

CLAY MINERAL IDENTIFICATION USING DIFFUSE SPECTRAL REFLECTANCE

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ABSTRACT

Traditionally, the principle means of identifying clay minerals has been through X-ray diffraction (XRD). While effective, there are some disadvantages to using XRD for this application. XRD requires a good deal of sample preparation before measurements can be made. These sample preparation methods consume the sample in the process of doing the analysis. XRD instrumentation can also be expensive, a constraint which may place the technology out of the reach of some institutions.

As an alternative, we have explored the use of Diffuse Spectral Reflectance (DSR), as a means of eliminating these disadvantages (Hunt, 1977). The method has been used extensively in satellite applications but less so in marine sedimentology (Balsam and Deaton, 1991; Ortiz *et al.*, 1999; Vandenberg and Jarrard, 2002). Clay minerals have distinct spectral features, which make them relatively easy to identify with this method. The method is fast, non-invasive, and less expensive. With proper calibration the method can provide quantitative estimates of clay mineral concentration, rather than simple presence-absence estimates.

Using an Analytical Spectral Devices, LabSpec™ Pro FR we have developed a simple, and inexpensive means of constraining measurement geometry for use with its standard fiber optic probes. Our approach enables reproducibility of DSR measurements to better than 0.2% throughout much of the instrument's measurement range which spans the UV/VIS/NIR from 350–2500 nm. Replicate measurements of known clay mineral samples and fine grain separates (<63 μm) provide proof of concept.

REFERENCES

- Balsam W.L. and Deaton B.C., 1991. Sediment dispersal in the Atlantic Ocean: Evaluation by visible light spectra, *Reviews in Aquatic Sciences*, 4, 411-447.
 Hunt, Graham R., 1977. Spectral Signatures of Particulate Minerals in the Visible and Near Infrared., *Geophysics*, Vol.42 No. 3 April p.501-513, (and references therein).
 Ortiz, J.D., Mix, A., Harris, S., and O'Connell, S. 1999. Diffuse spectral reflectance of as a proxy for percent carbonate in North Atlantic sediments, *Paleoceanography*, 14, 171-186.
 Vandenberg, M.D., and Jarrard, R.D., 2002. Determination of equatorial Pacific mineralogy. In Lyle, M., Wilson, P.A., Janecek, T.R., et al., *Proc. ODP. Init. Repts.*, 199, 1-20 (CD-ROM). Available from: Ocean Drilling Program, Texas A&M University, College Station TX 77845-9547, USA.

THE INSTRUMENT

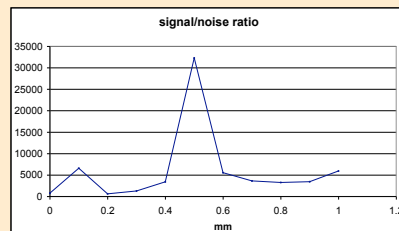


Analytical Spectral Devices LabSpec Pro FR

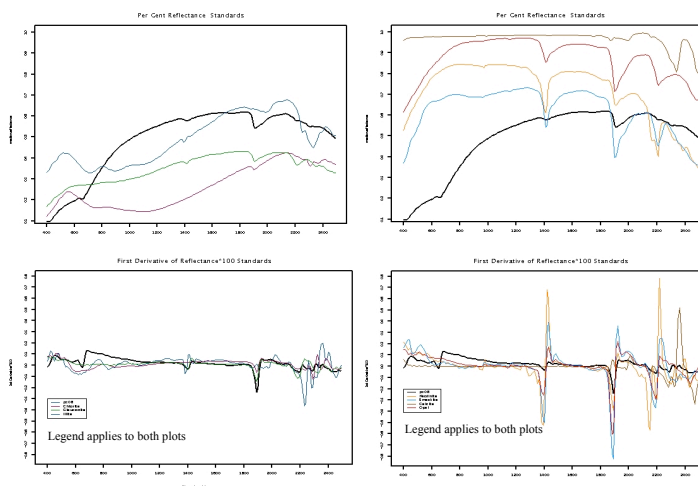
- UV/VIS/NIR spectrometer with 2 nm resolution, select-series detector
- Spectral range of 350-2500 nm. 400-2500nm is usable
- Uses a variety of fiber optic probes to allow easy changes to measurement geometry.
- We have attached a 3mm diameter probe to an existing microscope stand to enable accurate measurement of the distance between the custom designed probe tip and sample (~0.1mm).

CALIBRATION AND ERROR REDUCTION

Prior to each use, the instrument is calibrated using a Spectralon™ standard with known reflectance. All reflectance values are relative to this standard. Factors such as the distance between the probe tip and the sample, and the angle from which the measurement is taken can affect the quality of the data. We built a measurement jig to hold the probe tip normal to the sample, and a depth guide to maintain the probe at a constant height above the sample. We determined the optimal measurement height by taking replicate measurements of the standard at 0.1mm height intervals, and then dividing the peak visible photon counts by the standard deviation of the replicates. This creates a signal-to-noise ratio at 0.1 mm intervals above the sample. It was found that the ratio peaked at 0.5 mm. Using this setup can reduce measurement error from as much as 4% down to 0.2%.



