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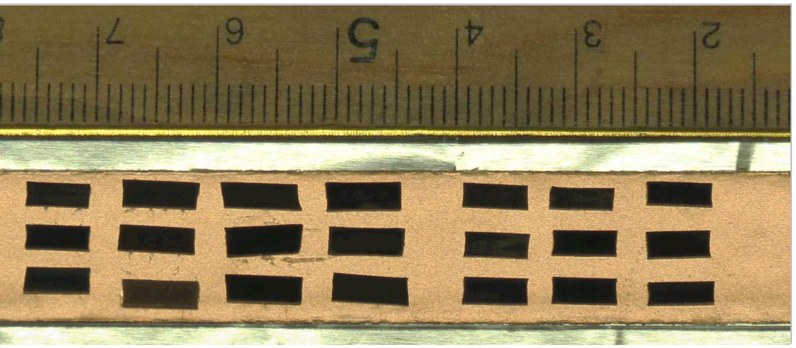

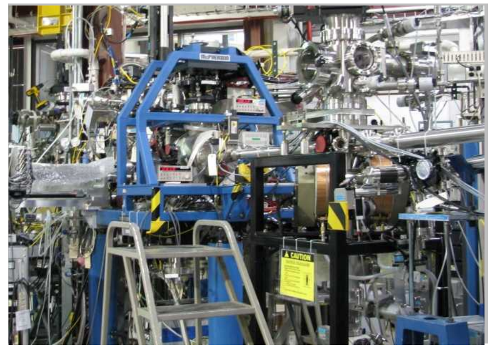

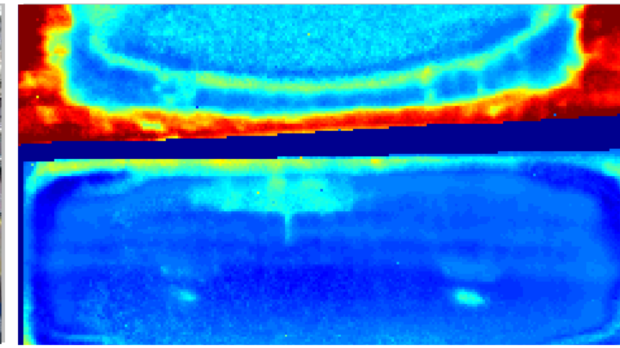

Measuring the Oxidation of Artificially Aged Elastomers with Multivariate Analysis and Imaging NEXAFS

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Sandia National Laboratories

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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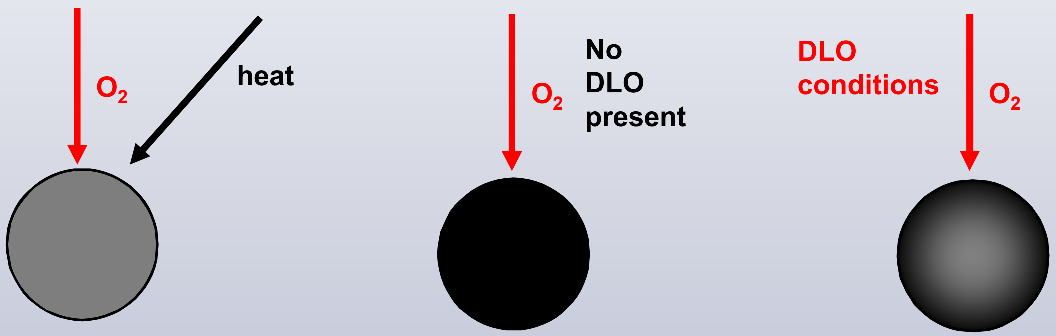
Outline

- Introduction
- NEXAFS and the Imaging Instrument
- Sample Preparation
- Multivariate Analysis
- NEXAFS Interpretation
- Data and Results
  - Filled Butyl Nitrile
  - Filled Neoprene
- Conclusions
- Acknowledgements

Elastomers age by Oxygen diffusion and reaction

- DLO: Diffusion Limited Oxidation
- Oxidation in material is faster than oxygen can diffuse into it
- Will lead to oxidation profile formation, heterogeneous degradation
- Oxidation rate (consumption) versus permeability (supply)
- Accelerated aging tests can completely misrepresent real aging

