allows you to program different analytical methods as you wish and also to export results into excel sheets as well as pyrogram graphics which you can view in different windows, you can also overlay several samples results pyrogram views and resize and down size as need be and the software also gives you a tracking feature that you can slide along the pyrograms to view temperatures, and hydrocarbon yields or carbon dioxide and carbon monoxide yields of interest. The software also allows you to use not only single point calibration but also multi-point calibration. The quality control feature on the software flags any errors one might have made in setting up the sequence for analysis as well as any errors made when defining the method parameters. The quality control feature also flags any out of range measurements on samples whose values have been previously documented. In addition, the quality control feature also flags any out of range gas flows and instructs the instrument to automatically stop if gas flows are out of previously set acceptable ranges. A HAWK dynamic report can also be generated to facilitate the sending to other computers or mobile phones of HAWK pyrograms that can be viewed with the software's tracking feature in real-time while drilling.

Wildcat Technologies has recently developed the HAWK Petroleum Assessment Method (HAWK-PAM) that utilizes five zones using multiple ramp and isotherm routines assigned during a single sample analysis. A ramp rate of 25°C is utilized to generate five petroleum peaks – four on oil fractions and one on kerogen. Each isotherm has its own specific Tmax indicative of the maximum evolution temperatures. Because HAWK-PAM measurement is initiated at 50 °C, it enables better quantification of volatile oil than was previously possible on pyrolysis instruments. In addition, this method enables measurement of API Gravity from drill cuttings, cores, outcrop samples, soil samples, oils and other fluids.

### Classical Pyrolysis Method

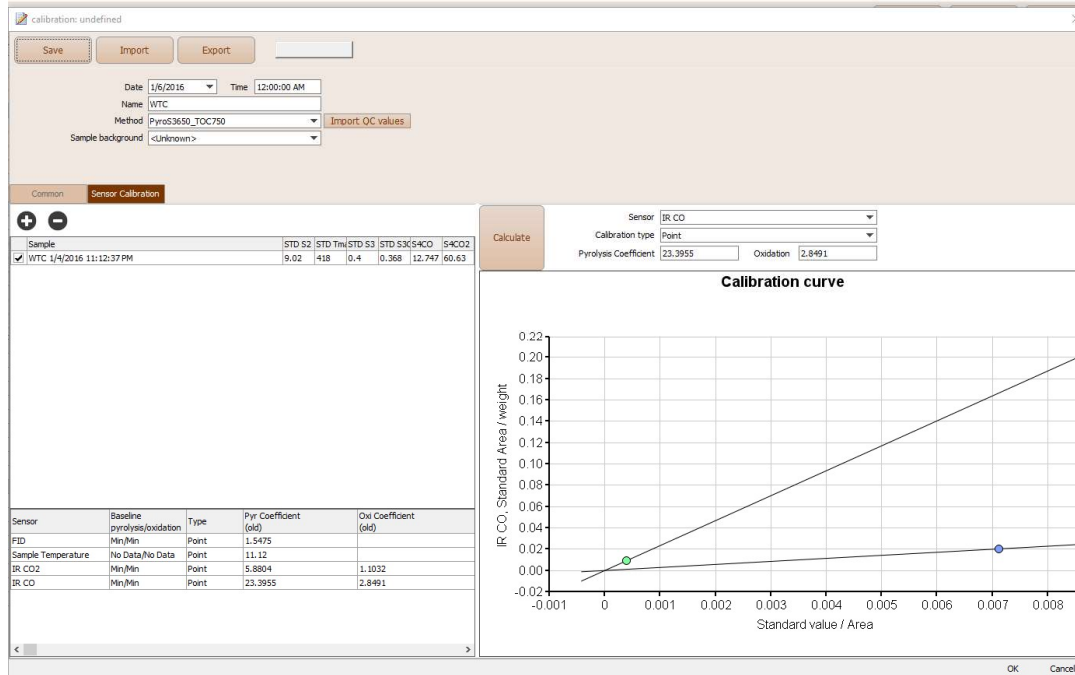
Classical pyrolysis method is the typical one used on pyrolysis instruments and is initiated at a stand by temperature of 100 °C, then through ballistic heating a rock sample is heated up to 300 °C and the thermally extracted hydrocarbons are quantified as S1<sub>free oil</sub> in mg HC/g rock. A ramp rate of 25 °C per minute is then utilized as the sample is pyrolyzed from 300 °C to 650 °C with the generated hydrocarbons being quantified in mg HC/g rock as S2<sub>kerogen yield</sub>. The temperature at which maximum generation of S2<sub>kerogen yield</sub> occurs, is designated as Tmax and it is a measure of the maturity of the rock sample in °C. After attaining the maximum pyrolysis temperature, the oven is then cooled down to 300 °C and then the oxidation cycle is performed whereby a ramp rate of 25 °C is utilized as the sample is heated to a maximum temperature of either 750 °C (if only the thermally extracted hydrocarbons, kerogen yield and TOC are required) or 850 °C ( if in addition to the thermally extracted hydrocarbons, kerogen yield and TOC, Carbonate determination is required as well). In addition to the hydrocarbons, CO and CO2 are measured as well during both the 100 °C to 400 °C temperature range of the pyrolysis cycle (S3, S3CO) and the 400 °C to 650 °C temperature range of the pyrolysis cycle (S3', S3'CO) as well as the oxidation cycle (S4CO, S4CO2 and S5). S4CO is limited to organic source while whenever inorganic carbon is present, S4CO2 and S5 are bounded from each other by a drop to a minimum in CO2 generation which occurs during the 550 °C to 720 °C temperature range. TOC in wt.% (Total Organic Carbon) is computed from S1<sub>free oil</sub>, S2<sub>kerogen yield</sub>, S3, S3CO, S4CO and S4CO2 while the Carbonate Carbon and per cent Calcium Carbonate equivalent (CaCO<sub>3</sub> equivalent (wt. %)) is computed from S3' and S5. The HAWK enables differentiation of carbonate minerals such as siderite, calcite and dolomite based on their respective CO2 pyrograms. Whereas hydrocarbons are detected using a Flame Ionization Detector (FID), both CO and CO2 are detected using an Infra-Red detector (IR).

