

# **Reduction of Absorption Spectra for NIR-SWIR Absorbing Dyes Using Critical Feature Identification and Projection**

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<b>14. ABSTRACT</b>  This study describes a reduction of absorption spectra for NIR-SWIR absorbing dyes on cotton-fabric substrates for critical feature isolation and projection. The critical features are identified through a structural analysis of the peaks, troughs, and points of inflection in the calculated Kubelka-Munk absorption spectra from diffuse reflectance measurements. These features are then parameterized and projected into a reduced feature subspace to effectively capture the fundamental characteristics of the absorbing dyes. The critical feature parameterization and projection supports construction of parametric models capable of estimating dielectric functions for various dyes, substrates, and mixtures.						
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## Table of Contents

1. Introduction.....	1
2. Kramers-Kronig Analysis of Diffuse Reflectance Spectra .....	1
3. Spectral Reduction and Critical Feature Projection.....	2
4. Case-Study Analysis .....	4
5. Aspects of Analysis.....	16
6. Kramers-Kronig Case-Study Analysis.....	17
7. Conclusion .....	23
8. Acknowledgements.....	24
9. References.....	24

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## 1. Introduction

This study describes inverse spectral analysis of diffuse reflectance from NIR-SWIR absorbing dyes on cotton-fabric substrates for the estimation of dielectric response functions [1]. The calculated functions provide dielectric-response characteristics of the dyes and information on the sensitivity of their interactions with substrates. Inverse spectral analysis is based reduction of absorption spectra for critical feature isolation and projection. The critical features are identified through structural analysis of the peaks, troughs, and points of inflection in the calculated Kubelka-Munk absorption spectra from diffuse reflectance measurement [2-5]. These features are then parameterized and projected into a reduced feature subspace to effectively capture the fundamental characteristics of the absorbing dyes. The critical feature parameterization and projection supports construction of parametric models capable of estimating dielectric functions for various dyes, substrates, and mixtures. The IR-absorbing dyes considered in this study are characterized by robust spectral features, whose inverse spectral analysis demonstrate the concept, as emphasized by reference [6], of applying Kramers-Kronig analysis to diffuse reflectance, which has significant practical value with respect to reduced effort for sample preparation (for spectroscopic analysis).

## 2. Kramers-Kronig Analysis of Diffuse Reflectance Spectra

The Kramers-Kronig analysis provides an estimation of dielectric responses using diffuse reflectance from materials on substrates and their absorption functions obtained using inverse-analysis. For this analysis, normalized extinction functions  $\langle\alpha_N(\lambda)\rangle$  are determined by inverse spectral analysis of diffuse-reflectance spectra using the Kubelka-Munk model, i.e.,

$$\langle\alpha_N(\lambda)\rangle = \frac{f_{KM}(\lambda)}{\max[f_{KM}(\lambda)]} \quad (Eq. 1)$$

and

$$f_{KM}(\lambda) = \frac{(1 - R_n(\lambda))^2}{2R_n(\lambda)}. \quad (Eq. 2)$$

where  $R_n$  is the normalized reflectance relative to background, e.g., substrate. Before proceeding, it should be noted that the inversion procedure defined by Eqs. (1) and (2) has a specific sensitivity property with respect to NIR-SWIR absorbing dyes, and accordingly, is essentially equivalent to other inversion procedures, applied to different types of spectroscopic measurements. This sensitivity property is discussed below.

Next, an imaginary index of refraction, scaled according to the normalized extinction functions  $\langle\alpha_N(\lambda)\rangle$ , is calculated by

$$\langle k_N(\lambda)\rangle = \frac{\langle\alpha_N(\lambda)\rangle\lambda}{4\pi}, \quad (Eq. 3)$$

and a real-refractive-index change, consistently scaled, is calculated by the Kramers-Kronig relation,

$$\langle\Delta n_N(\lambda)\rangle = \frac{2\lambda^2}{\pi} P \int_0^\infty \frac{\langle k_N(z)\rangle dz}{z(\lambda^2 - z^2)}. \quad (Eq. 4)$$

Note that a multiplicative factor approximates the dependence on scatterer density, and that the Kubelka-Munk function in Eq. (2) is correlated with the absorbance function. Further, we assume that the wavelength integration range of Eq. (4) is incomplete, but of sufficient expanse for estimation of the real-refractive-index change  $\langle \Delta n_N(\lambda) \rangle$ . Sensitivity with respect to this incompleteness can be quantified by extrapolation procedures at the limits of the measured spectral range.

Continuing the analysis procedure, a scaling parameter  $C_s$  represents the dependence on scatterer density, defined by

$$\alpha_s(\lambda) = C_s \langle \alpha_N(\lambda) \rangle. \quad (\text{Eq } 5)$$

Accordingly, the dependence of the complex index of refraction on scatterer density is

$$k_s(\lambda) = C_s \langle k_N(\lambda) \rangle \quad (\text{Eq } 6)$$

and

$$n_s(\lambda) = n_0 + C_s \langle \Delta n_N(\lambda) \rangle. \quad (\text{Eq } 7)$$

Numerical integration of Eq. (4) uses methods described in references [7-9] and references therein. Our spectral-reduction procedure entails decomposition of  $\langle \alpha_N(\lambda) \rangle$  in terms of reduced basis-function expansions, consisting of Lorentzian functions, and thus integration defined by Eq.(4) is performed analytically, by Hilbert transformation of analytic functions. Accordingly, letting

$$\langle \alpha_N(\lambda) \rangle = \lambda \sum_{k=1}^{N_k} \left( \frac{A_k}{\lambda_k} \right) \frac{(\gamma_k/2)^2}{(\lambda - \lambda_k)^2 + (\gamma_k/2)^2}, \quad (\text{Eq. } 8)$$

it follows that

$$\langle k_N(\lambda) \rangle = \frac{\lambda^2}{4\pi} \sum_{k=1}^{N_k} \left( \frac{A_k}{\lambda_k} \right) \frac{(\gamma_k/2)^2}{(\lambda - \lambda_k)^2 + (\gamma_k/2)^2} \quad (\text{Eq. } 9)$$

and

$$\langle \Delta n_N(\lambda) \rangle = \frac{\lambda^2}{4\pi} \sum_{k=1}^{N_k} \left( \frac{A_k}{\lambda_k} \right) \frac{(\gamma_k/2)(\lambda - \lambda_k)}{(\lambda - \lambda_k)^2 + (\gamma_k/2)^2}. \quad (\text{Eq. } 10)$$

### 3. Spectral Reduction and Critical Feature Projection

The key features of the dyes, including their absorption peaks and troughs, can be characterized within a dimensionally reduced space using concepts from principle-component analysis (PCA) [10]. This method allows the full spectral data to be projected into a smaller subspace of spectral components while still maintaining the essence of the critical features – such as the peak wavelengths, peak heights, and inflection points.

The projection is obtained by first convoluting a finite impulse response over causal discrete wavelengths with the full spectral input signal. The coefficient of the impulse response filter corresponds to the amplitude of the normalized absorption peak at the discrete wavelength of the local maxima (Eq. 11). The feature analysis also captures a similar convolution vector for the peak widths at half-height. In this case the filter coefficients correspond to the half-height full-width of

the peak at the discrete wavelength of the local maxima (Eq. 12). For both convolutions, filter coefficients of zero are applied to any non-peak location.

$$p[\lambda] = a_0x[\lambda_0] + a_1x[\lambda_1] + \dots + a_Nx[\lambda_N] \quad (\text{Eq. 11})$$

$$w[\lambda] = b_0x[\lambda_0] + b_1x[\lambda_1] + \dots + b_Nx[\lambda_N] \quad (\text{Eq. 12})$$

In this case, for each local peak identified within the spectra at  $x[\lambda_i]$  the coefficient  $a_i$  represents the peak amplitude and the coefficient  $b_i$  represents the half-height full-width.

This effectively projects the dye's absorption peak characteristics into a reduced subspace, consisting of only three vectors for the critical feature components: peak wavelengths, peak amplitudes, and peak half-height full-widths.

It is important to note, that these peaks are not necessarily easily identifiable as the local maxima within the calculated absorption function, as the fundamental peaks interact with each other, such that the characteristic peaks may not always align in wavelength with a peak in amplitude. To address this issue, the following steps were followed.

1. Applied an automatic algorithm for initial peak detections based on amplitude – such that the local peak is larger than its two neighbors. Variable median smoothing and minimum thresholds in both wavelength separation and absorption amplitude, were applied to avoid minor/measurement fluctuations. This analysis returns vectors for the local maxima across the spectral wavelengths, which includes the wavelength locations, the peak amplitudes, and the approximated half-height full-width.
2. Manually added and adjusted peaks to ensure the critical absorption features are sufficiently captured within the peak dataset. This included accounting for “hidden” peaks that do not present themselves as local maxima locations.
3. Verified peak selection with a Lorentzian analysis to ensure critical absorption behavior – including inflection points and peak/trough locations - is accurately captured. The Lorentzian analysis involved projecting all peak parameters using a Lorentzian curve (Eq. 13), constructively summing their interactions, and comparing to the original absorption spectra for additional tuning.

$$L_p[\lambda] = p[\lambda_p] \cdot \frac{1}{\pi} \frac{\frac{\Gamma_p}{2}}{(\lambda - \lambda_p)^2 + \left(\frac{\Gamma_p}{2}\right)^2} \quad (\text{Eq. 13})$$

$$y_{sub}[\lambda] = \sum_{p=1}^P L_p[\lambda] \quad (\text{Eq. 14})$$

The Lorentzian equation for each critical feature (Eq. 3) includes the amplitude of the peak,  $p[\lambda_p]$ , and the half-height full-width of the peak,  $\Gamma_p$ .  $\lambda_p$  corresponds to the wavelength location of the peak feature. The individual Lorentzian functions for all  $P$  critical features identified within the spectra are then combined to form a new projected subspace of absorption spectra (Eq. 14).