O-ring cross section



Unaged o-ring

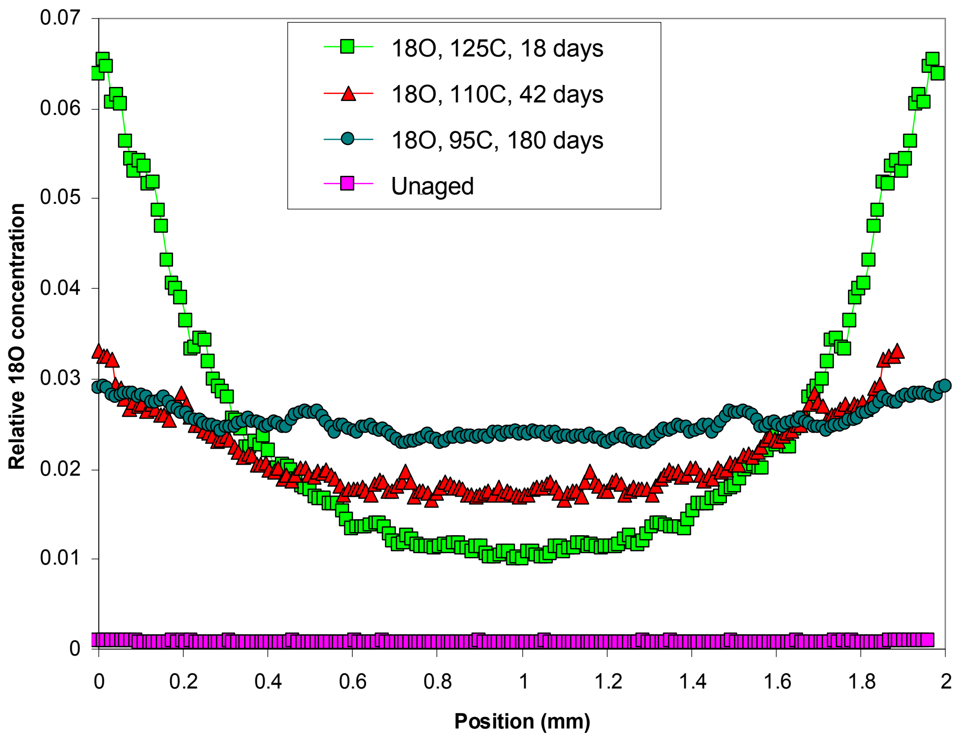
Uniform oxidation Through to bulk
Ambient slow aging
•Normal

Oxidation primarily on surface
Accelerated aging test
•Laboratory

We need a way to measure oxidation from normal (ambient slow aging) or real materials.

We have successfully measured Diffusion-Limited Oxidation using ToF-SIMS in Controlled Experiments

ToF-SIMS analysis of Filled Nitrile Aged in ^{18}O (New Oxidation)



Can we measure total oxidation of entire cross section with NEXAFS without using isotopic labeling?

Main Goal:
Develop technique to measure oxidation of real systems so that "unknowns" can be analyzed quantitatively.

Sample Preparation and Analysis

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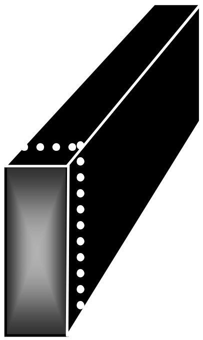
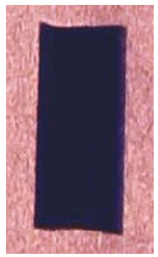
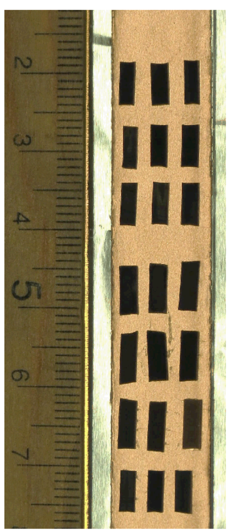
- Oxidize under controlled conditions
  - Filled Neoprene
  - Filled Butyl Nitrile
- Section Sample
  - Cleaned (remove Teflon) and sharpened razor blade
- Perform NEXAFS image analysis on entire cross section surface
- Extract region of interest (ROI) for each sample
- Create image montage for sample series
- Perform multivariate analysis
- Process data

