218 Higgins Street
Humble, TX 77338
(281) 540-3208

Non – Petroleum Industry Applications of HAWK Instrument

Non – Petroleum Applications of the HAWK instrument include the following:

- Carbonate minerals identification and determination of carbonate percentage.
- Coal deposits exploration and characterization.
- Cement manufacture.
- Soil pollution studies for environmental protection.

1. Carbonate minerals identification and determination of Carbonate Percentage

Occurrence of carbonates together with their associated calcium carbonate percentage can be measured on the HAWK instrument. Therefore using the HAWK, one can distinguish the various types of carbonate minerals. The associated calcium carbonate percentages of these minerals can then be calculated and these match the values that are obtained through using the X-Ray Diffraction (XRD) method.

Table 1 below shows an example of HAWK results obtained when carbonate minerals were analyzed.

Sample ID	S3 (mgCO2/g rock)	S3' (mgCO2/g rock)	Carbonate Carbon (CC) (wt. %)	Calcium Carbonate (CaCO3) (wt. %)
Siderite	0.55	95.12	2.78	23.14
Calcite	0.23	1.91	11.84	98.69

Note: $CaCO_3$ equivalent (wt. %) = (CC x 100)/12

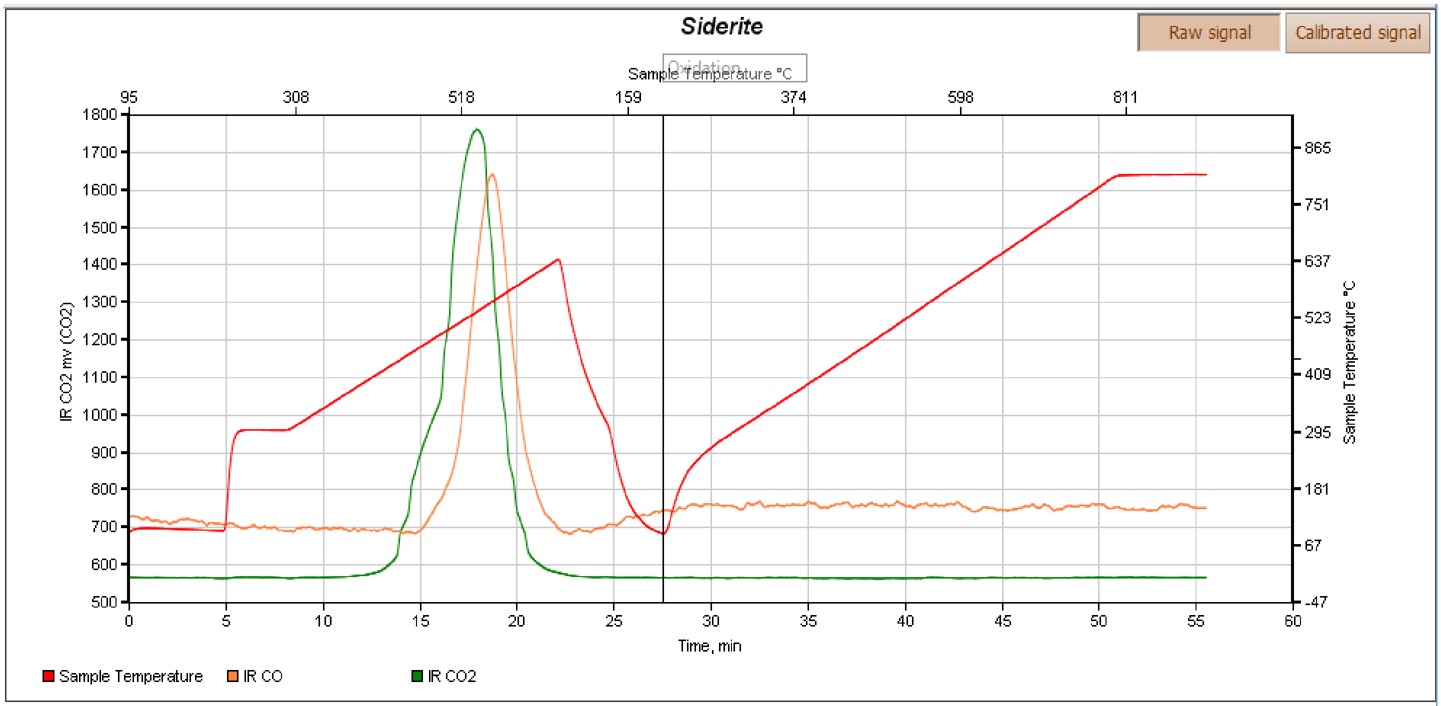
Table 1. Example of Carbonate minerals analytical results obtained on the HAWK instrument

