ABSTRACT
Qualitative and quantitative analysis of the elemental contents of limestone samples by Xenemetrix's X-Calibur SDD detector equipped with special light element optimized window.

OBJECTIVE
To make a qualitative and quantitative analysis of limestone samples using X-Calibur equipped with silicon drift detector with a very thin detector window optimized for analysis of light elements such as Na and Mg.

BACKGROUND
Energy Dispersive X-ray Fluorescence (EDXRF) is a fast and non-destructive technique used to identify and quantify any type of sample in solid, powder or liquid at minute scale time. EDXRF spectrometers play an important role in raw materials and end product tests and assure that consistent quality of samples is retained throughout a manufacturing process and in final product.

EDXRF is an ideal method for a quick and simple elemental analysis for industrial control purposes offering the following advantages: (1) Fast analysis, requiring minimal sample preparation, (2) Automated analysis process, (3) Limited or no exposure to corrosive and hazardous reagents as practiced by other analytical techniques, (4) Almost no training is required; easy to operate by non-technical or non-specialized personnel.

ANALYTICAL CONFIGURATION

Table 1: Analytical Configuration of X-Calibur SDD

Instrument	X-Calibur SDD EDXRF Bench top Spectrometer System.
Excitation	Rh-Anode X-ray Tube, 50W
Detector	High Performance Silicon Drift Detector with Light Element Optimized Window
Analysis Time	180 seconds
Type of analysis	Qualitative analysis of the limestone samples and quantitative analysis using standardless fundamental parameter software
Excitation	Direct excitation
Environment	vacuum atmosphere
Sample Preparation	no sample preparation

EXPERIMENTALS
Five limestone samples were obtained by the customer and analyzed qualitatively and quantitatively for the main and trace elements using X-Calibur SDD EDXRF analyzer. The SDD detector was equipped with a light element optimized window with improved the transmission of the low energy photons compared to detector with standard Be window. This results in enhanced light element signals and improved limit of detection by the EDXRF analyzer.

Quantitative analysis of the elements of interest was performed, by fundamental parameter software without the use of "calibration standard". This is the best available option in the absence of calibrated standards.

The samples were prepared by transferring the powder into the X ray cups with special prolene thin film support followed by slight tapping of the cup in order to compact the soil and eliminate the air voids. Vacuum was used to eliminate the oxygen in the x-ray beam path, since otherwise oxygen absorbs the weak low energy signal of the light elements.

The samples were acquired using different acquisition parameters in order to optimize the detection of the specified elements in the spectrum. Summary of elements present in the samples is summarized in table 2.

RESULTS AND DISCUSSIONS

QUALITATIVE ANALYSIS

The goal of this section of the work was to perform a qualitative elemental analysis of the limestone samples.

All the samples were found to be similar in the elements present (table 2).

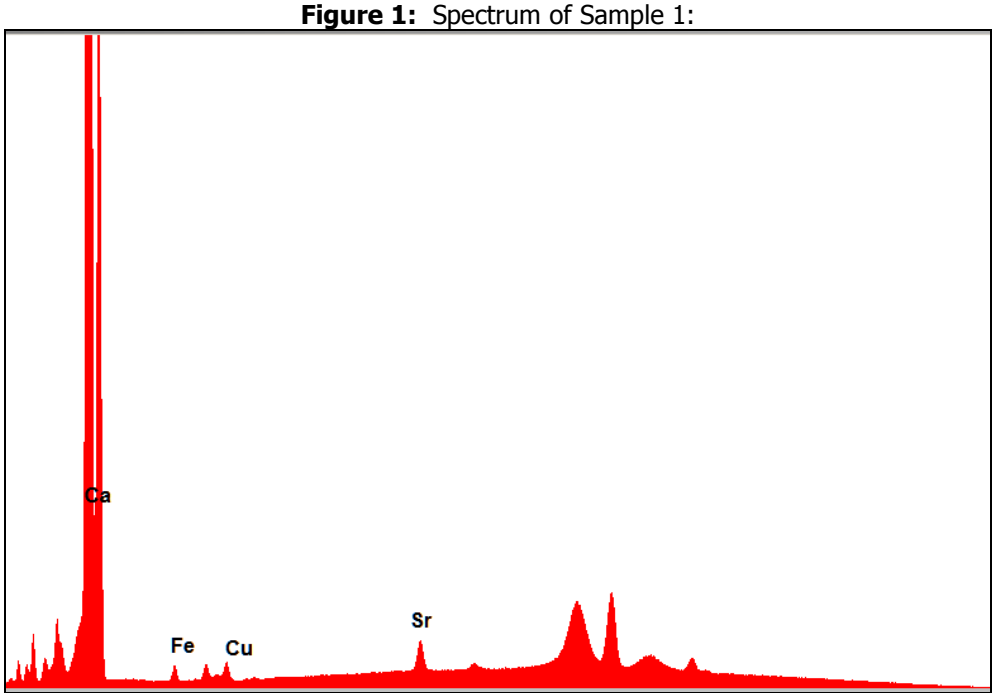
Table 2: Summary of main elements present in the samples

Sample ID	Elements present in all samples
Sample 1 C1/16811 Sample 2 C1/16811 Sample 3 C1/16811 Sample 4 C1/16811 Sample 5 D1/13711	Mg, Al, Si, S, Ca, Fe, Cu, Sr

The samples were acquired using different acquisition parameters in order to optimize the conditions for different groups of elements. The result of the qualitative analysis is listed in table 2.