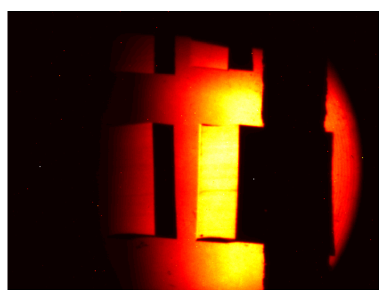




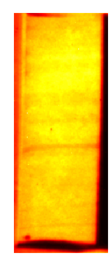
Accelerated aging: (known time and temperature)



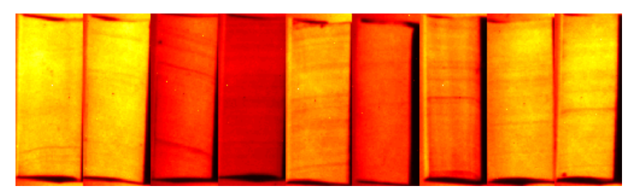
NEXAFS Sample Bar



18x16mm^2 FOV NEXAFS Image



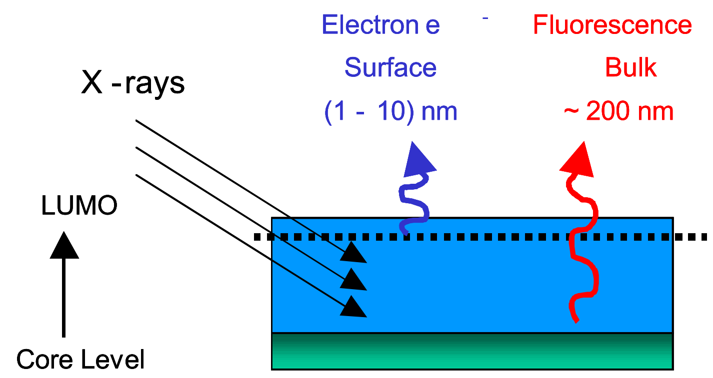
Sample ROI Extracted

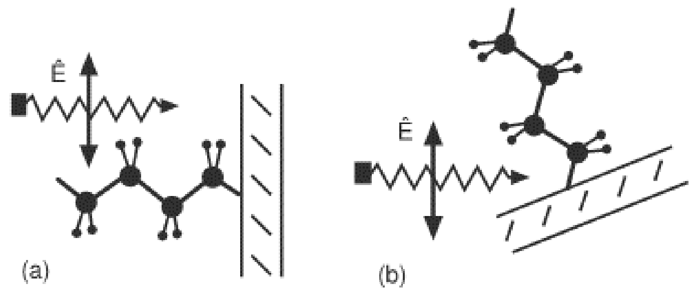


ROI from all samples from a series created sample series data

Why Use NEXAFS (Near Edge X-ray Absorption Fine Structure) ?

- A synchrotron-generated variable energy x-ray beam irradiates the sample surface.
- Resonant excitation and relaxation yields both secondary electrons (surface) and photons (bulk).
- Benefits of NEXAFS:
  - Element specific
  - Edge energy related to oxidation state
  - Sensitive to local bonding
  - Peak intensity directly related to the number of core holes and concentration.
  - Polarized light from the synchrotron allows probing of molecular orientation

