

Upstream Exploration & Production (E&P) with the Thermo Scientific Niton FXL with z-CAL

Introduction

The worldwide exploration of shale gas is driving North American and European natural gas production. Shale gas, or tight gas, is a gas found in very low permeability rock that requires hydro fracturing. Recent studies have linked the abundance of redox sensitive trace metals – vanadium (V), chromium (Cr), uranium (U), thorium (Th), molybdenum (Mo), and rhenium (Re) – to strata that are enriched in organic material. This abundance serves as an indicator of gas potential in shale. Accurate stratigraphic correlations in these monotonous sequences of shale can be enhanced by chemostratigraphic techniques, employing the major, minor, and trace element abundances and ratios. X-ray fluorescence (XRF) is a technology that can be used to rapidly log the inorganic geochemistry of cuttings and cores in minutes.

Application

Thermo Scientific™ portable XRF analyzers prove their value in upstream exploration and production (E&P) by providing rapid, on-site, bulk chemical analysis of rocks that can be used for identifying formations, as well as identifying the bulk chemical composition of the rock. The geochemical characteristics of the rocks can be used (whether at the rig site or remotely via a data connection) to infer rock properties that are favorable to oil & gas. There also are benefits in using portable XRF in the lab because the analyzer results have the ability to create detailed cm scale logs during the core logging process. This has the value of reducing laboratory costs.

These portable XRF analyzers provide users with the ability to 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 of 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 metal mining, portable XRF cannot analyze hydrocarbon fluids. However, portable XRF 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, magnesium (Mg)), and trace metal content.

Recent internal studies show that the analyzer has the ability to log dolomite content of gas shale 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. This indicates the usefulness of portable XRF in upstream E&P applications on a scale from cm to kilometers (km).

Uses of Elemental Chemistry by XRF in Upstream E&P

The elemental chemistry provided by XRF analysis assists upstream E&P in a variety of ways:

- Identification of major elements – as well as light elements: (Si), aluminum (Al), calcium (Ca), potassium (K), magnesium (Mg), and iron (Fe).
- Bulk chemistry gives sample mineralogy: silicates, aluminosilicates, carbonates, sulfides, (i.e., lower Si/Al indicates greater aluminosilicate content of rock).

- Element ratios such as Si/Al, Ca/K, Fe/S, Si/Ca can be used for semi-quantitative mineralogy: For example, Si/Al ratios between 5 and 22 indicate mixtures of clays, quartz, and feldspar. Ca/Mg ratios can provide a quantitative determination of the dolomite content of the carbonate rock. Furthermore, bulk chemistry combined with mineral phase identification by other techniques (e.g., fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), petrography, etc.) can provide quantitative mineralogy.
- Geochemical information adds value to petrophysical logs (i.e., gamma “hot sands,” etc.).
- Mineralogy determines hydrocarbon potential, reservoir quality, casing points, and fracture potential.

Method

Thermo Scientific™ Niton™ Field X-ray Lab (FXL) equipped with the new Thermo Scientific z-CAL, a

fit-for-purpose calibration and operation methodology for light elemental analysis is ideal for the light element and trace metal analysis required for gas shale applications.

The certified samples were loaded into standard 32 mm sample cups and fitted with a 4 micron polypropylene support film. A total measurement time of 240 seconds was used. Analytical results can often be improved by using longer measurement time or by preparing sample pellets which don't require support film.



Niton FXL with z-CAL is a break-through technology for oil and gas E&P.