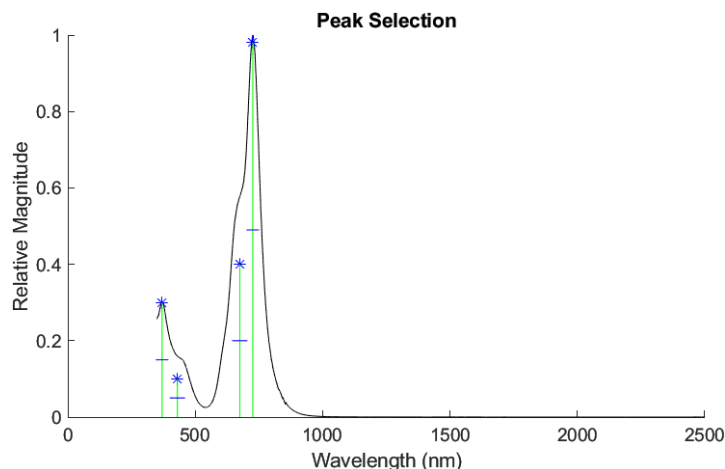
The characterization of the complex absorption behavior within simplified critical feature vectors can support further analysis of the key absorption characteristics and the potential dye mixture interactions. Additionally, this simplified parametric subspace can support the construction of approximate effective medium models capable of estimating reflectance from dyed fabrics.

#### 4. Case-Study Analysis

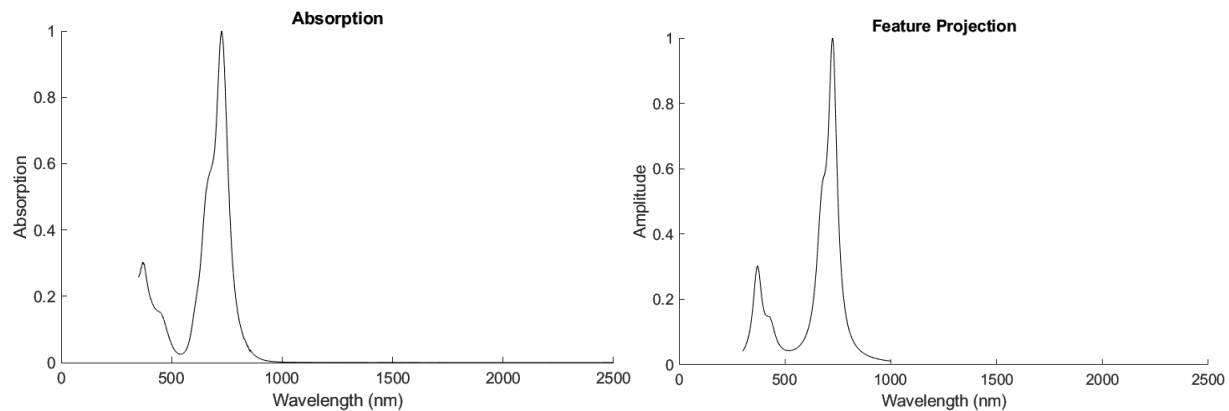
The critical feature isolation and projection was performed for 12 NIR-SWIR absorbing COTS dyes. The results from this analysis establish a proof of concept for the spectral reduction of fundamental material properties, which can support the characterization of future prediction models.

The dyes chosen for analysis have maximum-absorption wavelengths in either the NIR or SWIR bands, with appreciable spectral features extending into the visible spectrum. Reference [11] describes the procedures used for dye and dyed-fabric sample preparation, and reflectance-spectrum measurements of dyed fabric samples. For this study, these dyes are designated according to their maximum absorption wavelengths, using the designation “KM-Maximum-Absorption-Wavelength,” similar to references [12,13], where chemical formulae for these dyes are given. For each of these results, the absorption spectra was calculated from diffuse reflectance measurements using the normalized Kubelka-Munk inverse analysis method.

#### KM-720



**Figure 1:** KM-720 absorption spectra and peak characterization.

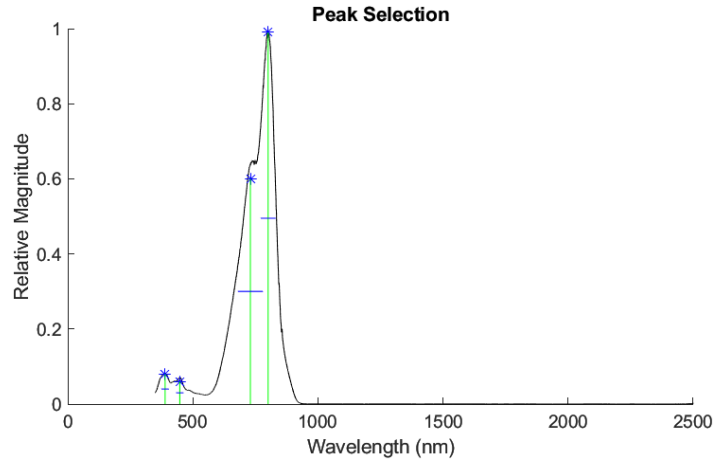


**Figure 2:** KM-720 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

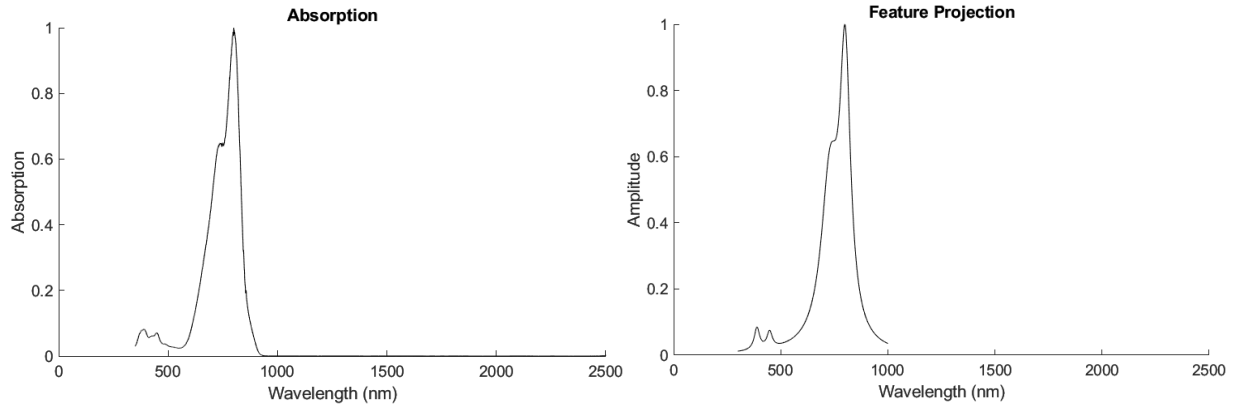
**Table 1:** KM-720 Critical Peak Parameters

<b>Wavelength</b>	<b>Peak Amplitude</b>	<b>Full-Width Half-Height</b>
370	0.30	50
430	0.10	60
675	0.40	60
726	0.98	50

**KM-775**



**Figure 3:** KM-775 absorption spectra and peak characterization.

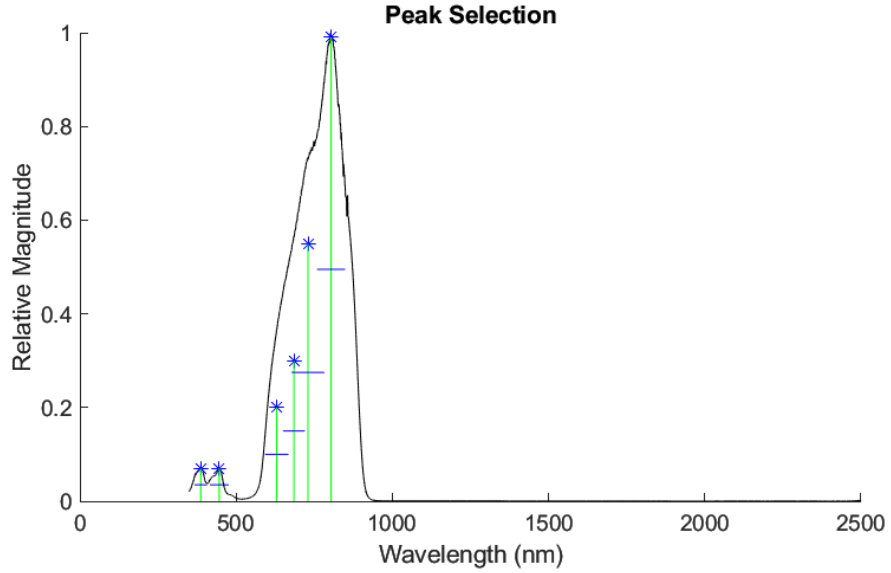


**Figure 4:** KM-775 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

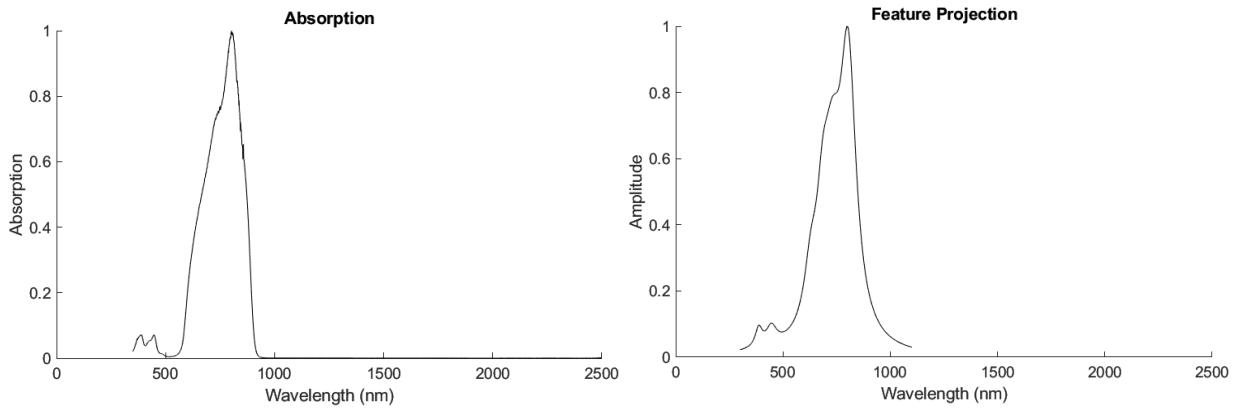
**Table 2:** KM-775 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
389	0.08	30
448	0.06	30
730	0.60	100
801	0.99	60

# KM-778



**Figure 5:** KM-778 absorption spectra and peak characterization.

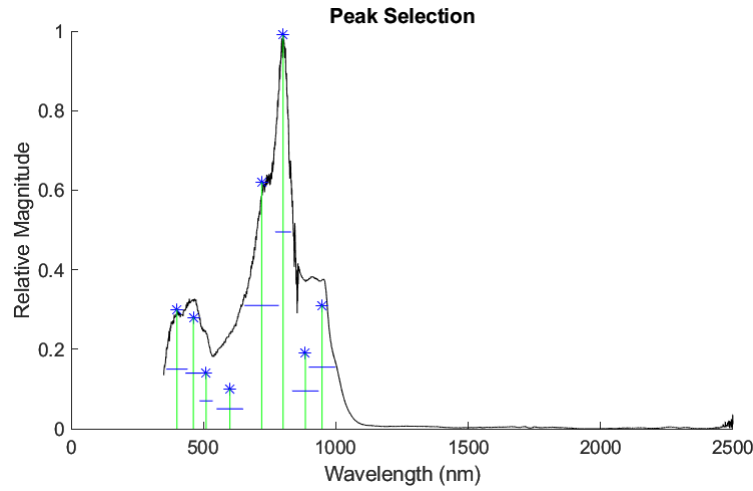


**Figure 6:** KM-778 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

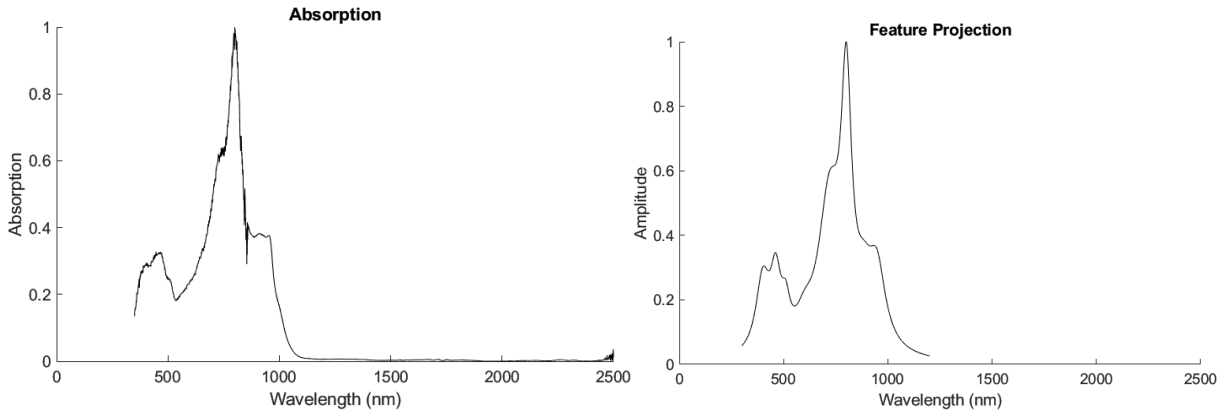
**Table 3:** KM-778 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
387	0.07	40
446	0.07	60
630	0.2	75
685	0.3	70
730	0.55	105
804	0.99	90

## KM-780



**Figure 7:** KM-780 absorption spectra and peak characterization.

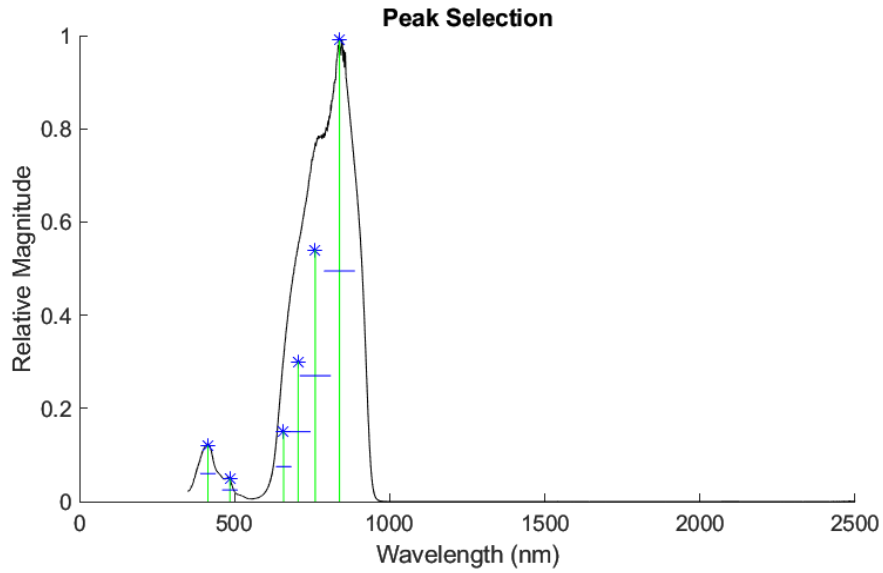


**Figure 8:** KM-780 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

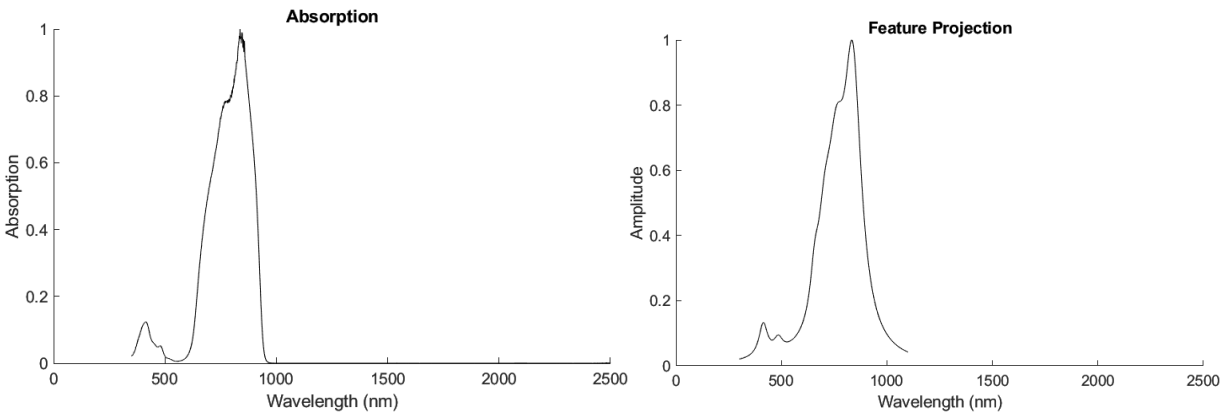
**Table 4:** KM-780 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
400	0.30	80
462	0.28	60
510	0.14	50
600	0.10	100
720	0.62	130
801	0.99	60
885	0.19	100
948	0.31	100

# KM-825



**Figure 9:** KM-825 absorption spectra and peak characterization.

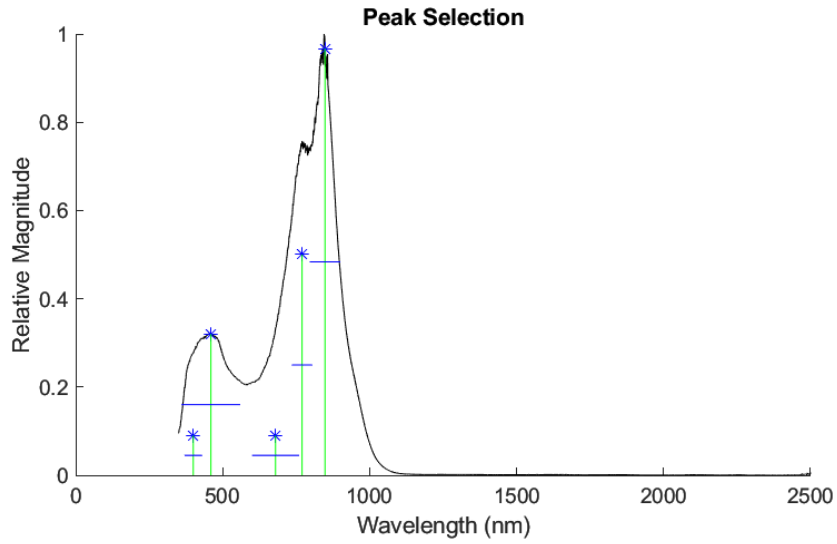


**Figure 10:** KM-825 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

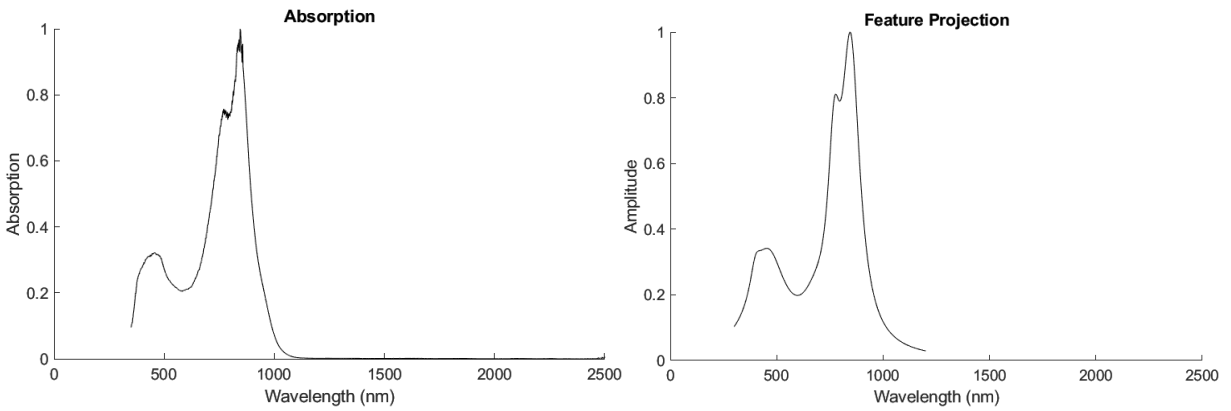
**Table 5:** KM-825 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
414	0.12	50
485	0.05	50
658	0.15	50
705	0.3	80
760	0.54	100
838	0.99	100

# KM-832



**Figure 11:** KM-832 absorption spectra and peak characterization.

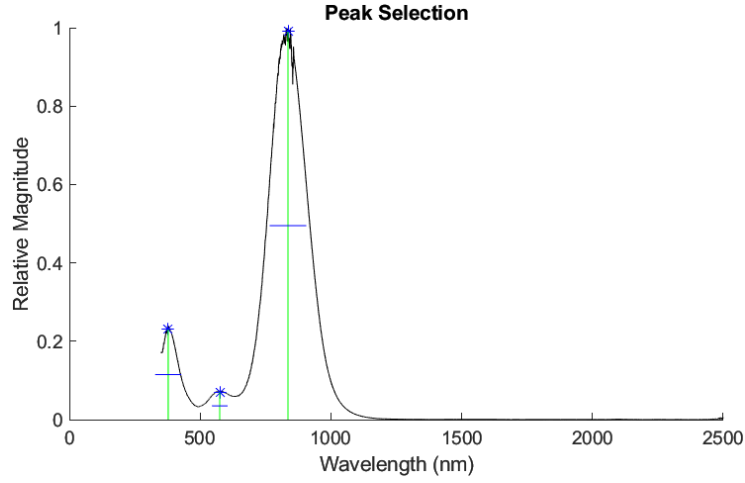


**Figure 12:** KM-832 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

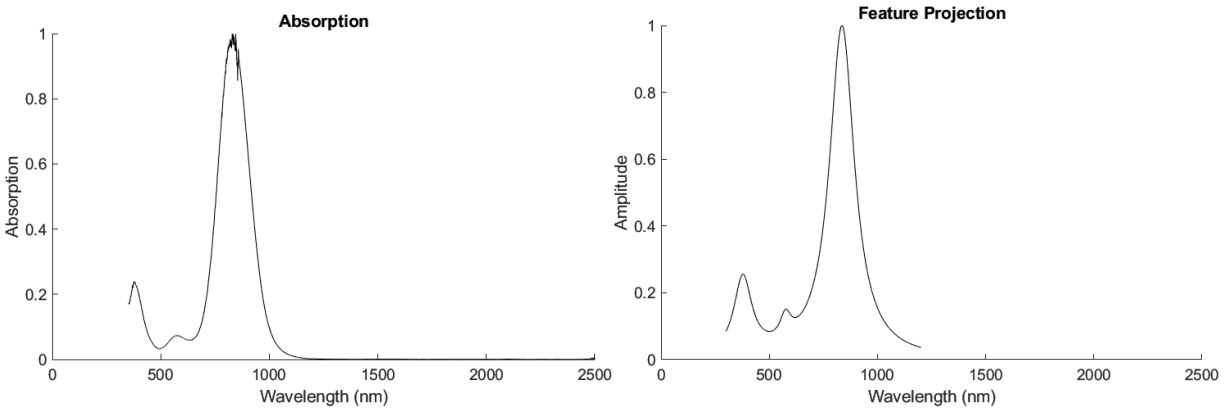
**Table 6:** KM-832 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
400	0.09	60
460	0.32	200
680	0.09	160
770	0.50	70
848	0.99	104

**KM-836**



**Figure 13:** KM-836 absorption spectra and peak characterization.

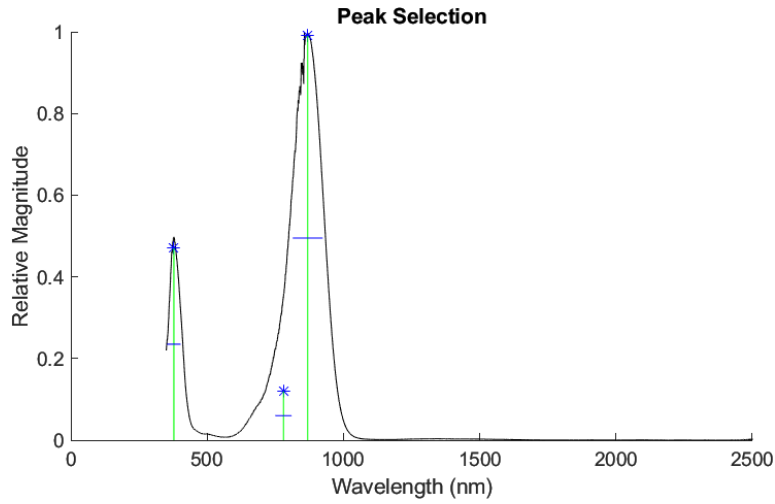


**Figure 14:** KM-836 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

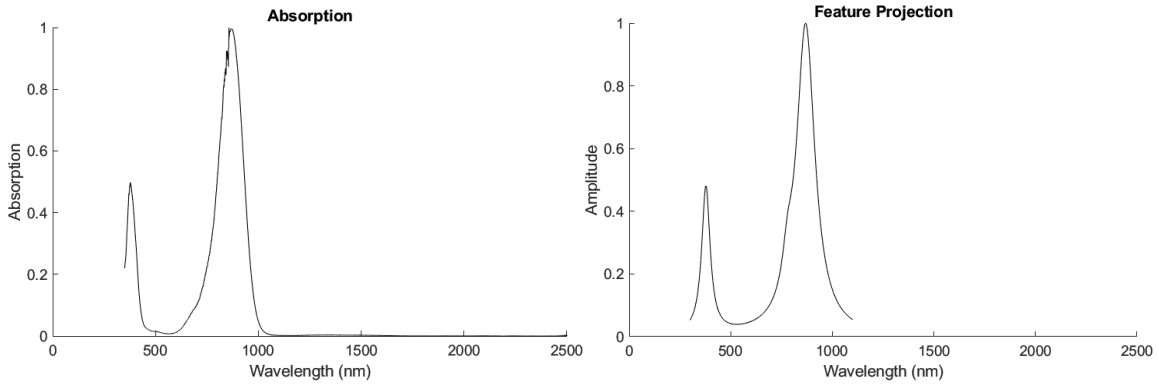
**Table 7:** KM-836 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
378	0.23	100
575	0.07	60
836	0.99	140