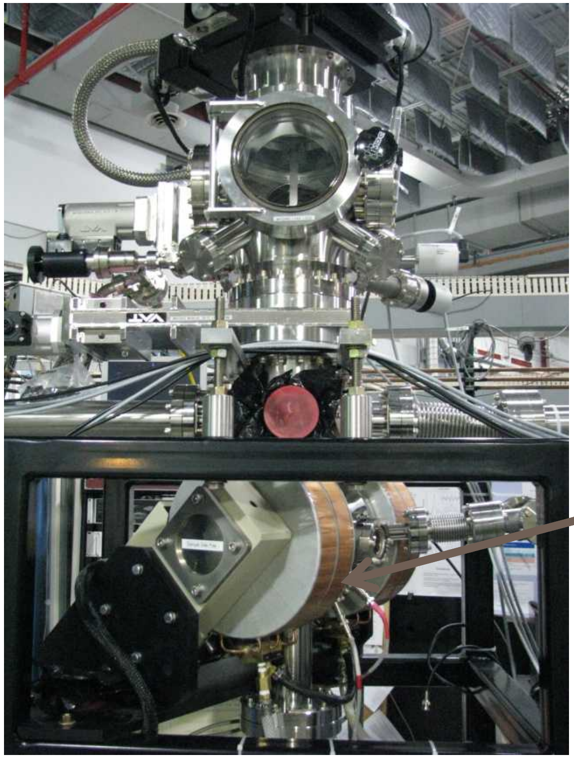




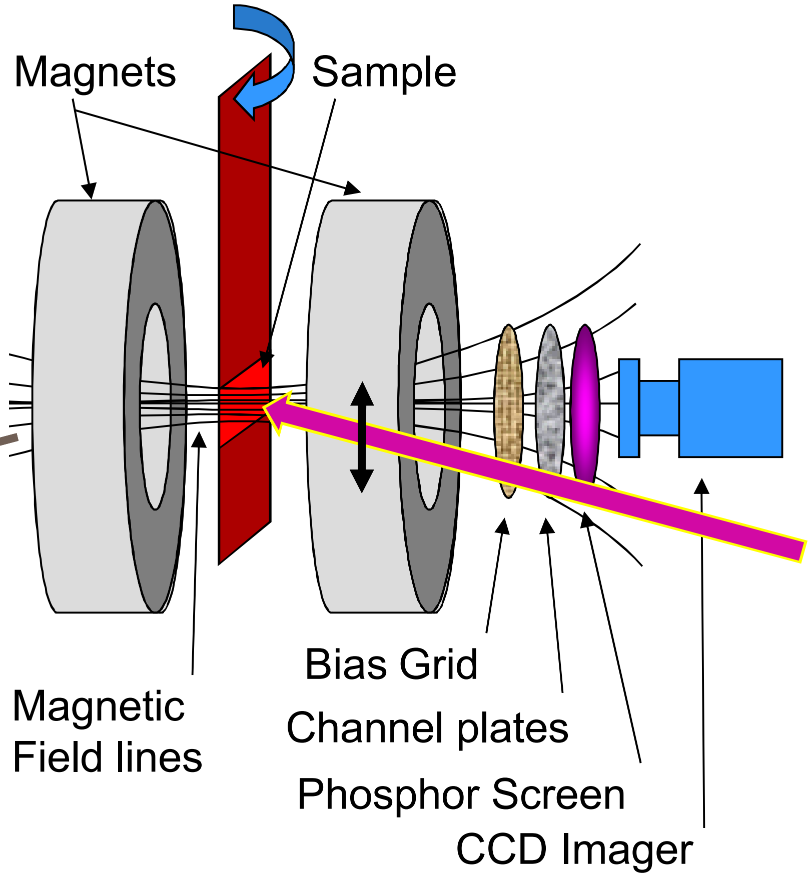
The maximum intensity of transition is achieved when the electric field vector is parallel to the respective bonding orbital; thus, when the beam is normal (a) the dominant transition will be the C-H* and at glancing angle geometry (b) the major transition will be the C-Cσ.

(J. Mat. Sci. Let., 17 (1998) 1223-1225.)

Imaging NEXAFS Instrument at National Synchrotron Light Source (NSLS), Brookhaven National Laboratories (BNL)