A typical pyrogram of the Classical Pyrolysis method from both the pyrolysis and oxidation cycles of the HAWK appears as shown below:



## Calibration

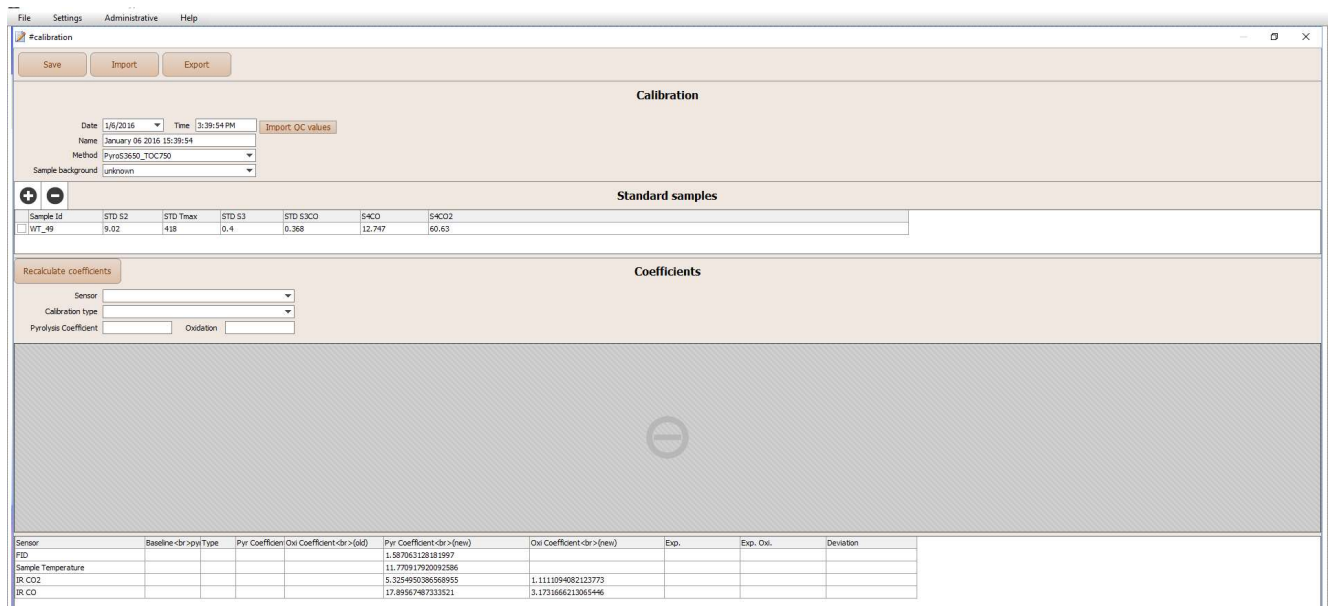
To create new calibration, first select the sample of interest, designate it as std, open it and import std values into it for the respective method. Save and close. Go to “Calibration” and then “New Calibration”. Open new calibration. Using the “+”, add in the sample of interest, name it, assign a method and then click on “Calculate” to populate coefficients. Save, close, select this “new calibration”, run calculation and then use this new calibration as needed.



To select calibration and then calculate coefficients:

- Click on Calibrations and then click on Select Calibration
- Double click on the calibration you require so as to open it
- Either add (+) or remove (-) as need be
- Ensure the standard values are input
- Calculate Coefficients

After calculating coefficients, they should appear as shown in the chart below:



Or

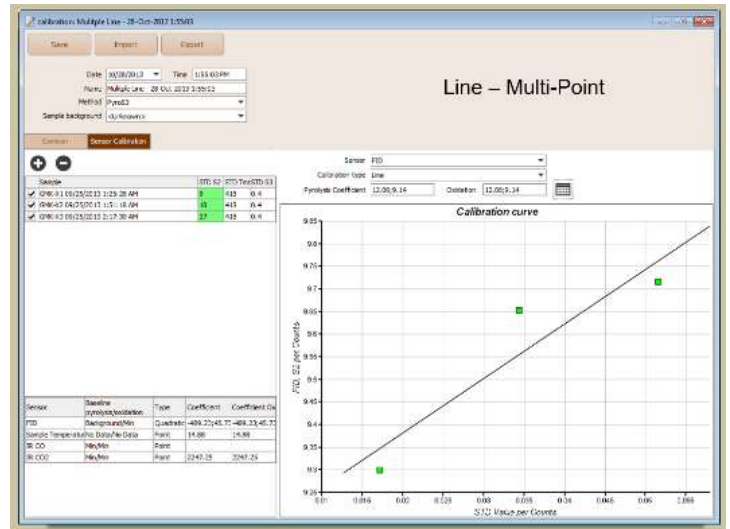
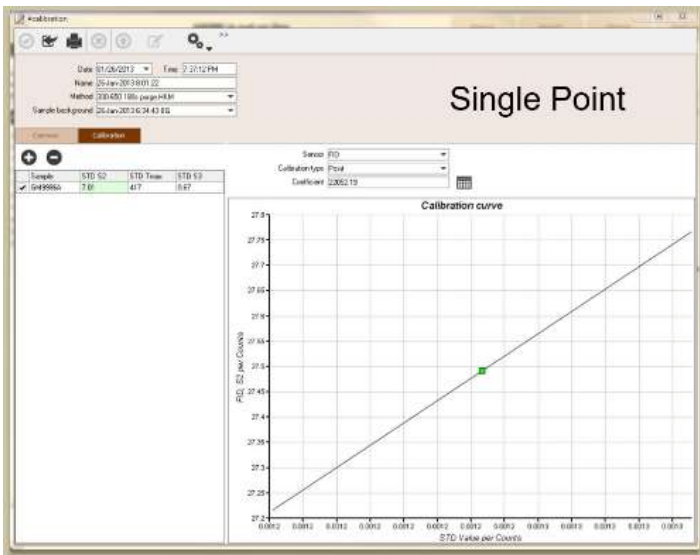
The screenshot shows the 'Calibration' window in the software. It includes fields for Date (1/12/2016), Time (12:10:09 PM), Name (January 12 2016 12:10:09), Method (PyroS3650\_TOCT50), and Sample background (Unknown). Below these are sections for 'Standard samples' and 'Coefficients'. The 'Standard samples' table is as follows:

Sample Id	STD S2	STD Tmax	STD S3	STD S3CO	S4CO	S4CO2
WT_A	9.02	418	0.4	0.368	12.747	60.63

The 'Coefficients' section has a 'Recalculate coefficients' button and dropdowns for Sensor, Calibration type, and Pyrolysis Coefficient. At the bottom, there is a table with columns: Sensor, Baseline-cbr>pyl>Type, Pyr Coefficient, Oxi Coefficient-cbr>{old}, Pyr Coefficient-cbr>{new}, Oxi Coefficient-cbr>{new}, Exp., Exp. Oxi., and Deviation.

