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Analysis of Borehole Gas with Direct Quadrupole Mass Spectrometry

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Introduction: Direct quadrupole mass spectrometry (DQMS) applied to analysis of borehole gas while drilling provides useful insight into petroleum systems, and can be used for reservoir characterization and modeling. The technique has been applied to a number of wells worldwide over the last few years, but predominantly within unconventional reservoirs in the U.S. Theory, practice, application and examples will be discussed.

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 inorganics in 90 seconds), and baseline sensitivity for C₄₊ species on the order of 0.1 ppm. Even nominally liquid-range petroleum species with finite (but measurable) vapor pressures can be analyzed at normal mud temperatures (Fig. 1). The resulting fragmentation patterns are complex for multicomponent mixtures and unavoidable overlap occurs among species with the same mass-to-charge ratio (e.g., CO₂ and propane molecular peaks at m/z 44). Species overlap issues are generally adequately addressed by considering relatively "clean" ions for a given compound (e.g., m/z 22 for CO₂; m/z 26 for propane), and by concentrating on families of species (e.g. paraffins, naphthenes, aromatics) rather than specific compounds. Approximate "GC equivalent" C₁-C₅ compositions can be calculated for use in standard gas ratio analysis and historical interpretive diagrams, with some restrictions. Interpretation of DQMS data benefits from the large body of information available from fluid inclusions trapped in rock material, and the analysis of these fluids with analogous instrumentation. Five potential application areas are discussed.

Petroleum Type and Quality: Applications include distinction between oil and gas, wetness (i.e., via light/heavy hydrocarbon ratios), fingerprinting multiple oils or gases in stacked pay reservoirs, and identifying and quantifying undesirable gases (e.g., sulfur species, CO₂). This is possible to a much greater extent with DQMS than with conventional mud-gas logging methods due to the range, accuracy, and sensitivity of chemical species analyzed.

Fluid Contacts: DQMS has been used to identify oil-water, gas-water and gas-oil contacts using variations in hydrocarbon wetness, inorganic species (e.g., hydrogen and helium) and water soluble species, such as benzene and toluene. Concomitant increases in selected species, and decreases in others (in response to solubility, for instance) are particularly useful and geosteering applications are apparent. An example is shown in Figure 2, a DQMS log containing a show in a zone of regional interest, but with no historical production. The OWC is clearly

shown on the second track from the right. Here, absolute benzene is green, and the benzene/toluene ratio is red. Absolute benzene is high in the show - the ultimate source of all the organic species. The transition to the water leg is marked by a decrease in absolute benzene, but an increase in the ratio of benzene to toluene, due to higher relative benzene solubility. Thin sections of cuttings material collected at well site were prepared from the anomalous interval, and document high abundance of moderate gravity oil inclusions. Thus, the feature is interpreted to represent a bypassed (unrecognized by conventional technology and/or untested) oil column with a definable OWC. CO₂ content of the petroleum phase was estimated at about 2%.

Water Saturation and “Proximity to Pay”: The selective concentration of certain hydrocarbon and non-hydrocarbon species in water is well established, and this concept has been used for many years to assess proximity to charge, and transitions from petroleum columns to water bearing intervals. As an example, the relative (not necessarily absolute) concentration of benzene will typically increase with respect to the less water soluble toluene, and much less soluble n-hexane as the water cut within a formation increases (as noted in the previous example). This water-soluble halo typically extends several miles away from the petroleum-water contact, providing a method of detecting nearby accumulations from water bearing reservoirs. If producible water is localized, and can be isolated or avoided in tight or fractured formations, water treatment and disposal issues may be less severe.

Porosity/Permeability and Fracture Detection: Porous intervals in tight rock often show higher light organic and/or inorganic species concentrations (including helium) with respect to heavier components (Fig. 3). Part of this phenomenon arises due to differential mobility of species as a function of molecular size. Faults or fractures have variable chemical character on DQMS data, depending on whether they are open, and whether they are localized within the penetrated formation or are through-going to shallower or deeper formations. Sealed fractures may manifest themselves as offsets in chemistry without a specific anomaly at the healed fracture itself. Formation constrained open fractures tend to occur as thin irregular anomalies that are not related to drilling operations, and may or may not show distinctive chemistry as compared to conventional porosity in the same unit (Fig. 3). Through-going open fractures may access other gas chemistries, and can imbibe exotic species into the specific formation they transect. If not vertically sealed in horizontal wells, these fractures can represent leak points that may cause production problems, including water production. Often these so-called depleted fracture or porosity zones (Fig. 3) resemble residual hydrocarbon occurrences in that they display lower absolute and/or relative concentrations of light organic and inorganic species (C₁, C₂, He), and may have higher implied water saturation (e.g., via Ben/Tol, Ben/nC₆).