NEXAFS Imaging Spectrometer
U7A Beamline, NSLS



FOV: 18x16 mm^2
~40µm resolution

Dan Fischer, NIST, NSLS, BNL

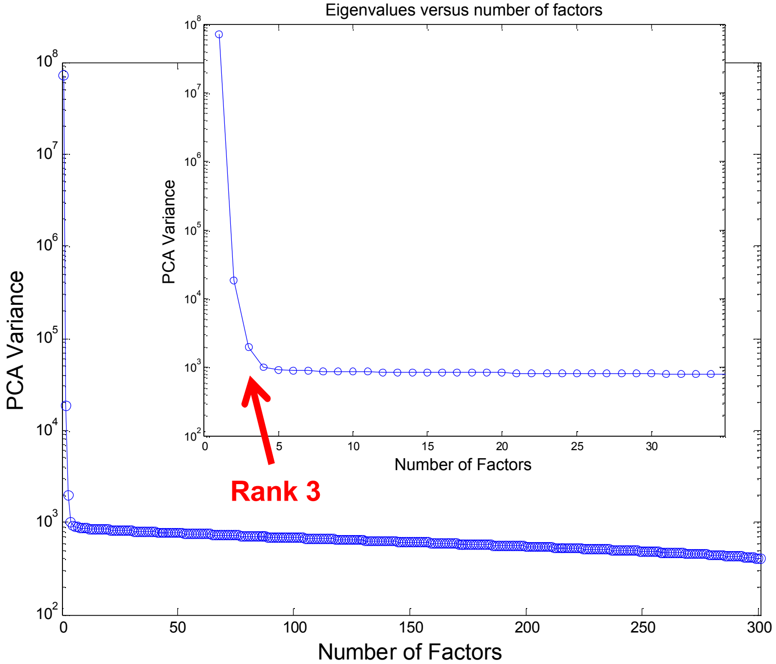
Multivariate Analysis Method Customized for NEXAFS

Multivariate Procedure using a custom SNL-developed Tool

- Obtain replicate spectral images as part of data acquisition
- Compute sum and variance from replicates
- Compute scaling matrices
- Scale Data
  - Scale each spatial pixel by root
- Find and Remove Outliers
  - Various methods of outlier detection
    - Dark image acquisition and analysis
    - Spectral outlier detection
    - Image filtering to detect hot or cold pixels
- Solve $D = TP^T$ to obtain principal components in region of interest
- Perform varimax rotation for spatial simplicity

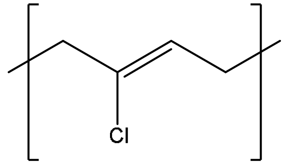
Estimating Number of Factors:

- Select region of interest (ROI) in image to analyze
- Perform eigenanalysis on outlier-free, variance-scaled data
- Determine number of factors from variance model

