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Methodology for shale analysis of onshore basins, Northern Territory: a compilation of analytical methodologies used by Weatherford Laboratories (Australia) Pty Ltd

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Methodology for shale analysis of onshore basins, Northern Territory: a compilation of analytical methodologies used by Weatherford Laboratories (Australia) Pty Ltd.


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This report contains the methodology used in the analysis of the organic geochemistry and rock properties of selected shales from on shore basins, Northern Territory, Australia.

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.
- X-ray diffraction for bulk and clay mineral fractions

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 CO2 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. $S_1$ bitumen content of the source rock, mg/g of rock
2. $S_2$ future hydrocarbon generating potential of the source rock, mg HC/g of rock
3. $S_3$ CO$_2$ generated by thermal decomposition, mg/g of rock
4. $T_{max}$ 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.

\[
HI = \frac{S_2}{w_{toc}} \\
OI = \frac{S_3}{w_{toc}}
\]

where:

- $HI$: hydrogen index, mg of hydrocarbons/g of total organic carbon
- $S_2$: 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
- $S_3$: CO$_2$ generated by thermal decomposition, mg CO$_2$/g rock
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.

\[
\begin{align*}
\text{PI} < 0.10 & \quad \text{immature} \\
0.10 \leq \text{PI} \leq 0.40 & \quad \text{oil window} \\
\text{PI} > 0.40 & \quad \text{gas window}
\end{align*}
\]

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.

\[
\begin{align*}
400^\circ C \leq \text{Tmax} < 435^\circ C & \quad \text{immature} \\
435^\circ C \leq \text{Tmax} < 470^\circ C & \quad \text{potential source rock for oil} \\
\text{Tmax} \geq 470^\circ C & \quad \text{potential source rock for gas}
\end{align*}
\]

**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 cm³ (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
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**

<table>
<thead>
<tr>
<th>Item</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>depth</td>
<td>Average sample depth.</td>
</tr>
<tr>
<td>bulk density</td>
<td>Bulk density determined by mercury displacement and sample mass.</td>
</tr>
<tr>
<td>crushed bulk density</td>
<td>Sample density determined by helium pycnometry soon after crushing. The density includes the rock minerals, free and bound water, liquid hydrocarbons, kerogen, and bitumen.</td>
</tr>
<tr>
<td>apparent grain density</td>
<td>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%.</td>
</tr>
<tr>
<td>total porosity</td>
<td>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.</td>
</tr>
<tr>
<td>gas-filled porosity</td>
<td>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.</td>
</tr>
<tr>
<td>water saturation</td>
<td>Volume of water divided by the total pore volume including free and bound water; also referred to as the total water saturation.</td>
</tr>
<tr>
<td>oil saturation</td>
<td>Volume of oil divided by the total pore volume; also referred to as the total oil saturation.</td>
</tr>
<tr>
<td>gas saturation</td>
<td>Volume of gas divided by the total pore volume; also referred to as the total gas saturation.</td>
</tr>
<tr>
<td>pressure-decay permeability</td>
<td>Permeability to nitrogen determined at low hydrostatic pressure conditions on a crushed sample excluding natural fractures.</td>
</tr>
<tr>
<td>effective porosity</td>
<td>Total porosity less the bound water saturation.</td>
</tr>
</tbody>
</table>
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:
- \(\phi_e\)  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
- \(\phi\)  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
- \(\rho_b\)  bulk density, g/cm\(^3\)
- \(\rho_{bc}\)  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.

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

where:
- \(\rho_{ma}\)  inorganic grain density, g/cm\(^3\)
- \(\rho'_{ma}\)  apparent grain density, g/cm\(^3\)
- \(w_{toc}\)  total organic carbon, weight fraction
- \(\rho_{loc}\)  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 rock's 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 polynantanes. 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 autosampler, 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., \( \text{CO}_2, \text{H}_2\text{O}, \text{N}_2 \). 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:

<table>
<thead>
<tr>
<th>Theoretical Range (%)</th>
<th>Sample Size (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1-2</td>
<td>10-20</td>
</tr>
<tr>
<td>2-5</td>
<td>5-10</td>
</tr>
<tr>
<td>5-10</td>
<td>3-8</td>
</tr>
<tr>
<td>10-15</td>
<td>3-5</td>
</tr>
<tr>
<td>&gt;15</td>
<td>1-2</td>
</tr>
</tbody>
</table>

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

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 an 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 sulfur 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.
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.