**KM-845**



**Figure 15:** KM-845 absorption spectra and peak characterization.

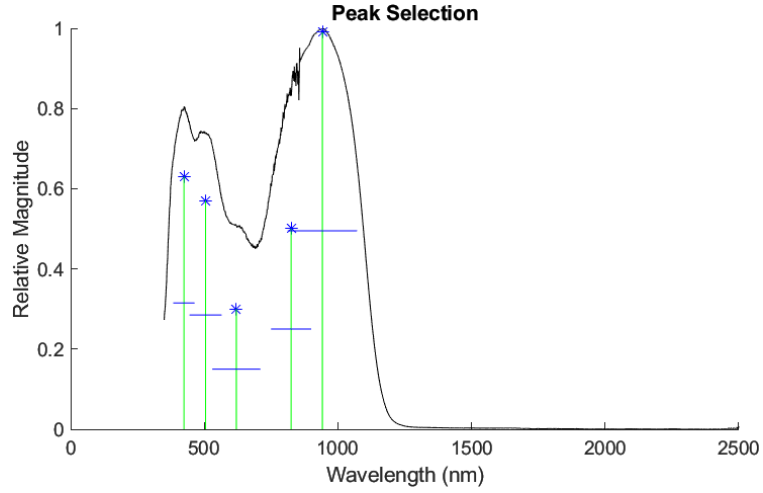


**Figure 16:** KM-845 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

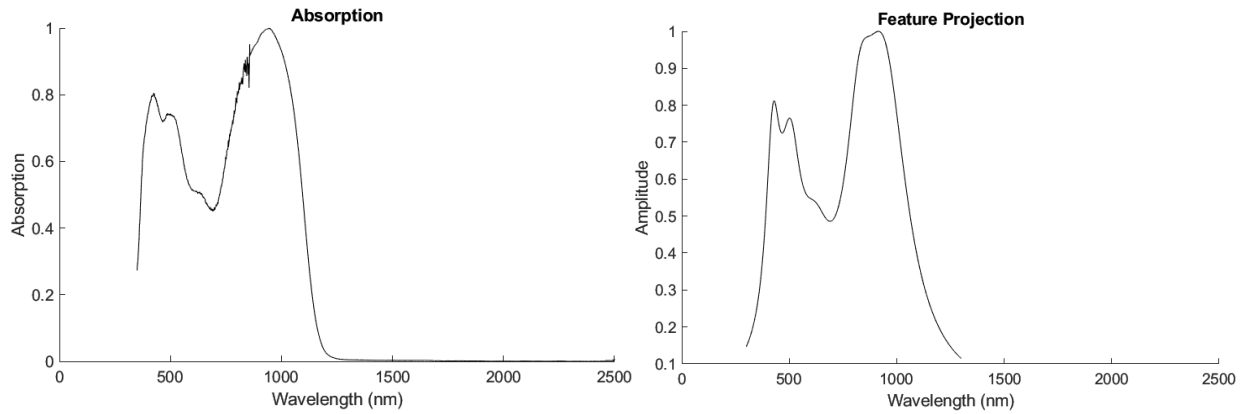
**Table 8:** KM-845 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
378	0.47	50
780	0.12	60
869	0.99	110

## KM-920



**Figure 17:** KM-920 absorption spectra and peak characterization.

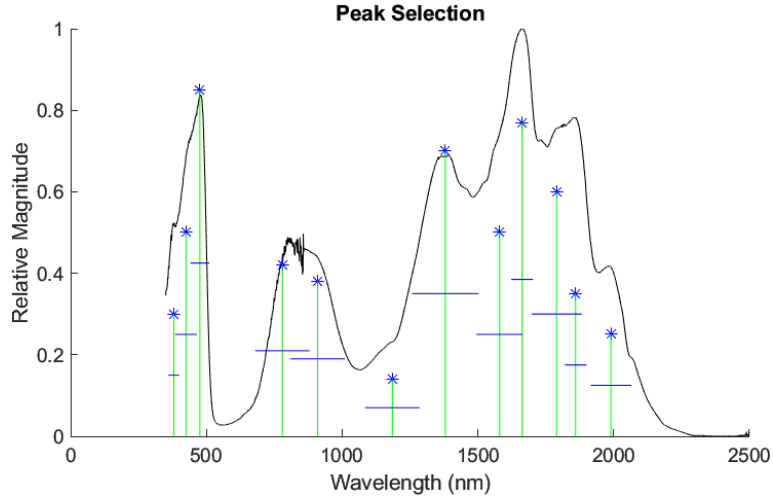


**Figure 18:** KM-920 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

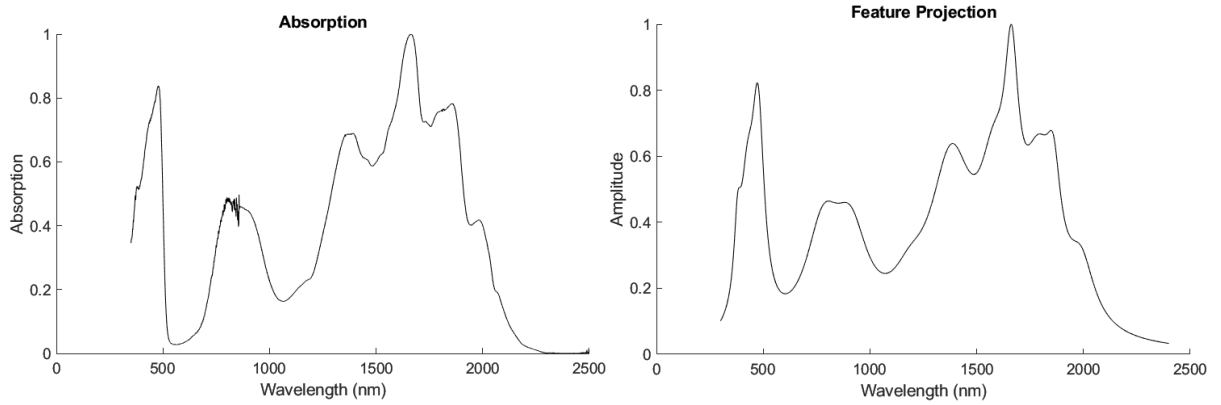
**Table 9:** KM-920 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
424	0.63	80
505	0.57	120
620	0.30	180
825	0.50	150
942	0.99	260

## KM-949



**Figure 19:** KM-949 absorption spectra and peak characterization.

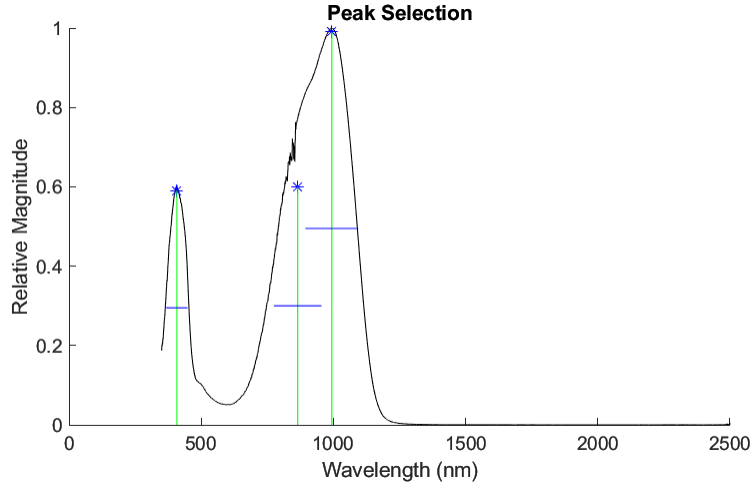


**Figure 20:** KM-949 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

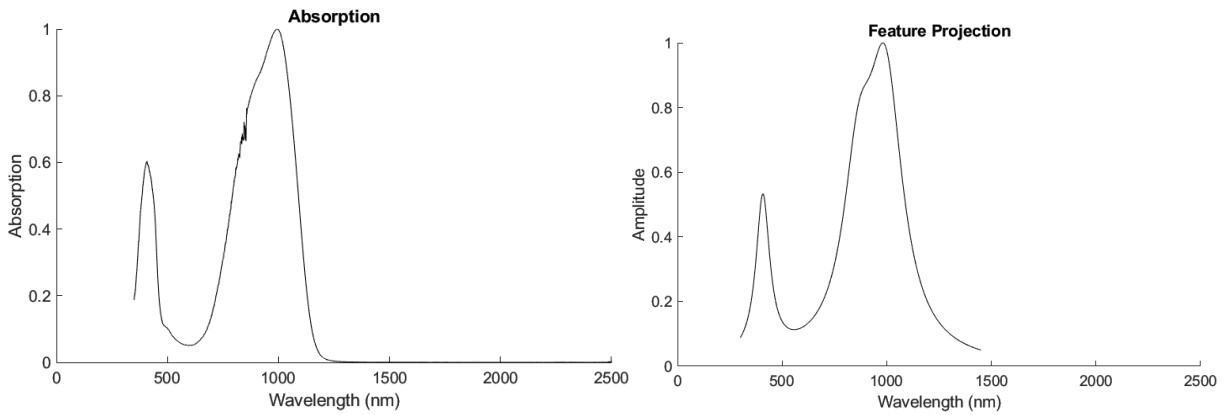
**Table 10:** KM-949 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
380	0.30	40
425	0.50	80
476	0.85	70
780	0.42	200
910	0.38	200
1185	0.14	200
1380	0.70	245
1580	0.50	170
1663	0.77	80
1790	0.60	185
1860	0.35	80
1990	0.25	150

**KM-978**



**Figure 21:** KM-978 absorption spectra and peak characterization.

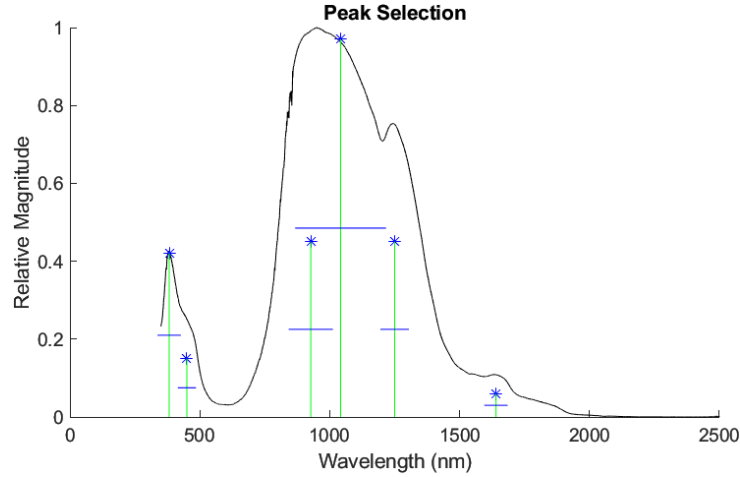


**Figure 22:** KM-978 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

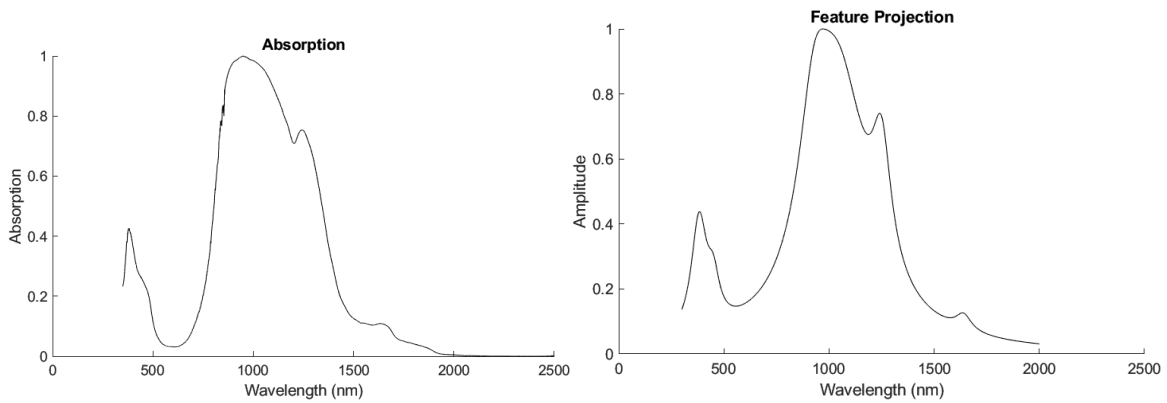
**Table 11:** KM-978 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
408	0.59	80
865	0.60	180
994	0.99	200

## KM-1072



**Figure 23:** KM-1072 absorption spectra and peak characterization.



**Figure 24:** KM-1072 comparison between the original Kubelka-Munk absorption spectra and the subspace feature projection.

**Table 12:** KM-1072 Critical Peak Parameters

Wavelength	Peak Amplitude	Full-Width Half-Height
382	0.42	90
450	0.15	70
927	0.45	170
1042	0.97	350
1250	0.45	110
1640	0.06	90

## 5. Aspects of Analysis

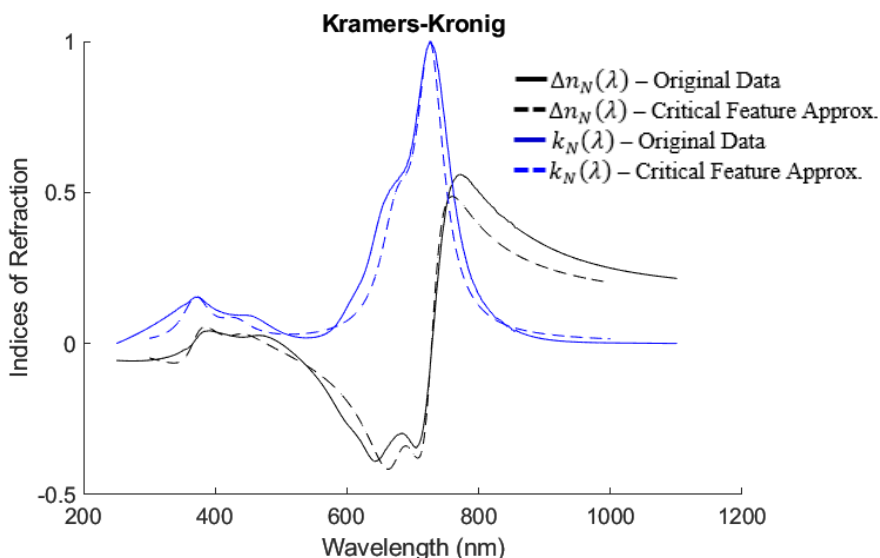
This analysis continues that of [14] by construction of reduced basis-function representations of IR absorption spectra. These constructions provide extrapolation of spectra beyond measurement ranges. As with reference [14], this analysis provided useful insight into Kramers-Kronig sensitivity with respect to incomplete measurement ranges. So long as the behavior of the

absorption data does not significantly change beyond the measurement range (i.e., no significant changes in slope), the estimated indices of refraction resulting from the Kramers-Kronig analysis can sufficiently represent the dye behavior. Additionally, reduced basis-function representations are smoothing filters for dye spectra with measurement noise, and thus prevent the noise from transferring into the Kramers-Kronig analysis.

## 6. Kramers-Kronig Case-Study Analysis

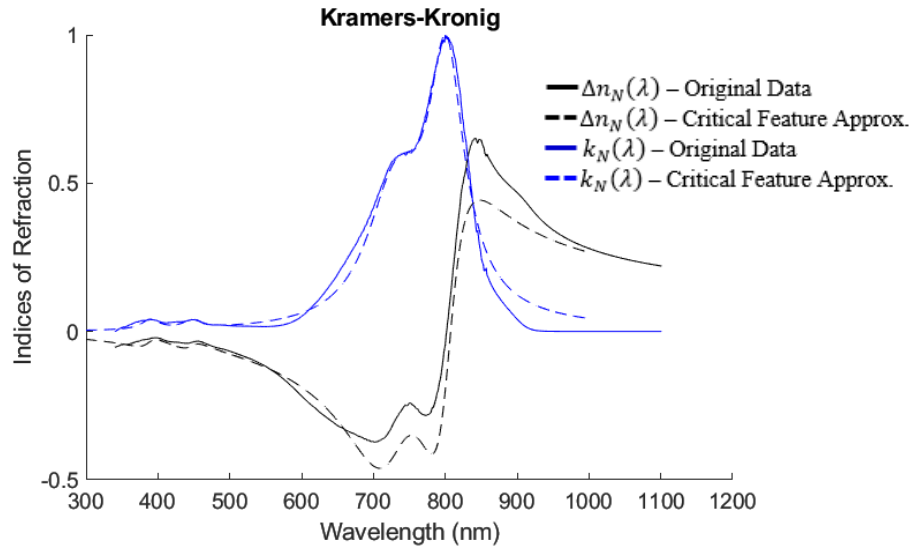
The complex indices of refraction for the reduced absorption subspaces were estimated and evaluated using Kramers-Kronig analysis (Eq. 9-10). Kramers-Kronig analysis establishes fundamental material properties that can support the characterization of the dielectric response functions. The intermediate index of refraction properties,  $\Delta n_N(\lambda)$  and  $k_N(\lambda)$ , are of particular interest, as they can be scaled – based on the scatterer density – to effectively estimate these dielectric response functions. The Kramers-Kronig results from the reduced subspace absorption were compared to the complex index of refraction for the full dataset with extrapolation, termination, and smoothing corrections, as calculated in reference [14]. The results from these comparisons are shown in Figures 25-36.

### KM-720



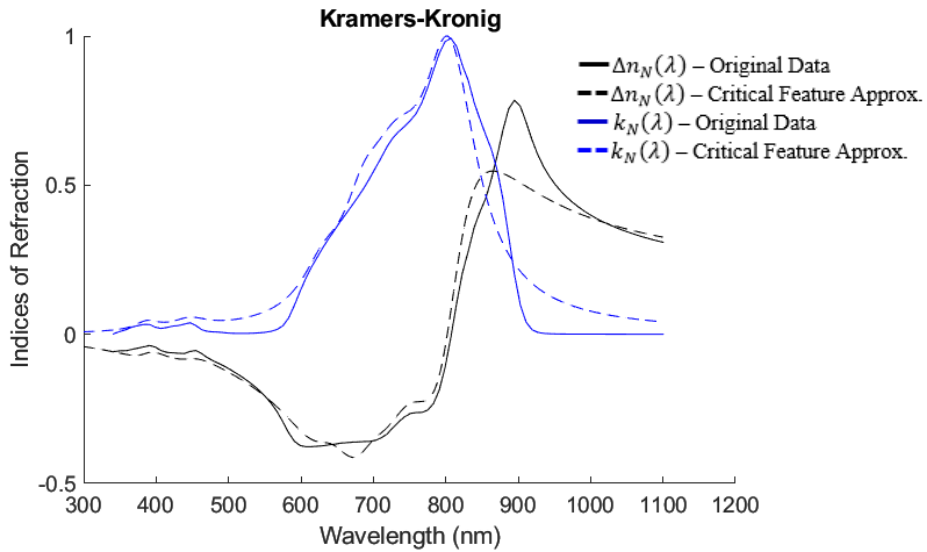
**Figure 25:** KM-720 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

### KM-775



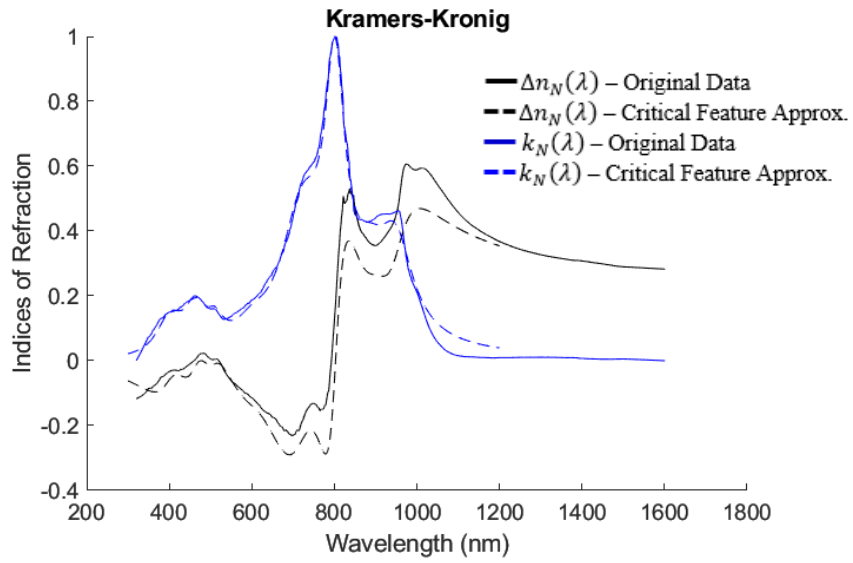
**Figure 26:** KM-775 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

### KM-778



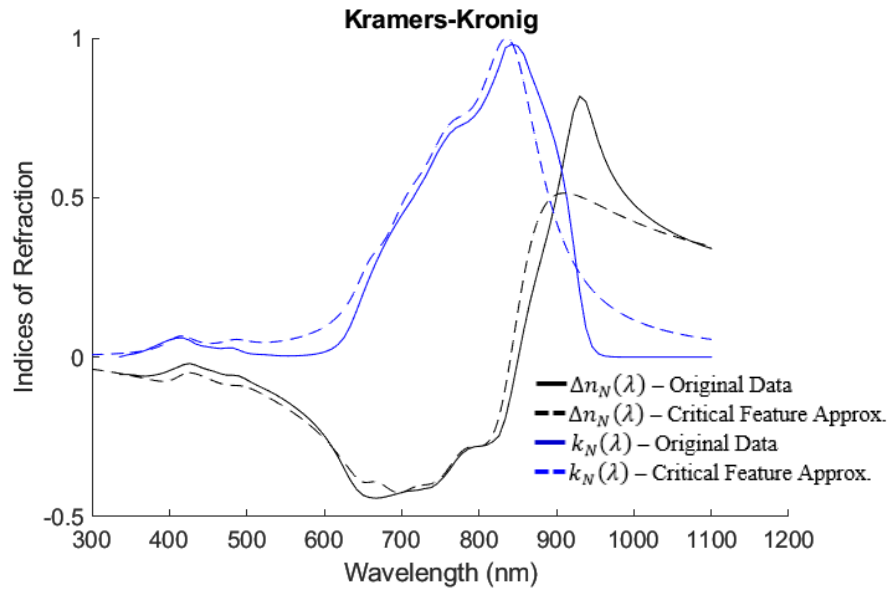
**Figure 27:** KM-778 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

