Upstream Exploration and Production
with the Thermo Scientific Niton XL3t 900 GOLDD Series XRF Analyzer
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Introduction
The handheld Thermo Scientific Niton x-ray fluorescence (XRF) analyzer proves its value in upstream exploration and production (E&P) by providing rapid, onsite bulk chemical analysis of rocks that can be used for identifying formations, identifying the bulk mineral composition of the rock, and inferring rock properties favorable to oil & gas production from the data in a real-time environment – whether at the rig site or remotely via a data connection. Benefits of using the analyzer in the lab also accrue in that the data, still used to log and infer rock properties and mineralogy, has the added value of reducing laboratory costs as well as the ability to create detailed cm scale logs during the core description process.

Application
With a Thermo Scientific Niton XRF analyzer, users can analyze a variety of sample types common in the upstream E&P industry, including drill cuttings, cores, surface outcrops, and piston-cored sediments that are used in the exploration for hydrocarbons. Because the inorganic chemistry and, ultimately, the mineral composition of the rocks, give geologists important information about how the hydrocarbon is hosted within the rock and how it will be produced, the elemental analysis of those rocks is critical. Unlike metals mining, we cannot analyze hydrocarbon fluids by XRF. However, we can analyze bulk elemental chemistry of a reservoir that reflects properties that influence porosity (cement types), permeability (clays, cement type), fracturability (Si content), and productivity (Si, Mg, and trace metal content).

Recent internal studies show that the analyzer has the ability to log dolomite content of gas shales from drill cuttings, map the distribution of clays and cements in fault systems and show subtle, but important variations of trace metals in gas shale and piston cores, indicating the usefulness of handheld XRF in upstream E&P applications on a scale from cm to km.

Uses of Elemental Chemistry by XRF in Upstream E&P
Specifically, the elemental chemistry provided with XRF analysis assists upstream E&P in a variety of ways:

- Light elements and Fe are major rock-forming elements (Si, Al, Ca, K, Na, Mg, Fe)
- Bulk chemistry gives sample mineralogy: silicates, aluminosilicates, carbonates, sulfides (e.g., lower Si/Al indicates greater aluminosilicate content of rock).
- Element ratios can point the way to quantitative mineralogy: Si/Al, Ca/K, Fe/S, Si/Ca (e.g., Si/Al ratios between 5 and 22 indicate mixtures of clays, quartz, and feldspar)
- Geochemical information adds value to petrophysical logs (e.g., gamma “hot sands,” etc.) that are run on every well drilled
- Bulk chemistry combined with mineral phase (structure) identification (FTIR, XRD, petrography, etc.) provides quantitative mineralogy
- Mineralogy determines hydrocarbon potential, reservoir quality, casing points, fracture potential
- Ca/Mg ratios can provide a quantitative determination of the dolomite content of the carbonate rock
Method
Comparison of the Thermo Scientific Niton ® XL3 Series 900 SDD hand held XRF analyzer with independent laboratory results obtained by ICP-MS on 160 sedimentary rock samples and standards show typical correlations (R^2) > 0.90 and repeatability < 5 % relative standard deviation (RSD) for most major, minor and trace elements from Mg to U. Optimal results were obtained on pressed powder pellets with the use of a He purge system. Counting times were 30 seconds each on the low, main and high energy filters (for analyzing elements Ti to U), and 60 seconds on the light filter setting (Mg to S) for a total analysis time of 150 seconds. Studies of solid cores and cuttings provide results within 5 to 20 % of this data quality.

Gas Shale Case Studies
Shale gas is driving the growth in North American and European natural gas production and is being explored worldwide. Shale, or tight gas, is gas found in very low permeability rock that requires hydro fracturing (must have high Si). Recent studies have linked the abundance of redox sensitive trace metals (V, Cr, U, Th, Mo, Re) to strata with increased organic paleo-productivity indicators and gas potential in shales\textsuperscript{1,2}. Accurate stratigraphic correlations in these monotonous sequences of shale can be enhanced by chemostratigraphic techniques employing major, minor and trace element abundances and ratios. Handheld XRF provides a tool to rapidly log the inorganic geochemistry of cuttings and cores in minutes at the cm scale. The Niton® XL3 Series 900 with geometrically optimized large area drift detector (GOLDD\textsuperscript{TM}) technology is ideal for light element and trace metal analysis required for gas shale applications.