Compartmentalization: One key potential application in horizontal wells involves using the detailed chemistry available with DQMS to define vertical and lateral compartmentalization. Changes in fluid chemistry often correlate with differences in rock characteristics that may affect completions. Constraining stages wholly within sections of rock that have similar fluid chemistry, rock chemistry and rock properties (particularly conventional or fracture porosity) generally results in more efficient distribution of induced fractures; thus more effective use of stimulation materials. If higher water saturation, CO₂ or unwanted heavier hydrocarbons are shown to be localized, those zones can be avoided. An example is illustrated from a strongly compartmentalized horizontal shale well (Fig. 3). Sulfur species, higher Sw zones, possible

depleted (vented) intervals, and fractures are illustrated. Monitoring these species in real time with an accurate wellbore path can distinguish between horizontal and vertical compartmentalization and has potential for geosteering. Often, an undulating wellbore will cross successive vertical compartments multiple times, producing a repeating chemical pattern on cross plots of appropriate species.

DQMS Vapor Analysis of Atmosphere Collected Over A Beaker of Oil at Room T; Selected Species are Labeled

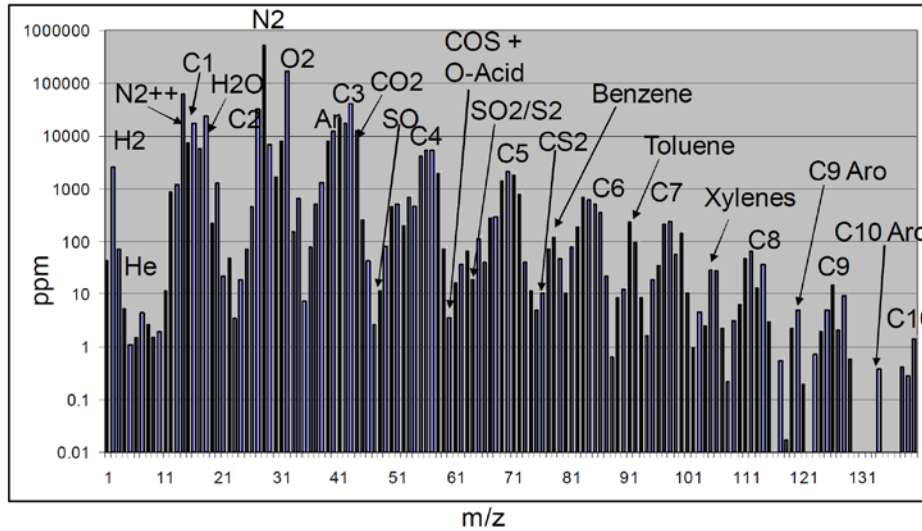


Figure 1. Selected species analyzed with DQMS.