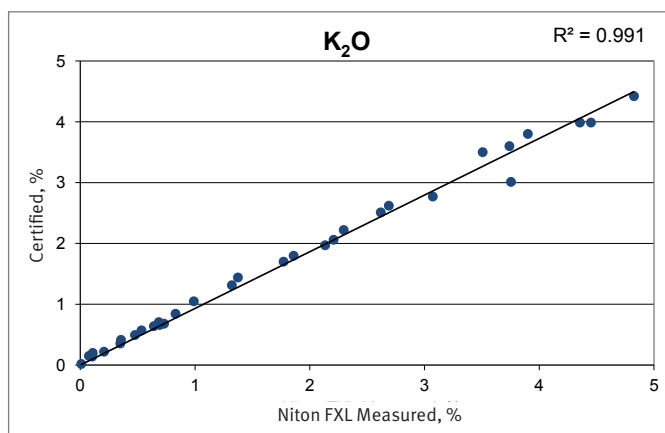
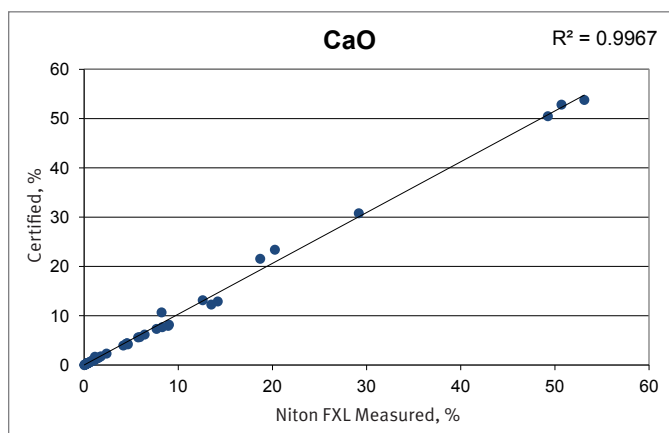
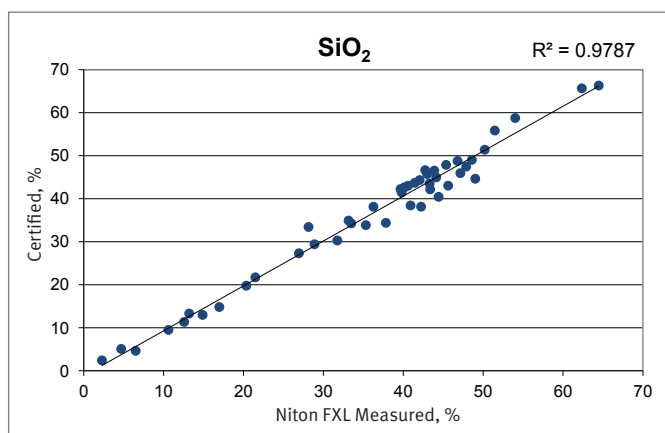
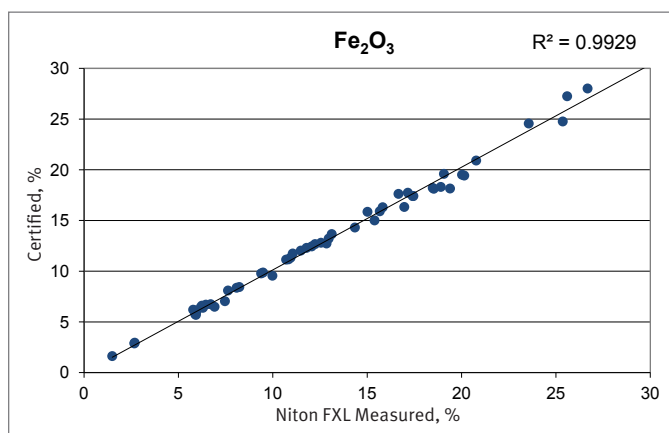
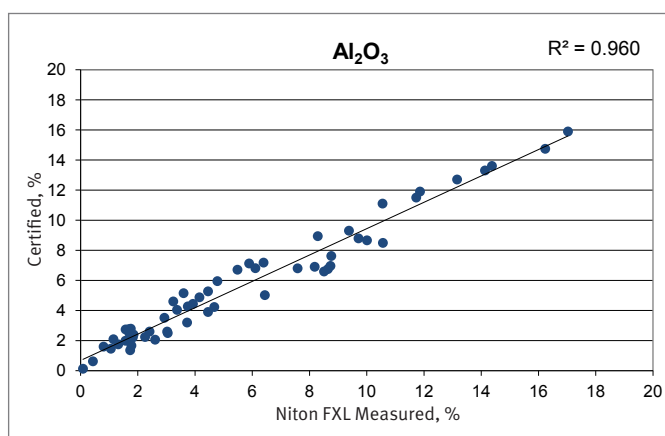
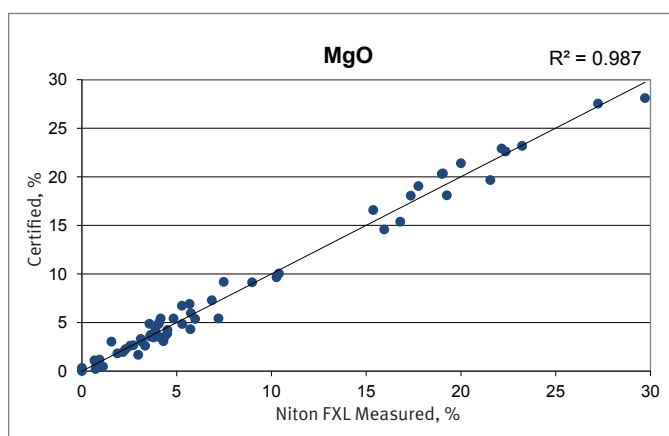


Figure 1. Correlation between various major elements in certified reference material analyzed by Niton FXL.