Eagle Ford Case Study
The Eagle Ford Formation is a sequence of shale, siltstone, and limestone that is an important source rock and shale gas play in Texas. Within the shale, there are very few visual indicators of stratigraphic position and an important contact between the Turonian/Cenomanian age rocks separates low from high total organic carbon (TOC) content sequences. TOC controls how much gas can be generated within the shale. Redox sensitive trace elements, elements with multiple oxidation states such as U, Mo, Cr, V, Ni, and Re, can pinpoint this boundary and can be related to the paleo-productivity of the rock.

The Mn, V, Cr and Mo data presented in Figure 1 show a marked decrease in Mn and increase in V+Cr and Mo below the stage boundary, correlating with increased TOC content of the cuttings. The sharp contrast in trace metals above and below the Turonian/Cenomanian boundary allows us to pinpoint the contact within feet. This case study clearly demonstrates that the Niton XL3 Series 900 GOLDD can be used to accurately define stratigraphic intervals by chemical proxies. Bulk chemistry can be used to determine productive regions in gas shales – which will be a major tool used in onsite well logging and as an aid to routine core analysis.
Figure 1. Gamma, total organic carbon (TOC), and elemental logs plotted as a function of depth in feet (6900' to 7300' total depth). Gamma intensity increases to the right; high values indicate the presence of radioactive elements trapped in shale. Note the minor changes in the gamma log throughout the depth interval. TOC and gamma data are from a previous Shell study. Mn, V, Cr, and Mo were analyzed with a 900 SDD on sand-sized drill cuttings in 20’ composites. Samples were analyzed in mining mode (30 sec/filter, 60 sec/light filter) and soil mode (30 sec/filter). Data presented here is from soil mode data set. Note the marked decrease in Mn and increase in V+Cr and Mo below the boundary. This suggests anoxic conditions that preserved more organic material, which is consistent with the higher TOC values below the boundary.

Montney Shale Case Study
The Montney Formation is a Triassic sequence of very-fine-grained sandstone and siltstone in northeast British Columbia and western Alberta. Gas is hosted in the lower permeability (tight), finer-grained members of the formation (see Figure 2).

Figure 2. Gray fine-grained sandstone and siltstone of the Montney Formation. Note the lack of distinguishing features.
The formation is composed of quartz with variable amounts of clays and calcite cement; pyrite also can be present. Knowing the mineralogy of the various intervals encountered while drilling gives insight into the total porosity of the formation (see Figure 3). High Si/Al ratios tend to indicate lower total microporosity in shale gas reservoirs\(^3\). From the total porosity, investigators can calculate an accurate estimate of the gas content of the shale.

![Figure 3. Major element plots help define relative mineralogy in the Montney using handheld XRF analysis.](image)

On the left: elemental abundance plot of Fe vs. S shows that the host mineral for the S is pyrite \((\text{FeS}_2)\) rather than gypsum \((\text{CaSO}_4\cdot\text{H}_2\text{O})\). On the right: elemental ratios of Si/Al is a basic indicator of the abundance of quartz \((\text{SiO}_2)\) vs. aluminosilicates, such as clays and feldspars. The combination of Si/Al and Ca/K ratios can show the relative amount of clay, quartz, and feldspar in the formation; for example, high Ca/K indicates the presence of calcite cement and high Si/Al shows increased quartz in the sandstone.

Elemental ratios offer an advantage over elemental abundances because the accuracy of the analyses is not a factor when comparing data acquired under the same conditions (matrix type and sample prep). Relative shifts in elemental ratios can be used to quickly note increasing calcite, quartz, and clays in a formation for further follow up. Gas shales produce best in fracture prone intervals that are quartz and calcite-rich. By identifying these intervals in the field, the geologist is better able to plan for the well’s completion program. Rapid elemental analysis by handheld XRF and elemental ratio plots is a valuable tool in well logging and exploration.

**Conclusion**

Elemental analysis using the handheld Thermo Scientific Niton XRF analyzer imparts important information to the explorationist. Elemental chemistry gives clues to the rock properties that could affect oil & gas accumulation like porosity (Si and Ca content), permeability (Si/Al, Mg, Ca and K as proxies for clays and dolomite), and the presence of undesirable minerals (clays, pyrite, and carbonate cement from Si/Al, Fe/S, and Mg/Ca ratios). This information can be included in the well logs, adding valuable information to aid in the interpretation of petrophysical data and offering greater value to the exploration program.

To discuss your particular applications and performance requirements, or to schedule an on-site demonstration and see for yourself how Thermo Scientific Niton XRF analyzers can help save you time and money, please contact your local Thermo Scientific Niton Analyzer representative or contact us directly by email at niton@thermofisher.com, or visit our website at www.thermo.com/niton.
References:
