Color Reflectance Workshop Report

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Attendees: Tomohisa Irino, Gary Acton, Peter Blum, Denise Kulhanek, Carlos Alvarez-Zarikian, Trevor Williams, Leah LeVay, Margaret Hastedt, David Houpt'

Comments *in absentia*: Liviu Giosan

Executive Summary

Following the SODV upgrades, IODP JRSO switched from using a Minolta CM-2002 spectrophotometer to an Ocean Optics USB4000 system. The new system was selected because it had major advantages in speed and resolution, which allowed faster coreflow through the shipboard laboratories. The older system was a potential bottleneck in the processing of cores.

The new Ocean Optics system produces color space data (e.g., Tristimulus XYZ and CIELAB L*a*b*) of good quality that serve the needs of the general science user. Unfortunately it has a very large noise level compared to the Minolta, a fact that made the use of spectral and first derivative spectral data from the USB4000 problematic and disappointing. The new system was also more sensitive to the quality of contact with the surface of the core section than the Minolta. Evaluations from scientists and an NSF review all indicated that making improvements to the color measurements on the *JOIDES Resolution* (JR) was a priority. For these reasons, the JRSO has sought to improve the contact the sensor makes with the core section, has searched for alternate sensors, and has solicited support from the scientific community to evaluate these improvement efforts.

The panel evaluated the Minolta and both the Ocean Optics USB4000 and QE Pro spectrometers on geologic cores and standard reference materials. In short, the QE Pro appears to be a significant improvement over the USB4000 and should be adopted immediately on the JR. In addition, the Minolta should remain available on the ship in order to assure scientists as to the quality of the QE Pro data.

It is important to note that the spectral effect of the GLAD Wrap™ and the quality of contact between the integrating sphere and the sample will continue significantly affect data quality. Steps have been taken to improve the contact, but it is still a potential source of erroneous measurements. These are well-known issues and no satisfactory solution has ever been proposed that resolves them. High quality GLAD Wrap™ (uncolored and ideally unwrinkled) should be used to minimize these problems. The panel also recommends that additional parsed data be stored in LIMS: spectral data and RGB conversion from the other color space data. The RGB derived from color space data and that obtained from the SHIL image should be used to cross-check image and spectral quality between the color measurement and the imaging logger and to identify potential trouble spots. Perhaps in the future, multispectral or hyperspectral techniques (that do not require contact) will overcome these issues, but those techniques are too immature for adoption at this time.

Evaluation of Sensors

The panel was provided by an overview created by JRSO staff that evaluated a number of potential replacement detectors from Ocean Optics. Three systems were evaluated: the FLAME, the MAYA, and the QE Pro. Based on the results given in Appendix A, the QE Pro was clearly superior and was purchased as a replacement for the USB4000 system. Implementation of the QE Pro on the JR was delayed in order to convene the Color Reflectance Workshop and allow the community to evaluate the new detector, or to suggest an alternate path forward. The panel members were given the opportunity to experiment with the Minolta CM-2002, the USB4000, and the QE Pro in a side-by-side comparison.

Comparison Methodology

Geologic cores were obtained from the GCR, representing a wide variety of colors and brightness. These were covered with fresh GLAD Wrap™, and data were acquired from selected points on all three detectors under as close to identical conditions as possible.

In addition, a number of photographic standards as well as synthetic hematite/goethite paint swatches were scanned.

Fundamental Differences between Ocean Optics and Minolta Detectors

- The spectral resolution of the Minolta CM-2002 (10 nm) is two orders of magnitude less than the Ocean Optics USB4000 and QE Pro
- The Minolta uses a xenon flash and near-instantaneous integration; the Ocean Optics systems use a combined halogen/LED light source and integrate on a continuous basis
- The Minolta uses a capacitor to charge the flash and has a relatively fixed 3-second acquisition + recovery time; the Ocean Optics systems have a much shorter integration time (on the order of 0.2 to 0.5 seconds)
- The Minolta has a slightly smaller contact point for its integration sphere; the Ocean Optics integration sphere has a large circular footprint (40 mm in diameter)
- The Minolta has a 6 mm aperture, which is the same as the Ocean Optics sphere used for the comparison experiments; note that the aperture on the JR is a custom 10 mm size to improve quality

Detector Comparison Results

Comparison of Raw Spectra and Output

Generally, the spectra from all three spectrometers (Minolta CM-2002, Ocean Optics USB4000, and Ocean Optics QE Pro) have a similar shape and character. However, notable differences exist between spectra generated by the three systems.