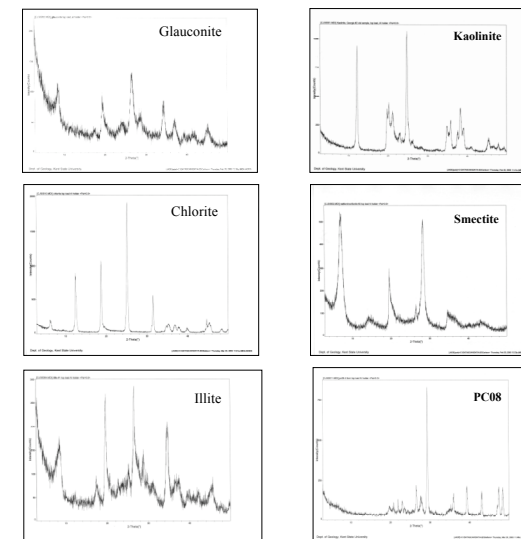
UV/VIS/nIR DATA



The percent reflectance charts show the variability between the minerals being analyzed well enough to easily identify pure minerals with no more preparation than sieving and hand grinding the sample. The deep sea core data in which we are trying to identify minerals is a mixture and therefore presents slightly more challenging identification. Certain features due to the presence of one mineral may be masked by the presence of another. Interaction of this occurs between calcite, opal, kaolinite and smectite. Calcite shows a strong absorption feature just before 2400 nm, while the other three minerals all have increased reflectance at the same point, this results in a masking effect of the calcite feature when it is mixed with any or all of these minerals. Despite these difficulties, the presence/absence of clay minerals can be determined by correlation of reflectance spectra of known minerals with those of unknown samples (see table at right).

The mineral standards were compared against reflectance data gathered from 77 fine grain separates (<63 μm) from deep sea core OXMZ01MV PC08, a 13.85 m long piston core taken off of Baja California (23°28' N, 111°35.91' W). The core was raised from a water depth of 705 m.

XRD DATA



These XRD patterns from bulk samples clearly show the variability in the clay minerals, and all demonstrate that the samples used are fairly pure representatives of their species. The PC08 material shows numerous small clay peaks, but these are dwarfed by several large calcite peaks, the largest just before 30 degrees. Unlike the DSR method, this makes identification of the clay minerals within the marine sample difficult without additional sample processing.

Below is a correlation table for percent reflectance and first derivative values for the clay minerals and the median reflectance for the 77 samples from PC08. The bold face numbers are significant correlations. The significant correlations between the standards make it difficult to tell the difference between these two minerals using this parameter. While this is a serious problem for the raw percent reflectance data, but there are fewer significant correlations between the standards when a first derivative transformation is used. Using first derivative transformed data, the correlation suggests the presence of illite, smectite, and opal, within these marine sediments.

Linear Correlation Coefficient Between Reflectance of Standards and PC-08 Median Wavelength range 1000-2500nm @ 10nm resolution

	Chlorite	Glauconite	Illite	Kaolinite	Smectite	Calcite	Opal	PC-08
Chlorite	1.00							
Glauconite	0.78	1.00						
Illite	0.86	0.52	1.00					
Kaolinite	-0.24	-0.72	0.08	1.00				
Smectite	-0.27	-0.70	0.11	0.91	1.00			
Calcite	-0.08	-0.46	0.20	0.73	0.67	1.00		
Opal	-0.32	-0.74	0.03	0.91	0.98	0.71	1.00	
PC-08	0.74	0.31	0.94	0.24	0.33	0.39	0.26	1.00

Linear Correlation Coefficient Between First Derivatives of Standards and PC-08 median

	Chlorite	Glauconite	Illite	Kaolinite	Smectite	Calcite	Opal	PC-08
Chlorite	1.00							
Glauconite	0.49	1.00						
Illite	0.15	0.42	1.00					
Kaolinite	-0.04	0.22	0.51	1.00				
Smectite	-0.02	0.23	0.82	0.66	1.00			
Calcite	0.60	0.23	0.15	0.04	-0.02	1.00		
Opal	0.05	0.39	0.80	0.59	0.94	0.02	1.00	
PC-08	0.27	0.55	0.78	0.45	0.71	0.22	0.77	1.00

Wavelength range 1000-2500nm @ 10nm resolution, thus n=150
 Average lagged decorrelation scale is ~ 200nm Thus df = (150-2)/20 = 7.4

5% < r < 0.65
 1% < r < 0.78
 Based on interpolation of Table A10 from "Statistical Methods", 8th ed.

CONCLUSIONS AND FUTURE DIRECTION

- DSR is a quick and efficient way to gather data on samples
- It is possible to make measurements with error as low as 0.2%
- Clay minerals have distinct reflectance patterns that should make them identifiable with this method, although masking of some features can be a problem
- To extract quantitative information from DSR measurements, we are exploring the use of normative analysis of reflectance data (e.g. Vandenberg and Jarrard, 2002) and principle component analysis of first derivative transformed data (e.g. Balsam and Deaton, 1991).