<table>
<thead>
<tr>
<th>Theoretical Range (ppm)</th>
<th>Sample Size (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 – 10.0</td>
<td>25 – 100</td>
</tr>
<tr>
<td>10.0 – 100.0</td>
<td>10 – 25</td>
</tr>
<tr>
<td>&gt; 100.0</td>
<td>3 – 10</td>
</tr>
</tbody>
</table>

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 \( \varepsilon_L = \Delta L/L_0 \) (where \( L_0 \) is the initial length and \( \Delta L \) is the length change) and radial strain \( \varepsilon_R = \Delta D/D_0 \) (where \( D_0 \) is the initial diameter and \( \Delta D \) is the diameter change). Differential stress \( \sigma_d \) is defined as the difference between the total axial stress \( \sigma_1 \) 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 ($\sigma_d$) 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 ($\nu_s$) 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 ($\rho_b$) of the specimen. Dynamic Young’s modulus ($E_d$) is expressed as

$$E_d = \left(\frac{\rho_b V_s^2 (3V_p^2 - 4V_s^2)}{(V_p^2 - V_s^2)}\right).$$

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

$$\nu_d = 0.5 \left[\left(\frac{V_p}{V_s}\right)^2 - 2\right]/\left[\left(\frac{V_p}{V_s}\right)^2 - 1\right].$$

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 ($\tau_c$) 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), $\sigma_n$ is the normal stress across the incipient fracture plane, $\tan\phi$ is the coefficient of internal friction and $\phi$ 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 1,170 psi.
DENSITY SEPARATION BY KEROGEN FLOTATION USING ZNBR\textsubscript{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 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\textsubscript{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\textsubscript{2} solution and the procedure used for the sink/float separation are described below.

**Preparation of ZnBr\textsubscript{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\textsubscript{2} and stir. Pour this into the large beaker. Use the remaining water to rinse the remaining ZnBr\textsubscript{2} 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. \[ D = \frac{(CB-AB)}{(1-C)} \]
   \[ A = \text{Density that you have} \]
   \[ B = \text{Volume that you have} \]
   \[ C = \text{Density that is needed} \]
   \[ D = \text{Volume of water to add} \]
4. Mix water with ZnBr\textsubscript{2} 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 ZnBr₂ 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 ZnBr₂ 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.
**X-Ray Diffraction (XRD) Analysis Procedures – Includes Micronizing Milling and Spray Drying Techniques**

**Sample Preparation**

A representative portion (6 grams minimum, preferably 10 grams) of each sample is selected for XRD analysis. Samples are disaggregated using mortar and pestle and portioned out for bulk and clay analyses.

**Bulk/Whole Rock Analysis**

The bulk portion is ground into a slurry using a McCrone Micronizing Mill. The slurry is transferred to an air brush assembly and spray dried using a James Hutton Institute Spray Drying Oven. Randomly oriented spherical aggregates are then loaded into stainless steel sample holders. This method eliminates preferred orientation of minerals and allows for improved reproducibility of the bulk XRD patterns (Bish and Reynolds 1989, Hillier 2002).

These bulk sample mounts are scanned with a Bruker AXS D4 Endeavor X-ray diffractometer using copper K-alpha radiation. To eliminate K-beta peaks and reduce background noise, nickel filter slits and air scatter screens are utilized, respectively. The scanning parameters for a bulk scan are from 5° 2θ to 70° 2θ. The step size is 0.020°, and the dwell time at each step is 0.5 seconds. Full scanning parameters are defined below (for both bulk and clay):

- Operating voltage: 50Kv
- Operating amperage: 40mA
- Axial soller slit is in place
- Goniometer diameter: 400mm
- Lynx Eye High speed detector with a 2θ scanning range of 4°
- A nickel filter for K beta peaks
- An air scatter screen to reduce fluorescence
- Variable divergent slit at 0.3mm for bulk and 0.5mm for clay

**Bulk Mineral Quantification**

MDI Jade™ 9+ software and ICDD PDF 4+ 2013 database, with over 790,000 known compounds, are used to identify mineral phases present in the bulk diffractograms. Reference Intensity Ratio (RIR) method is used to quantify the whole rock. The RIRs (eg Mineral Intensity Factors (MIF)) are generated for each diffractometer using pure mineral standards mixed with quartz in a 50:50 weight percent ratio. When pure mineral standards are not available, Jade™ intensity ratios are applied. The primary peaks of the minerals present are measured using the area under the curve to one standard deviation (subtracting the background).

X-ray diffraction cannot identify non-crystalline (amorphous) material, such as organic material and volcanic glass. However, samples containing amorphous material show an anomalous “hump” in the XRD pattern. If further evaluations are required, Bruker AXS TOPAS v4.2 software is used to provide an
estimate of the amount of amorphous material. Scans undergo full-pattern-fitting and Rietveld refinement using structure phase files previously identified by Jade and ICDD software (see above).

**Clay Sample Preparation**

An oriented clay fraction mount is prepared for each sample from hand ground powder. The samples are treated with a small amount of sodium hexa-meta-phosphate as a deflocculant mixed with distilled water. The samples are then physically dispersed using a Fisher Scientific Ultra Sonifier to bring the clays into suspension. The samples are sized fractionated by centrifuging. After centrifuging, the supernatant containing the less than 2 micron clay fraction is vacuumed through a filter membrane glass tube that collects the solids on to a millipore filter.

These oriented solids are mounted on glass slides, loaded into desiccant bowls containing 99.9% ethylene glycol for an extended period of time at a temperature of 110°C. The samples are loaded directly from the desiccant bowl to ensure maximum sample glycolation. The glycolated clays are also scanned in a Bruker AXS diffractometer using the following scan parameters: 2° 2θ to 30° 2θ at a step size of 0.025° per step and a dwell time of 0.26 seconds at each step.

After the glycolated slide is scanned, the slides are heat-treated in a furnace at 375°C for one hour and rescanned at the same clay parameters stated above. This process aids in identifying the expandable, water-sensitive minerals.

When samples contain high levels of carbonates combined with low clay quantities, we may need to return to the sample and remove the carbonates to obtain a better clay scan for accurate identification and quantification.

**Clay Mineral Identification and Quantification**

Mixed-layer clays, particularly illite/smectite (I/S) are identified following the multiple peak method of Moore and Reynolds (1997). This entails measuring the 001/002 and 002/003 peaks of the illite/smectite. NEWMOD clay mineral generation program is used to create theoretical clay patterns, clay mixtures, and illite crystallinity. Identification of the amount of smectite (percent expandability) is also verified using the heat treated diffractogram overlain on the glycolated diffractogram in MDI Jade.

Kaolinite and chlorite are identified by the relative proportions of the peaks at 3.59 Å (kaolinite 002) and 3.54 Å (chlorite 004).

Clay mineral quantification includes: (1) the actual amount of discrete clay mineral species in the sample, and (2) the “expandability” or amount of smectite in mixed-layer clays, if present. Illite/Smectite (I/S) is the most common mixed-layer clay, but there are also chloride/smectite (corrensite) and kaolinite/smectite. There are several tables in Moore and Reynolds (1997) that list 2θ positions and their correlative percent smectite in I/S (Table 8.3, p.273) or C/S (Table 8.4, p.281).

The Mineral Intensity Factor (MIF) method of Moore and Reynolds (1997) is applied to quantify the clay species. Weatherford has calculated MIFs for most clay minerals encountered. The area of the specific mineral peak being used is divided by the MIF in the quantification process. The clay species is normalized to the total clay value derived from the bulk analysis.
References