- Most obvious, amount of noise in the USB4000 is an order of magnitude larger than the other two systems, and is even noisier in the blue end of the spectrum
- The spectra for the Ocean Optics systems were consistently lower by a few percent relative to the Minolta except for the 99% reflectance standard, which we suspect is above the linear range of the Minolta—its standard is approximately 93%–94% reflectance
    - The lower spectra in the Ocean Optics systems produces lower color space results
    - We suspect these differences may be related to contact given the high sensitivity to even a small gap and the need for a nonlinearity correction to be applied to the Ocean Optics data; the non-linearity correction is applied to the shipboard system, but was not available for the testing done during this workshop
- The Minolta produces more accurate color space values on the photographic cards than the Ocean Optics systems
- The Ocean Optics spectrometers exhibit apparent non-linearity, and a correction factor (supplied with the QE Pro devices) must be applied to the raw spectral counts prior to data reduction; this is being done in the current SHMSL code for USB4000 data
- The Ocean Optics spectrometers are sensitive to distance from sample as seen in Fig. 3. The Minolta demonstrates much less fall-off over the same gap.

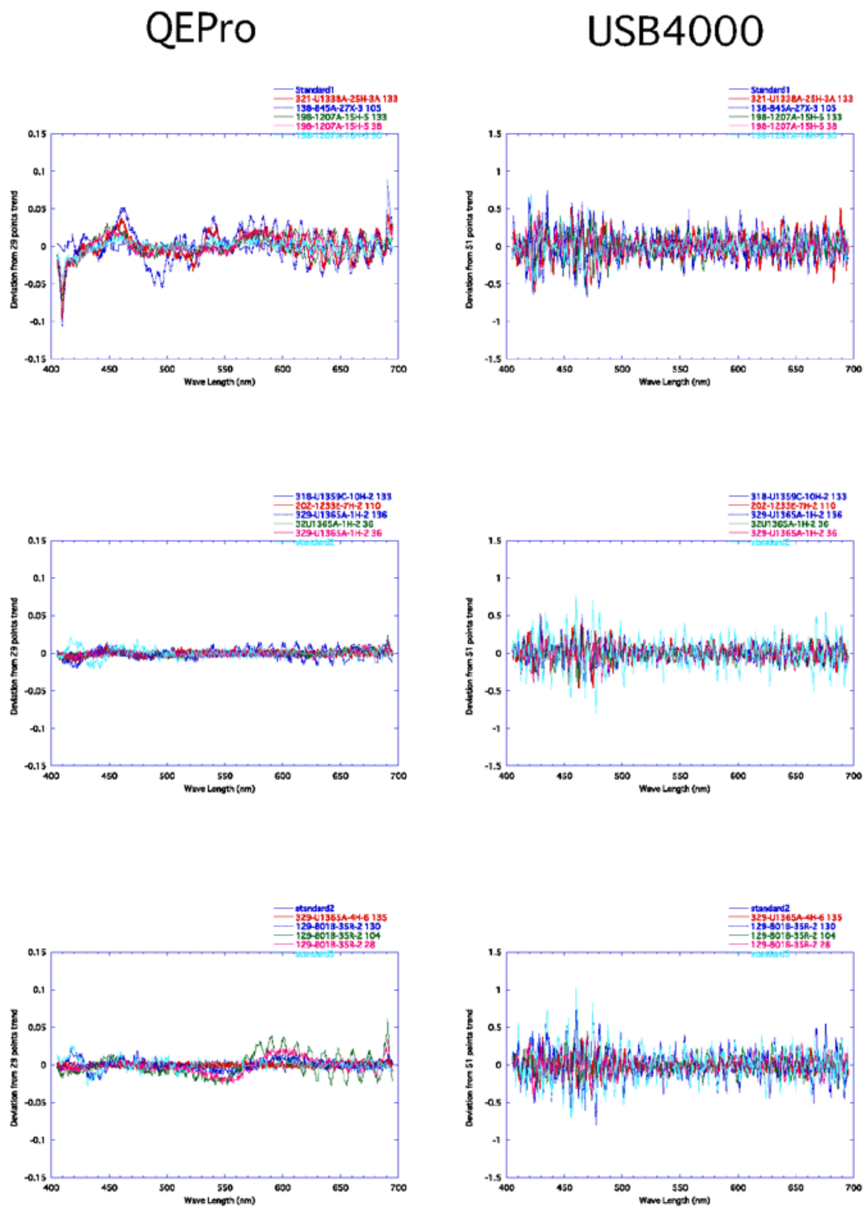

Fig. 1. Illustration of noise difference between QE Pro and USB4000. Noise was defined as the difference between the raw spectrum and smoothed spectrum (10 nm window).