Results

The coefficient of determination, the R^2 value, is a measure of how closely the data sets correlate with each other, where a perfect correlation would have an R^2 of 1. Correlation plots are shown in Figures 1 and 2 for elements of interest in gas shale studies.

Comparison of the results of the Niton FXL instrument in certified reference materials from different rock types show typical correlations (R^2) > 0.90 and repeatability < 5% relative standard deviation (RSD) for most major, minor, and trace elements.

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 preparation). Relative shifts in elemental ratios can be used to quickly note increasing calcite, quartz, and clays in a formation for further follow up. Gas shale produces best in fracture prone intervals that are enriched in quartz and calcite. By identifying these intervals in the field, geologists are better able to plan for the well's completion program. Rapid elemental analysis by XRF and elemental ratio plots is a valuable tool in well logging and exploration. These ratios can be calculated easily using the Pseudo-element feature of the software on the field x-ray lab.

Long-Term Instrument Stability

Good instrument stability is an important factor when measuring trends and elemental ratios in the analysis of oil and gas shale samples. Table 1 and Figure 3 show the stability of the Niton FXL over an 8-hour period.

Time, h	Mg	Al	Fe
0	1.50	7.76	3.25
0.5	1.51	7.73	3.23
1	1.45	7.70	3.23
1.5	1.49	7.83	3.24
2	1.44	7.75	3.22
2.5	1.53	7.65	3.22
3	1.43	7.69	3.23
3.5	1.50	7.79	3.23
4	1.33	7.82	3.22
4.5	1.52	7.73	3.23
5	1.40	7.69	3.24
5.5	1.63	7.77	3.24
6	1.36	7.82	3.23
6.5	1.51	7.72	3.24
7	1.64	7.77	3.24
7.5	1.45	7.77	3.23
8	1.45	7.72	3.23
average	1.48	7.75	3.23
stdev	0.08	0.05	0.01
% rsd	5.69	0.66	0.24

Table 1: Stability of instrument over an 8-hour period demonstrated by Mg, Al and Fe measurements every half an hour.

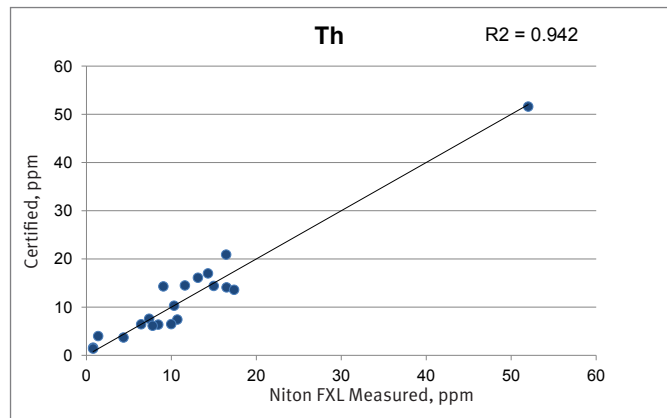
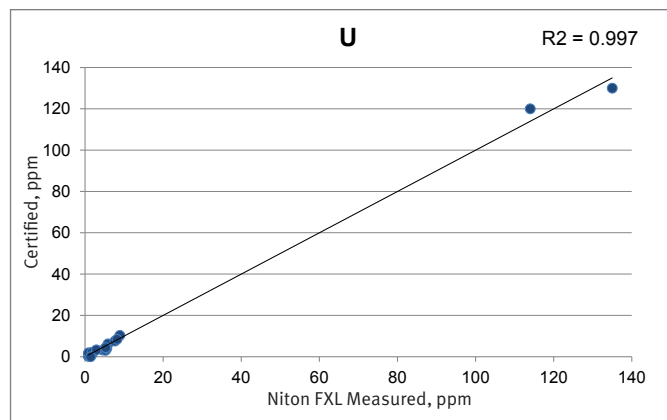


Figure 2. Correlation between trace elements (U and Th) in certified reference material analyzed by Niton FXL.

