**Introduction**

Exploration and production (E&P) of unconventional oil and gas requires advanced and innovative technologies. Horizontal drilling and fracking are examples of innovations that opened the door to unconventional hydrocarbon resources.

Well site geochemistry is another new technique that can provide invaluable and near real-time data, with practical applications from precise rock identification to mineralogy and mineral modeling, chemostratigraphy, geo-steering, reservoir characterization (permeability, porosity, fracture population, brittleness) and even productivity (TOC inference). This technique is not unknown in E&P and is currently used in chemostratigraphy and mud logging.

The data for well site geochemistry is commonly provided by using laboratory instruments, an often expensive and time-consuming process. A supplemental technique is portable X-ray fluorescence (PXRF), which utilizes small, portable and rugged handheld or benchtop analyzers (Fig. 1). These analyzers can provide timely data on a variety of samples, from drill cuttings to cores and outcrops, without the need for a highly skilled workforce.

**Calibration**

When using PXRF, a common question is, “Do I need to calibrate the analyzer?” There are three calibration methods that are used in PXRF: Empirical, Fundamental Parameter (FP), and Compton Normalization.

Both FP and Compton Normalization calibrations are performed at the factory, without standards. Empirical calibration needs known samples (i.e. standards) and uses the correlation between the readings obtained from these samples and their known values in order to quantify elements in unknown samples. This calibration can provide precise and accurate assay data for a narrow range of sample types and matrices. Unreliable data can be created, however, if the sample type or matrix differs from the ones that were used for calibration.

Compton Normalization only works with a sufficient scatter (Compton Peak) in a spectrum related to the sample matrix. As the average atomic mass of the sample increases, the Compton peak decreases. Therefore, samples with a high percent of heavy elements cannot be analyzed with Compton Normalization. As a result, this calibration is used for very specific sample types, and it is not common in oil and gas wellbores.
FP calibration is an algorithmic approach based on the predictable detector response to known parameters, such as sample geometry, source energy, distance and angle between the detector and the sample, as well as other factors. FP calibration is preferred when a wide range of samples and matrices are analyzed. In such sample sets, FP can provide very precise data with good accuracy. Accuracy in the analysis can be increased by a cal-factor adjustment, which can be done internally in handheld analyzers and externally in FXL analyzers. The cal-factor adjustment uses a few known samples to adjust calibration by changing the slope and y-intercept of the factory calibration.

**Method**

One hundred sixty sedimentary rock samples and standards with independent laboratory ICP-MS results were analyzed by a Thermo Scientific™ Niton™ XL3t GOLDD handheld analyzer equipped with a silicon drift detector (SDD). Counting times were 30 seconds each on the low, main and high energy filters (for analyzing elements K to U), and 60 seconds on the light filter setting (Mg to S), for a total analysis time of 150 seconds. Optimal results were obtained on pressed powder pellets with the use of a He purge system.

**Results**

Comparison of two sets of analytical data (one set from handheld XRF and the other from an independent lab) shows typical correlations ($R^2 > 0.90$ and relative standard deviation (RSD; repeatability) ≤5% for most major, minor and trace elements from Mg to U (Fig. 2). The high correlation indicates that the factory FP calibration is capable of providing reliable and repeatable (high precision) analytical results for a wide range of samples and matrices. However, cal-factor adjustment is needed to improve the accuracy.

![Figure 2. Comparison of Niton handheld data with samples run by ICP-MS in an independent laboratory shows strong correlations with precision ≤5 % RSD for most elements from Mg to U.](image-url)
Conclusion
Well site geochemistry, particularly with PXRF, is a fast growing technique that can provide invaluable, rapid data that can be used in rock identification, mineralogy and mineral modeling, chemostratigraphy, geo-steering, reservoir characterization (permeability, porosity, fracture population, brittleness) and even productivity (TOC inference). Each analysis using PXRF is done in a few minutes without the need of a highly skilled workforce.

This case study shows that Thermo Scientific Niton handheld analyzers can deliver reliable, repeatable and accurate data on elements from Mg to U using FP factory calibration. To further increase the accuracy of the analytical data, cal-factor adjustment is recommended. This adjustment takes a few minutes and it is done using a set of known samples such as standards or even previously analyzed samples from the same well site.

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.