Table 1. L* comparison between models. Demonstrates the apparent non-linearity of the Ocean Optics detector (see Fig. 2, below). Data are from measuring a QP color card.

QP Card	QE Pro	Minolta	% QE Pro/ Minolta
95 L*	93.71	93.75	99.96
80 L*	77.21	79.29	97.38
48 L*	45.06	47.87	94.14
35 L*	33.19	35.01	94.81

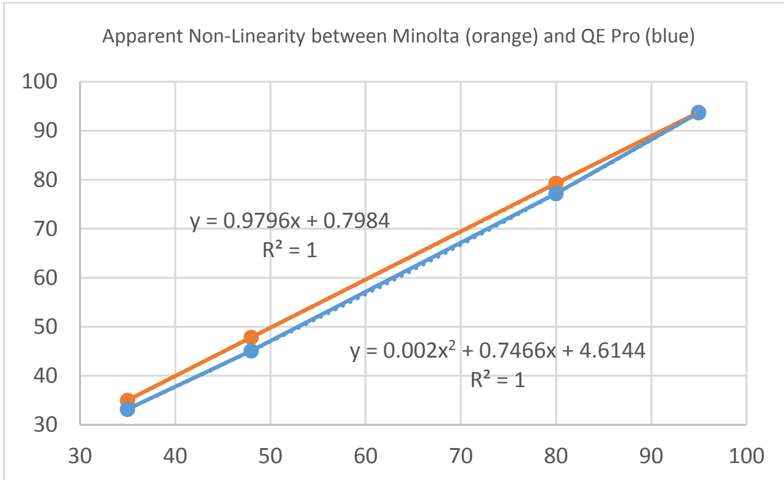

Fig. 2. Non-linearity of QE Pro without application of 7th-order correction factors. LabVIEW code takes these factors into account before evaluating percent reflectance. Data are from measuring a QP color card; orange is from Minolta CM-2002 and blue is from Ocean Optics QE Pro.

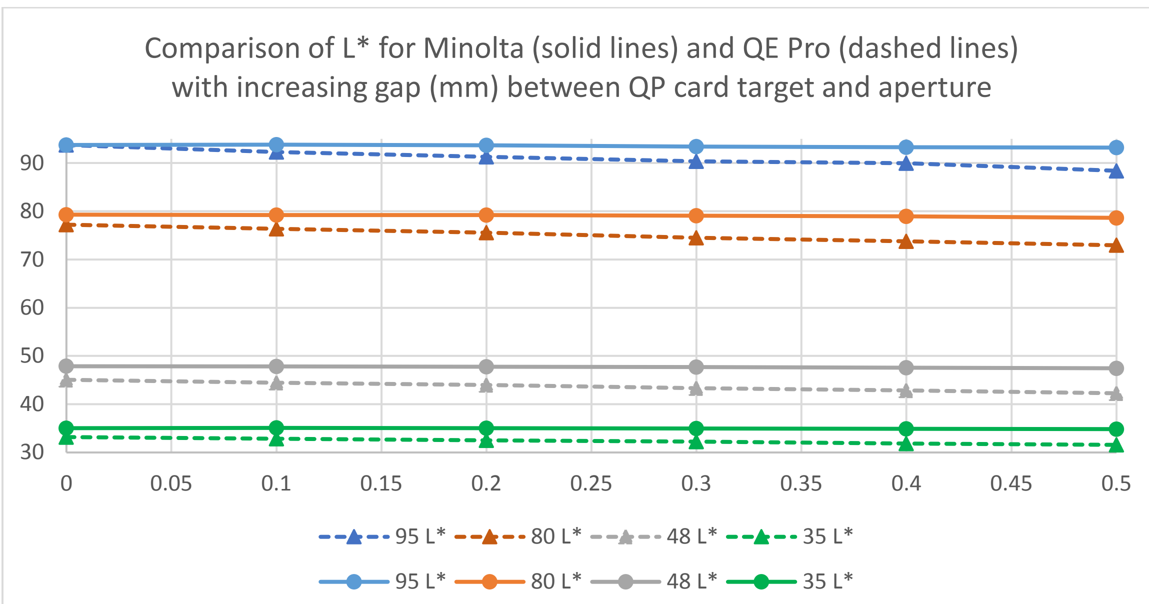

Fig. 3. Comparison of L* signal loss with increasing gap between aperture and QP card target. The Minolta loss is present but much smaller than the Ocean Optics loss.