Sensor	Baseline-cbr>pyl>Type	Pyr Coefficient	Oxi Coefficient-cbr>{old}	Pyr Coefficient-cbr>{new}	Oxi Coefficient-cbr>{new}	Exp.	Exp. Oxi.	Deviation
FID				1.6215401895774535				
Sample Temperature				9.77691984348093				
IR CO				15.87683321235898	2.84150489412429			
IR CO2				5.75129484400873	1.1039023468234512			
FID				1.6215401895774535	1.6215401895774535			
Sample Temperature				9.77691984348093	9.77691984348093			
IR CO2				5.75129484400873	1.1039023468234512			
IR CO				15.87683321235898	2.84150489412429			

The calibration should then appear as shown below for either single-point calibration or multi-point calibration.





## Sample Preparation

The HAWK™ requires an Electronic Analytic Balance with readability of 0.1 mg (typical sample quantity is 60 - 100 milligrams). Additional suggested equipment include Mortar, Pestle and Sample Sieve (60 mesh). Sample loading device and spatula are provided.



## HAWK Petroleum Assessment Method™ (HAWK-PAM)

HAWK Petroleum Assessment Method (HAWK-PAM), utilizes five zones using multiple ramp and isotherm routines assigned during a single sample analysis. A ramp rate of 25°C is utilized to generate five petroleum peaks – four on oil fractions and one on kerogen (Maende, 2016). Each isotherm has its own specific Tmax indicative of the maximum evolution temperatures. The peak names and associated temperature of occurrence are as shown in the table below:

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

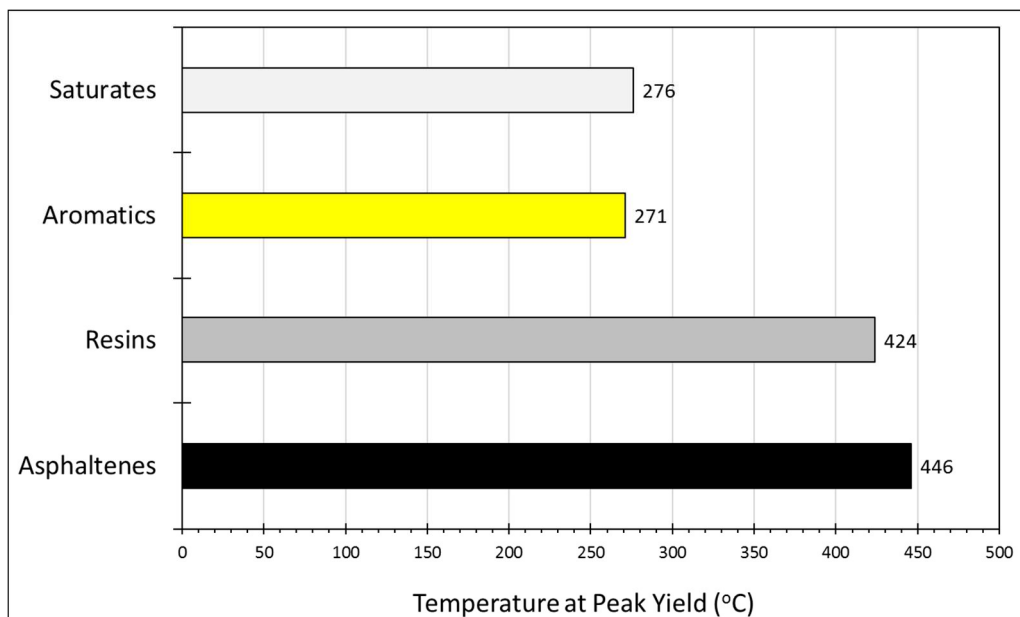
### Approximation of carbon number ranges and SARA fraction disposition utilized in the multiple ramp and isotherm program used in the HAWK-PAM

The generalized categories for these five HAWK Petroleum Assessment Method peaks as well as their SARA (Vazquez and Mansoori, 2000) fractions including polar constituents (resins vs asphaltenes) are depicted above.

The HAWK-PAM technique is based on initiating pyrolysis on whole rock or fluid samples at 50 degrees C and then in a single run ramp up to 650 degrees C through 5 separate zones whereby the resulting 5 peaks represent the oil fraction at 50 to 100 degrees C, at 100 degrees C, at 100 to 180 degrees C, at 180 to 350 degrees C and finally the last peak from 350 to 650 degrees C, which is mainly Kerogen or Asphalt

if the latter happens to be present. The pertinent Carbon number grouping for these 5 peaks are C4 – C5, C6 – C10, C11 – C19, C20 – C36 and C37+. Using HAWK-PAM quantification of each of these petroleum fractions as Oil-1, Oil-2, Oil-3, Oil-4 and K-1 is done.

Additional methodologies partially segregate the polars into resin and asphaltenes fractions based on their Tmax differences. This was shown by Jarvie et al. (2015) where the saturates and aromatics largely volatilize whereas the resins and asphaltenes decompose during pyrolysis at different temperature (Tmax) values.



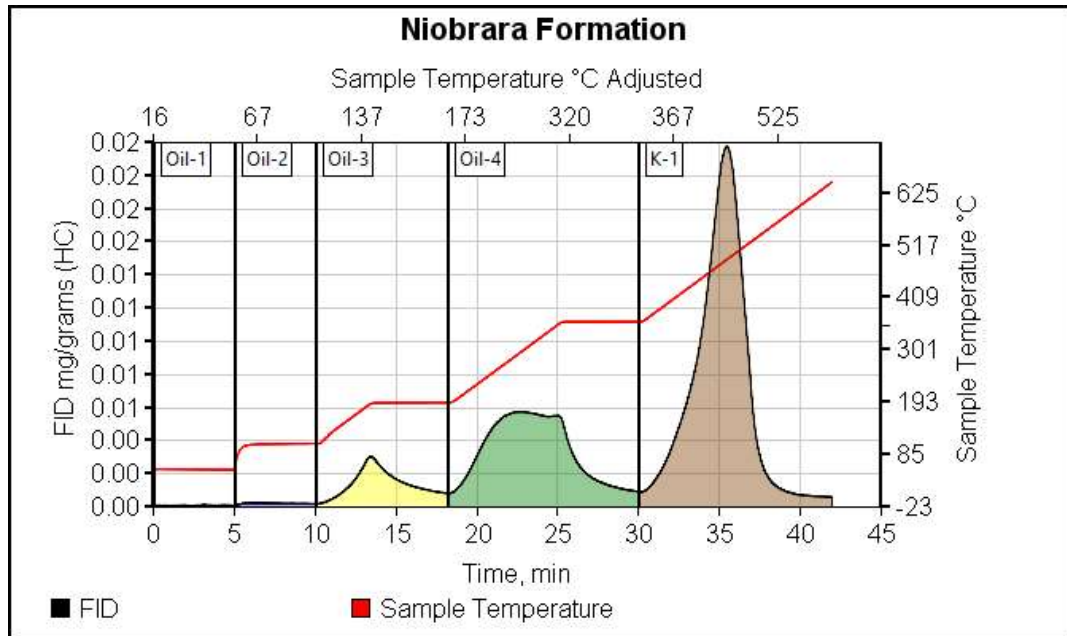
**Volatilization and Tmax temperatures for saturates and aromatics and resins and asphaltenes, respectively**

#### **n-Alkane and SARA fractions that were analyzed for Calibration of HAWK-PAM**

<b>n-Alkane and SARA fractions that were analyzed using HAWK-PAM</b>	<b>Carbon Number</b>	<b>HAWK-PAM Oil fraction and K-1 fraction designation</b>
2 Pentane samples	5	Oil-1
3 Toluene samples	7	Oil-2
3 Decane samples	10	Oil-2
3 Tetradecane samples	14	Oil-3
2 Saturates samples		Oil-3
3 Eicosane samples	20	Oil-4
3 Hexacosane samples	26	Oil-4
3 Triatriacontane samples	33	Oil-4
4 Aromatic samples		Oil-4 and K-1
3 Tetratetracontane samples	44	K-1
6 NSO samples		K-1
3 Kerogen samples		K-1
2 Asphalt samples		K-1

**n-Alkane and SARA (Saturates, Aromatics, Resins & Asphaltenes) fractions that were analyzed for Calibration of HAWK-PAM (Maende et. al., 2017)**

A typical pyrogram generated using the HAWK Petroleum Assessment Method using five different ramp and isotherm times and temperatures appears as shown below:



Five ramp temperatures and isotherms using a HAWK PAM program. Programming can be assigned for any given ramp and isotherm values in the methodology

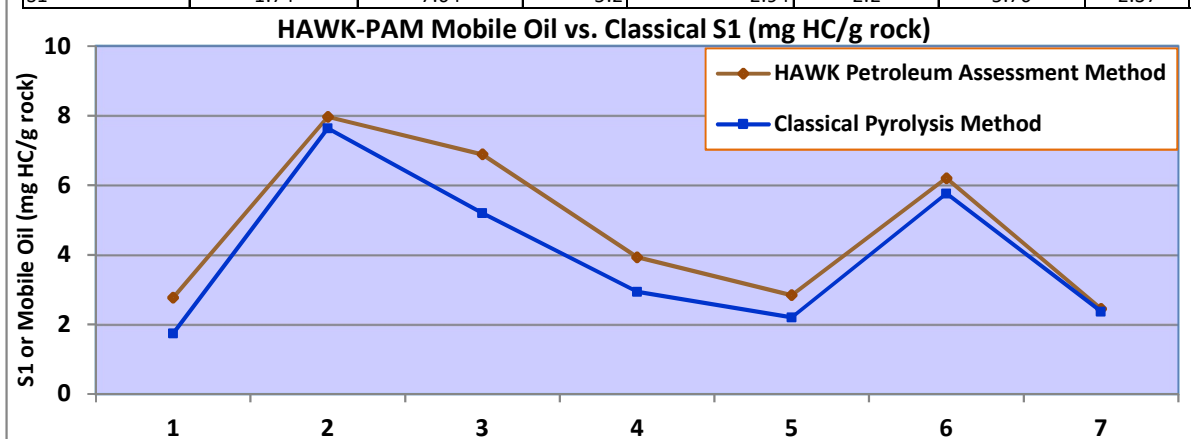
### Reservoir Assessment using the HAWK Petroleum Assessment Method™ (HAWK-PAM)

Results on analyses of samples from seven source rocks using this new method are shown below and so are the results of analysis of this same group of samples when the classical pyrolysis method (initiate pyrolysis at 300 °C and ramp at 25 °C up to 650 °C) is utilized.

### Comparison of results of HAWK Petroleum Assessment Method™ with those of the Classical Pyrolysis Method

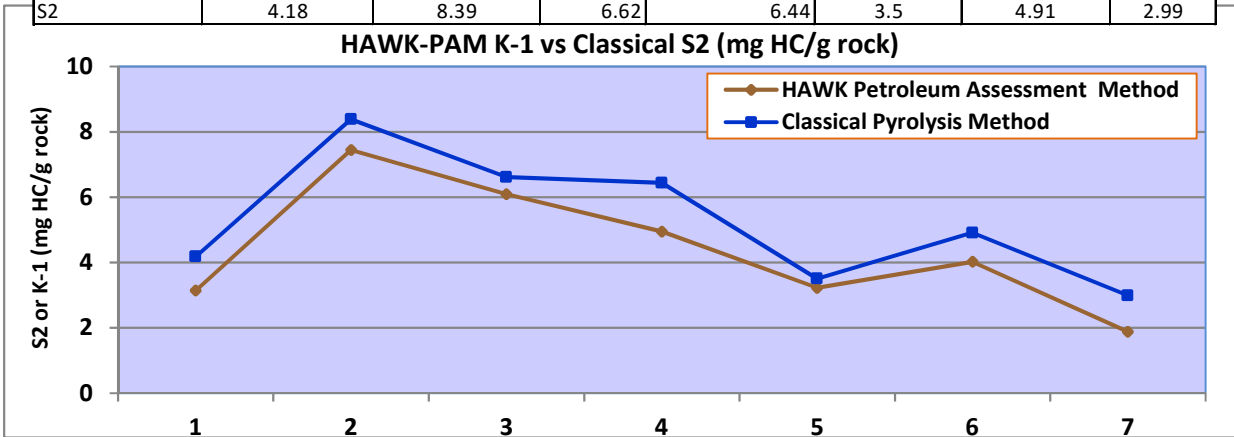
The tables and charts below show a comparison of various unconventional resource plays using HAWK.