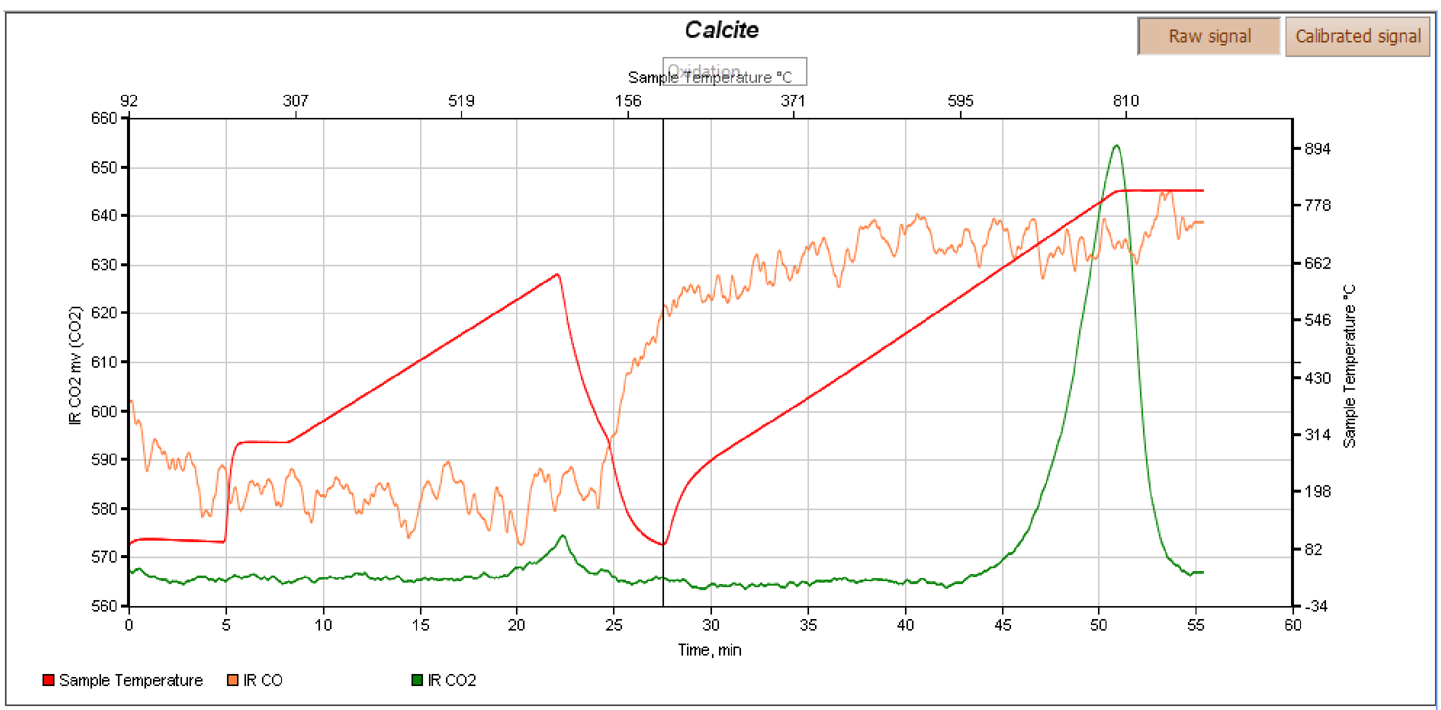
A comparison of HAWK instrument results with those of XRD measurements on Carbonate rocks are shown in Table 2.