Comparison of First-Derivative Data

First derivatives are used by researchers to identify and to attempt to quantify the existence certain minerals in samples, as shown in Appendix A. Reflectance methods allow quantification of these minerals at lower concentration levels than other common methods such as XRD and at high spatial resolution. For example, hematite has a peak around 565 nm and goethite has a double peak at 535 nm and 435 nm. The USB4000 can detect the presence of some of these minerals, but the noise level is so high that the effective detection limit is significantly compromised. After the introduction of the BLULOOP light source (late 2015), the first derivative spectra of the USB4000 improved significantly with filtering and it is possible to extract mineral data using smoothed spectra (e.g., 20 nm smoothing window, see Fig. 6). The Minolta and QE Pro both generate identical good quality first-derivative spectra and are both suitable for this purpose.

- Both the Minolta and the QE Pro have similar sensitivity to the mineral peaks as represented by similar-magnitude responses
- The QE Pro's higher spectral resolution can resolve peaks that the Minolta cannot
- The QE Pro's results are smoother/less jagged, indicating less noise in the spectra than the Minolta

Potential detection of higher resolution spectral features is useful to science. For example, mineral components such as hematite and goethite can be determined with good spectral data. Another example is the detection of the redox state in clay minerals. Chromophores from hydrothermal settings could potentially be detectable in the visual spectrum range if such sediments are drilled in the future and proper experiments are set up. The increased resolution of the QE Pro would not only give better quality spectral results but may also yield more scientific information.

