NORTHERN TERRITORY GEOLOGICAL SURVEY

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Shale analysis methodology of the greater McArthur Basin shale study: a compilation of analytical methodologies used by Weatherford Laboratories (Australia) Pty Ltd

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BACKGROUND

This report contains the methodology used in the analysis of the organic geochemistry and rock properties of selected shales from the greater McArthur Basin, Northern Territory, Australia. It supersedes the same titled Record 2015-004.

The services of Weatherford Laboratories (Australia) Pty. Ltd. were procured to conduct the analysis for the Northern Territory Geological Survey, Department of Mines and Energy (NTGS) in 2014. This report is a compilation of the methodologies employed by the laboratory, as designed and implemented by Weatherford Laboratories.

These methodologies employed are standard across the petroleum industry for the analysis of the organic geochemistry and rock property parameters of:

- Total Organic Carbon
- Shale Rock Properties including porosity, permeability, oil/water/gas saturation
- Fluid extraction
- Kerogen isolation
- Kerogen kinetic analysis
- Diamondoid and biomarker analysis
- Elemental analysis for Carbon, Hydrogen, Oxygen, Nitrogen, Sulfur and Iron content of the kerogens
- Density separation by kerogen flotation
- Mechanical rock properties including tri-axial cleavage, Young’s Modulus and Mohr-Coulomb failure analysis.
- Sorption isotherm technology summary

All listed figures and tables were produced by Weatherford Laboratories (Australia) Pty. Ltd.

SHALE ANALYSIS METHODOLOGY

of

McArthur Basin Shale Study

for

NORTHERN TERRITORY GEOLOGICAL SURVEY DEPARTMENT OF MINES AND ENERGY

by

WEATHERFORD LABORATORIES (AUSTRALIA) PTY LTD

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INTRODUCTION

This report summarizes the procedures and results of the shale characterization program conducted on core samples recovered from various wells. WFT Labs conducted analyses on the shale samples. The goals of this project were to assess reservoir properties at the various locations

Many of the values presented in this report are time specific. For instance, references to gas content and gas composition are valid on the date the reservoir was sampled. These properties may have been affected by fluid production from the study well, offset wells, or drainage by mining activities since the samples were collected.

LABORATORY PROCEDURES

WFT Labs performed shale property analysis including Leco TOC analysis measurements on all samples. If TOC reached >0.4% the sample was designated for Programmed Pyrolysis by SRA. Other analyses were selected by NTGS. The following details typical laboratory procedures and analyses conducted for a shale reservoir property assessment.

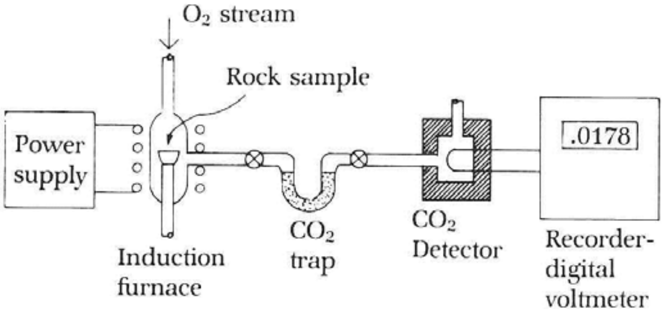
Samples were processed using systematic procedures that minimized sample aerial oxidation, and aerial desiccation (moisture loss).

Total Organic Carbon (TOC) and Pyrolysis Analysis

TOC and pyrolysis analysis (commonly referred to as RockEval™ pyrolysis) are the two most common analysis methods for evaluating the quantity and type of organic material present in rocks. These measurements are summarized in this section based upon material extracted from Waples.

The quantity of organic material present in sedimentary rocks is almost always measured as the total organic carbon (TOC) content, which is determined by combustion. Carbonates are removed from the rock sample of interest with hydrochloric acid before combustion as these minerals would yield carbon dioxide during combustion. TOC analyses are then run in a LECO® carbon analyzer that combusts a 140 mg sample of powdered rock at 1,300°F (704.4°C) in the presence of a large excess of oxygen. A schematic of this apparatus is included in Figure 1. All organic carbon is converted to carbon dioxide that is trapped within the instrument and released into a detector once combustion is complete. The amount of carbon dioxide measured is proportional to the total organic carbon content.

Figure 1. LECO Carbon Analyser Schematic



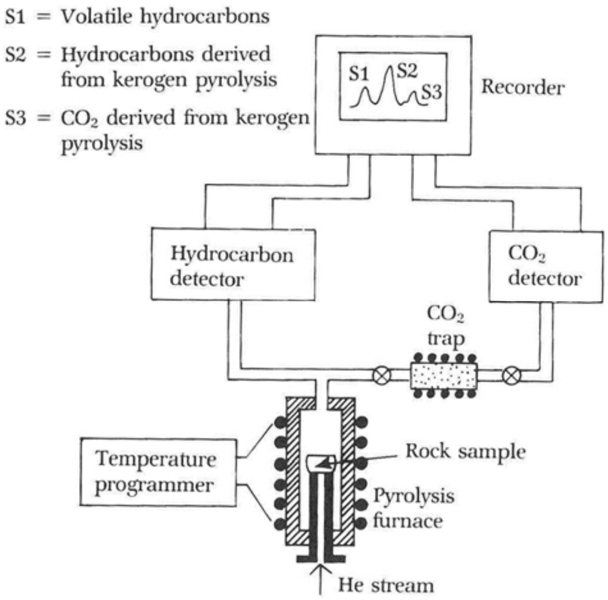
Pyrolysis mimics the natural hydrocarbon generation process that occurs over geologic time at much lower temperatures. Roughly 50 to 100 mg of sample is heated slowly in the absence of oxygen from 300 to 550°C. Exclusion of oxygen insures that only thermal decomposition reactions occur. Figure 2 illustrates a schematic of the Pyrolysis analyser apparatus.

During heating, the first volume of hydrocarbon is released when heated at a temperature of 300°C for three minutes. These hydrocarbons are analogous to solvent-extractible bitumen. The hydrocarbon volume is monitored by a detector and a peak referred to as S1 is recorded. High S1 values indicate large volumes of bitumen in an active source rock or the presence of migrated hydrocarbons.

The temperature is then increased by 25°C per minute to a maximum of 600°C. A second volume of hydrocarbon begins to emerge above approximately 350°C, reaches a maximum flux rate somewhere between 420 and 480°C, and then declines. This second volume of hydrocarbons is referred to as S2 and represents the hydrocarbon volume generated by thermal decomposition of kerogen. The S2 peak is the most important indicator of the present-day ability of the kerogen to generate hydrocarbons. The temperature at which the S2 peak occurs is referred to as Tmax. Tmax may not be reliable when S2 is less than approximately 0.2 mg/g.

Carbon dioxide is also released from the kerogen during pyrolysis. It is recorded by the CO_2 detector as a peak referred to as S3 and is detected in the temperature range of 300 to 390°C. The amount of carbon dioxide released is generally believed to be related to the oxygen content of the kerogen. High oxygen content is considered a negative indicator of source rock potential.

Figure 2. Pyrolysis Analyser Schematic



In summary, the four parameters obtained from pyrolysis are as follows.

1. S1 bitumen content of the source rock, mg/g of rock
2. S2 future hydrocarbon generating potential of the source rock, mg HC/g of rock
3. S3 CO_2 generated by thermal decomposition, mg/g of rock
4. Tmax the temperature at which maximum hydrocarbon generation occurs, °C

These four parameters are evaluated to determine the thermal maturity and source rock characteristics of the organic material. Waples defines three source rock types.

1. Effective source rock: any sedimentary rock that has already generated and expelled hydrocarbons.
2. Possible source rock: any sedimentary rock whose source potential has not been evaluated but may have generated and expelled hydrocarbons.
3. Potential source rock: any immature sedimentary rock known to be capable of generating and expelling hydrocarbons if the level of thermal maturity were greater.

Kerogen type and thermal maturation are characterized by two indices: the hydrogen index, HI defined by the below equation, and the oxygen index, OI also defined by the below equation. These data are plotted on the graph illustrated in Figure 3 to determine the kerogen type and thermal maturity.

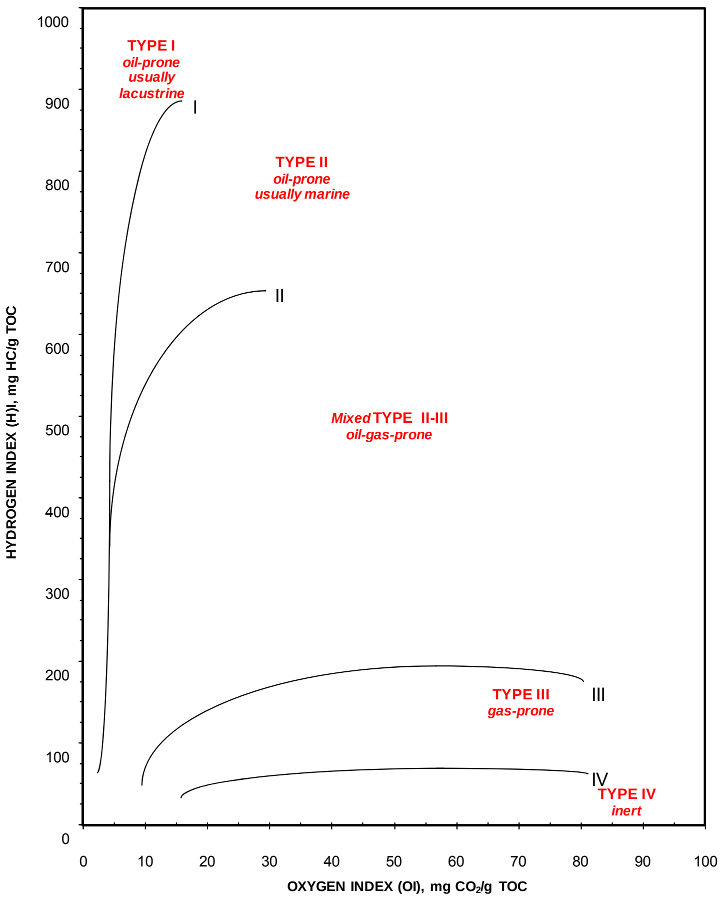
$$HI = \frac{S2}{w_{toc}}$$

$$OI = \frac{S3}{w_{toc}}$$

where:

HI	*hydrogen index, mg of hydrocarbons/g of total organic carbon*
$S2$	*future hydrocarbon generating potential of the source rock. mg HC/g rock*
w_{toc}	*total organic carbon, weight fraction*
OI	*oxygen index, mg of CO_2/g of total organic carbon*
$S3$	*CO_2 generated by thermal decomposition, mg CO_2/g rock*

Figure 3. Modified Van Krevelen Diagram



Type I kerogen is mainly aliphatic in nature and is derived from fresh water algal lipids (usually lacustrine in origin) and can have very high oil or gas generating potential. Type II kerogen is predominately naphthenic in nature and is usually formed from marine organic matter (plankton) in an oxygen-free environment. The oil generating potential of Type II kerogen is high; although, less than for Type I. Type III kerogen is mainly aromatic in nature and is formed by decomposition of terrestrial plants. This type of kerogen is similar to vitrinite in humic coals. The oil generating potential of Type III kerogen is low and the gas generated is primarily methane. Type IV kerogen is essentially inert carbon and has no oil or gas generating potential. As thermal maturity increases, one cannot determine the source of the organic material as all merge together in the Type IV category.

Besides the HI and OI values, there are other combinations of the raw pyrolysis data that are useful. Kerogen is converted to bitumen during hydrocarbon generation. At greater maturity, the S2 values decrease while the S1 values increase. The ratio of S1 to the sum of S1 and S2 is referred to as the production index (PI) or transformation ratio defined by the below equation.

$$PI = \frac{S1}{S1 + S2}$$

This ratio increases with increasing maturity to a point. When the thermal maturity progresses further into the gas window, S1 will decrease as the bitumen is converted to gas. Until S1 is converted to gas, the guideline for estimating thermal maturity from the production index is as follows. These numbers are dimensionless.

$PI < 0.10$	immature
$0.10 \leq PI \leq 0.40$	oil window
$PI > 0.40$	gas window

Thermal maturation can be related to Tmax, which often increases with depth. Tmax is also dependent on kerogen type, which can cause Tmax values to not increase with depth as expected. Therefore, isolated Tmax values are not considered representative. The thermal maturity is classified as follows.

400°C ≤ Tmax < 435°C	immature
435°C ≤ Tmax < 470°C	potential source rock for oil
Tmax ≥ 470°C	potential source rock for gas

Shale Rock Properties (SRP) Analysis

The shale rock properties (SRP) analysis performed by WFT Labs determines a suite of petrophysical properties, including bulk density, crushed density, grain density, porosity, fluid saturations, and matrix permeability. The properties are used to calibrate open-hole log interpretation and to compute the volume of gas stored by compression in the gas-filled porosity.

The SRP analysis is performed in the following general steps. The definitions of the resulting data are summarized in Table 2.

1. The bulk volume of a roughly 100 cm^3 (300 g) sample is determined using mercury displacement.

2. The sample weight is measured and bulk density is computed from the mass divided by volume.

3. The sample is crushed rapidly to a -20 mesh size and split into two fractions: one approximately 80 g and the other approximately 220 g.

4. The 220 g sample is weighed and the sample volume is determined with a helium pycnometer. This sample volume is an intermediate step used to compute the gas-filled porosity (porosity-gas saturation product) of the sample as discussed earlier.

5. The 220 g sample is then cleaned using toluene in a Dean-Stark extraction apparatus to remove all free and bound water and liquid hydrocarbons, but not bitumen or kerogen. The extracted water volume is measured. The extracted mass of oil is determined from the loss in sample weight minus the mass of water extracted. The

volume of oil extracted is estimated by assuming an oil density of 0.8 g/cm^3. The sample is then dried to remove the remaining toluene.

6. The grain volume of the cleaned sample is determined using a helium pycnometer. Grain density is determined by dividing the cleaned sample mass by the volume. This density is affected by kerogen and bitumen that remain in the sample. If the TOC content is significant, the grain density must be corrected to estimate the grain density of the TOC free sample.

7. The grain volume and the extracted fluid volumes are used to compute the total pore volume and total porosity of the sample.

8. The fluid saturations are computed by dividing the extracted fluid volumes by the sample pore volume.

9. The gas permeability of the 80 g split of the crushed sample is determined using the pressure-decay method derived from work pioneered by Luffel and others.

Table 1. Shale Rock Property Definitions

Item	Definition
depth	Average sample depth.
bulk density	Bulk density determined by mercury displacement and sample mass.
crushed bulk density	Sample density determined by helium pycnometry soon after crushing. The density includes the rock minerals, free and bound water, liquid hydrocarbons, kerogen, and bitumen.
apparent grain density	Dried sample density determined by helium pycnometry after removal of all free and bound water and liquid hydrocarbons by toluene solvent extraction. Kerogen and bitumen are still included in this grain density, which is less than the mineral density when TOC content is significant, i.e., more than 0.25 wt%.
total porosity	Total pore volume to bulk volume ratio including the pore volume originally occupied by gas, liquid hydrocarbons, free water, and water bound into the clay materials.
gas-filled porosity	Porosity-gas saturation product of the pore volume originally occupied by natural gas. The effective porosity-effective gas saturation product is equal to the total porosity-total gas saturation product.
water saturation	Volume of water divided by the total pore volume including free and bound water; also referred to as the total water saturation.
oil saturation	Volume of oil divided by the total pore volume; also referred to as the total oil saturation.
gas saturation	Volume of gas divided by the total pore volume; also referred to as the total gas saturation.
pressure-decay permeability	Permeability to nitrogen determined at low hydrostatic pressure conditions on a crushed sample excluding natural fractures.
effective porosity	Total porosity less the bound water saturation.
effective gas saturation	Gas volume divided by the effective pore volume.

bound water saturation	Immobile water volume in clay divided by the bulk volume.
free water	Water present in the effective pore volume that may be immobile due to low permeability and capillary forces.

The crushed bulk density is usually greater than the bulk density and is related to the gas-filled porosity with the below equation. The total porosity-total gas saturation product is equal to the effective porosity-effective gas saturation product because of a difference in the effective and total gas saturation.

$$\phi_e S_{ge} = \phi S_g = 1 - \frac{\rho_b}{\rho_{bc}}$$

where:

ϕ_e	*effective porosity excluding the porosity within clay filled with bound water, volume fraction*
S_{ge}	*effective gas saturation, volume of gas / pore volume of the effective porosity, volume fraction*
ϕ	*total porosity including the porosity within clay filled with bound water, volume fraction*
S_g	*total gas saturation volume of gas / total pore volume, volume fraction*
ρ_b	*bulk density, g/cm^3*
ρ_{bc}	*crushed bulk density, g/cm^3*

The grain density that is estimated is the apparent grain density as it contains kerogen and bitumen and is less than the grain density expected from X-ray diffraction data. The apparent grain density can be corrected to an inorganic grain density with the below equation.

$$\rho_{ma} = \frac{\rho'_{ma}(1 - w_{toc})}{1 - \frac{w_{toc}}{\rho_{toc}}\rho'_{ma}}$$

where:

ρ_{ma}	*inorganic grain density, g/cm^3*
ρ'_{ma}	*apparent grain density, g/cm^3*
w_{toc}	*total organic carbon, weight fraction*
ρ_{toc}	*total organic carbon density, g/cm^3*

Accurate data concerning the density of the total organic carbon density are unavailable. This value probably ranges from 1.25 to 1.40 g/cm^3. A value of 1.25 g/cm^3 is used throughout this report unless otherwise stated.

Soxhlet Extraction

Soxhlet extraction is generally performed on a rock sample (outcrop, side-wall core, cuttings, cores, etc.) for the purposes of quantifying the amount of extractable organic matter (EOM) present in the rock, and also to provide a sample of the soluble organic material, also called bitumen, for further geochemical analysis. Soxhlet extraction may also be used to prepare the rock sample for further analysis, such as the removal of contamination from cuttings prior to RE and TOC, or for the removal of bitumen prior to pyrolysis GC of residual kerogen. Generally, about 50g of rock, if available, is ground to -60 mesh, weighed, placed in a cellulose soxhlet thimble and then extracted with dichloromethane using soxhlet apparatus. Both the soxhlet thimble and apparatus are run through the extraction process before the addition of the sample to make sure no contamination is present within the extraction system. Freshly activated copper metal is added to the refluxing solvent at the beginning of the extraction process for the removal of any elemental sulfur that may be extracted along with the bitumen. Removal of elemental sulfur is necessary since it interferes with subsequent tests that are performed on the bitumen, and because it would artificially inflate the EOM value that is measured. The extraction is allowed to continue until no additional color is observed leaching from the sample (typically overnight). At this point the extraction is stopped and the extract filtered through a pre-extracted Whatman #40 filter paper. Solvent is then carefully evaporated from the filtrate and the amount of EOM obtained by transferring it to a pre-weighed sample vial.

Kerogen Isolation

10-20g of cleaned sample that has been ground to pass a 40 mesh sieve is used. The samples are reacted with concentrated HCl to remove any mineral carbonates. After the reaction is complete the samples are rinsed and centrifuged to separate the solids. A solution of Zinc Bromide is added and the samples are centrifuged once more. Methanol is then added and the samples centrifuged several times while adding more Methanol. Once this is complete the samples are rinsed in water twice then with distilled water.

Kinetics Analysis

Reaction rate profiles derived from pyrolysis FID are used to determine kinetic parameters. These kinetic parameters can be incorporated into hydrocarbon generation models to quantitatively simulate the thermal conversion of various kerogen types to oil and gas. Combining this data with basin modeling and geochemical analysis of the source rock can provide more accurate estimates of a source rocks' contribution to oil and/or gas in a basin and determine the timing of oil and/or gas generation and migration.

Whole rock or isolated kerogens are analyzed with the Source Rock Analyzer (Weatherford Laboratories) or with the Rock-Eval 6 by Vinci Technologies to acquire accurate temperature and reaction rate profiles. Our instrumentation contains a temperature measuring device at the sample being analyzed and this reduces the temperature correction factor necessary to acquire accurate data. The samples are analyzed using multiple constant heating rates, for example (1, 2, 5, 15, and 50°C/min) from 250 to 650°C.

The Lawrence Livermore National Laboratory KINETICS program is used for the calculation of the kinetic parameters. A multiple reaction model is applied which fits the curves with a discrete distribution of activation energies and a common pre-exponential factor, using nested non-linear and constrained linear regressions. A 1000 cal/mol activation energy spacing is used which is considered sufficient to avoid local minima. All parallel and independent reactions are considered first order. The calculations are made both with a free and fixed (A=1.00x1014/sec) pre-exponential factor. Tabular and graphical data of the activation energy distribution and the selected frequency factor are provided. Graphs of the measured and computed rate profiles are included.

Diamondoid Analysis

Diamondoids are hydrocarbons often found in petroleum samples which have chemical structures based upon the carbon atom framework found in diamond. For this reason they are also known as nanodiamonds or condensed adamantanes, and may include multiple carbon atom cages as well as numerous isomeric and structural variants of adamantanes and polymantanes. Traditional biomarkers analysis often gives source and thermal maturity information for oils generated in the main oil window; however, for oils and condensates generated by highly mature source rocks and those which have undergone secondary cracking, biomarker concentrations may be below conventional detection limits. In these samples the analysis of diamondoids can be used to derive such information as (1) Determine the percentage of oil that has been converted to gas, (2) the floor of the economic oil window, (3) calibrate oil-to-gas conversion models, (4) recognize mixes of highly mature oil with less mature oil, (5) estimate expulsion efficiencies of "poor" source rocks.

A series of diamondoid standards were acquired from a commercial source and used to establish an internal standard calibration GCMS method using Cholane and OTP as internal standards. Multiple concentration level standards were prepared to provide a reliable calibration across a range of concentrations, and from this relative response factors were calculated.

Samples are examined using a HP 6890 gas chromatograph equipped with a HP 7683 auto-sampler, on-column injector and the HP5973 mass selective detector (MSD). The samples are separated using a 60 meter DB-1 column using a column oven program that starts 130 °C and ends at 315°C with a total run time of 131.33 minutes. Helium is used as carrier gas. The on-column injection technique with an injector temperature programmed at 3°C above that of the column oven is used. The MSD is operated in the selected ion mode (SIM).

Elemental Analysis

Elemental or CHONS analysis provides the elemental composition of oxygen, carbon, hydrogen, sulfur, and nitrogen. The standard method for elemental analysis specifies that carbon and hydrogen of the kerogen will be determined from the gaseous products of the material's complete combustion. The total sulfur, nitrogen and ash are to be determined from the entire material in separate calculations.

For lack of a suitable test for oxygen, its percentage content in the kerogen is determined by subtracting from 100 the sum of the percentages of the other components.

Elemental Analysis
CHN Normal

Analysis: Carbon, Hydrogen, and Nitrogen

Sample Requirements: 1.5 – 3 mg

Note: This technique is suitable for a reporting limit of $\geq$0.1% for carbon, hydrogen and nitrogen.

Accuracy: $\pm$ 0.3-0.4% Absolute

Compatible Sample Types: Solids, Liquids, Oils

Incompatible Samples Types: Gases

Interferences: High levels of fluorine or inorganics

Note: It is recommended that samples which contain high amounts of fluorine or inorganics should be analyzed by optimum combustion analysis.

Analysis Technique: normal combustion

Sample Preparation: Approximately 2 mg of sample is weighed accurately into a tin sample boat.

Method Summary: Carbon, Hydrogen, Nitrogen are determined using a Perkin-Elmer 2400 Elemental Analyzer. This analyzer uses combustion to convert the sample elements to simple gases, i.e., CO_2, H_2O, N_2. Upon entering the analyzer, the sample is combusted in a pure oxygen environment. The product gases are separated under steady state conditions, and measured as a function of thermal conductivity. The instrument is calibrated prior to sample analysis with an NIST traceable organic standard. System suitability is confirmed by analyzing an NIST traceable organic standard. The standard must check to within 0.1% of its theoretical value.

Elemental Analysis
Sulfur

Analysis: Total Sulfur (S)

Sample Requirements:

Theoretical Range (%)	Sample Size (mg)
0.1-2	10-20
2-5	5-10
5-10	3-8
10-15	3-5
>15	1-2

Note: This analysis is suitable for samples containing >0.1%. Samples requiring lower limits of detection must use ion chromatography or inductively coupled plasma optical emission.

Accuracy: ± 0.3-0.4% Absolute

Compatible Sample Types: Solids, Liquids, Oils,

Incompatible Samples Types: gases

Interferences: F, P

Analyte	Intereferences
S	F, P,I

Note: Samples requiring sulfur, which contain F, and P require an analysis or theory in order to correct the sulfur value.

Analysis Technique: Colormetric Titration

Sample Preparation: The appropriate amount of sample is weighed accurately into an aluminum sample boat and wrapped in an ashless filter paper. The sample is combusted in a oxygen combustion flask containing hydrogen peroxide. The sample is set aside for 20 minutes.

Method Summary: QTI utilizes a colormetric titration for the percentage determination of sulfur for a wide variety of materials. Upon combustion, samples containing sulfer are converted to sulfate. Sulfate, in the presence of DMSA III, can then be titrated with barium perchlorate to a distinct blue end point. Each titration unit is calibrated by determining a solution factor which is based on the normality of the titrant. System suitability is confirmed prior to any sample analysis by combusting and titrating an NIST traceable standard. The standard must check to within 0.4% of its theoretical value. Upon completion the total sulfur can afterwards be calculated with a common formula.

Elemental Analysis
Inductively Coupled Plasma

Analysis: Inductively Coupled Plasma

Sample Requirements: Sample requirements vary by element. The following table is provided as a guide. Consult the laboratory for a refined sample size estimate, if needed.

Theoretical Range (ppm)	Sample Size (mg)
1.0 – 10.0	25 – 100
10.0 – 100.0	10 – 25
> 100.0	3 - 10

Note: This analysis is suitable for the following elements; Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, Ir, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Os, P, Pb, Pd, Pr, Pt, Re, Rh, Ru, S, Sb, Sc, Se, Si, Sn, Sr, Ta, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, and Zr. The elements Hg, Os and S may be analyzed by special arrangement with the laboratory. Solid samples requiring lower limits of detection must use ICPMS in most cases. Cesium can only be measured by ICPMS.

Accuracy: ± 2 - 10% (analyte and concentration dependent)

Compatible Sample Types: n/a

Incompatible Samples Types: Multi-element samples, such as those containing W and P show spectral interference.

Interferences: Samples may be interfered with by other metals in the sample. Each element has a unique interference upon other analytes. The elemental composition of the sample needs to be specified to determine if the technique is applicable to a given sample.

Note: Sample matrix interferences are common and are most often addressed by acid matrix matching and vigorous digestion of the sample. Since the analytical technique is a multiple-wavelength technique spectral overlaps with other elements are better detected than with AA or GFAA. In those cases where overlap cannot be overcome a different analytical technique is recommended (ICPMS).

Analysis Technique: Inductively Coupled Plasma spectrometry.

Sample Preparation: The sample may be prepared by a variety of techniques. The exact sample preparation scheme is dependent on the chemical composition of the sample and the analyte to be measured. Preparations may include dissolution into acid or base, thermal decomposition in oxygen atmosphere, thermal decomposition after chemical char using a furnace, general ashing techniques, vigorous acid digestion in open vessels, and acid digestion in sealed microwave vessels.

Method Summary: A high-energy radio frequency field is impinged upon a stream of argon gas. A spark is used to ionize the argon gas, which forms a sustained plasma due to inductive coupling with the high energy radio frequency field and the continuous supply of fresh argon to the plasma torch. This plasma then has solutions passed into it in the form of a fine aerosol. The aerosol is dried, the dried particles broken apart and the individual elements are excited by interaction with the excited state argon in the plasma. As each element returns to its ground state from the excited state the element will emit light at wavelengths which are characteristic of that element. The emission intensity for each element is monitored for each standard solution and a calibration curve of emission intensity versus element concentration is constructed. Each wavelength for each element will have different sensitivities and potential spectral interferences. Since it is often not possible to know the detailed history of a sample and what elements may be present in high concentrations (which would lead to additive or suppressive interferences) all major wavelengths are monitored. After the calibration has been confirmed a method blank is analyzed, if applicable, and the sample solutions are then analyzed.

A Perkin-Elmer Optima ICP spectrometer is used for the sample analysis. This spectrometer is a simultaneous instrument. The instrument is calibrated using NIST traceable standards and a calibration curve constructed. Calibration is confirmed by reading a Calibration Check Standard prepared independently from the calibration standards. This Calibration Check Standard is analyzed as a sample and must return an acceptable analytical result before samples can be analyzed. The Calibration Check Standard is analyzed periodically throughout the analytical run and as the final sample to ensure that the instrument has maintained its calibration. The prepared sample solution is then analyzed and the measured emission or absorbance is compared with the calibration curve and a concentration of analyte in the prepared sample solutions determined. The sample solution is analyzed in duplicate with the average result reported. The concentration of analyte in solution is then back calculated to the original sample taking into account the sample mass digested, the final sample solution volume and any dilutions performed on the digested sample solutions.

Accuracy for a given sample type is best determined for an individual compound by pre-digestion spike and recovery experiments. The sample preparation and sample heterogeneity tend to have a greater impact on apparent accuracy as the concentration of analyte drops below approximately 100 ppm in the sample (this will vary by sample and analyte tested). Thus, the larger the sample size which can be provided the better the confidence will be at the lower levels of analysis.

Characterization of Mechanical Properties

Background

Mechanical or elastic properties of reservoir rocks are widely used for many engineering applications. The mechanical properties (Young's modulus and Poisson's ratio) of reservoir rocks can be determined by either static or dynamic method. The static elastic properties of reservoir rocks are determined by the stress-strain response of the reservoir rocks in a triaxial compressive test conducted under confining pressure simulating in-situ reservoir stress condition. In contrast, the dynamic elastic properties are computed from the sonic wave (compressional and shear) velocities and bulk density using equations based on a linear elastic theory.

It is well known that the dynamic elastic moduli (Young's modulus and bulk modulus) are higher than the static elastic parameters. The dynamic to static Young's modulus ratios of more than 20 are reported in the literature. While sonic and dipole sonic logs along with density logs are widely used to determined the mechanical properties of the reservoir rocks (i.e., dynamic method), it is also known that the static properties are much more representative for the mechanical properties of the reservoir rocks. However, the static mechanical properties are not readily available over the large interval of reservoir due to the constraints placed by the availability of core materials. The elastic properties derived from the sonic or dipole sonic logs are dynamic properties and therefore, it is necessary to correct these dynamic mechanical properties to the static properties equivalent to in-situ reservoir properties before using for the engineering applications, such as hydraulic fracture design, wellbore stability and sanding prediction.

Triaxial Compressive Strength Test

Triaxial compressive strength tests are conducted in a standard triaxial rock testing system consisting of pressure vessel with specimen assembly, servo-controlled stiff loading frame, hydraulic pump system to supply pressurized oil, confining and pore pressure intensifiers and computer data acquisition. All pressures and stress (confining pressure, pore pressure and axial stress) can be independently controlled using electro-hydraulic servo-controlled feedback systems. Two linear variable differential transducers (LVDT) attached to the endcaps record axial displacement. Radial displacement measurements are recorded with a circumferential chain gauge wrapped around the sample near the mid point. Axial load is measured with an internal load cell and confining and pore pressures are measured by hydraulic pressure transducers.

The general procedures for triaxial compressive test are summarized in the following:

a) A right cylindrical plug is cut from the sample core and its end-surfaces ground parallel to each other within 0.001 inch. A length to diameter ratio of 2:1 is recommended to obtain representative mechanical properties of the sample. Physical dimensions of the specimen are recorded and the specimen is saturated with simulated formation brine if needed.
b) The specimen is then placed between two platens and a heat-shrink jacket is placed over the specimen.
c) Axial strain and radial strain devices are mounted in the platens and on the lateral surface of the specimen, respectively.
d) The specimen assembly is placed into the pressure vessel and the pressure vessel is filled with hydraulic oil.
e) Confining pressure is increased to the desired hydrostatic testing pressure.
f) Measure optional P-wave and S-wave velocities at the initial hydrostatic condition.
g) Specimen assembly is brought into the contact with a loading piston that allows application of axial load.
h) Increase axial load at a constant displacement rate until the specimen fails while confining pressure is held constant.
i) Reduce axial stress to the initial hydrostatic condition after sample fails.
j) Reduce confining pressure to zero and disassemble sample.

Data Analysis for Triaxial Compressive Strength Test (Static Elastic Parameters)

The axial stress is determined by dividing the measured load by the initial cross-sectional area of the specimen. Differential stresses are plotted against both axial strain ε_L (= $\Delta L/L_o$, where L_o is the initial length and ΔL is the length change) and radial strain ε_R (= $\Delta D/D_o$, where D_o is the initial diameter and ΔD is the diameter change). Differential stress (σ_d) is defined as the difference between the total axial stress (σ_1) and the confining pressure (P_c). For the sign conventions, compressive stress and contraction (shortening) are considered positive. Therefore, positive axial strain indicates a shortening of the specimen length and negative radial strain indicates an increase of the specimen diameter during the test.

The compressive strength of the specimen is determined by the maximum differential stress (σ_d) achieved during the test plus the confining pressure. However, it should be noted that the differential stresses ($\sigma_1 - P_c$) are plotted in the stress-strain curves (Figure 1). Static Young's modulus (E_s) is determined by the linear-least-square slope of the differential stress versus the axial strain curve. Likewise, static Poisson's ratio (ν_s) is determined by the linear-least-square slope of the radial strain versus the axial strain curve at the same interval as the Young's modulus is determined.

Acoustic Velocities and Dynamic Elastic Parameters

Compressional (P) and shear (S) wave velocities are determined using a system composed of endcaps fitted with piezoelectric crystals, a pulser/receiver, and a high-speed digital storage oscilloscope. The pulse transmission technique is used with 1MHz frequency for both P- and S-waves. Ultrasonic velocities (compressional- and shear-wave velocities) are calculated from transit times of the compressional and shear waves in the sample after correcting transit times for the platens.

Dynamic elastic properties (Young's modulus, Poisson's ratio, bulk modulus, and shear modulus) are calculated from the measured compressional-wave velocity (V_p), shear-wave velocity (V_s) and bulk density (ρ_b) of the specimen. Dynamic Young's modulus (E_d) is expressed as

$$E_d = [\rho_b V_s^2 (3V_p^2 - 4V_s^2)]/(V_p^2 - V_s^2).$$

Dynamic Poisson's ratio (ν_d) depends on the ratio of the compressional-wave velocity to the shear-wave velocity (V_p/V_s) and can be expressed as

$$\nu_d = 0.5 [(V_p/V_s)^2 - 2]/[(V_p/V_s)^2 - 1].$$

Dynamic shear modulus (G_d) is expressed as

$$G_d = \rho_b V_s^2.$$

Dynamic bulk modulus (K_d) is expressed as

$$K_d = \rho_b (3V_p^2 - 4V_s^2)/3.$$

Applications of Triaxial Compressive Test

The static and dynamic mechanical properties from triaxial compressive tests with concurrent ultrasonic velocity measurements can be used to solve many practical problems:

- Hydraulic fracture design (compressive strength, Young's modulus and Poisson's ratio)
- Wellbore stability, sand production and critical drawdown analysis (angle of internal friction, cohesion and uniaxial compressive strength)
- Sonic or dipole sonic log calibration

In addition to the triaxial compressive test, proppant embedment test can be performed to evaluate the interaction between proppant and fracture face with increasing closure stress.

Hydraulic Fracture Design Optimization

Hydraulic fracturing is the primary stimulation method for improving well productivity. Completion engineers generally need mechanical properties of the reservoir rocks and frac fluid properties to design the hydraulic fracturing. The properties of the frac fluid are usually known and considered as controllable parameters that can be varied to maximize fracture treatment. However, the mechanical rock properties are uncontrollable and should be provided by either static lab tests on core plugs or by dipole sonic logs calibrated to static laboratory values.

Triaxial compressive strength tests are conducted on the samples from the interested pay zone and bounding barrier zones at confining pressures simulating downhole stress conditions (Figure 1). The static elastic parameters (Young's modulus and Poisson's ratio) and compressive strength are provided as the deliverables for the optimized fracture designs. Ultrasonic velocities can be measured in conjunction with the triaxial compressive strength tests and used for sonic or dipole sonic log calibration. Stress differences between the pay zone and confinement zone are important factor in the arrestment of the vertical fracture growth, therefore, the triaxial compressive tests on the top and bottom barrier zones are also highly recommended.

Wellbore Stability and Sand Production

Wellbore stability problems cost over $1 billion annually to the oil and gas industry and are important during not only drilling but also production period of oil and gas wells. Wellbore instability and sanding problems occur when near-wellbore stress exceeds formation strength. Therefore, an accurate failure criterion of reservoir rocks based on the triaxial compressive strength tests is great importance along with the correct estimation of formation stresses acting on the wellbore and perforation channel.

The triaxial compressive strength tests are commonly used to generate the accurate failure criterion for the formation of interest, which is reservoir specific. The compressive strengths from a suite of triaxial compressive tests at different confining pressures are used to construct a Mohr-Coulomb failure criterion. Based on the Coulomb failure criterion, the critical shear stresses (τ_c) associated with onset of shear failure of intact rocks can be expressed as:

$$\tau_c = S_0 + \sigma_n \tan\phi$$

where S_0 is the cohesion (inherent shear strength), σ_n is the normal stress across the incipient fracture plane, $\tan\phi$ is the coefficient of internal friction and ϕ is the angle of internal friction. Mohr-Coulomb failure analysis provides cohesion, angle of internal friction and unconfined compressive strength (Figure 2), which are necessary parameters for the wellbore stability analysis and sanding prediction.

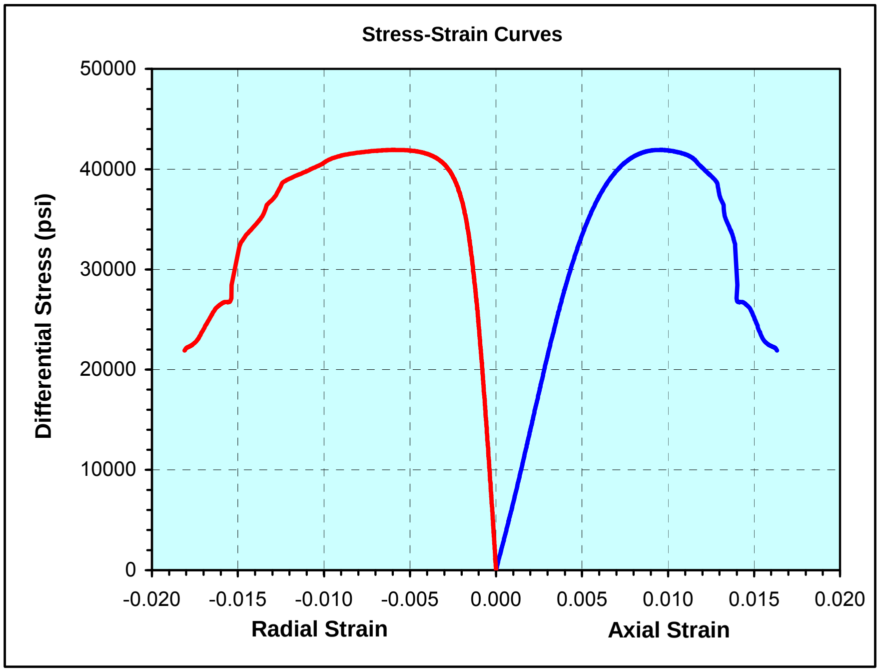


Figure 4. Example of triaxial compressive test. The static Young's modulus and Poisson's ratio determined from the triaxial test are 7.37x10^6 psi and 0.32, respectively. In contrast, the dynamic Young's modulus and Poisson's ratio determined for the same sample are 10.19x10^6 psi and 0.31, respectively.

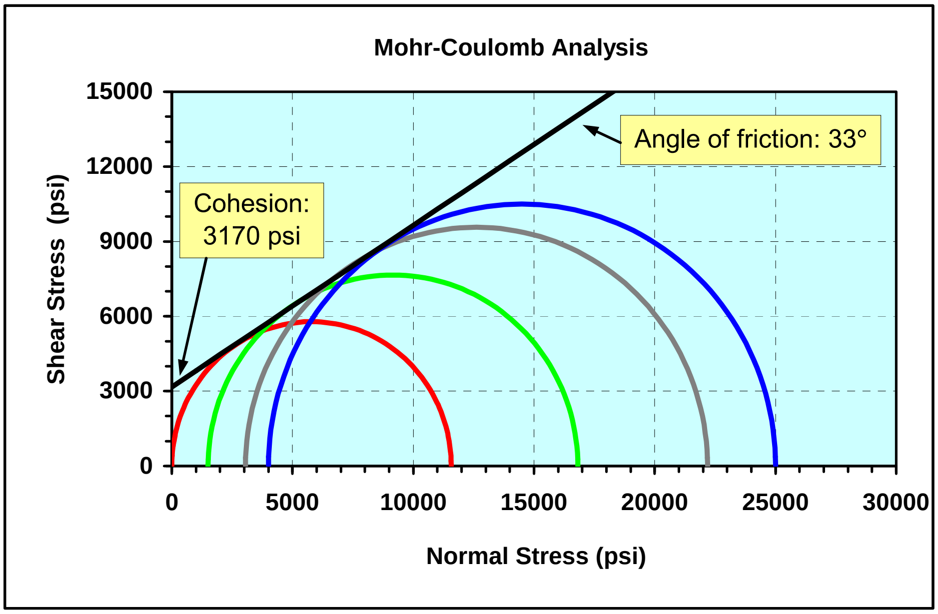


Figure 5 Example of Mohr-Coulomb failure analysis. The unconfined compressive strength determined from the Mohr-Coulomb analysis is 1,1700 psi.

DENSITY SEPARATION BY KEROGEN FLOTATION USING $ZNBR_2$ SOLUTION

Introduction.

Kerogen isolated by acid digestion (HCl and HF) rarely is completely mineral free. Pyrite for example is a typical contaminant in the kerogen concentrate from acid digestion since it is does not dissolve in HCL or HF. While this is generally not a problem if the kerogen is being isolated for vitrinite reflectance or MOA (the petrographer simply ignores the pyrite when making kerogen observations), the residual mineral matter does interfere with elemental analysis (especially sulfur content when pyrite is present).

For this reason it is often necessary to perform a density based separation on the kerogen concentrate so that the less dense kerogen is floated away from the more dense mineral matter. This sink/float type density separation can be achieved with solutions of various salts, but typically we employ zinc bromide ($ZnBr_2$) for this purpose. While most pyrite is removed in this process it is typical for some to remain in the floated kerogen due to the very close association of the organic matter with finely dispersed pyrite.

The preparation of the $ZnBr_2$ solution and the procedure used for the sink/float separation are described below.

Preparation of $ZnBr_2$solution.

1. Put 350 ml DI water in a 1000ml glass beaker with a stir bar and put on a stirring hot plate. Heat the water but don't boil. Pour about 100ml of the water into a smaller beaker. Pour the remainder of the water into a bottle of 500g $ZnBr_2$ and stir. Pour this into the large beaker. Use the remaining water to rinse the remaining ZnBr2 into the large beaker.
2. Stir the solution until all crystals are dissolved. Set aside and allow to cool to room temperature. Measure the density by weighing a known volume.
3. If the density is lower than needed heat the solution to remove water and measure density again after it cools. If the density is too high use the following formula to get the needed density. $D=(CB-AB)/(1-C)$
   A= Density that you have
   B= Volume that you have
   C= Density that is needed
   D= Volume of water to add

4. Mix water with ZnBr2 solution and verify the density.

Procedure for sink/float separation of kerogen concentrate.

1. Follow Acid digestion procedure through one rinse after 2nd HCL.

2. Make sure sample is thoroughly spun down (use longer time or higher speed if necessary) Pour off water and add $ZnBr_2$ solution to near the top. Use density specified by client. Thoroughly agitate the sample and spin at high speed for 20 minutes. If you have an uneven number of samples use a blank with the same $ZnBr_2$ solution.

3. While samples are spinning make a second set of centrifuge tubes with the same information as the original plus a large F. After centrifuge stops pour approximately the top 1/3 from the first tube into the second. Recap first tube, fill second tube with MeOH, agitate and cap.

4. Centrifuge both tubes for 20 minutes at high speed. Be sure centrifuge is balanced. First tube should be balanced by a first tube and a second by a second tube.

5. After centrifuge stops pour off the liquid in the second tube, being careful not to lose sample. Pour offs go into approved waste container. Again, pour off about 1/3 of the first into the second. Add MeOH to both tubes, agitate and spin for 10 minutes.

6. After centrifuge stops pour off both tubes into waste container, add water, agitate and centrifuge for 10 minutes.

7. When centrifuge stops, pour off water, add 5 ml HCL, fill with water to top, agitate and spin for 10 minutes.

8. Rinse twice with water and then twice with distilled water.

Weatherford Laboratories Sorption Isotherm Technology Summary

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Introduction

Weatherford Laboratories (WFT Labs) and its predecessors developed our initial sorption isotherm technology in 2002 and have been improving and refining our capabilities ever since. Our latest generation of isotherm instruments is illustrated in Figure 1. Their primary function is to measure the adsorbed gas storage capacity of a variety of gases in both coal and shale samples. This document summarizes WFT Labs' technology used to measure and interpret the data. We believe that our data is the highest accuracy available due to the measurement hardware, our sample handling and preparation procedures, and our data interpretation procedures. The purpose of this document is to summarize our procedures for our clients.

The first section of this report summarizes our capabilities; particularly those that have improved isotherm accuracy. The later sections summarize our interpretation procedures, fluid property estimates, and application of the Langmuir isotherm relationship to predict in-situ gas storage capacity data.

Figure 1. Weatherford Laboratories Isotherm Equipment featuring two independent covered oil baths, metal to metal seals on pressure cells, pressure capabilities to 10,000 psi, and temperatures up to 400 °F.

Summary of Weatherford Laboratories Isotherm Capabilities

Weatherford Laboratories has over ten years of experience measuring isotherms, and is now using a fourth generation machine (see Figure 1) designed to expand capabilities, reduce noise, and improve isotherm measurements. There have been a variety of design, sample handling, and data interpretation features and improvements that result in excellent data accuracy as summarized in this section. Design features include:

1. The isotherm apparatuses are enclosed in a temperature controlled room to minimize ambient air temperature fluctuations that can affect the isotherm cells and baths as well as the electronic equipment. Electronics and measurement equipment are powered from an Uninterruptible Power Supply (UPS) to minimize electronic noise in the measurements.

2. The reference and sample cell sizes were enlarged over standard designs to accommodate larger sample sizes for increased accuracy, especially for low storage capacity samples such as shale and subbituminous coal.

3. The reference and sample cells are sized so that the void volume within the sample cell when it contains coal or shale is roughly the same volume of the reference cell. This improves material balance accuracy. For improved accuracy in special cases, both the reference and sample cell sizes can be varied.

4. The pressure cells are immersed in an oil bath to minimize errors due to transient temperature fluctuations. In our low temperature machines (with open baths), temperature can be maintained within less than 0.2 °F of the desired temperature. Our high temperature baths allow the pressure cells to be totally submerged. The baths are heavily insulated and have a cover so that temperature stability is on the order of 0.05 °F. With refrigeration, our machines are able to handle temperatures between 10 and 400 °F.

5. The temperature is monitored continuously using a thermocouple or RTD for each sample. The accuracy of the thermocouple is ±0.05 °F. High temperature machines use RTDs with an accuracy of ±0.02 °F.

6. The pressure transducers are directly immersed into the oil bath reducing temperature effects upon the transducers themselves. The transducers are temperature compensated and for low temperature baths are accurate to 0.05% of full scale which corresponds to ±2.5 psi for a 5,000 psia transducer.