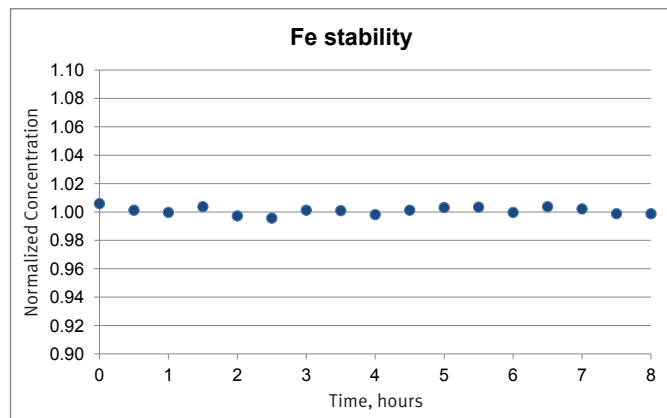
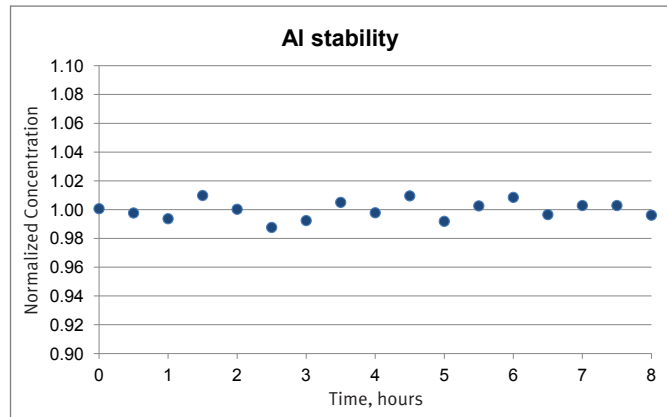


Figure 3. Stability of instrument indicated by Al and Fe measurement every half an hour over an 8-hour period.

Conclusion

Elemental analysis using the Niton FXL field x-ray lab provides important information to petroleum geologists. The Niton FXL with z-CAL analysis enables users to accurately detect oil bearing strata thus improving geo-steering and aiding mud-logging, thanks primarily to its improved ability to detect trace elements and light elements such as Mg and Al.

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 special minerals (e.g., clays, pyrite, and carbonate cement from Si/Al, Fe/S, and Mg/Ca ratios; figure 4). 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, please contact your local Thermo Scientific portable XRF analyzer representative or contact us directly by email at niton@thermofisher.com, or visit our website at www.thermoscientific.com/niton.

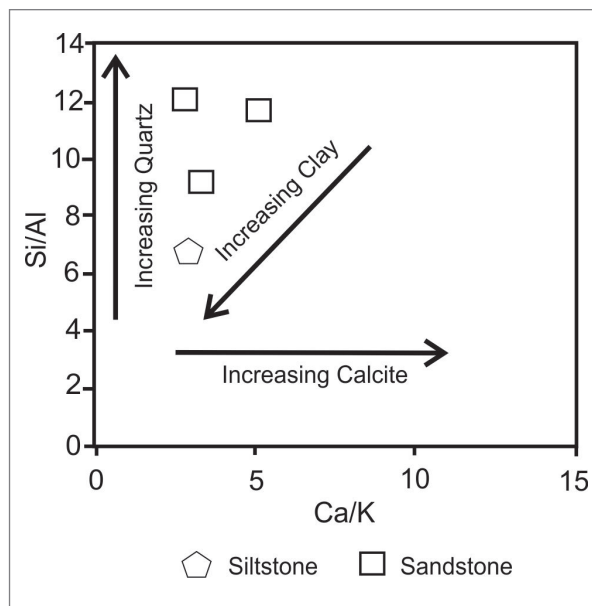


Figure 4. Elemental ratio of Si/Al is a basic indicator of the abundance of quartz (SiO_2) vs. aluminosilicates such as clays and feldspars. The combination of Si/Al and Ca/K ratios can show the relative amount of clay, quartz, and feldspar in the formation; for example, high Ca/K indicates the presence of calcite cement and high Si/Al shows increased quartz in the sandstone.

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