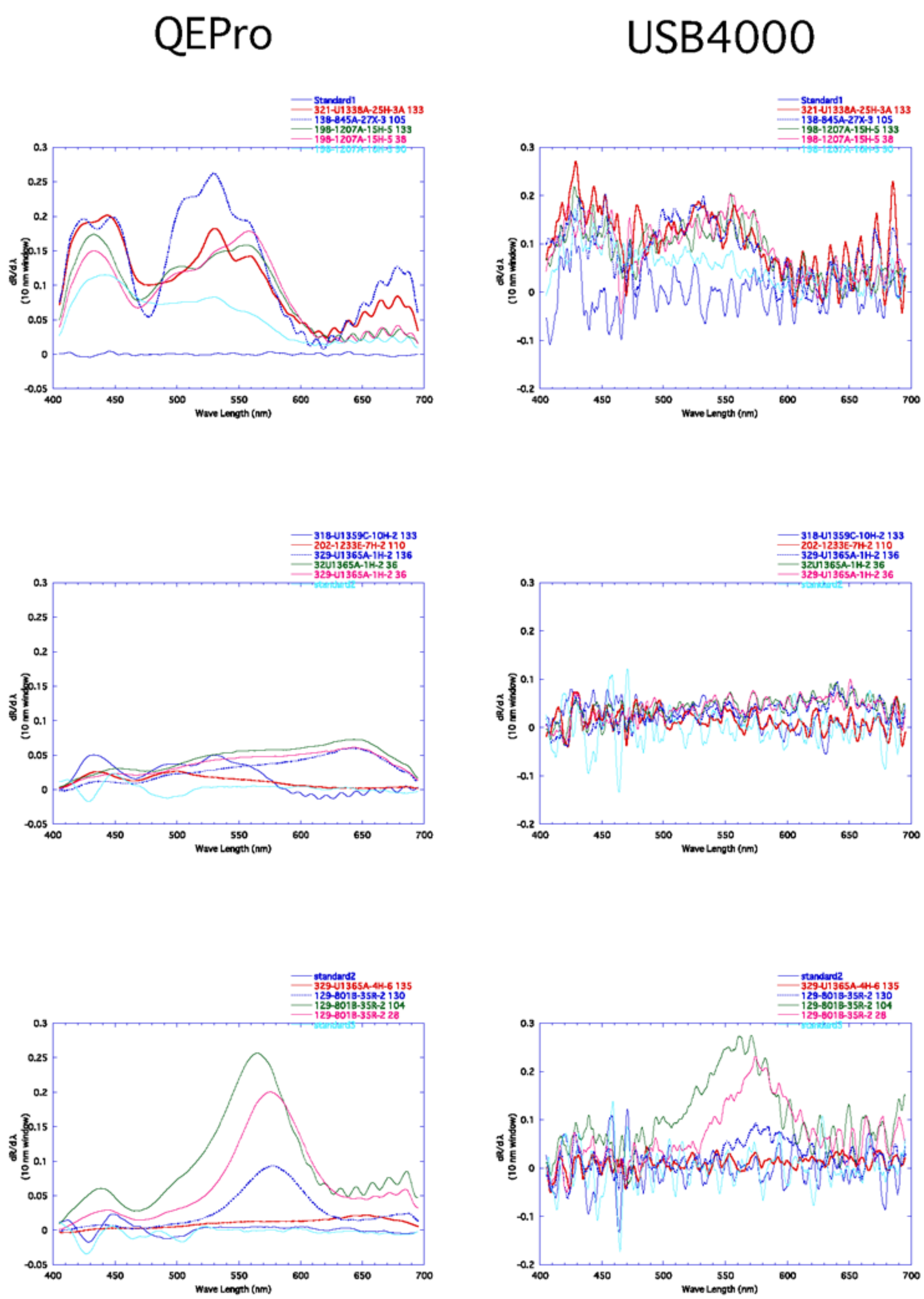

Fig. 4. Comparison of first derivative performance between QE Pro and USB4000 spectrometers; USB4000 data are smoothed on a 20-nm running average and QE Pro is unsmoothed. First derivative is defined as slope using 10 nm window. Note that the mineral peaks are still visible.

