Direct Quadrupole Mass Spectrometry Advanced Borehole Gas and Cuttings Volatile Analysis for Oil and Gas Wells

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Introduction

New quantitative methods of borehole gas detection and analysis have begun to change the way oil and gas operators are analyzing their mud gas data. Traditionally, gas chromatographs have been used to determine where gas shows exist within the borehole. These chromatographs generally were able to detect

hydrocarbons up to C5, and ratios such as Wetness, Balance, and Character could be used to analyze the gas properties. With the Fluid Inclusion Technologies (FIT) Direct Quadrupole Mass Spectrometer (DQ1000TM) (www.fittulsa.com), a much more complete picture of the petroleum system and reservoir can be obtained, due to the chemical breadth of species that are analyzed.

The DQ1000TM Mass Spectrometer was developed and patented by FIT, a spinoff of Amoco Production Research. It has been run on hundreds of wells worldwide, but particularly within unconventional reservoirs in the U.S. The ultimate goal is to enable clients to use this technology to drill,

test and produce wells more effectively (Hall, et al., 2010; Hall and Sterner, 2012; Ramaswami et al., 2012).

The DQ1000TM is a ruggedized portable instrument designed for on-site, 24/7, real-time formation fluid analysis and evaluation. Conditioned gas (particulates and excess moisture removed) is continuously presented to the instrument through a standard gas line, and is sampled via a short capillary bleed without boiling point separation (in contrast to GC or GCMS). This allows rapid analysis of high molecular weight species (complete analysis of C1-C10 and inorganic compounds

in 90 seconds), and baseline sensitivity for C4+ species

on the order of 0.1 ppm, and can help pinpoint zones of interest even in very low pressure reservoirs. Even nominally liquid-range petroleum species with finite (but measurable) vapor pressure can be analyzed (Fig. 1). The instrument is capable of discriminating among major classes of organic compounds (e.g.,

A Beaker of Oil at Room T; Selected Species are Labeled 1000000 COS+ C3 CO2 O-Acid 100000 Benzene 10000 Toluene C5 C9 Aro 1000 **Xylenes** C10 Aro 100 10 0.1 91 101 111

DQMS Vapor Analysis of Atmosphere Collected Over

Figure 1. Selected species analyzed with DQMS.

paraffins, naphthenes, aromatics) as well as inorganic species such as CO₂, He, N₂, O₂, H₂, Ar, organic acid, sulfur species, and mud additives. Interpretation of DQMS data, although potentially complex, benefits from the large body of information available from fluid inclusions trapped in rock material, and the analysis of these fluids with analogous instrumentation by FIT over the last 23 years (Hall et al., 1997).

Companies such as Field Geo Services, Inc. (www. fieldgeoservices.com) are operating this system on location and providing in-depth analysis on applications

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such as compartmentalization, water saturation, depletion, fractures and faults, type and quantity of hydrocarbon zones, porosity and permeability, drill bit wear and more. Some of these applications are illustrated in Figures 2-5. Field Geo Services, Inc. will plot the data on a 30" widestrip-log and provide an LAS file with over 100 chemical species and ratios as well as provide full analysis and cross-plots of zones of interest.

Figure 2 records an oil-water contact below a bypassed oil zone. Absolute benzene concentration follows the hydrocarbon phase, but the ratio of benzene to toluene increases in the water leg due to the relative increase in benzene solubility in water as compared to toluene. Similar logic can be used to identify hydrocarbon zones with high producible water content, and water bearing zones that contain an updip hydrocarbon column.

Figure 3 illustrates compartmentalization within several shows in a wellbore. A cross plot of methane to ethane illustrates that shows 1-3 are not in chemical equilibrium, and are variable in terms of wetness (steeper sloped shows indicate drier gas). Show 1b is a slightly

depleted version of shows 1a and 1c, which otherwise have similar C1-C2 ratios. Defining compartmentalization in unconventional reservoirs can be useful for completion operations.

Figure 4 shows a through-going high angle fault in a horizontal shale borehole. In this case, helium (ultimately derived from radioactive decay of uranium, thorium and potassium) is preferentially transported from a deeper horizon into the shale. The damage zone around the fault is identified as a general increase in helium around the main fault, but in this case, the more prominent break is associated with the highest helium concentration. Note that the ratio of helium to total gas is much higher than outside the fault zone, reinforcing the interpretation that an exotic fluid is being introduced from outside the main formation.

Another complementary lab-based service available from FIT is called fluid inclusion volatile analysis or Fluid Inclusion Stratigraphy (FISTM). FISTM is a rapid, automated process conducted on unpreserved cuttings, core or outcrop samples of any age. Approximately 1 gm of material is crushed in a vacuum system and

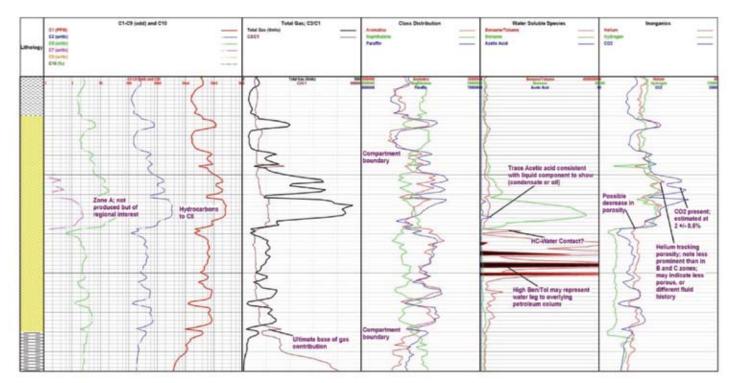


Figure 2. Oil-water contact within a bypassed oil zone. The transition from oil to water is indicated by an increase in the ratio of benzene to toluene in this case (red curve, second track from right).

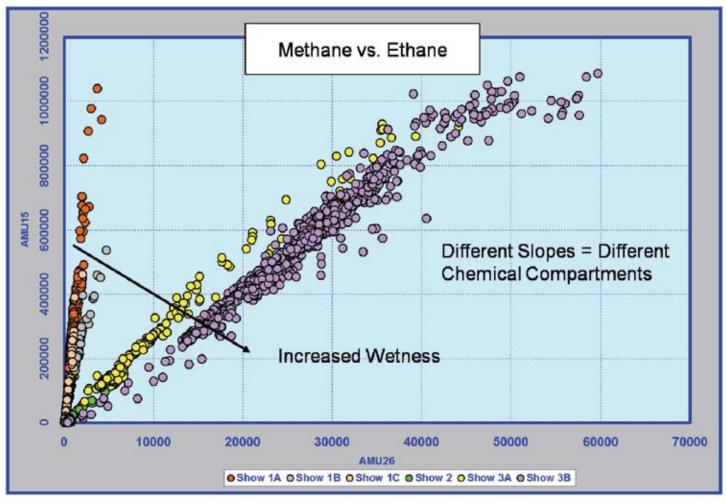


Figure 3. Compartmentalization indicated on a cross plot of C1 vs. C2.

the evolved gas and liquid range species (C1-C13 hydrocarbons and various inorganic compounds) are analyzed via direct quadrupole mass spectrometry. Fluid inclusions are encapsulated pore fluids, generally included in the rock by diagenetic processes or fracture healing events (**Fig. 5**). In organic rich shales, conversion of kerogen to oil and gas creates nanoporosity within converted kerogen structures and provides significant storage capacity for fluids within these lithologies. These nanopore fluids contribute significantly to FIS responses in source rocks.

Depth profiles of the entire wellbore are constructed by automated FIS analysis of hundreds of samples per well and are used to map migration pathways, charge, paleocharge, proximity to pay, seals, compartmentalization and fluid type and quality. An example is shown in **Figure 6**. Here, a flanking dry hole had no conventional

drilling shows. Archived cuttings analysis indicates that a shallow microseep is present, that light undersaturated oil migrated through the reservoir section, and that the hydrocarbon is still reservoired within approximately 5 miles (8 km). Cumulatively, the data lower the risk associated with drilling updip.