7. Multiple gases can be used for measurements including methane, ethane, propane, carbon dioxide, and nitrogen. Others may be available on special request. Ethane and propane maximum pressures may be limited by available gas tank pressure and the critical temperature of the gas. All other gases are available at pressures up to 10,000 psia using pressure boosters.

8. Our new high temperature isotherm units use pressure cells incorporating metal to metal seals in place of O-ring seals. These virtually eliminate any leakage from the pressure cells even at high pressures. They also avoid damage to the seals from gases such as carbon dioxide. This previously limited carbon dioxide isotherms to around only 2000 psia.

9. Pressure and temperature data are monitored by a computer data acquisition system that can collect data at 0.5 second intervals. We have developed methods to calculate diffusivity from these data and will be incorporating these estimates in future isotherm reports.

10. Currently, sixteen isotherm cells of varying capabilities are available at WFT Labs' Golden Colorado facility and eight more will be located at our Brisbane offices in Australia. To increase our capacity, we are currently building twelve more isotherm cells bringing the total number of available cells to 36 worldwide. The build out of the new equipment should be completed in 2013-2014 timeframe.

The advantages of our sample handling procedures are as follows.

1. Sample preparation is a very important item to obtain accurate storage capacity data. WFT Labs has developed special methods to determine the moisture holding capacity (similar to equilibrium moisture content at reservoir temperature) on coal samples to insure that the isotherm data are measured at the in-situ moisture content as accurately as possible. For shale samples we ensure immediate preservation at the well site so that in-situ fluids are not altered via desiccation or imbibition.

2. When necessary, all samples can be prepared in a glove box under an inert atmosphere to eliminate oxidation effects.

3. Sample density is determined in triplicate and compared to the sample density determined by the isotherm apparatus for quality control. If the densities do not agree, there is a discrepancy with the isotherm sample; the cause of which is investigated and corrected.

4. We have implemented technology to insure that moisture content of the isotherm samples cannot change significantly during the measurement steps. In addition, for quality control, moisture content is determined before and after the isotherm measurements. Storage capacity is a function of moisture content and moisture content changes must be avoided.

Proper interpretation of the data requires a variety of steps. The critical interpretation items are as follows.

1. Reference cell, sample cell, and void volumes are determined with helium using six to nine pressure steps. This redundancy improves the accuracy of the volume determination.

2. Calibration and sorption isotherm data are highly sensitive to the estimated properties of the free gas phase. We have determined and are using the most accurate methods currently available to estimate the free gas density (z factors) and sorbed gas density of helium, methane, ethane, propane, carbon dioxide, and nitrogen.

3. We have implemented a full computerized interpretation that accounts for slight temperature and pressure variations to improve the accuracy of the measured stabilized pressure and temperature conditions at the end of each isotherm step. This improvement greatly increases the repeatability and consistency of the isotherm measurements.

4. All measurements made by WFT Labs are recorded in a strictly confidential internal data base so that WFT Labs can compare measurements to past data to identify inconsistencies if any are present.

5. If WFT Labs determines that there are discrepancies in the data, WFT Labs will rerun the measurement at no charge to the client.

6. As expected, we have confirmed the accuracy of all calculations incorporated in the data acquisition and interpretation software.

One concern that WFT Labs has always had with reported isotherm data, is that one cannot check the calculations as most laboratories do not report sufficient data to do so. As a result, WFT Labs reports the following items.

1. The pressure, temperature, z factor, and duration of each endpoint isotherm step.

2. Langmuir parameters of pressure and storage capacity will be computed with 95% confidence intervals and statistical error bars to report the accuracy of the regression.

3. Upon special request, all temperature and pressure data as a function of time can be supplied.

These three items will allow one to estimate the range in possible storage capacity at in-situ conditions.

Although it is at the client's discretion, we recommend that a full suite of data be measured to properly characterize each isotherm sample. These measurements are required to determine why storage capacity data may vary from sample to sample. For coal, these data include the following.

1. Moisture holding capacity (the moisture content of the isotherm sample)
2. Proximate analysis for ash, moisture (before equilibration to moisture holding capacity), volatile matter, and fixed carbon content
3. Ultimate analysis for carbon content, hydrogen, sulfur, nitrogen, and oxygen content
4. Helium density in triplicate
5. ASTM rank, based upon proximate analysis, moist-mineral-matter free heating value, and sulfur trioxide in ash
6. Vitrinite reflectance
7. Maceral analysis for organic composition

For shale samples, the characterization data include the following.

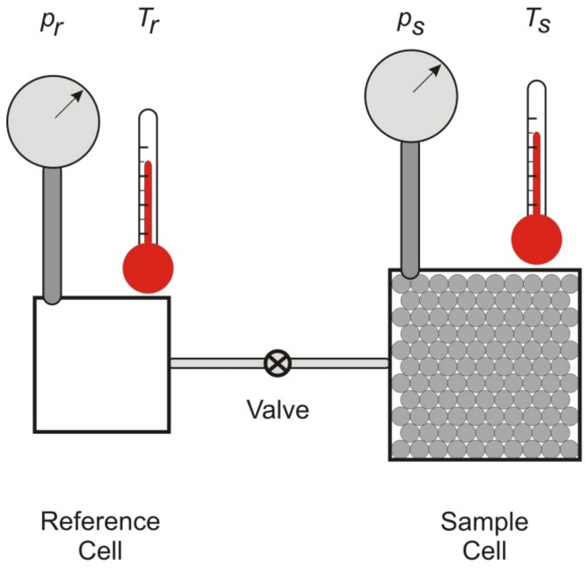
1. Grain density, and bulk density of crushed samples
2. X-ray diffraction for inorganic composition
3. Total organic content (TOC)
4. Programmed Pyrolysis for organic matter characterization
5. Shale Rock Properties analysis (shale permeability, porosity, and fluid saturations).

Endpoint Data Interpretation

The determination of the gas storage capacity of a sample is based upon material balance interpretation of the stabilized pressure and temperature at the end of each pressure step. This section discusses the endpoint interpretation methods used by WFT Labs.

Figure 2 illustrates a general schematic of the isotherm apparatus. A reference cell is connected to a sample cell. Independent pressure transducers monitor the pressure within each cell. A thermocouple or RTD monitors the temperature for the sample cell. The cells are immersed in an oil bath maintained at constant temperature that eventually forces the cells to return to the bath temperature as transient effects subside.

Figure 2. Weatherford Laboratories Isotherm General Schematic

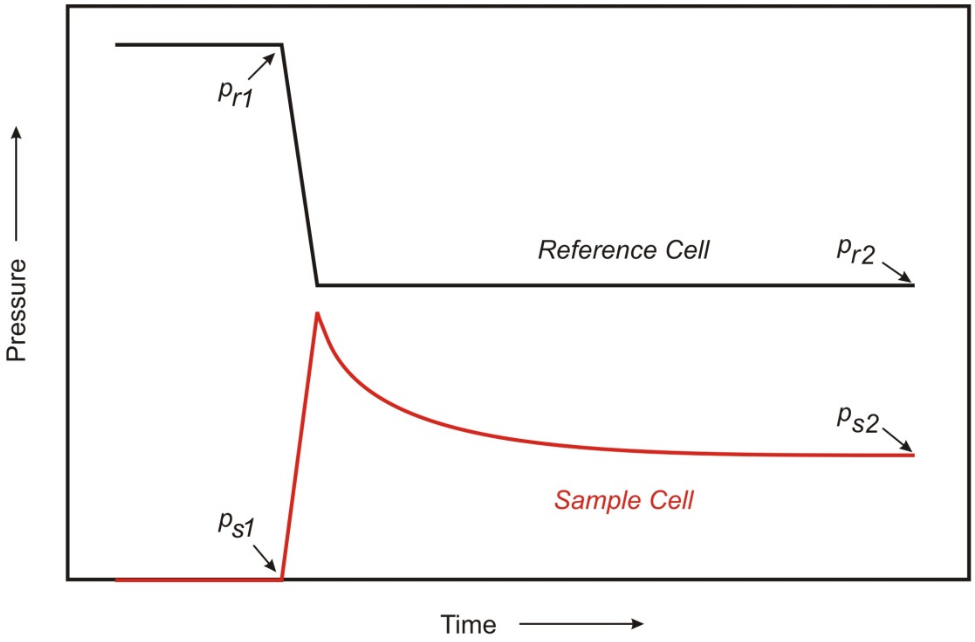


A single isotherm step as illustrated in Figure 3 includes several sub-steps. With the valve between the reference and sample cells closed, the reference cell is charged to a pressure p_{r1} that is greater than the desired sample cell stabilization pressure at the end of the step, p_{s2}. Pressure p_{r1} is allowed to stabilize as the reference cell temperature returns to the bath temperature. The sample cell remains at pressure p_{s1} from the previous step. When both p_{r1} and p_{s1} are stable, the valve between the reference and sample cells is opened allowing the reference cell to drop to a pressure near the final stabilization pressure, p_{r2}. The sample cell pressure increases to a level less than p_{r2} at which time the valve is closed. The sample cell pressure declines with time as the gas adsorbs into the sample and eventually stabilizes at p_{s2}. A variation on this procedure is to leave the valve open; in this situation, p_{r2} and p_{s2} are equal.

This process is repeated a number of times to measure endpoints with between 3 and 9 pressure steps. We have found that six steps across the pressure range of interest is usually sufficient. The maximum stabilized sample cell pressure is selected to be above the maximum in-situ reservoir pressure whenever possible.

We refer to the free gas phase as the gas that is contained within the void volume of the cells while the sorbed gas phase is contained in the micro-pores of the sorbing material within the sample cell. Interpretation of the pressure and temperatures at the end point steps is based upon material balance analysis of the change in the number of molecules (or moles) of gas stored in the reference cell and the change in the number of molecules in the free gas phase within the sample cell. The difference between the two is the number of molecules that were sorbed during the pressure step.

Figure 3. Isotherm Pressure Step Schematic



The endpoint analysis is based upon the real gas law[1] to relate gas density to pressure and temperature conditions. Equation 1 lists the form of the real gas law used during this evaluation. This form is commonly used in the petroleum industry.

$$pV = nzRT \tag{1}$$

where:

p	*pressure, psia*
V	*volume,* ft^3
n	*number of lb moles, dimensionless*
z	*real gas deviation factor, dimensionless*
R	*gas constant,* $psia\text{-}ft^3/lbmole\text{-}^oR$
T	*temperature, degrees Rankine*

In this unit system, *R* has the value 10.7316.[2] Absolute temperature in degrees Rankine is equal to temperature in degrees Fahrenheit plus 459.67. (Reference 2, p. I-33).

There are two primary steps in measuring isotherm data, a calibration step and an isotherm measurement step. During calibration, the empty reference and sample cell volumes are determined with helium. Calibration also involves determination of the void volume within the sample cell after it is filled with a sorbing material. This step is also performed with helium as this gas does not adsorb into the sample. The isotherm measurement step involves repeated pressure steps with a sorbing gas to determine the stabilized endpoint pressure and temperature conditions for each step. The interpretation of the data during these primary steps is discussed in the following sections.

Cell Volume Calibration

The calibration step involves three steps. Step one is expansion of gas from the reference cell to the sample cell when the sample cell is empty. Step two involves expansion of gas from the reference cell to the sample cell when the sample cell contains a calibration blank of known volume. The two sets of pressure and temperature endpoints are used to solve simultaneously for the unknown reference and sample cell volumes. This calibration need only be performed after changing the mechanical configuration of the apparatus or when necessary to verify the volume data. The third step involves expansion of gas from the reference to the sample cell when the sample cell contains the sample for which sorption data are desired. The third step is performed before all isotherm measurements.

This calibration is done with helium since the void volume determination step requires a non-sorbing gas. However, conceptually the calibration during the first two steps can be done with any gas whose z factor values as a function of temperature and pressure are accurately known.

