EDXRF APPLICATION NOTE

ANALYSIS OF LIMESTONE

$^{\#}$1108 REV2

SCOPE

The analysis of limestone is demonstrated using the empirical approach.

BACKGROUND

Limestone has historically been used as a major material in the construction of buildings and monuments, as well as the production of glass. More modern uses of limestone include as a raw material in the production of quicklime, cement and mortar, as well as a basic aggregate in road construction. Limestone is also used as a scrubber stone in the desulfurization of flue gas and is used as a reagent in blast furnaces to extract iron from ore. Purified, limestone has many uses as a calcium supplement in foods and animal feeds, and well as a whitener in cosmetics. The high calcium content of limestone is also an ideal ingredient in remineralization and can be used in water, toothpaste, mouth rinses, etc. Because of the wide variety of uses for limestone, quality control and precise characterization is an important part of limestone mining and processing operations.

INSTRUMENTATION

Model:	Rigaku NEX CG
X-ray tube:	50 W Pd-anode
Excitation:	Indirect with polarization
Detector:	High performance SDD
Analysis Time:	140 sec
Environment:	Helium Purge (optional vacuum available)
Standard:	15-position Sample Tray (32mm)

SAMPLE PREPARATION

A sample is first ground to a homogeneous powder approximately 100-200 mesh and dried to remove excess moisture. Limestone is somewhat hygroscopic and carbonates give limestone a pseudo-crystalline nature, and so sample preparation for EDXRF is done by making a hydraulically pressed pellet using wax binder. To prepare a pressed pellet 6.0g of powder is homogeneously mixed with 0.6g of wax binder (such as Chemplex SpectroBlend powder or tablets) and the resulting mix of sample and binder is pressed in hydraulic press using 20 tons pressure. This creates a pellet that minimizes mineralogical effects and creates a stable sample for analysis. Use the same recipe of binder and powder for all calibration standards and unknown samples.

CALIBRATION

Empirical calibrations were built using a set of 8 assayed standards, including NIST SRM 1d (Limestone, Argillaceous). The standards are representative of the limestone ores at the mine site. Using the empirical approach, “alpha corrections” are then employed to compensate for variations in X-ray absorption and enhancement effects within the sample due to the independent variations in element concentration, thus yielding a very accurate model characterizing the ore type. A summary of each empirical calibration is shown here.

8 Standards

Component	Concentration Range (%)	RMS Deviation	R^2 Confidence
$MgCO_3$	0.53 – 8.66	0.344	0.9937
Al_2O_3	0.19 – 2.35	0.031	0.9991
SiO_2	0.95 – 8.67	0.168	0.9981
$CaCO_3$	84.95 – 95.12	0.294	0.9980
Fe_2O_3	0.12 – 0.86	0.006	0.9998

REPEATABILITY

To demonstrate repeatability (precision), one representative samples were chosen from the set of calibration standards. Each sample was measured in static position for ten repeat analyses using a total analysis time of 140 sec per measurement, with typical results shown below.

Sample: NIST SRM 1d

Component	Assay Value (%)	NEX CG Average Result	Standard Deviation	% Relative
$MgCO_3$	0.63	0.64	0.047	7.5
Al_2O_3	0.526	0.535	0.010	1.9
SiO_2	4.08	3.99	0.035	0.9
$CaCO_3$	94.32	94.57	0.23	0.2
Fe_2O_3	0.136	0.138	0.002	1.5

REPEATABILITY (*continued*)

Sample: Quarry Sample 7A

Component	Assay Value (%)	NEX CG Average Result	Standard Deviation	% Relative
$MgCO_3$	1.64	1.69	0.022	1.3
Al_2O_3	0.29	0.26	0.004	1.4
SiO_2	2.58	2.50	0.020	0.8
$CaCO_3$	95.12	95.32	0.19	0.2
Fe_2O_3	0.120	0.127	0.002	1.7

TYPICAL DETECTION LIMITS

To determine the Lower Limit of Detection (LLD) using the empirical method, ten repeat analyses of a blank sample (boric acid) were measured and the standard deviation calculated. The LLD is then defined as three times the standard deviation. This approach ensures that analyses above the determined LLD are measuring signal above background. The following LLDs were determined using the same analysis times employed for calibration and repeatability. Actual detection limits may vary based on analysis time used, combinations of elements present and elemental concentration levels.

Component	LLD (%)
$MgCO_3$	0.020
Al_2O_3	0.007
SiO_2	0.009
Fe_2O_3	0.001

DISCUSSION

A typical approach for creating the most accurate empirical calibrations is to develop the set of calibrations from actual quarry samples. To improve the model of the matrix and to allow for changes in limestone composition, the initial calibrations can be expanded and augmented using addition assayed samples.

Performance, precision and limits of detection can be improved by using longer analysis times. The results shown here indicate performance in a “real-world” situation where a short analysis time of 140 sec is required. Two secondary targets are used to measure the elements shown here. The RX9 polarizer is ideal for light elements (Na-Cl) and was set to 100 sec, and the Cu target was employed using a count time of 40 sec. Quadrupling the analysis time to a total of 560 sec improves precision and detection limits by a factor of two.

Sodium is rarely monitored in limestone, typically only for a few specialty limestone products. The samples measured for this App Note did not contain Na.

CONCLUSION

The Rigaku NEX CG combines indirect excitation with secondary targets, polarization targets and a high performance SDD detector to yield the optimum performance for elemental analysis of limestone. During the entire quarrying and processing cycle, oxide composition of the limestone material must be reliably monitored to ensure optimal process control and profitability. The Rigaku NEX CG analyzer is an ideal tool throughout the quality control process. In addition, the NEX CG can be used to monitor air filters for air quality emission control, and UltraCarry can be used to monitor process effluents to ppb range detection limits, making the NEX CG a versatile and valuable tool for several applications within limestone mining and processing.