Formation	Barnett	Marcellus	Burkett	Niobrara	Upper Avalon	Eagle Ford	Bazhen
Mobile Oil	2.77	7.97	6.89	3.93	2.84	6.2	2.45
S1	1.74	7.64	5.2	2.94	2.2	5.76	2.37

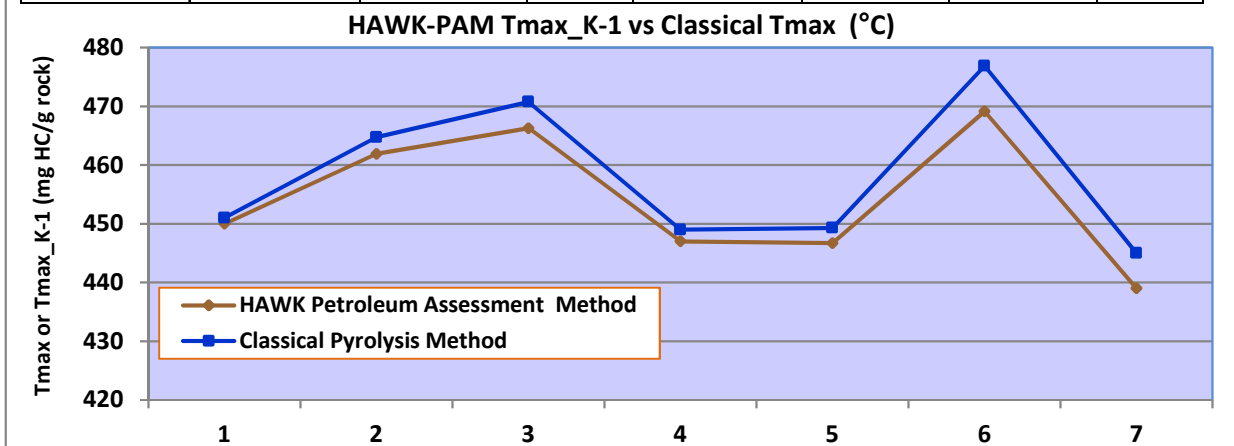




Formation	Barnett	Marcellus	Burkett	Niobrara	Upper Avalon	Eagle Ford	Bazhen
K-1	3.14	7.45	6.09	4.95	3.23	4.02	1.88
S2	4.18	8.39	6.62	6.44	3.5	4.91	2.99



Formation	Barnett	Marcellus	Burkett	Niobrara	Upper Avalon	Eagle Ford	Bazhen
K-1 Tmax	450	462	466	447	447	469	439
Tmax	451	465	471	449	449	477	445

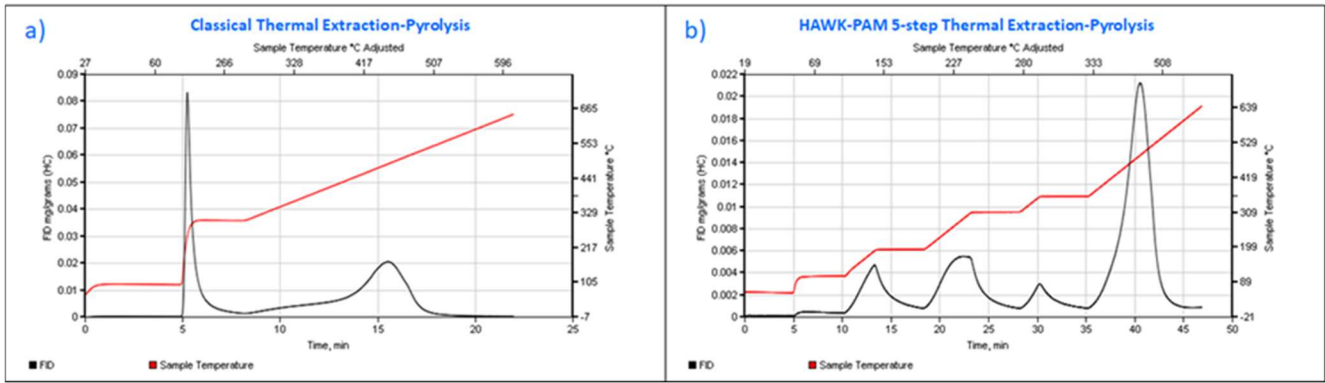


### Comparison of Classical Pyrolysis Method and HAWK Petroleum Assessment Method™ Parameters

This comparison shows that for all the analyzed samples, the mobile oil computed using the HAWK Petroleum Assessment Method exceeds the S1 value obtained from the Classical Pyrolysis Method.

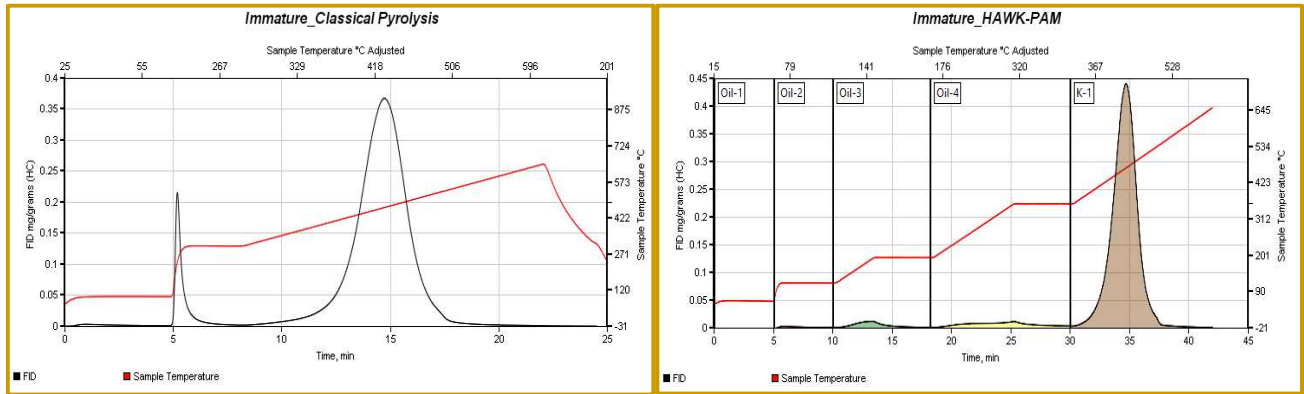
Whenever the Tmax K-1 turns out to be a number of degrees different from the classical pyrolysis Tmax, the implication is that the rock sample is impregnated with petroleum or is contaminated by oil-based mud additives. It is only through the Petroleum Assessment method that separation of the heavy oil/asphaltene from kerogen is almost completely achieved thereby enabling a more accurate kerogen Tmax.

Classical (a) and HAWK-PAM (b) thermal extraction and pyrolysis analysis. Classical pyrolysis (a) shows a large free oil peak (S1) but the pyrolysate has a shoulder that is also volatile (extractable) organic matter; it is necessary to extract the rock to obtain the total oil and the S2 Tmax value is skewed to a lower value. The HAWK-PAM methodology (b) separates the total oil peak into four different compositional ranges and removes the shoulder from the kerogen peak yielding a more reliable Tmax value.