The mass balance on the initial system when the cells are empty is given by Equation 2 which states mathematically that the mass within the system before opening the valve between the two cells is the same as the mass within the system after closing the valve.

$$V_r \rho_{r1} + V_s \rho_{s1} = V_r \rho_{r2} + V_s \rho_{s2} \tag{2}$$

where:

V_r *reference cell volume, ft^3*
V_s *sample cell volume, ft^3*
ρ_{r1} *reference cell free gas density at initial condition, lbm/ft^3*
ρ_{r2} *reference cell free gas density at final condition, lbm/ft^3*
ρ_{s1} *sample cell free gas density at initial condition, lbm/ft^3*
ρ_{s2} *sample cell free gas density at final condition, lbm/ft^3*

Gas density in the free gas phase is computed with Equation 3.

$$\rho = \frac{m}{V} = \frac{\hat{M}p}{zRT} \tag{3}$$

where:

m *free gas mass, ft^3*
$\hat{M}$ *gas molecular weight, lbm/lbmoles*

Combination of Equations 2 and 3 after eliminating the common molecular weight and gas constant results in Equation 4. This equation has two unknowns, the reference and sample cell volumes.

$$V_r \left(\frac{p_{r1}}{z_{r1}T_{r1}} - \frac{p_{r2}}{z_{r2}T_{r2}} \right) + V_s \left(\frac{p_{s1}}{z_{s1}T_{s1}} - \frac{p_{s2}}{z_{s2}T_{s2}} \right) = 0 \tag{4}$$

The process is repeated after a blank calibration volume is placed into the sample cell. Equation 5 describes the material balance relationship in this situation.

$$V_r \left(\frac{p_{r1}}{z_{r1}T_{r1}} - \frac{p_{r2}}{z_{r2}T_{r2}} \right) + V_s \left(\frac{p_{s1}}{z_{s1}T_{s1}} - \frac{p_{s2}}{z_{s2}T_{s2}} \right) = V_b \left(\frac{p_{s1}}{z_{s1}T_{s1}} - \frac{p_{s2}}{z_{s2}T_{s2}} \right) \tag{5}$$

where:

V_b *blank calibration volume, ft^3*

These equations are solved simultaneously to determine V_r and V_s. Equation 4 uses the pressure and temperature conditions measured within each cell when the sample cell was empty and Equation 5 uses the pressure and temperature conditions measured within each cell when the sample cell contained the blank volume.

The void volume within the sample cell when containing the sample of interest can then be determined by expansion of helium from the reference to the sample cell. Equation 6 is the basis of the interpretation which is solved for the material volume, V_m, with Equation 7. The void volume is computed with Equation 8.

$$V_r\left(\frac{p_{r1}}{z_{r1}T_{r1}}-\frac{p_{r2}}{z_{r2}T_{r2}}\right)+\left(V_s-V_m\right)\left(\frac{p_{s1}}{z_{s1}T_{s1}}-\frac{p_{s2}}{z_{s2}T_{s2}}\right)=0 \qquad (6)$$

where:

V_m *volume of sample material, ft*^{3}

$$V_m=V_r\frac{\left(\frac{p_{r1}}{z_{r1}T_{r1}}-\frac{p_{r2}}{z_{r2}T_{r2}}\right)}{\left(\frac{p_{s1}}{z_{s1}T_{s1}}-\frac{p_{s2}}{z_{s2}T_{s2}}\right)}+V_s \qquad (7)$$

$$V_v=V_s-V_m=-V_r\frac{\left(\frac{p_{r1}}{z_{r1}T_{r1}}-\frac{p_{r2}}{z_{r2}T_{r2}}\right)}{\left(\frac{p_{s1}}{z_{s1}T_{s1}}-\frac{p_{s2}}{z_{s2}T_{s2}}\right)} \qquad (8)$$

The interpretation of the pressure data measured with a sorbing gas requires the reference and void volume estimates, V_r and V_v, respectively. These volumes are usually reported in units of cm^3 while all of the equations in this section assume that the volume is in units of ft^3. Units of ft^3 are converted to units of cm^3 by dividing ft^3 by 3.531467(10^{-5}).

Single Component Gas End Point Interpretation

Once the reference cell and void volumes have been determined, a sorbing gas is introduced into the apparatus to determine the gas storage capacity as a function of pressure and temperature. The mass balance with a sorbing gas is given by Equation 9.

$$V_r\frac{p_{r1}\hat{M}}{z_{r1}RT_{r1}}+V_{v1}\frac{p_{s1}\hat{M}}{z_{s1}RT_{s1}}=V_r\frac{p_{r2}\hat{M}}{z_{r2}RT_{r2}}+V_{v2}\frac{p_{s2}\hat{M}}{z_{s2}RT_{s2}}+\left(n_2-n_1\right)\hat{M} \qquad (9)$$

where:

n_1 *number of sorbed molecules at the start of the pressure step, lbmoles*
n_2 *number of sorbed molecules at the end of the pressure step, lbmoles*

Solving for the change in the number of molecules in the sorbed state and eliminating the common molecular weight results in Equation 10.

$$n_2-n_1=V_r\left(\frac{p_{r1}}{z_{r1}RT_{r1}}-\frac{p_{r2}}{z_{r2}RT_{r2}}\right)+V_v\left(\frac{p_{s1}}{z_{s1}RT_{s1}}-\frac{p_{s2}}{z_{s2}RT_{s2}}\right) \qquad (10)$$

The void volume is reduced by the volume of the sorbed phase. Therefore, the number of sorbed molecules determined by Equation 10 must be corrected as discussed below.

The number of molecules can be converted to the volume of gas at standard temperature and pressure (STP) with Equation 11.

$$V_s = \frac{n z_{sc} R T_{sc}}{p_{sc}} \tag{11}$$

where:

V_s	*sorbed gas volume at STP, ft^3*
z_{sc}	*real gas deviation factor at STP, dimensionless*
T_{sc}	*temperature at standard conditions, degrees Rankine*
p_{sc}	*pressure at standard conditions, psia*

For example, 1 lbmole of methane at 14.73 and 60 °F, occupies a volume of 377.8504 scf as z_{sc} is generally 0.998 for methane at these conditions. The gas storage capacity at the stabilized reference cell pressure and temperature is then computed with Equation 12 by dividing by the sample mass that was measured before placing the sample in the sample cell.

$$G'_s = \frac{2000 V_s}{m_m} \tag{12}$$

where:

G'_s	*Gibbs isotherm gas storage capacity, scf/ton*
m_m	*material mass, lbm*

Note that the material mass is often reported in grams. Grams are converted to lbm by multiplying grams by 2.204622622(10^{-3}). Gas storage capacity in cm^3/g is equal to the gas storage capacity in units of scf/ton divided by 32.036929.

The isotherm determined in this manner is referred to as a Gibbs isotherm due to the simplification assumed by Gibbs during his study of sorption thermodynamics. The resulting Gibbs isotherm can be corrected to the true isotherm through the use of Equation 13. The free gas density is computed with Equation 3 at the stabilized sample cell end point pressure and temperature conditions. The sorbed phase density is assumed to be equal to the liquid density of the molecules of interest at the atmospheric pressure boiling point. The sorbed phase density will be discussed in more detail later.

$$G_s = \frac{G'_s}{1 - \frac{\rho_f}{\rho_s}} \tag{13}$$

where:

G'_s	*Gibb's isotherm storage capacity, scf/ton*
G_s	*total isotherm storage capacity, scf/ton*
ρ_f	*free gas density, lbm/ft^3*
ρ_s	*sorbed gas density, lbm/ft^3*

Gas Properties

Density information is required for both the free and sorbed gas phases to interpret the end point pressure and temperature conditions. The free gas density is dependent upon the *z* factors. The sorbed gas density is based upon an equivalent liquid density. This section discusses the methods used to arrive at the free gas z factors as well as the sorbed gas density.

The method used to estimate the *z* factor has a substantial impact upon the accuracy and quality of the gas storage capacity estimates. By quality, we are referring to the ability to accurately correlate gas storage capacity with pressure through the use of a Langmuir isotherm relationship. Correlation to a Langmuir relationship will be discussed in the following section.

Methane

Methane has been extensively studied due to its value as a fuel and will be the most common gas used for isotherm measurements. Table 1 summarizes methane properties.

Table 1. Summary of Methane Properties

Property	Units	Value
Molar mass	lb/lbmole	16.0428
Critical pressure	psia	667.06
Critical temperature	°F	-116.655
Critical density	lbm/ft^3	10.154
Triple point temperature	°F	-296.421
Atmospheric pressure boiling point temperature	°F	-258.669
Liquid density at atmospheric pressure boiling point temperature	lb/ft^3	23.2572
	g/cm^3	0.372545

Methane density is based upon information reported in Reference 3 and Reference 10. The accuracy of the methane density data, and thus *z* factor, was reported to be within ±0.03% for pressures below 1,740 psia and temperatures below 170 °F while uncertainty was between ±0.03% and ±0.15% at greater temperatures and pressures. This reference summarizes modern methane property data in detail. Because of the accuracy of these data and the thoroughly researched equation of state, we have chosen to use Reference 3 for our *z* factor estimates.

The sorbed gas density is generally assumed to be equal to the liquid density at the atmospheric pressure boiling point. It can be calculated from equation 14:

$$\text{Density} = 8MP_c/(RT_c) \tag{14}$$

where:

M = 16.0428 lbm/lbmole

R = 10.7316 psia·ft^3

P_c = 667.06 psia and

T_c = 343.015 °R

This gives a value of 23.572 lb/ft^3 or using equation 15 to convert units, 0.372545 gm/cc.

$$\text{Density (g/cc)} = 0.01601846337 * \text{Density (lb/ft}^3\text{)} \tag{15}$$

This is the methane liquid density that we use to correct methane Gibbs isotherm relationships.

Carbon Dioxide

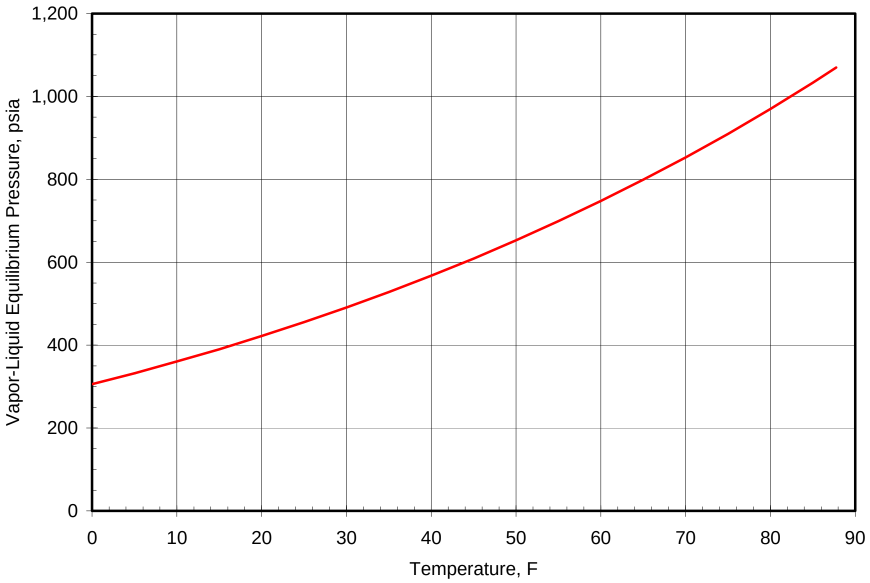
Carbon dioxide is an unusual compound in that in that it has great deviation from ideal gas behavior. In addition, the critical point of CO_2 (87.76076 °F, 1,069.9869 psia) and can be approached while measuring CO_2 storage capacity. At temperatures greater than the critical temperature, CO_2 will remain in the vapor phase. At lower temperatures, CO_2 can liquefy in the isotherm apparatus. Table 2 summarizes CO_2 properties.

Table 2. Summary of Carbon Dioxide Properties

Property	Units	Value
Molar mass	lbm/lbmole	44.0098
Critical pressure	psia	1,070.0
Critical temperature	°F	87.76076
Critical density	lbm/ft^3	29.1913
Triple point temperature	°F	-69.804
Atmospheric pressure boiling point temperature	°F	-109.12
Liquid density at atmospheric pressure boiling point temperature	lbm/ft^3	64.12531
	g/cm^3	1.027189

Reference 4 lists the most accurate data concerning CO_2 density available. The accuracy of density, and hence z factors, are ±0.03% to ±0.05% in the range of temperature up to 482 °F and pressure up to 4,350 psia.

Figure 4. CO_2 Vapor-Liquid Saturation Line



Because CO_2 liquefies at temperatures that may be in the range of interest of isotherm measurements, there is a limit to the maximum pressure for CO_2 sorption measurements below the critical temperature. Figure 4 illustrates the vapor-liquid saturation line. At any given temperature below the critical temperature, the maximum cell pressure that can be used without liquefaction is indicated by the saturation line. Above the critical temperature, this is not a problem. Using equations 14 and 15, the saturated liquid density at the critical temperature is 1.027189 g/cm^3 (64.12531 lbm/ft^3). This is the CO_2 liquid density that we use to correct the CO_2 Gibbs isotherm relationships.

Nitrogen

The properties of nitrogen have been well documented due to its use as a reference fluid for many physical models and calibration purposes. The most up to date properties and equation of state for nitrogen are listed in Reference 5. The uncertainty in density, hence z factor, ranges from ±0.01% between 26 and 170 °F at pressures less than 1,740 psia, ±0.02% overall other temperatures less than 530 °F and pressures less than 1,740 psia, up to a maximum of ±0.6% at the highest temperatures. Nitrogen properties are summarized in Table 3.

Table 3. Summary of Nitrogen Properties

Property	Units	Value
Molar mass	lbm/lbmole	28.01348
Critical pressure	psia	492.52
Critical temperature	°F	-232.524
Critical density	lbm/ft^3	19.5587
Triple point temperature	°F	-346.00
Atmospheric pressure boiling point temperature	°F	-320.43
Liquid density at atmospheric pressure boiling point temperature	lbm/ft^3	45.28051
	g/cm^3	0.725324

Using equations 14 and 15, the saturated liquid density at the atmospheric pressure boiling point temperature of -320.43 °F is 0.725324 g/cm^3 (42.28051) lbm/ft^3. This is the N_2 liquid density that we use to correct the N_2 Gibbs isotherm relationships.

Helium

Helium z factor information is required to calibrate the cell and void volumes. The small size of the helium molecule allows it to penetrate into coal pores less than 0.3 nm in diameter. It also has such a small heat of adsorption that adsorption is negligible (Reference 6, page 194). Therefore density determined with helium is considered the true density of the sample. During calibration of the isotherm sample cell and void volumes, the volume of the sample is also determined, which, given the weight, results in accurate density estimates. Table 4 summarizes helium properties (Reference 1).

Table 4. Summary of Helium Properties

Property	Units	Value
Molar mass	lbm/lbmole	4.0026
Critical pressure	psia	33.011
Critical temperature	°F	-450.32
Critical density	lbm/ft^3	4.5302
Triple point temperature	°F	-455.75
Atmospheric pressure boiling point temperature	°F	-452.055
Liquid density at atmospheric pressure boiling point temperature	lbm/ft^3	10.53283
	g/cm3	0.16872

Ethane

Ethane is commonly present in sorbed gas reservoirs, and ethane isotherm data can be required. The most accurate ethane density data is listed in Reference 1. Density and z factor uncertainty is within ±0.2%. Table 5 summarizes ethane properties.

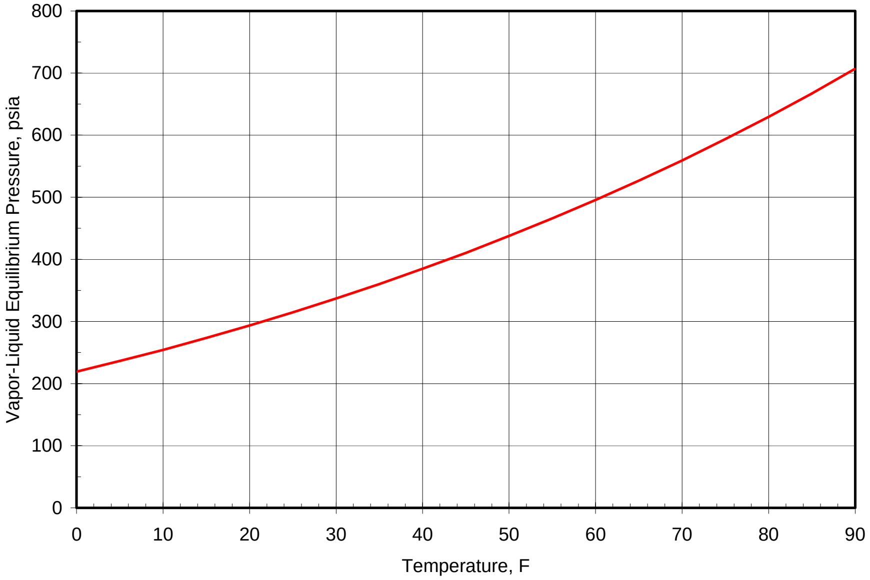
Table 5. Summary of Ethane Properties

Property	Units	Value
Molar mass	lbm/lbmole	30.069
Critical pressure	psia	706.65
Critical temperature	°F	89.91
Critical density	lbm/ft^3	12.871
Triple point temperature	°F	-297.01
Atmospheric pressure boiling point temperature	°F	-127.45
Liquid density at atmospheric pressure boiling point temperature	lbm/ft^3	28.82159
	g/cm^3	0.461678

As with CO_2, ethane can liquefy in the isotherm cell depending upon the measurement temperature. Figure 5 illustrates the ethane liquid-vapor saturation line. Isotherm measurements below the critical temperature are limited to the pressure indicated by the saturation line.

References 1 and 7 indicate that the saturated liquid density at the atmospheric pressure boiling point temperature of -127.45 °F is 0.461678 g/cm^3 (28.82159) lbm/ft^3. This is the ethane liquid density that we use to correct the ethane Gibbs isotherm relationships.

Figure 5. Ethane Vapor-Liquid Saturation Line



Propane

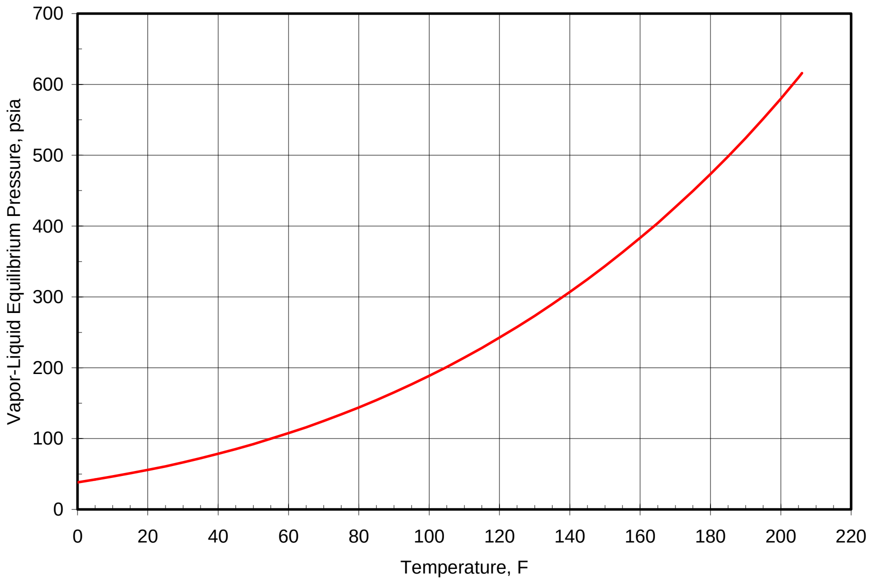
Propane can be present in sorbed gas reservoirs and propane isotherm data can be required, especially for shale. References 1 and 9 list the most accurate propane density data available. Density and *z* factor uncertainty is within ±0.2%. Table 6 summarizes propane properties.

Table 6. **Summary of Propane Properties**

Property	Units	Value
Molar mass	lbm/lbmole	44.096
Critical pressure	psia	616.58
Critical temperature	°F	206.13
Critical density	lbm/ft^3	13.764
Triple point temperature	°F	-305.73
Atmospheric pressure boiling point temperature	°F	-43.805
Liquid density at atmospheric pressure boiling point temperature	lbm/ft^3	30.4418
	g/cm^3	0.487631

Propane will liquefy at most temperature conditions of interest during isotherm measurements and the storage capacity data will be limited to low pressure. Figure 6 illustrates the vapor-liquid saturation line. Isotherm measurements below the critical temperature will be limited to the pressure indicated by the saturation line. This may not be a limitation since multicomponent storage capacity estimates depend upon the partial pressure. As propane is usually present in small quantities, the partial pressure of propane may be in the vapor phase range.

Figure 6. **Propane Vapor-Liquid Saturation Line**



References 1 and 9 indicate that the saturated liquid density at the atmospheric pressure boiling point temperature of -43.805 °F is 0.487631 g/cm^3 (30.4418) lbm/ft^3. This is the propane liquid density that we use to correct the propane Gibbs isotherm relationships.

Langmuir Isotherm Relationship

A Langmuir isotherm relationship is the most common method used to correlate gas storage capacity to pressure in the coal gas industry. The Langmuir relationship as used by WFT Labs is listed in Equation 16.

$$G_s = G_{sL}\left[1-\left(w_a + w_w + w_s\right)\right]\frac{p}{p+p_L} \tag{16}$$

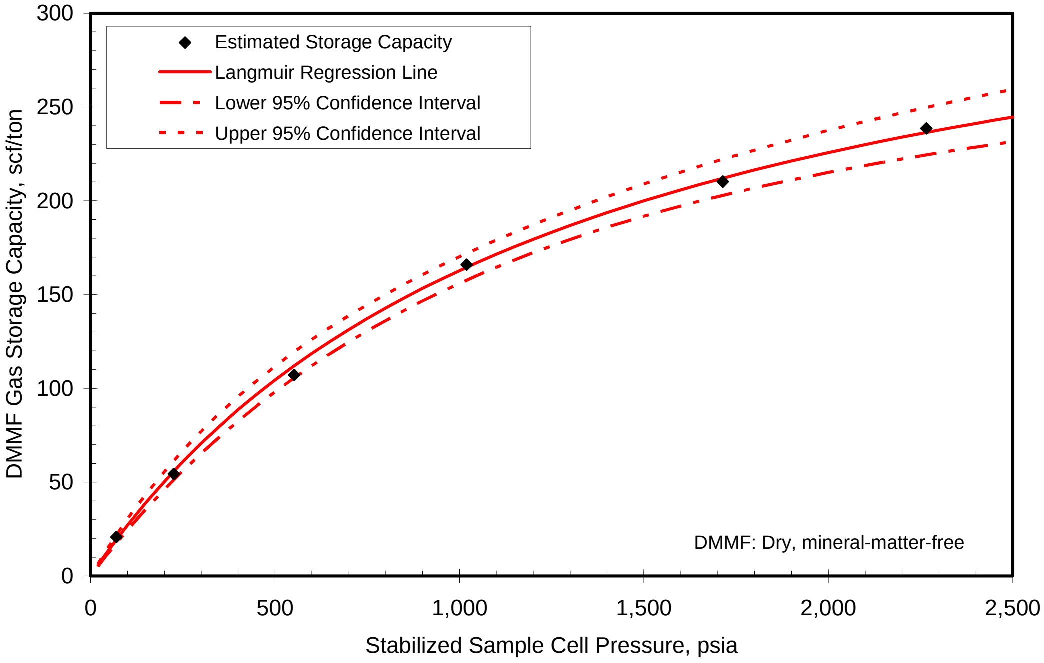
where:

G_s *gas storage capacity, in-situ basis, scf/ton*
G_{sL} *Langmuir storage capacity, dry, mineral-matter free basis, scf/ton*
w_a *ash content, weight fraction*
w_w *moisture content, weight fraction,*
w_s *sulfur content, weight fraction*
p *pressure, psia*
p_L *Langmuir pressure, psia*

The Langmuir storage capacity is the equivalent storage capacity at infinite pressure. The Langmuir pressure is the pressure at which the storage capacity is equal to half the Langmuir storage capacity. The weight fractions of ash, moisture, and sulfur dilute the storage capacity. We generally use in-situ values to convert the laboratory measurements to the average condition in the reservoir to predict reservoir behavior.

