## Multi-Camera Hyperspectral Imaging and Micro X-Ray Fluorescence Elemental Mapping for Multi-Range Geochemical Investigation

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Several hyperspectral modalities have been used in the past for the concurrent measurements of core samples. [1-3]. The purpose of these measurements was to survey stored lengths of core samples [4] as a function of drill depth using VNIR and SWIR hyperspectral regions and cameras. In some cases, a cooled long-wave infrared (LWIR) camera has also been used when the high camera cost was warranted.

Middleton Spectral Vision has developed the Via-Spec<sup>™</sup> Geo 5 Series instruments [5] that can have VNIR, SWIR, MWIR, LWIR and Polarized Fluorescence hyperspectral cameras configured in a serial format above a conveyor belt to analyze mineral samples. In this communication a common cement sample was examined and the abbreviated results are presented below. In addition to the optical hyperspectral analysis, showing the x-ray mapping elemental distribution of the same sample was performed and compared on the same scale.

The information content in the VNIR range is mostly the color and the various electronic transitions that show a signature below 1000 nm. The SWIR region (1000-2500 nm) for minerals is dominated by the mineral hydration (oxides, hydroxides – e.g., Calcium Hydroxide) around 1450 nm and around 1800-2000 nm. The overtones and combination bands of the fundamental molecular vibrations also contribute to the overall spectra of minerals and are characteristic to the chemical composition, although it is more difficult to identify the bands than organic materials. In the 2.5-25 um region the fundamental vibrations of the molecules including the crystalline modes are detected.

In addition to the broadband absorption hyperspectral imaging techniques discussed above, we have developed a unique macroscopic hyperspectral fluorescence imaging methodology for larger samples (4-inch spatial dimension) and apply it to mineral imaging. For crystalline minerals the polarization of the excitation laser is able to generate different polarized images. The degree of polarization sensitivity can also be used for further identification of the components of the sample.

Micro-X-ray fluorescence (microXRF) is a nondestructive elemental analysis technique based on the emission of characteristic X-rays following the excitation of the specimen by an Xray source. A broad range of specimens can be placed into the instrument chamber and data can be observed within minutes of setting the sample on the stage. The characteristic X-rays emitted by the specimen are detected using an energy dispersive X-ray detector and displayed as a spectrum of energy versus intensity. Qualitative analysis is accomplished by identifying elements present in the specimen based on their characteristic X-ray energies. Semi-quantitative analysis is accomplished by comparing the relative area under the peaks of characteristic X-rays of the elements. Limits of detection (LOD) are dependent on several factors, including instrument configuration and operating parameters, sample thickness, and atomic number of the individual elements. Typical LODs range from parts per million ( $\mu$ gg<sup>-1</sup>) to percent (%).

Nearly 99% of the minerals making up Earth's crust are made of just eight elements (O, Si, Al, Fe, Mg, Ca, Na, K). Oxygen is the most abundant. A majority of these eight elements are found combined with other elements as compounds. The abundance of oxygen dictates that many of these compounds are various inorganic oxides which are ubiguitous on Earth. X-ray fluorescence has been used in many aspects of mineral science analysis, with a particular emphasis on minerals in natural resources. The microXRF M4 Tornado simultaneously detects all elements from Na to U. This technique is therefore well suited to analyze most minerals whether as oxides, minerals with metals, or unique trace elements/inclusions within minerals. In addition to many other sample types, X-ray fluorescence is utilized frequently in the study of cements. Common materials which make up cement include many of these common oxide compounds. Bulk composition and individual mineral phases/phase distribution can be identified, and resolution of compositional variation within phases can be observed at the micron scale using the collected x-ray maps. MicroXRF is a highly complementary analytical technique to the optical reflectance technique described above. The combined element X-ray map in Figure 6 presents detected elements

(here Si, Mg, Ca, K, Sr, Fe), each with its own color. These elemental distribution maps quickly reveal some apparent phases which make up this sample. These phases can then be easily correlated with the reflectance spectra of known minerals.

The above hyperspectral imaging and elemental maps can be applied on the same scale for 4" diameter cut and polished cores or smaller mineral samples. To illustrate the power of the combined parallel measurements, a 4" diameter cement sample was cut, polished and measured with all the above described techniques. This application example is particularly suitable to show the power of the combination of the techniques due to the range of different minerals present in the particular sample.

The x, y, and spectral information data hypercubes were saved and analyzed using Middleton Spectral Vision KemoQuant<sup>™</sup> hyperspectral analysis software package. The special KemoQuant Fusion<sup>™</sup> version for multirange hyperspectral data is also able to scale and match the images derived from different wavelength ranges of the same sample measurements.

The scope of this application note only allows the illustration of some of the results.

As a reference the RGB image of the sample is shown. Even with the best camera, only the image morphology and location of the different color constituents could be detected. Chemical and elemental composition, crystallinity and other important information requires a broad range of spectral analysis afforded by the combination of the hyperspectral measurements and consequent data analysis shown below.



Fig 1. RGB image of cement sample disc. The image reveals the existence of the different stones mixed in the cement but cannot differentiate them based on their chemical composition or spectral signature. The image was created from the VNIR data using the red, green and blue wavelengths for the display.



Fig. 2. The VNIR image shows the high-resolution features and 400-1000 nm reflectance spectra of selected areas of the sample. The image was created using three selected MCR factors for the three colors of the display. The actual dataset contains all spectra for all points of the image, here three selected spectral components are shown, each assigned to red, green and blue color for display purposes.







Fig 3. SWIR composite image and example spectra of a few selected areas.



Fig 4. MWIR composite image and example spectra of a few selected areas.





Fig 5. Fluorescence composite image and example spectra of a few selected areas.



Fig 6. MicroXRF combined element distribution map. The identified elements are displayed in different colors as indicated in the lower left corner of the image. Elemental distribution is a proxy for identification of minerals.

The above Application Note illustrates the power of using different wavelength ranges and the hyperspectral components. Please note that similar color rocks show up very differently in the different multi-component images. This differentiation is the power of utilizing the spectra, not just the visible colors. It is further noted that the differentiating power of the different wavelength ranges is also very different, thus using additional hyperspectral cameras with different wavelength ranges brings new information, not just emphasizing the same chemical differences.

Each camera data cube was producing several more MCR factors than shown here. The methodology producing the images, correlating the spectra to mineral types and many other details will be published in the near future. The equipment used to produce the data are shown on Figs 7-8.



Fig 7. Via-Spec<sup>™</sup> Geo 5 Series multi-range hyperspectral scanner (Middleton Spectral Vision, Middleton, WI)

## References

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Fig 8. M4 Tornado MicroXRF instrument (Bruker Nano GmbH, Berlin, Germany)