Thus, while the DQ1000TM characterizes open pore fluids, FISTM can help identify paleo-charge that may have been lost to system or redistributed to other portions of the basin. FIS is also useful in wells where drilling conditions (e.g., overbalance) have resulted in limited formation gas being liberated to the mud system. In unconventional reservoirs FIS data can be used to help predict fluid type, composition and volume within tight rock, as well as identify variability along laterals that can be exploited for more effective completions.

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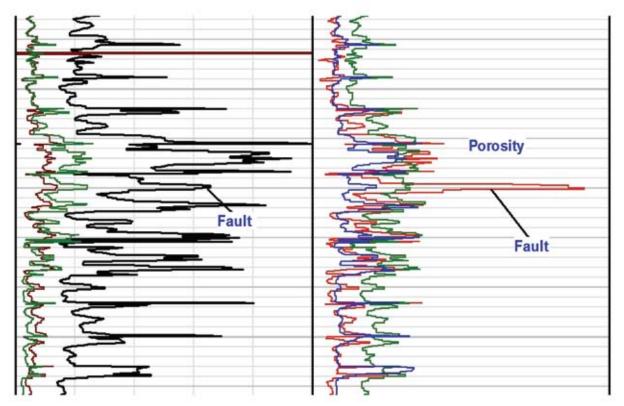


Figure 4. Through-going fault in horizontal shale well. Distinct fluid composition associated with fault suggests it transects deeper units, allowing exotic species to invade the faulted formation. Lack of offset in chemistry across the fault may indicate a small amount of throw, or strike-parallel displacement. Total gas in black; helium in red, CO₂ in Blue, hydrogen in green (right track).

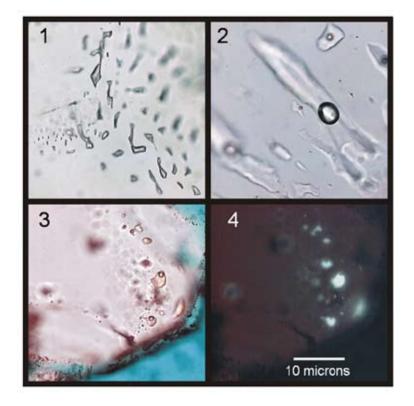


Figure 5. Fluid inclusions in sandstone. 1: Gas; 2: Brine; 3: Oil in white light; 4: Oil under UV light.

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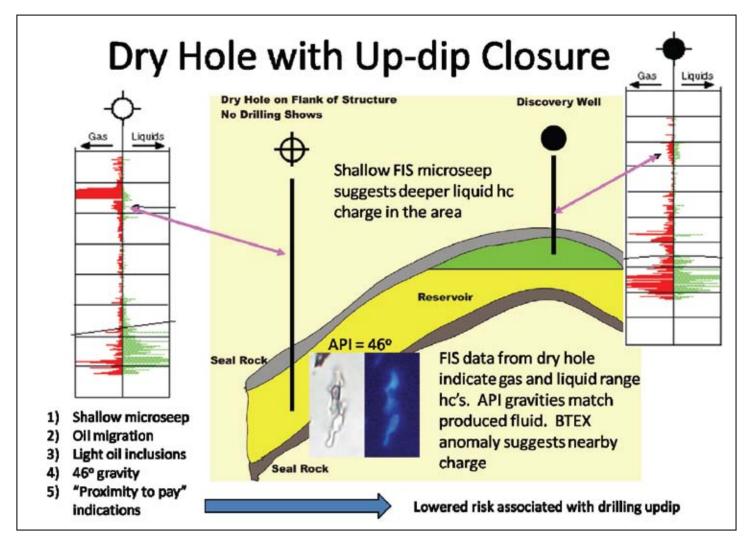


Figure 6. Fluid inclusion volatile analysis from cuttings from a dry hole and discovery well. No drilling shows were recorded in the dry well, but cuttings indicate the presence of active microseepage from crestal charge, light oil migration through the flanking well and water-soluble organic species indicative of nearby reservoired hydrocarbons.

For more information or for interest in using these systems and processes, please contact Field Geo Services, Inc. at 970-270-4940 or visit their webpage at www.fieldgeoservices.com or Fluid Inclusion Technologies' webpage at www.fittulsa.com.

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