Figure 7 illustrates a typical isotherm graph with confidence intervals determined by linear regression. The confidence intervals indicate the accuracy of the regression, not the accuracy of each data point. These data were measured on a low range, sub-bituminous C Powder River Basin coal sample.

Figure 7. **Typical Langmuir Isotherm Relationship**



The Langmuir parameters are determined by linear regression of the estimated storage capacity at the end point conditions through the use of Equation 17.

$$\frac{p}{G_s} = \frac{p_L}{G_{sL}\left[1-\left(w_a+w_w+w_s\right)\right]} + \frac{1}{G_{sL}\left[1-\left(w_a+w_w+w_s\right)\right]}p \tag{17}$$

Figure 8 illustrates a typical analysis graph. The Langmuir storage capacity is computed from the slope with Equation 18 and the Langmuir pressure is computed from the slope and intercept with Equation 19.

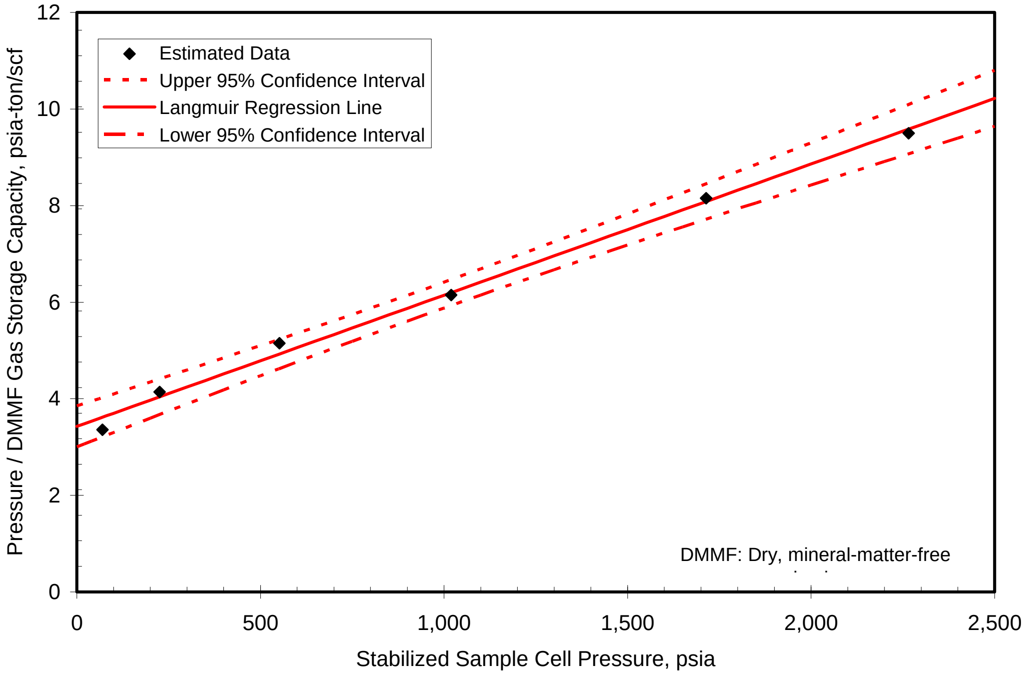
$$G_{sL} = \frac{1}{a_1\left[1-\left(w_a+w_w+w_s\right)\right]} \tag{18}$$

$$p_L = a_0 G_{sL}\left[1-\left(w_a+w_w+w_s\right)\right] \tag{19}$$

where:

a_0 *intercept, psia-ton/scf*
a_1 *slope, ton/scf*

Figure 8. **Typical Langmuir Isotherm Analysis Graph**



As with any regression, confidence intervals of each of the parameters can be computed. Reference 6 presents calculation methods that have been incorporated into WFT Labs software.

Multicomponent Isotherm Relationship

Although WFT Labs equipment can measure sorption data when using a mixture of pure gases, these data are generally determined only for research studies. It is more practical to compute multicomponent storage capacity measurements from pure component isotherm relationships using extended Langmuir isotherm models. In addition, coal gas reservoir simulation files often require the individual pure component storage capacity data (such as GEM developed by the Computer Modeling Group, Calgary, Alberta).

The extended Langmuir isotherm relationship (see reference 9) for component *i* in the presence of other sorbed gas components is listed in Equation 20.

$$G_{si} = G_{sLi}\left[1-\left(w_a + w_w + w_s\right)\right]\frac{\dfrac{py_i}{p_{Li}}}{1+p\displaystyle\sum_{j=1}^{nc}\frac{y_j}{p_{Lj}}} \tag{20}$$

where:

G_{si}	*multicomponent storage capacity of component i, in-situ basis, scf/ton*
G_{sLi}	*single component Langmuir storage capacity of component i, dry, ash-free basis, scf/ton*
p_{Li} or p_{Lj}	*single component Langmuir pressure of component i or j, psia*
y_i or y_j	*mole fraction of component i or j in the free gas (vapor) phase, dimensionless*
nc	*number of components*
p	*pressure of the free gas phase, psia*

The total storage capacity is the sum of the individual component gas storage capacity as shown by Equation 21.

$$G_s = \sum_{i=1}^{nc} G_{si} \tag{21}$$

where:

G_s	*total mixture storage capacity, in-situ basis, scf/ton*

The mole fraction of component *i* in the sorbed phase is simply the ratio of the storage capacity of component *i* to the total storage capacity as shown by Equation 22.

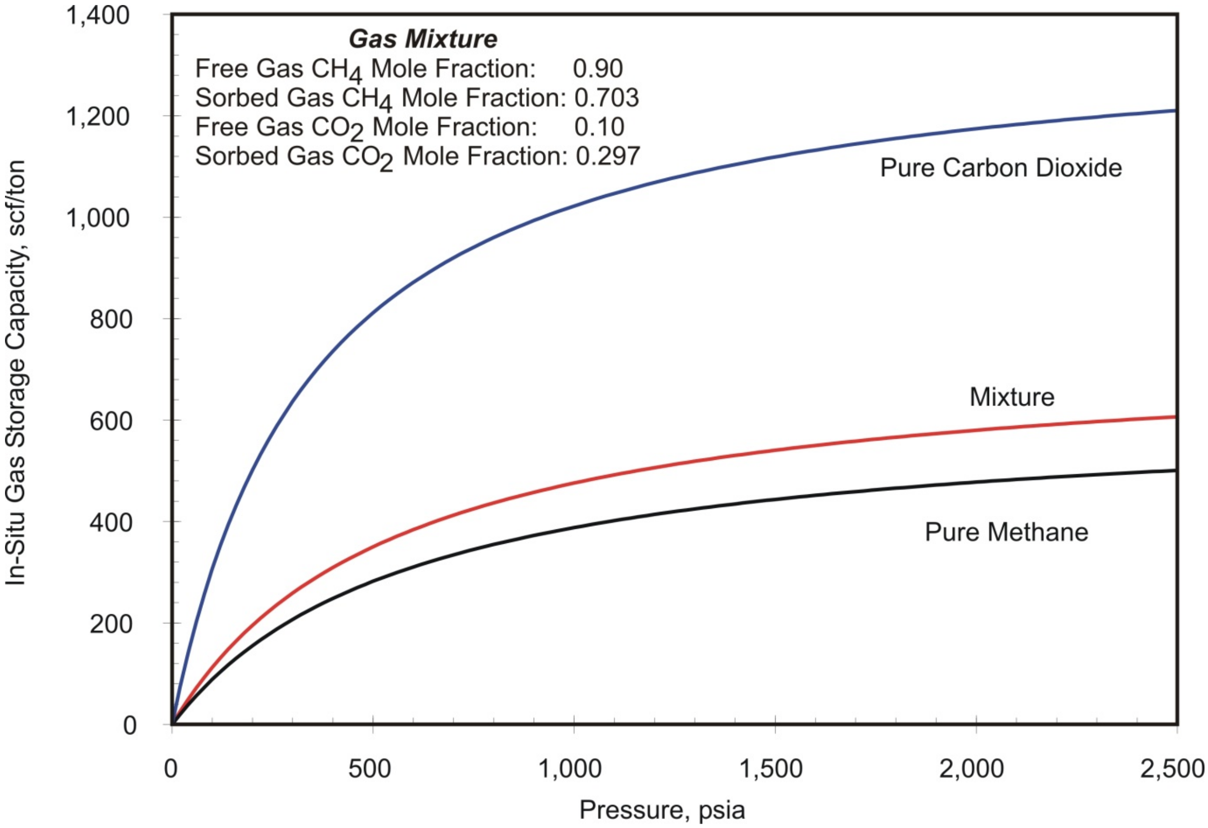
$$x_i = \frac{G_{si}}{G_s} \tag{22}$$

where:

x_i	*sorbed phase component i concentration, mole fraction*

The use of extended Langmuir isotherm theory allows one to mix the sorption data. As an example, Figure 9 illustrates a binary gas system including both methane and carbon dioxide. In principle, any number of gas components can be included as long as pure component isotherm data are available for each component.

Figure 9. **Example Methane and CO_2 Mixture Isotherm Data**



Summary

In summary, WFT Labs has spent a great deal of effort and time to develop modern state of the art isotherm equipment for maximum data accuracy.

The advantages of the equipment are as follows.

1. The isotherm apparatuses are enclosed in a temperature controlled room that is air conditioned and closely monitored

2. The reference and sample cell sizes were enlarged to accommodate larger sample sizes for increased accuracy, especially for low storage capacity samples such as shale and subbituminous coal.

3. The reference and sample cells are sized so that the void volume within the sample cell when it contains coal or shale is roughly the same volume of the reference cell. For improved accuracy, both the reference and sample cell sizes can be varied when necessary.

4. The pressure cells are immersed in an open oil bath maintained within less than 0.2 °F of the desired temperature or in insulated covered baths with temperature stability on the order of 0.05 °F.

5. The temperature within the sample cell is monitored directly with a thermocouple and is not assumed to be the same as the bath temperature. The accuracy of the thermocouple is ±0.05 °F. High temperature machines use RTDs with an accuracy of ±0.02 °F.

6. The pressure transducers are directly immersed into the oil bath reducing temperature effects upon the transducers themselves. The transducers are temperature compensated and accurate to 0.05% of full scale.

8. Isotherm measurements can be performed at temperatures from 10 °F to 400 °F and pressures up to 10,000 psia.

9. Isotherms can be measured with methane, ethane, propane, carbon dioxide, and nitrogen with others available upon request up to 10,000 psia as long as the measurement temperature is above the critical temperature.

10. Pressure and temperature data are monitored by a computer data acquisition system that can collect data at one second intervals.

The advantages created by the sample handling techniques are as follows.

1. WFT Labs has developed special methods to determine the moisture holding capacity at which the isotherm data are measured.

2. Samples can be prepared under an inert environment eliminating oxidation effects.

3. Sample density is determined in triplicate and compared to the sample density determined by the isotherm apparatus for quality control.

4. Moisture content of the isotherm samples cannot change significantly during the measurement steps.

The advantages of WFT Labs' data analysis techniques are as follows.

1. Reference cell, sample cell, and void volumes are determined redundantly.

2. We are using the most accurate methods currently available to estimate the free gas density (z factors) of helium, methane, ethane, propane, carbon dioxide, and nitrogen.

3. We have implemented full computerized interpretation that accounts for slight temperature and pressure variations to improve the accuracy of the measured stabilized pressure and temperature conditions at the end of each isotherm step.

4. We compare the measured data to previous measurements to insure consistency.

Finally, we report more information than other isotherm laboratories including the following information.

1. The pressure, temperature, z factor, and duration of each endpoint isotherm step.

2. Langmuir parameters of pressure and storage capacity will be computed with 95% confidence intervals and statistical error bars to report the accuracy of the regression.

3. Upon request, WFT Labs will provide the entire measured temperature and pressure history of the measurements.

WFT Labs can measure a full suite of coal and shale properties to characterize the isotherm samples.

We hope that the information included in this document assists with interpretation of WFT Labs isotherm data. Thank you for your interest in our technology.

Sincerely,

Weatherford Laboratories
Chad Hartman
Chief Technical Advisor, Golden Colorado

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