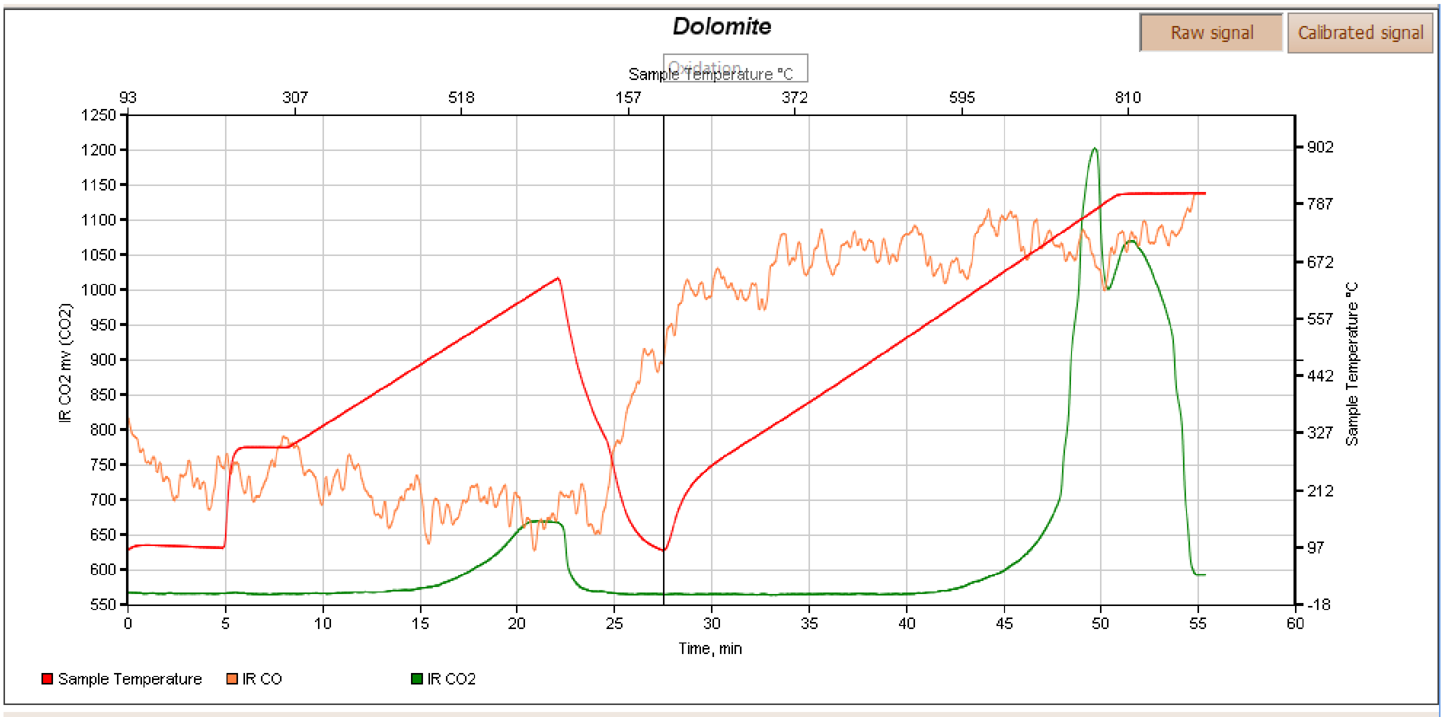
Sample ID	Calcium Carbonate (CaCO3) (wt. %) (Inorganic Carbon) determined on the HAWK instrument	Calcium Carbonate (CaCO3) (wt. %) (Inorganic Carbon) determined on the XRD instrument
TR-11-01	79.9	83.2
TR-11-02	45.2	57.6

Table 2. Comparison of HAWK and XRD results on Carbonate rock samples

Pyrograms of Carbonate minerals on the HAWK instrument occur as shown below. These HAWK pyrograms are for Siderite, Calcite and Dolomite.







HAWK pyrograms of Siderite, Calcite and Dolomite

Uses of Carbonates include those shown in Table 3 below.