### KM-780

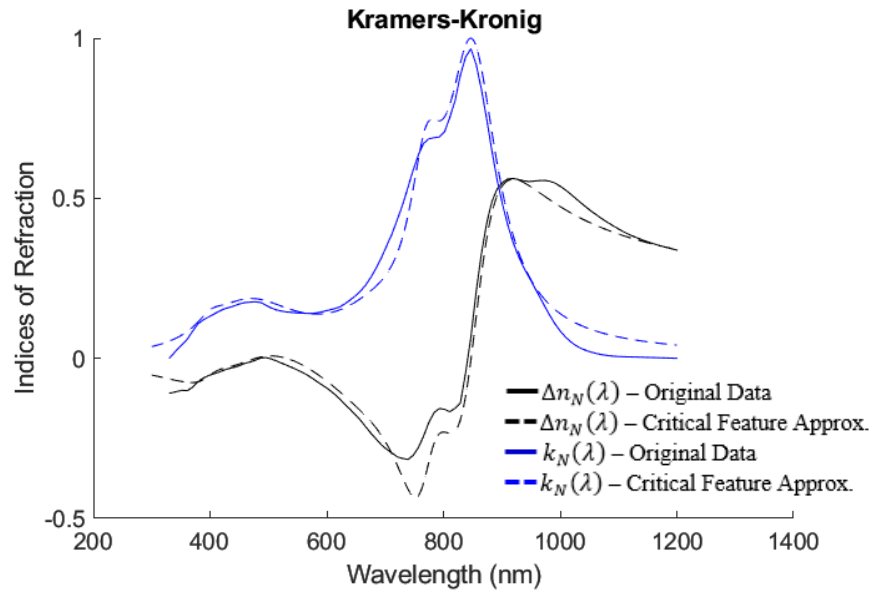


**Figure 28:** KM-780 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

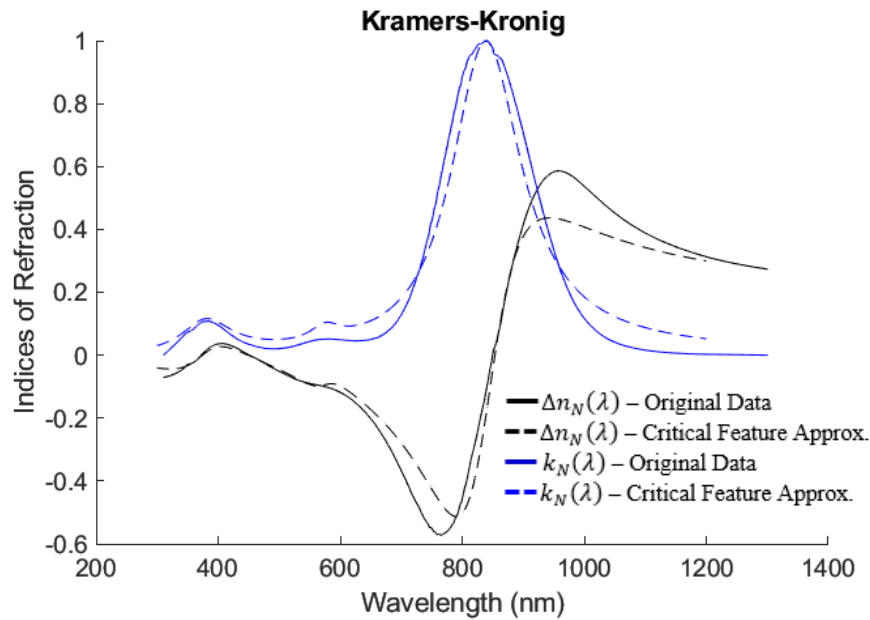
### KM-825



**Figure 29:** KM-825 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

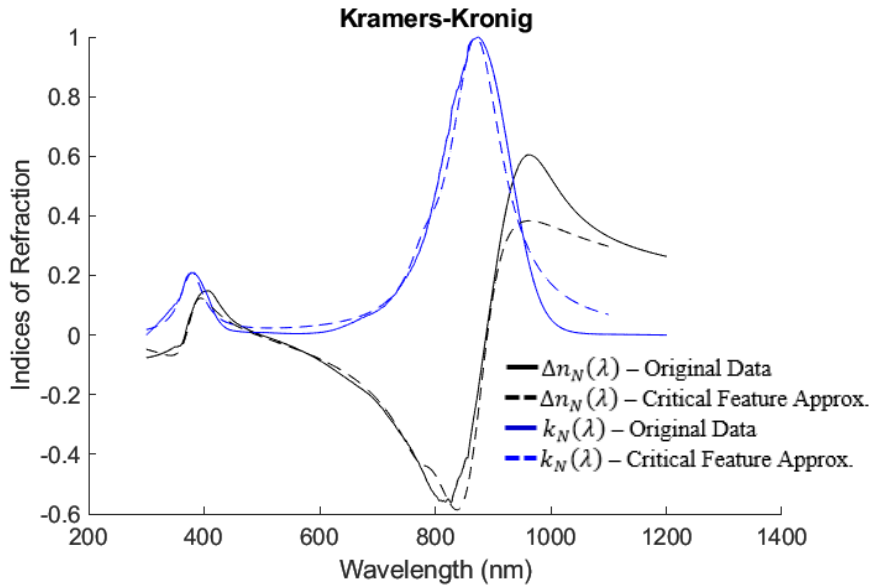
**KM-832**

**Figure 30:** KM-832 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

**KM-836**

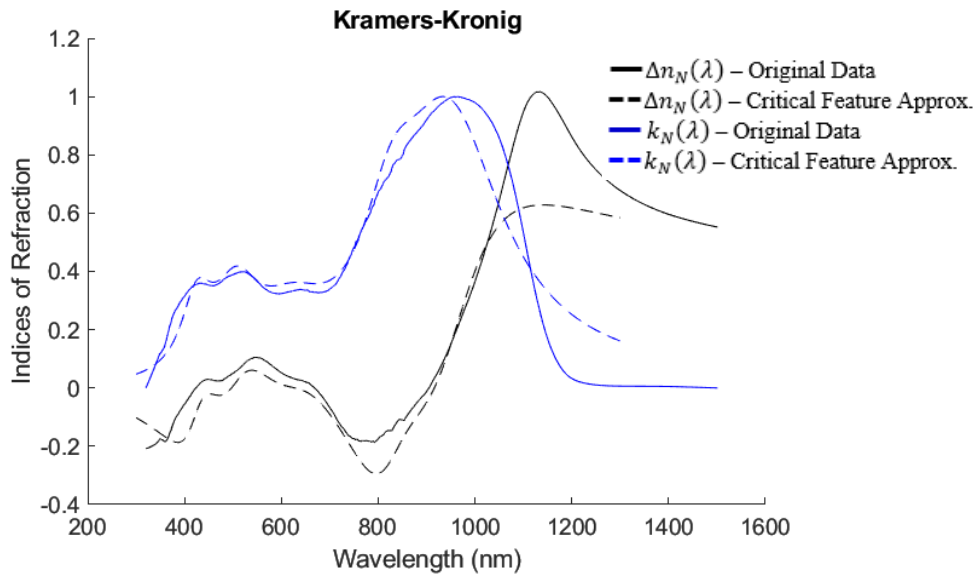
**Figure 31:** KM-836 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

### KM-845



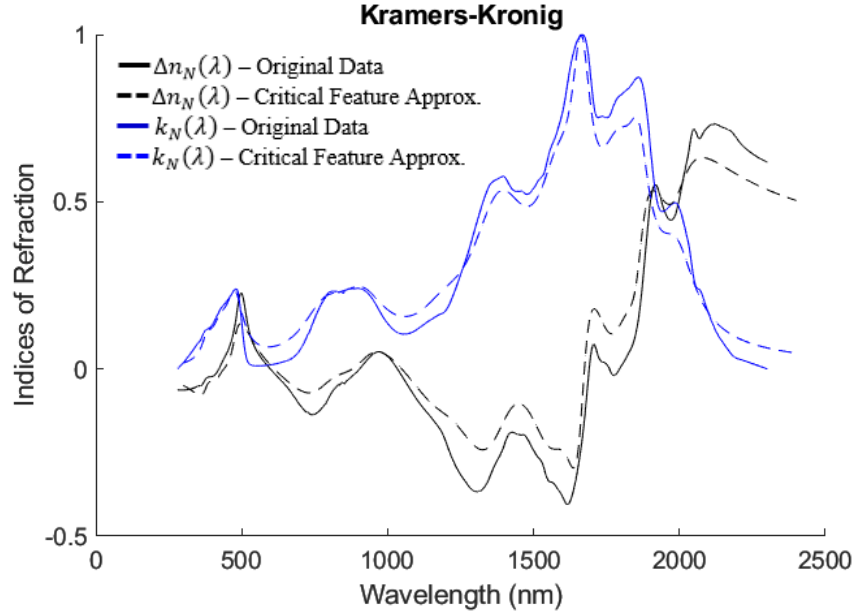
**Figure 32:** KM-845 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

### KM-920



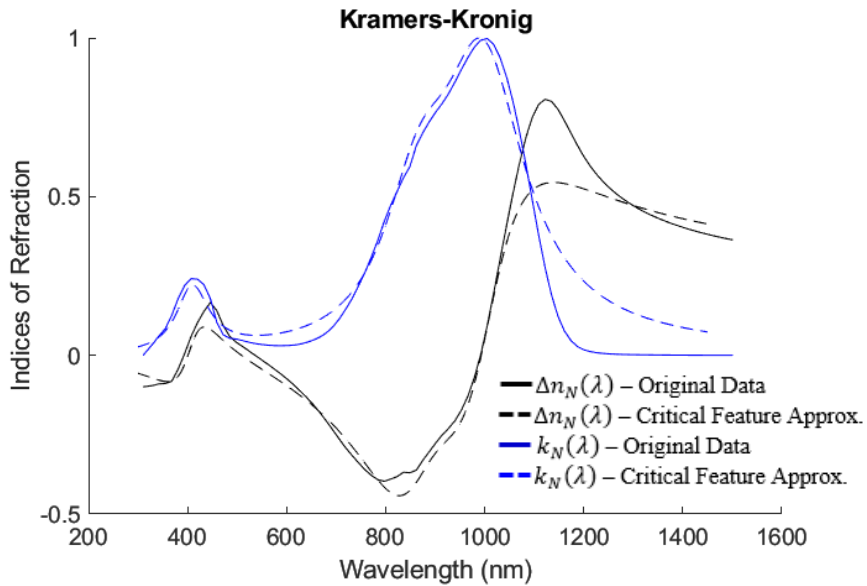
**Figure 33:** KM-920 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

### KM-949



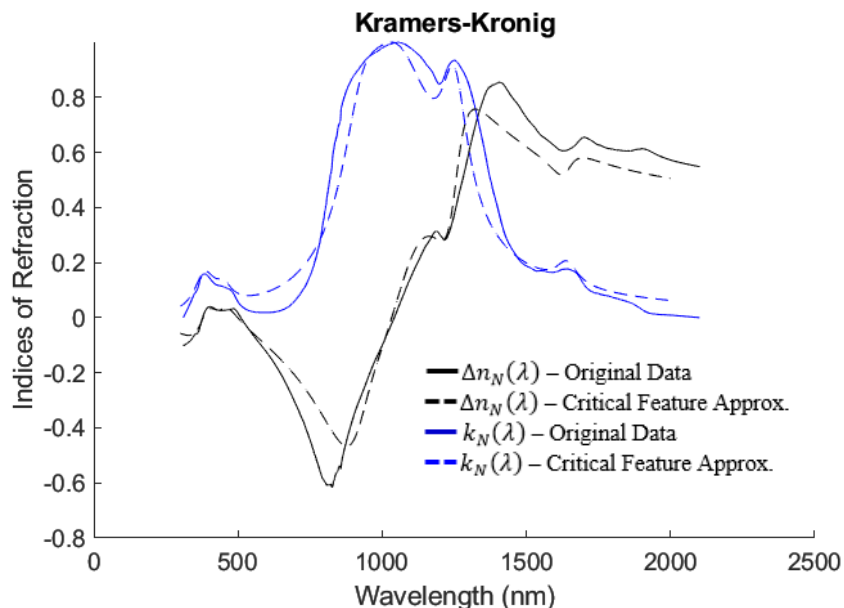
**Figure 34:** KM-949 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

### KM-978



**Figure 35:** KM-978 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

## KM-1072



**Figure 36:** KM-1072 Kramers-Kronig indices of refraction, comparing the results from the full extrapolated and smoothed KM dataset with the results from the critical feature approximation.

Figures 25-36 indicate that the absorption subspaces created from critical feature projection can capture the fundamental characteristics of the Kramers-Kronig indices of refraction, and in turn the dielectric response behavior. The Kramers-Kronig analysis of the critical feature subspace deviates some in magnitude and width from the full dataset Kramers-Kronig results; however, the critical points of interest within the Kramers-Kronig analysis – including inflection point location – remain similar.

This indicates that the underlying dielectric response characteristics can be maintained through the reduction of absorption data into a critical feature subspace. Additionally, reduced subspace datasets require no additional extrapolation, termination, or smoothing, unlike the original dataset, which is incomplete in the sense that it does not necessarily approach zero at the lower and upper wavelengths. These results support the reduction of complex measurement spectra into a significantly reduced critical feature subspace capable of maintaining dielectric response characteristics for effective-medium model analysis.

## 7. Conclusion

Determining estimates of the dielectric response of NIR/SWIR-absorbing dyes poses a specific problem. This study presents and demonstrates an inverse spectral analysis procedure for determining such estimates, which is based on reduction of absorption spectra by means of critical feature isolation and projection. The estimated dielectric response functions can be used to construct a parametric space for developing effective-medium models capable of estimating reflectance from dyed fabrics.

## Acknowledgements

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