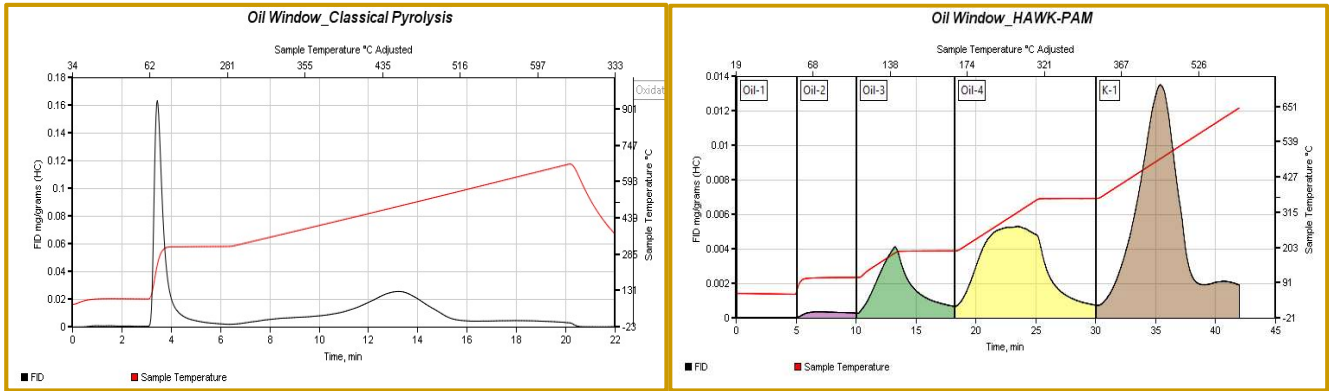


**Maturity characteristic HAWK-PAM Pyrograms compared with those of Classical Pyrolysis**

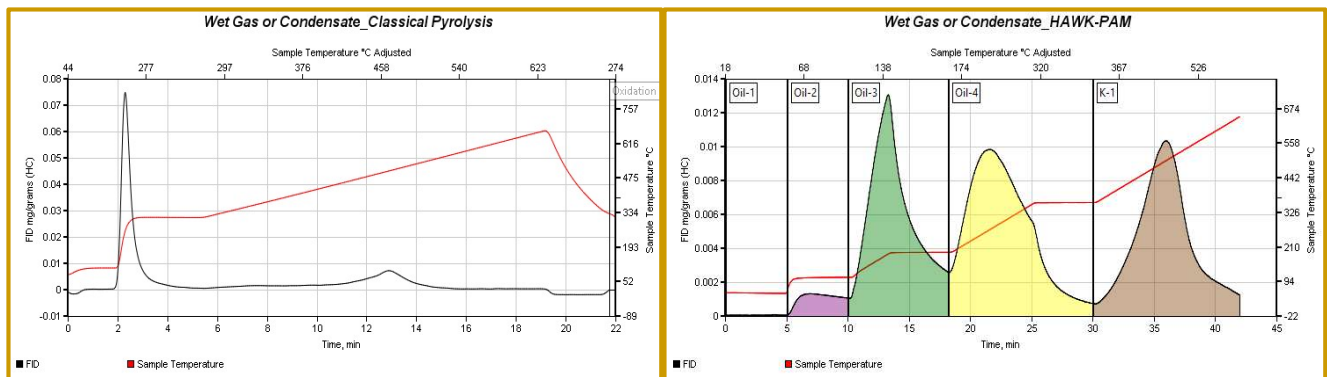
**Immature**



**Oil Window - Classical Pyrolysis "S2 shoulder" is resolved on HAWK-PAM**



**Wet Gas/Condensate**

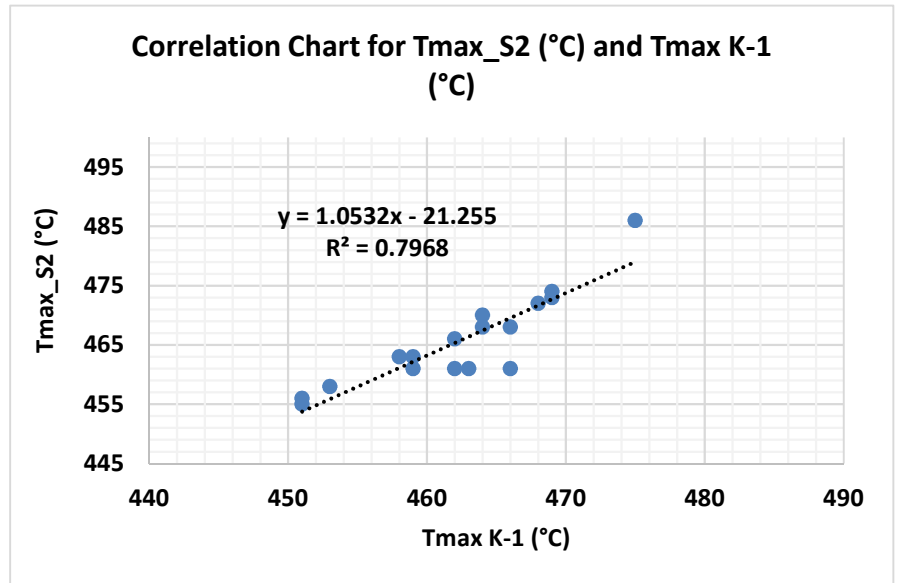


## Correlation of Classical Pyrolysis Method Maturity Parameter (Tmax\_S2 (°C)) with HAWK Petroleum Assessment Method™ Tmax K-1 (°C) Parameter

The Classical Pyrolysis Method maturity parameter, Tmax\_S2 (°C) correlates closely with the HAWK Petroleum Assessment Method's Tmax K-1 (°C) parameter as is depicted in the table and graph below:

### Correlation of Classical Pyrolysis Method Tmax\_S2 (°C) and HAWK Petroleum Assessment Method™ Tmax K-1 (°C) Parameters

Sampled Formation	Tmax_S2 (°C)	Tmax K-1 (°C)
Marcellus Shale	461	466
Marcellus Shale	466	462
Marcellus Shale	461	463
Marcellus Shale	468	466
Marcellus Shale	461	462
Marcellus Shale	463	458
Marcellus Shale	461	459
Marcellus Shale	463	459
Marcellus Shale	456	451
Marcellus Shale	455	451
Marcellus Shale	458	453
Marcellus Shale	486	475
Marcellus Shale	474	469
Burkett Formation	473	469
Burkett Formation	472	468
Burkett Formation	468	464
Burkett Formation	470	464

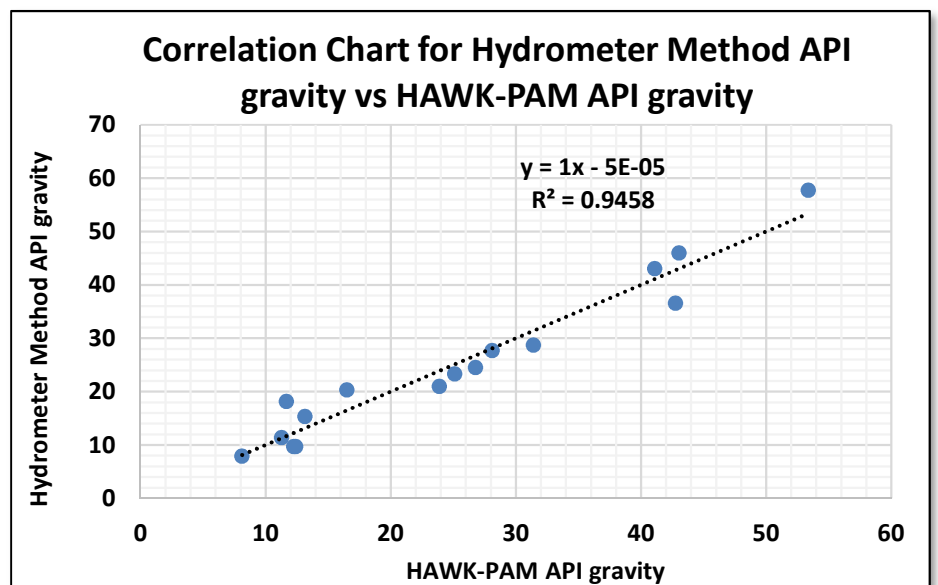


### HAWK-PAM measurement of API gravity

A derivation from the HAWK Petroleum Assessment method parameters is used for measuring API gravity. This derivation can be seen from the table and graph below which were obtained from running the HAWK Petroleum Assessment method on oils (Maende *et. al.*, 2017).

Hydrometer Method API gravity	HAWK-PAM API gravity
57.70	53.39
9.72	12.26
20.30	16.51
28.70	31.42
43.05	41.09
45.96	43.05
36.57	42.77
23.30	25.12
24.50	26.79
21.00	23.89
27.70	28.12
11.41	11.28
9.72	12.41
7.91	8.12
15.31	13.14
18.16	11.67

API prediction using HAWK. This can be used on source/reservoir rocks calibrated to oils



## HAWK-PAM, HAWK-PAM TOC and HAWK-PAM TOC/CC methods of analysis for Drill Cuttings, Cores, Outcrop Samples and Soil Samples

### Type of Samples

Drill Cuttings, Cores and Outcrop samples of Natural rock (Limestone, Shale, Clay, Sandstone) and Soil Samples including Soil samples that are contaminated by oil or other organic material and which may be in solid, sludge or liquid form.

### HAWK-PAM analytical capabilities

Whereas the Classical Pyrolysis method can be utilized to analyze for free oil (S1), TOC and Carbonate, the HAWK-PAM method can also be used to not only analyze for free oil (Oil-1, Oil-2, Oil-3 and Oil-4), but it can also be used to analyze for Volatile Organic Compounds and quantify them in the C4-C5, C6-C10 and C11-C19 groups as shown in the table below. As the table below demonstrates, HAWK-PAM can be used to quantify petroleum fractions and distinguish gasoline, kerosene + diesel, lubricating oil and asphalt, in addition to providing measurement of API gravity.

### HAWK-PAM API Gravity & Petroleum Oil Fractions

Sample ID	Oil-1 (mg HC/g rock)	Oil-2 (mg HC/g rock)	Oil-3 (mg HC/g rock)	Oil-4 (mg HC/g rock)	K-1 (mg HC/g rock)	Petroleum Fraction						
						API Gravity Prediction (°)	Sum (Oil-1, Oil-2, Oil-3, Oil-4, K-1) (mg HC/g rock)	C4 - C10 = Oil-1 + Oil-2 (wt. %)	C11 - C19 = Kerosene + Diesel = Kerosene + Jet Fuel = Oil-3 (wt. %)	C20 - C36 = Oil-4 (wt. %)	C37+ = Asphalt = K-1 (wt. %)	Total Per cent sum
Permian Basin; Rock Extract	0.01	1.66	33.95	94.57	12.31	39	142.50	1.17	23.82	66.36	8.64	100
Eagle Ford Shale; Oil	14.13	53.13	94.98	134.91	29.65	43	326.80	20.58	29.06	41.28	9.07	100

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

**HAWK-PAM can be used to analyze for oil fractions and TOC by using the method HAWK-PAM TOC and in addition, HAWK-PAM can be used to analyze for oil fractions, TOC and Carbonates by using the method HAWK-PAM TOC/CC.**

### Sample Preparation

#### 1. Sample Preparation for Crude Oil Contaminated Soil and Soil Samples

- Place HAWK sample crucible on weighing balance, zero out
- Using a spatula, scoop portions of the Crude Oil Contaminated Soil or Soil sample, as received, directly into the HAWK sample crucible, using weights of between 70 and 150 mg
- Analyze on the HAWK using either the HAWK-PAM, HAWK-PAM TOC method or the HAWK-PAM TOC/CC method.

## 2. Sample Preparation for Drilling Cuttings

### A. Sample Preparation for Drilling Cuttings that were drilled using either air or water-based mud

- Using a spatula, scoop a portion of the Drilling Cuttings sample into a Pyrex glass beaker of 600 ml volume
- Wash with running water together with a few drops of dawn soap.
- Decant off water as you continue washing and you may also splash a jet of water into the beaker to agitate the sample. Decant off all the contaminants that float upwards.
- Using an appropriate felt pen, label the top of the weigh boat with the Sample ID
- Transfer the Drilling Cuttings sample from the beaker into a weigh boat (VWR® Weigh Boat), and wash with running tap water followed by decanting off contaminants and muddy water, until clear water covering the sample is achieved.
- Leave the washed Drilling Cuttings sample to dry on the weigh boat in open air on a bench top in the Laboratory. Drying might take 2 to 3 days.
- Grind the dried Drilling Cuttings sample to "powder" size (60 mesh sieve size), using a mortar and pestle
- Using weighing balance, use weights at about 70 mg
- Analyze on the HAWK, using the HAWK-PAM TOC/CC method.