Carbonate	Uses
Soda ash or Sodium Carbonate (Na_2CO_3)	Manufacture of glass, paper, rayon soaps, and detergents. As a water softener. Control of pH through neutralizing of acids. Synthesis of sodium compounds, including sodium bicarbonate (baking soda), sodium silicate (used in detergents), sodium tripolyphosphate (a detergent builder), sodium hydroxide (lye), sodium chromate and sodium dichromate (used in chrome plating), sodium aluminate (used in refining aluminium), and sodium cyanide (for electroplating).
Limestone or Calcium Carbonate ($CaCO_3$)	Refining of iron ore and manufacturing of steel. Manufacture of fertilizers such as agricultural lime. Manufacture of cement. In scrubbers that remove sulfur from flue gases, and the manufacture of soda ash.
Potash or Potassium Carbonate (K_2CO_3)	Manufacture of glass.
Lithium carbonate (Li_2CO_3)	Manufacture of glasses, ceramics, pharmaceuticals and aluminium.
Strontium carbonate ($SrCO_3$)	Manufacture of CRT tubes for televisions and computers. Manufacture of red fireworks.
Nickel carbonate ($NiCO_3$)	Used in electroplating and manufacture of ceramics.
Cobalt carbonate ($CoCO_3$)	As a catalyst in the refining industry. As a ceramic pigment and as a mineral supplement for livestock.

Table 3. Uses of Carbonates (http://antoine.frostburg.edu/chem/senese/101/inorganic/faq/carbonate-uses.shtml accessed on 07.20.2016)

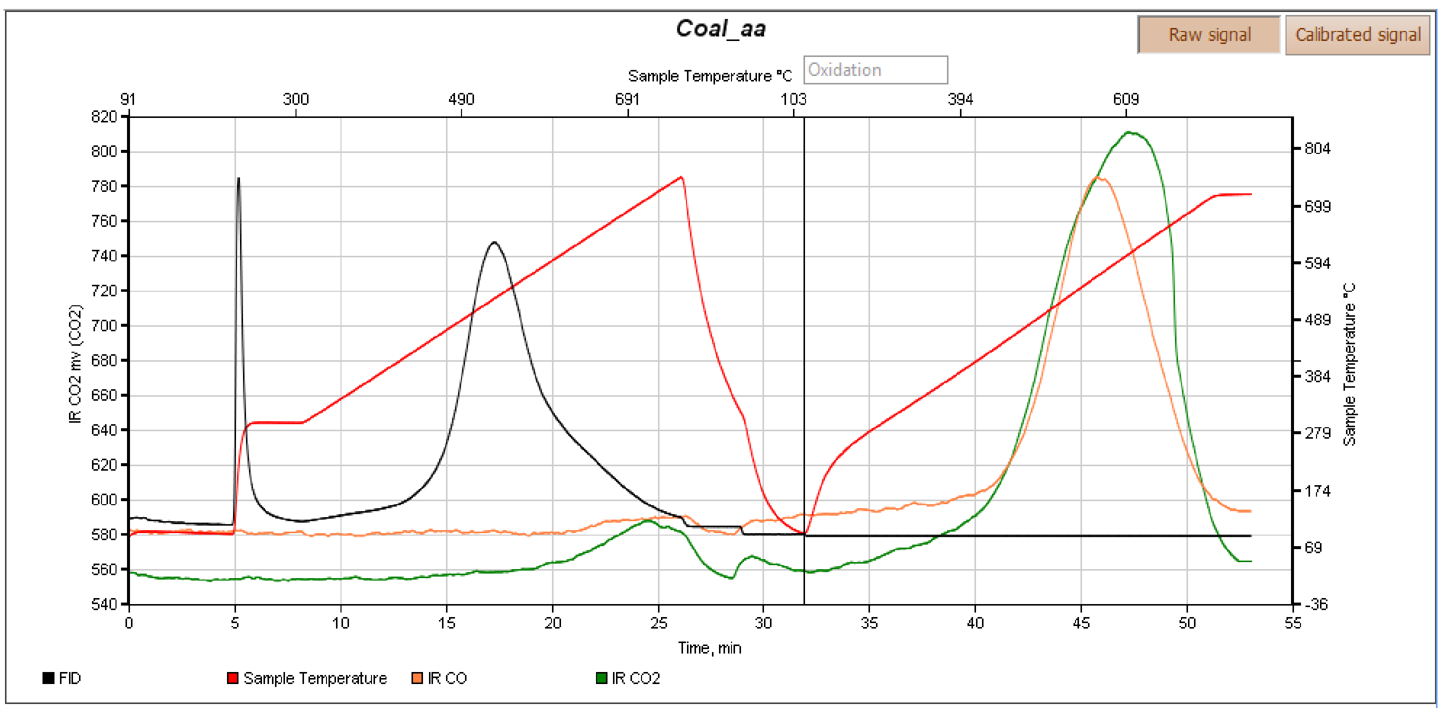
2. Coal deposits exploration and characterization