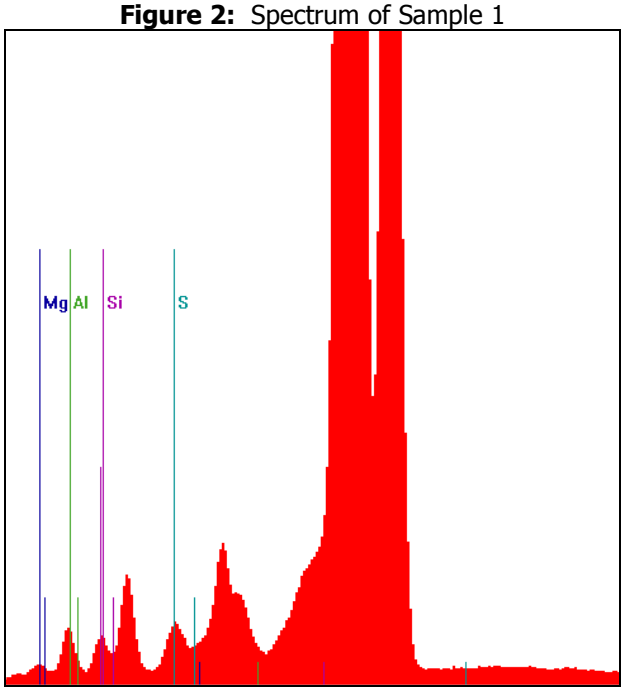
A spectrum of sample 1, is shown in figure 1.

Figure 1: Spectrum of Sample 1:



SDD detector with Light Element window is especially useful to enhance the signal of light elements. In this work this detector is useful for the detection of Mg an Al (figure 2). Since this detector window is characterized by high transmittance of the signals of low Z elements, emission peaks of Mg and Al were enhanced and clearly observed in the spectrum. Thus, the detection limit for these element was considerably improved. Figure 2 shows a zoom of the low Z elements which were present in all limestone samples.

Figure 2: Spectrum of Sample 1



QUANTITATIVE ANALYSIS

Quantitative analysis in EDXRF is best done with regression analysis based on certified calibration standards (samples of known concentration and of the same matrix as the samples to be analyzed) and building calibration curves per element of interest. When calibration standards are not available the quantitative analysis can be performed using Fundamental Parameter software that compares ratio of the elemental peaks in the spectra and uses theoretical considerations to calculate the absorption of X-rays and the inter-elements effect without the need of certified calibration standards.
In this application sample 1-5, were analyzed quantitatively using standardless fundamental parameter calculations. It should be noted based on the spectral information received that sample 1-4 were most probably the same material, while sample 5 was slightly different in composition. The quantitative results are shown in Table 3.

Table 3: Elemental composition of sample 1-5.

	sample 1 w/w%	sample 2 w/w%	sample 3 w/w%	sample 4 w/w%	sample 5 w/w%
$CaCO_3$	96.42	96.28	96.39	96.09	96.75
SiO_2	0.62	0.62	0.60	0.68	0.45
SO_3	0.36	0.33	0.38	0.36	0.23
Al_2O_3	1.45	1.53	1.47	1.54	1.38
Fe_2O_3	0.096	0.09	0.09	0.11	0.04
MgO	0.90	0.99	0.90	1.07	1.00
SrO	0.06	0.06	0.05	0.06	0.06
Cd	0.05	0.04	0.04	0.05	0.04
CuO	0.04	0.04	0.04	0.04	0.04

Conclusions

This work demonstrates the excellent performance of X-Calibur SDD detector with Light Element Optimized window for elemental analysis of limestone samples that contain light elements like Mg and Al in addition to other elements.

This work constitutes a good example of how fast and easy qualitative analysis of unknown limestone samples can be performed. Several elements were detected in the 5 limestone samples using the X-Calibur SDD while the absence of other elements (at least not above 100's of ppm) was confirmed by the use of different acquisition parameters, which are optimized and specific for a given element.
Due to the absence of real representative calibration standards powerful fundamental parameter software was Used, without the use of any "calibration standard", to quantify the elemental content of all five unknown limestone samples.
To conclude, X-CaliburSDD with Light Element Optimized window is good analytical tool for elemental analysis of limestone samples.