### B. Sample Preparation for Drilling Cuttings that were drilled using oil-based mud

- Pick out any obvious contaminants and foreign material
- Clean with Dawn soap using running water.
- Leave to stand in open air on a bench top in the Laboratory for 2 to 3 days to allow it to dry.
- Grind to 60 mesh size ("powder") state.
  - **Note:** it is necessary to grind the sample before continuing with the cleaning because oil-based contamination seeps into pore spaces of the rock.
- Clean again with Dawn soap in beaker of 50ml vol.
- Decant water out of the beaker.
- Leave to stand in open air on a bench top in the Laboratory for 2 to 3 days to allow it to dry.
- Add 87:13 Chloroform: Methanol organic solvent mix to sample in 50ml beaker until you are at 30 to 40 ml height (about 90% full).
- Stir
- Cover tray of beakers that contain samples tightly with aluminium foil and leave to extract in a fume hood cupboard up to 4 hours
- Start the procedure of decanting to clearness: uncover the samples and carefully decant out the chloroform: methanol solvent without losing samples. Add more chloroform: methanol to about 90% full, cover with aluminium foil and leave to extract up to 4 hours.
- Uncover the samples, carefully decant out the solvent and then add more chloroform: methanol solvent to about 90% full and then cover tightly again and leave to extract 4 hours or overnight if needed.
- Uncover the samples and see if the cloudy top is all gone:
  - If the clearness has not emerged, continue repeating previous solvent and decanting steps until all the cloudiness is gone, and clearness has emerged; the time duration can be a day to a week depending on the type of contamination.

- If clearness has emerged now thereby signifying that extraction of oil-based mud is now complete. Carefully decant out the solvent and leave the samples to dry out in the open air on a bench top in the laboratory for 2 to 3 days, then proceed to next step.
- Let the cleaned sample dry and if need be wash again with Dawn soap and dry.
- Smell the sample to confirm no smell of solvent is still there.
- Leave the sample to dry in the open air on a bench top in the laboratory
- Analyze on the HAWK using the HAWK-PAM TOC/CC method.

### 3. Sample Preparation for Liquid Oil or other Liquid samples

- For each of the Liquid samples that will be analyzed, fill a HAWK crucible to between one half (1/2) and two thirds (2/3) full silica gel or with clean sand that has previously been baked in an oven to 110 °C.

**Note:**

- The silica gel that is recommended can be obtained from Sigma-Aldrich using the following link: <https://www.sigmaaldrich.com/catalog/product/sial/243981?lang=en&region=US>.
- The sand that is recommended is “play sand” which should be prepared as follows:
  - Cleaned by first picking out any contaminants and other large objects
  - Sieving with 20 mesh size sieve before baking the sand in an oven
  - Leave it to cool in the open air before storing it in a Pyrex beaker and covering the beaker with aluminium foil, whenever the clean sand is stored.
- Place HAWK sample crucible onto the weighing balance, zero out
- Using a syringe, inject 30 micro-liters of the liquid, onto the silica gel or clean baked sand
- Record the weight of the injected Liquid
- Analyze the Liquid samples on the HAWK using HAWK-PAM TOC method

### 4. Sludge samples can be directly placed into a HAWK crucible and weighed on the Analytic Balance and then analyzed on the HAWK instrument using either HAWK-PAM, HAWK-PAM TOC or the HAWK-PAM TOC/CC method.

### 5. Grinding and Weighing

The HAWK requires a 4 decimal place Electronic Analytic Balance with readability of 0.1 mg (typical sample size is 60 - 100 milligrams with use of about 70 mg being optimal). Additional required equipment includes Mortar, Pestle, Sample Sieve (60 mesh) and optional Sand Sieve (20 mesh). It is a good idea to have both an iron steel mortar and pestles as well as a ceramic mortar and pestle because, it is easier to break-down chips from cores using an iron steel and mortar. Sample loading device and spatula are provided.





## HAWK-PAM, HAWK-PAM TOC and HAWK-PAM TOC/CC Methods

- HAWK-PAM method consists of the pyrolysis-based HAWK Petroleum Assessment Method (HAWK-PAM) that is run in the 50 °C to 650 °C.
- HAWK-PAM TOC method consists of the pyrolysis-based HAWK Petroleum Assessment Method (HAWK-PAM) that is run in the 50 °C to 650 °C, followed by oxidation from 300 °C to 750 °C.
- HAWK-PAM TOC/CC method which comprises of the HAWK-PAM method, followed by oxidation from 300 °C to 850 °C.

## REFERENCES

- Barker, C., 1974, Pyrolysis techniques for Source-Rock Evaluation, AAPG Bull., v. 58, no. 11, p. 2349-2361.
- Espitalie, J., M. Madec, B. Tissot, J.J. Mennig, and P. Leplat, 1977, Source rock characterization method for petroleum exploration, OTC paper #2935, 6p.
- Jarvie, Daniel M., Alejandro Morelos, and Zhiwen Han, 2001, Detection of Pay Zones and Pay Quality, Gulf of Mexico: Application of Geochemical Techniques, Gulf Coast Assoc. of Geol. Soc. Transactions, Volume LI, 2001, pp. 151-160.
- Jarvie, D. M., 2012, Shale resource systems for oil and gas: Part 2 – Shale-oil resource systems, in J. A. Breyer, ed., Shale reservoirs – Giant resources for the 21st century: AAPG Memoir 97, p. 89 – 119.
- Jarvie, D.M., B.M. Jarvie, W.D. Weldon, and A. Maende, 2015, Geochemical assessment of in situ petroleum in unconventional resource systems, URTEC paper 2173379, 20p.
- Jarvie, D.M., 2014, Components and processes affecting producibility and commerciality of shale resource systems, *Geologica Acta*, v. 12, no. 4, ALAGO Special Publication, p. 307-325.
- Jones, R., 1984, Comparison of carbonate and shale source rocks, in *Petroleum Geochemistry and Source Rock Potential of Carbonate Rocks*, AAPG Studies in Geology 18, J. Palacas, ed., pp. 163-180.p. 163-177.
- Maende, A., 2016, HAWK Petroleum Assessment Method (HAWK-PAM), Application Note 052016-1, [http://www.wildcattechnologies.com/application/files/1514/9686/0020/Application\\_Note\\_052016-1\\_HAWK\\_Petroleum\\_Assessment\\_Method.pdf](http://www.wildcattechnologies.com/application/files/1514/9686/0020/Application_Note_052016-1_HAWK_Petroleum_Assessment_Method.pdf)
- Maende, A., A. Pepper, D. M. Jarvie, and W. D. Weldon, 2017, 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, Search and Discovery Article #80596 (2017), Adapted from oral presentation given at AAPG 2017 Annual Convention and Exhibition, Houston, Texas, April 2-5, 2017. [http://www.searchanddiscovery.com/pdfz/documents/2017/80596maende/ndx\\_maende.pdf.html](http://www.searchanddiscovery.com/pdfz/documents/2017/80596maende/ndx_maende.pdf.html)
- Peters, K. E., 1986, Guidelines for Evaluating Petroleum Source Rock Using Programmed Pyrolysis, AAPG Bull. v. 70, No. 3, p. 318-329.
- Peters, K.E. and M.R. Cassa, 1994, Applied source rock geochemistry, in Magoon, L.B. and W.G. Dow, eds., *The petroleum system – from source to trap*, AAPG Memoir 60, p. 93-120.