Coal characterization using the HAWK instrument is achieved through measurement of volatile hydrocarbons, total organic carbon (fixed carbon) and maturity (Tmax). These are critical parameters that are required in characterizing coals (Pierce, 1999, https://pubs.usgs.gov/of/1999/0567/report.pdf accessed on 07.20.2016).The calorific value of a coal deposit can also be inferred from the coal type (coal ranking); peat, lignite, sub-bituminous, bituminous and anthracite (https://www.uky.edu/KGS/coal/coalkinds.htm accessed on 07.20.2016), whose characteristics are governed by its volatile hydrocarbons, total organic carbon and maturity values.

Total organic carbon (fixed carbon) and maturity (Tmax) measurements on coals are done using the classical pyrolysis method that initiates both pyrolysis and oxidation cycles at 300 with terminations being selectively at either 650, 750 or 850 °C. Table 4 below shows the results of analyses of a coal sample on the HAWK instrument using this classical pyrolysis method. The resultant HAWK pyrogram obtained from coal analysis is also shown below.

Sample ID	**S1-Free Oil (mgHC/g rock)**	**S2-Kerogen Yield (mgHC/g rock)**	**S3 (mgCO2/g rock)**	**Tmax-Maturity (°C)**	**TOC (Total Organic Carbon) (wt. %)**	**HI Hydrogen Index (S2/TOC x 100) mg HC/g TOC**	**OI Oxygen Index (S3/TOC x 100) mg CO_2/g TOC**
Coal_a	4.94	63.15	2.01	495	67.03	94	2

Table 4. Results of analysis of a coal sample on the HAWK instrument using the classical pyrolysis method



HAWK pyrogram of a coal sample

Volatile hydrocarbons component of the coal samples on the other hand, are analyzed on the HAWK instrument using the HAWK-PAM method.

HAWK-PAM method 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 hydrocarbon peaks – four on oil fractions and one on kerogen. 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 Table 5 below:

Oil-1 (mg HC/g rock)	**Tmax Oil-1 (°C)**	**Oil-2 (mg HC/g rock)**	**Tmax Oil-2 (°C)**	**Oil-3 (mg HC/g rock)**	**Tmax Oil-3 (°C)**	**Oil-4 (mg HC/g rock)**	**Tmax Oil-4 (°C)**	**K-1 (mg HC/g rock)**	**Tmax K-1 (°C)**
Oil peak obtained during purge (~50 °C to (100 °C). Hold time of 5 mins	Tmax for Oil-1 peak	Set oven temperature at 100 °C, hold for 5 mins. Record the generated oil	Tmax for Oil-2 peak	Ramp from 100 °C to 180 °C at 25 °C. Hold for 5 mins. Record the generated oil	Tmax for Oil-3 peak	Ramp from 180 °C to 350 °C at 25 °C. Hold for 5 mins. Record the generated oil	Tmax for Oil-4 peak	Ramp from 350 °C to 650 °C at 25 °C. Record oil that is generated from Kerogen (K) and any petroleum or oil based mud additive that may be present	Tmax for K-1 peak

Table 5. HAWK-PAM method description

The generalized categories for these five HAWK-PAM method peaks as well as polar constituents (resins vs asphaltenes) are depicted in Table 6 below:

	Oil-1	**Oil-2**	**Oil-3**	**Oil-4**	**K-1**
Petroleum Fractions	C1-C5	C6-C7	C8-C14	C15-C40	Kerogen and Heavy Oil (if present)
	Saturates and Aromatics			**Polars**	**Kerogen**

Table 6. Approximation of carbon number ranges and SARA fraction disposition utilized in one of the multiple ramp and isotherm programs used in the HAWK-PAM method.

Table 7 below shows the pertinent HAWK-PAM oil fractions that apply to the listed n-alkanes.

n-Alkane	**Formula**	**HAWK-PAM oil fraction**
Pentane	C_5H_{12}	Oil-1
Hexane	C_6H_{14}	Oil-2
Toluene	C_7H_8	Oil-2
Heptane	C_7H_{16}	Oil-2 and Oil-3
Decane	$C_{10}H_{22}$	Oil-2 and Oil-3
Tetradecane	$C_{14}H_{30}$	Oil-3
Eicosane	$C_{20}H_{42}$	Oil-4
Hexacosane	$C_{26}H_{54}$	Oil-4
Triatriacontane	$C_{33}H_{68}$	Oil-4
Tetratetracontane	$C_{44}H_{90}$	K-1

Table 7. n-alkanes disposition in the oil-fractions framework of the HAWK-PAM method

Results of analysis of a coal sample using the HAWK-PAM method are shown in Table 8 below.

Sample ID	Oil-1	Tmax Oil-1	Oil-2	Tmax Oil-2	Oil-3	Tmax Oil-3	Oil-4	Tmax Oil-4	K-1	Tmax K-1
Coal_a	0.17	16	0.4	61	1.34	146	4.78	313	54.29	498

Table 8. HAWK-PAM method analytical results on a coal sample

Uses of coal (http://www.worldcoal.org/coal/uses-coal accessed on 07.20.2016), include:

- Electricity generation.
- Steel production.
- Cement manufacturing.
- As a liquid fuel.
- Alumina refineries.
- Paper manufacturing.
- Manufacturing of chemical such as creosote oil, naphthalene, phenol, and benzene.
- Ammonia gas recovered from coke ovens is used to manufacture ammonia salts, nitric acid and agricultural fertilizers.
- Several different products have coal or coal by-products as components: soap, aspirins, solvents, dyes, plastics and fibers, such as rayon and nylon.
- Activated carbon - used in filters for water and air purification and in kidney dialysis machines.
- Carbon fiber - an extremely strong but light weight reinforcement material used in construction, mountain bikes and tennis rackets.
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3. Cement manufacture

The raw materials needed to produce cement are calcium carbonate, silica, alumina, and iron ore (http://www.lafarge-na.com/wps/portal/na/en/2_2_1-Manufacturing_process accessed on 07.20.2016). These raw materials are extracted from limestone rock, chalk, shale, or clay. The HAWK instrument's classical pyrolysis method alluded to above provides TOC (Total Organic Carbon) and Carbonate measurements that can be utilized to characterize these naturally occurring deposits of limestone, chalk, shale and clay. In addition measurement of the HAWK-PAM method's oil fractions alluded to earlier, provide characterization for the low volatile organic matter contents of the naturally occurring raw materials that are needed to manufacture cement.

In addition the fuel oil that is used to complement coal in cement manufacturing can be characterized using the HAWK-PAM method.

Cement is used mainly for buildings, roads, bridges and other infrastructure based construction.

4. Soil Pollution Studies for Environmental Protection

Whereas analysis of soil samples using the HAWK classical pyrolysis method will characterize their organic matter content (TOC) and carbonate content, further analysis of these soil samples using the HAWK-PAM method will reveal whether their hydrocarbon contents are in-line with background values associated with the low volatile hydrocarbons that are generated from bacterial action on soils or whether the soils have been polluted by hydrocarbons discharge or dumping from oil and gas transportation vessels (pipelines, ships, trains, tankers, lorries) or from leakages of hydrocarbons stored either in buildings or underground in the subsurface. The soil samples carbon monoxide and carbon dioxide levels can also be monitored using the HAWK instrument. Industrial sites can be monitored too for an increasing levels of hydrocarbons, Carbon monoxide and Carbon dioxide or carbonates generation or dumping that could pollute soils and in-turn pollute water sources too.

References

http://antoine.frostburg.edu/chem/senese/101/inorganic/faq/carbonate-uses.shtml accessed on 07.20.2016.

Pierce, 1999, https://pubs.usgs.gov/of/1999/0567/report.pdf accessed on 07.20.2016.

https://www.uky.edu/KGS/coal/coalkinds.htm accessed on 07.20.2016.

http://www.worldcoal.org/coal/uses-coal accessed on 07.20.2016.

http://www.lafarge-na.com/wps/portal/na/en/2_2_1-Manufacturing_process accessed on 07.20.2016).