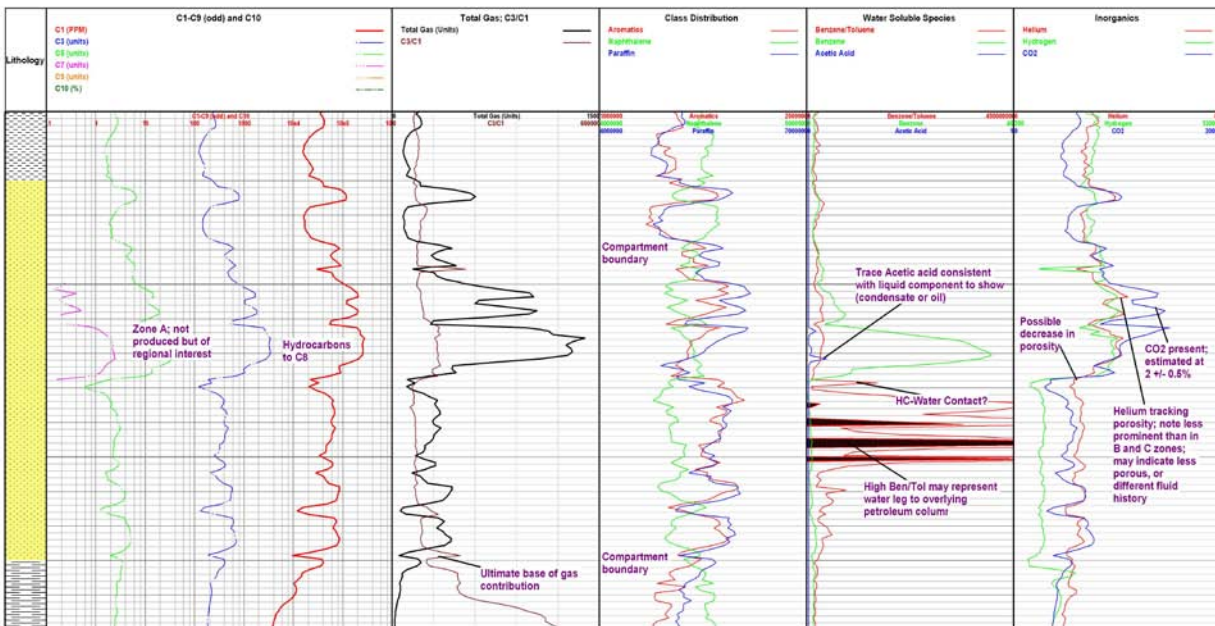


Figure 2. Probable oil-water contact in a bypassed oil zone.

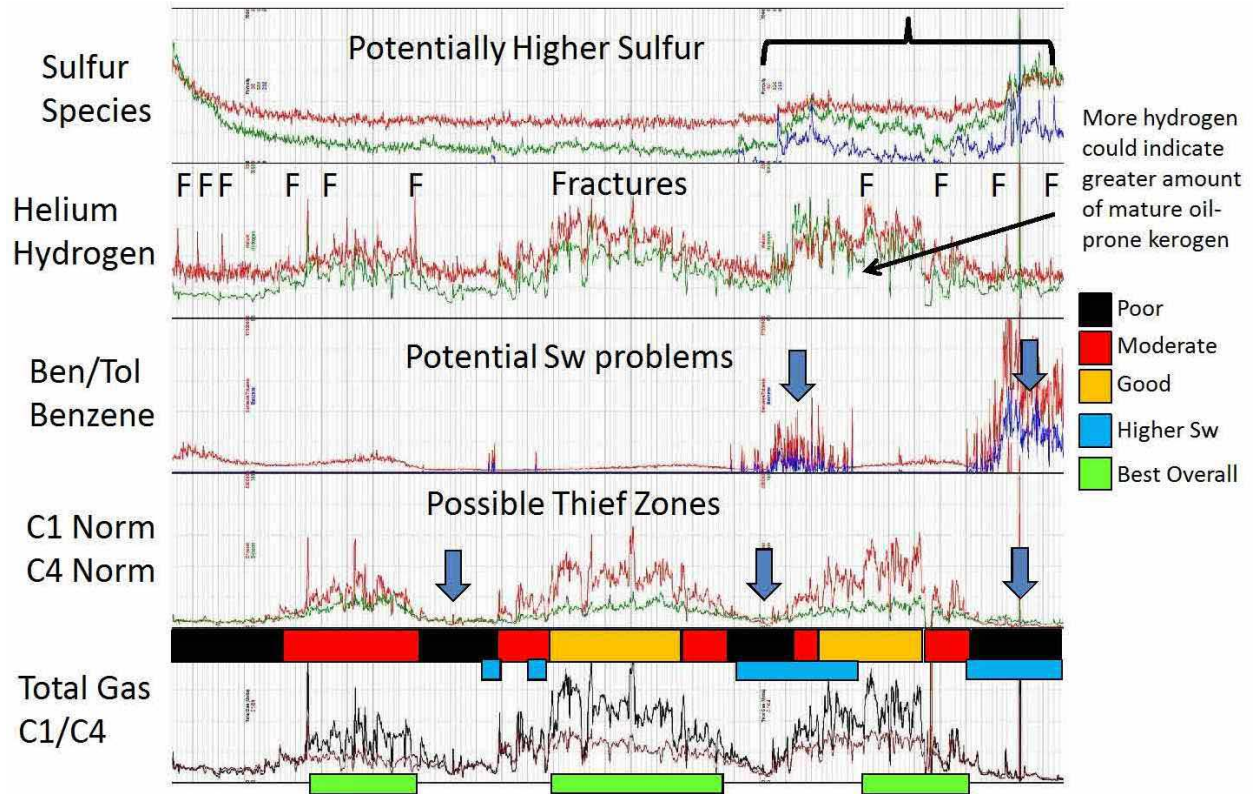


Figure 3. Horizontal well in strongly compartmentalized shale.