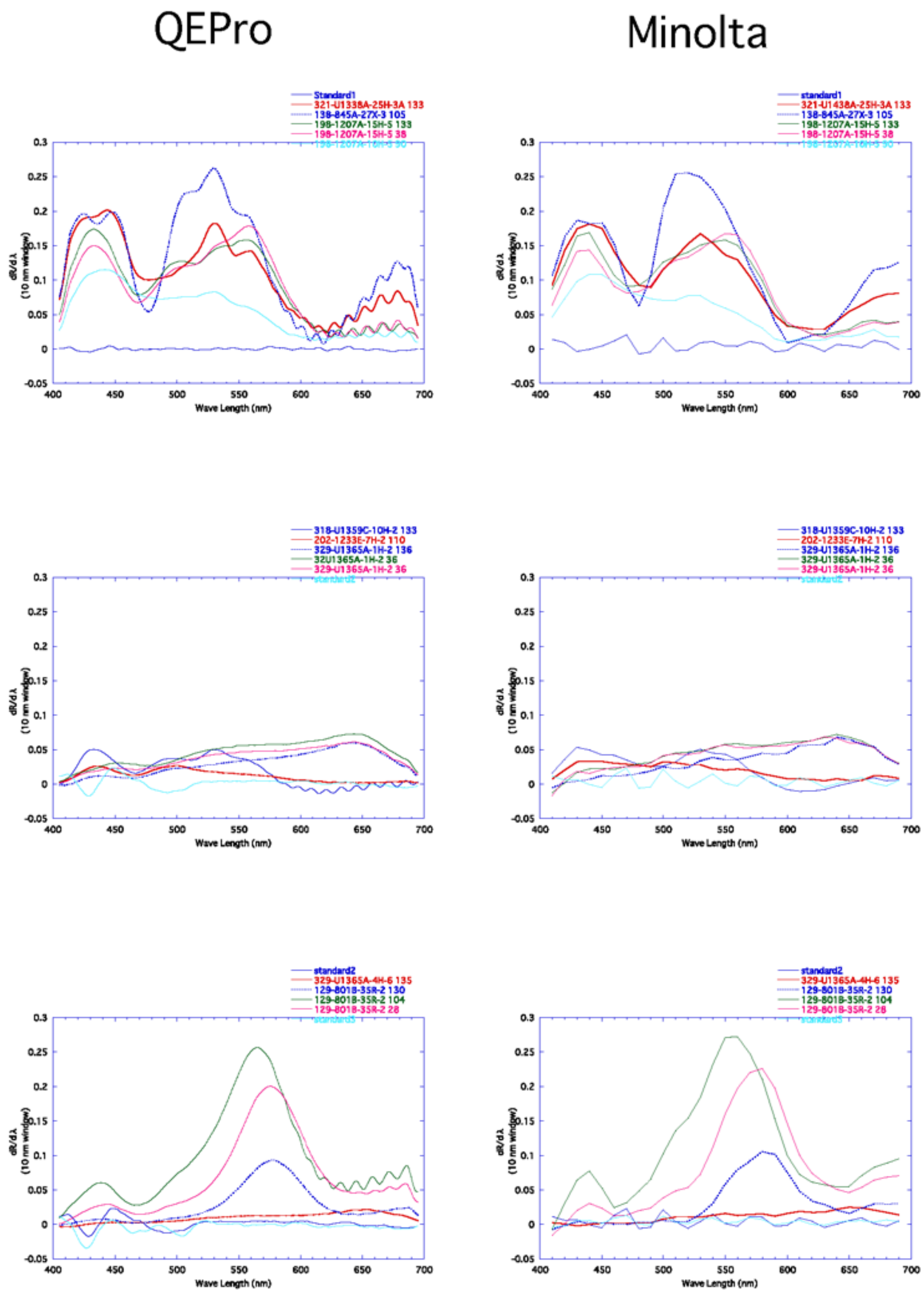

Fig. 5. Comparison of first-derivative spectra for the QE Pro and Minolta (no smoothing). First derivative is defined as slope of 10 nm window.

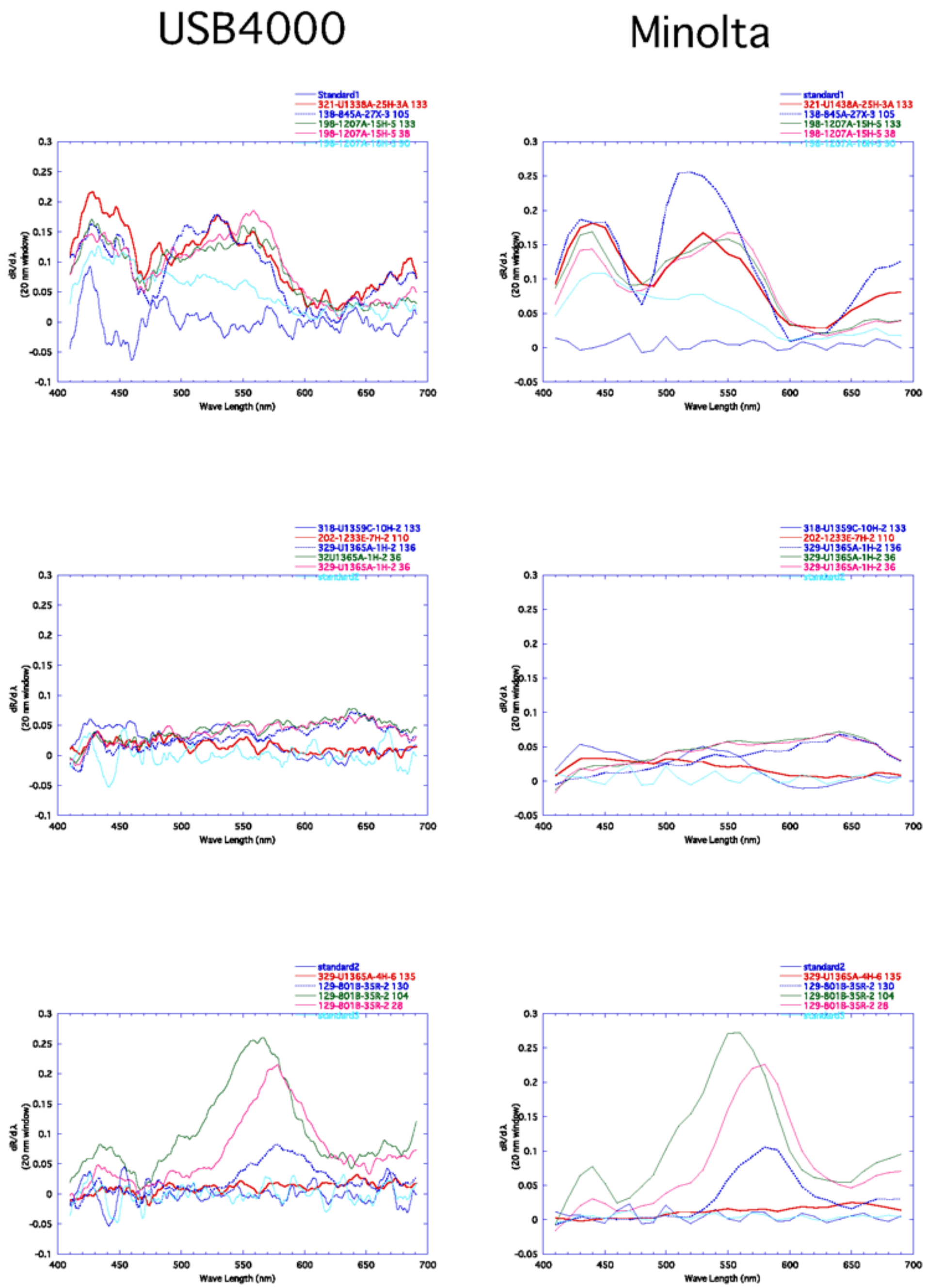

Fig. 6. First derivative spectra with a smoothing window of 20 nm for USB4000 and compared with Minolta (unsmoothed) data.

Problems with the Fiber-Optic Cables

During the experiments, the Ocean Optics systems appeared to perform extremely poorly (high degree of drift from standard value). This was traced to bending of the armored fiber cables to a tighter radius than that allowed by the design. The experiments were continued without putting undue stress on the cables with much better results: on the JR, the fiber cables are protected from this sort of stress.

Thin Film Interference Detected

A well-documented phenomenon in optical films is that they create an interference spectrum. The existence of this interference became apparent upon the evaluation of the higher-resolution, lower-background noise QE Pro. The Minolta does not have the resolution to detect this interference, and the USB4000 is too noisy to see it clearly, although both are clearly affected in the same manner. It will be important to educate users of the spectral data of the existence and unavoidable source of this interference.

In hindsight, we looked at USB4000 data acquired after late 2015 and the effect of the thin film interference is plainly evident as well, now that the spectral quality is improved by the BLULOOP/halogen dual light source. Prior to the advent of the BLULOOP on the JR, the interference was buried in the noise.

Thin film interference is exhibited throughout the visible spectrum, but is most obvious between 600 and 700 nm. This can be seen in several of the spectra in Figures 4 and 5 as a 10-nm sinusoidal wave function.

The effect of the required plastic film has been an issue since the start of diffuse color measurements during ODP, and it would be beneficial to remove the film from the setup. However, we are not likely to implement a non-contact method anytime soon. Therefore, removal of some of the plastic film effect by filtering out the thin film interference could convince users that we have significant control over the plastic film effect. However, such filtering will not overcome particularly noisy features and is likely to create a biasing effect from the filtering technique itself.

Recommendations

The JRSO should:

1. Implement the QE Pro as soon as practical;
2. Maintain the presence of the Minolta CM-2002 on board the JR to assist in the assessment of data quality; should both existing Minoltas fail, replace with modern model;
3. Make appropriate color cards (with flat surfaces) available to scientists to help assure quality of color measurement (e.g., QP cards, an inventory item in the physical properties lab so access is easy);
4. Change the nomenclature of “normalized” spectra to “percent reflectance,” as the terminology was confusing to the workshop attendees and is likely to be so for future users;
5. Save raw spectral data without averaging or binning at full resolution of detector as measurement files;
6. Parse 2 nm-binned spectral data into LIMS instead of in auxiliary files;
7. Add another LIMS Report to provide spectral data (cf. JANUS color report), “standard+spectra”;
8. Calculate RGB data from the XYZ data and parse that into LIMS as well;
9. Add RGB data to standard LIMS Report and the standard+spectra LIMS Report;
10. If practical, create a report that compares RGB from the SHMSL to RGB from the SHIL;
11. Continue to monitor surface contact and ensure it is as close to perfect as possible;
12. Continue research into methods to overcome the interference and spectral shift from the use of GLAD Wrap™, including but not limited to non-contact techniques or new optical film
13. Correct LIMS and SHMSL errors found during workshop[1]

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[1] Spectral files in LIMS are not being stored correctly (e.g., normalized and raw spectral ASMAN links both produce a normalized spectral file [raw spectral file is missing]); may also require fixing SHMSL code