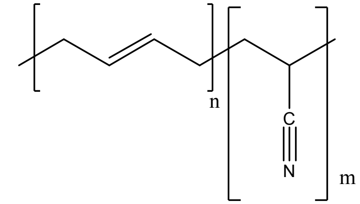


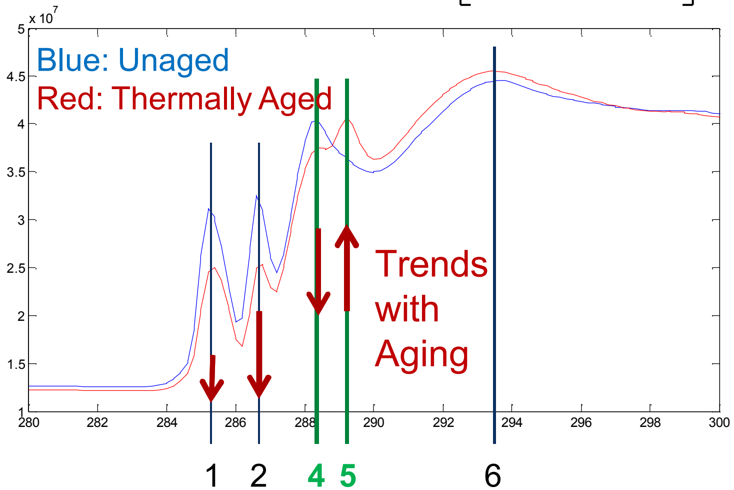
NEXAFS spectral features

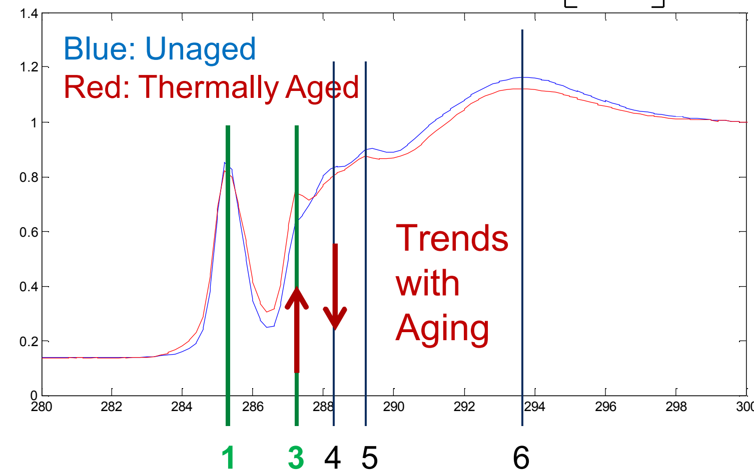
Neoprene



Butyl Nitrile





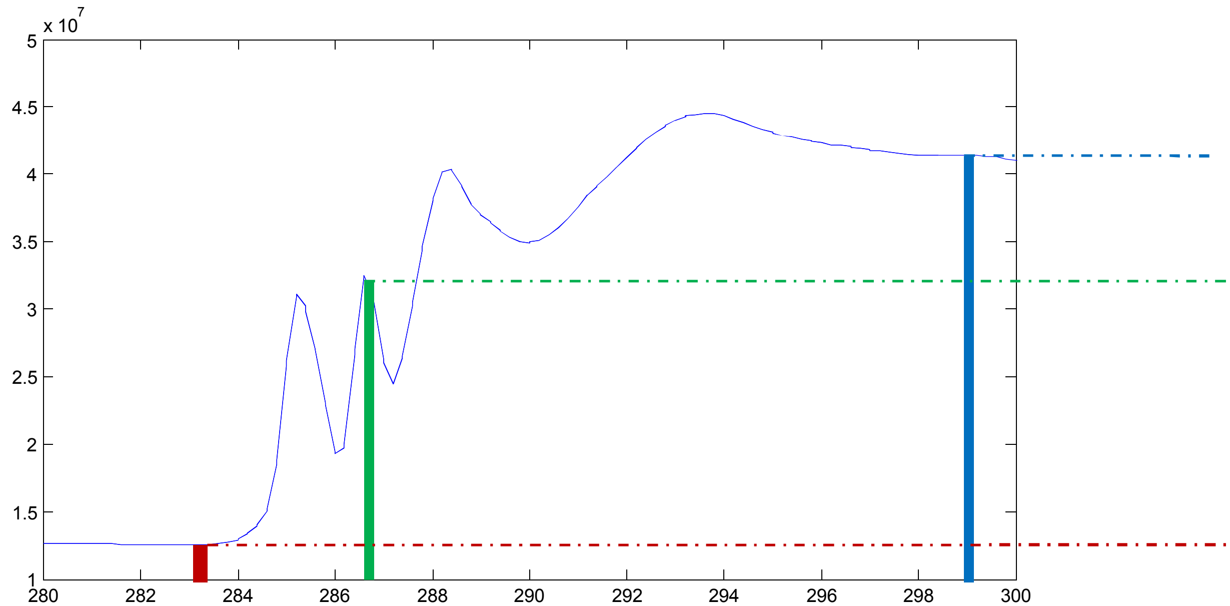


#	Neoprene (Energy)	Nitrile (Energy)	Assignment (optical orbital)					
			C-H	C-C	C=O	CH_2	C-Cl	C≡N
1	285.4	**285.4**	**$1\pi^*_{C=C}$**					
2	286.7				$1\pi^*_{C=O}$		$1\pi^*_{C-C}$	
3		**287.4**			**$1\pi^*_{C=O}$**			**$\pi^*_{C\equiv N}$**
4	**288.4**	288.4	**σ^*_{C-H}**					
5	**289.3**	289.3				**σ^*_{C-OH}**		
6	293.6	293.6		σ^*_{C-C}				

Overlapping Peaks (rows 2–3)

O. Dhez et. Al. Journal of Electron Spectroscopy and Related Phenomena 128 (2003) 85-96
H. Ade and S. G. Urquhart, "NEXAFS Spectroscopy and Microscopy of Natural and Synthetic Polymers", Chemical Applications of Synchrotron Radiation, T.K. Sham, Ed. World Scientific Publishing Co. Ltd. Singapore

Peak Images Are Created from Multivariate Results



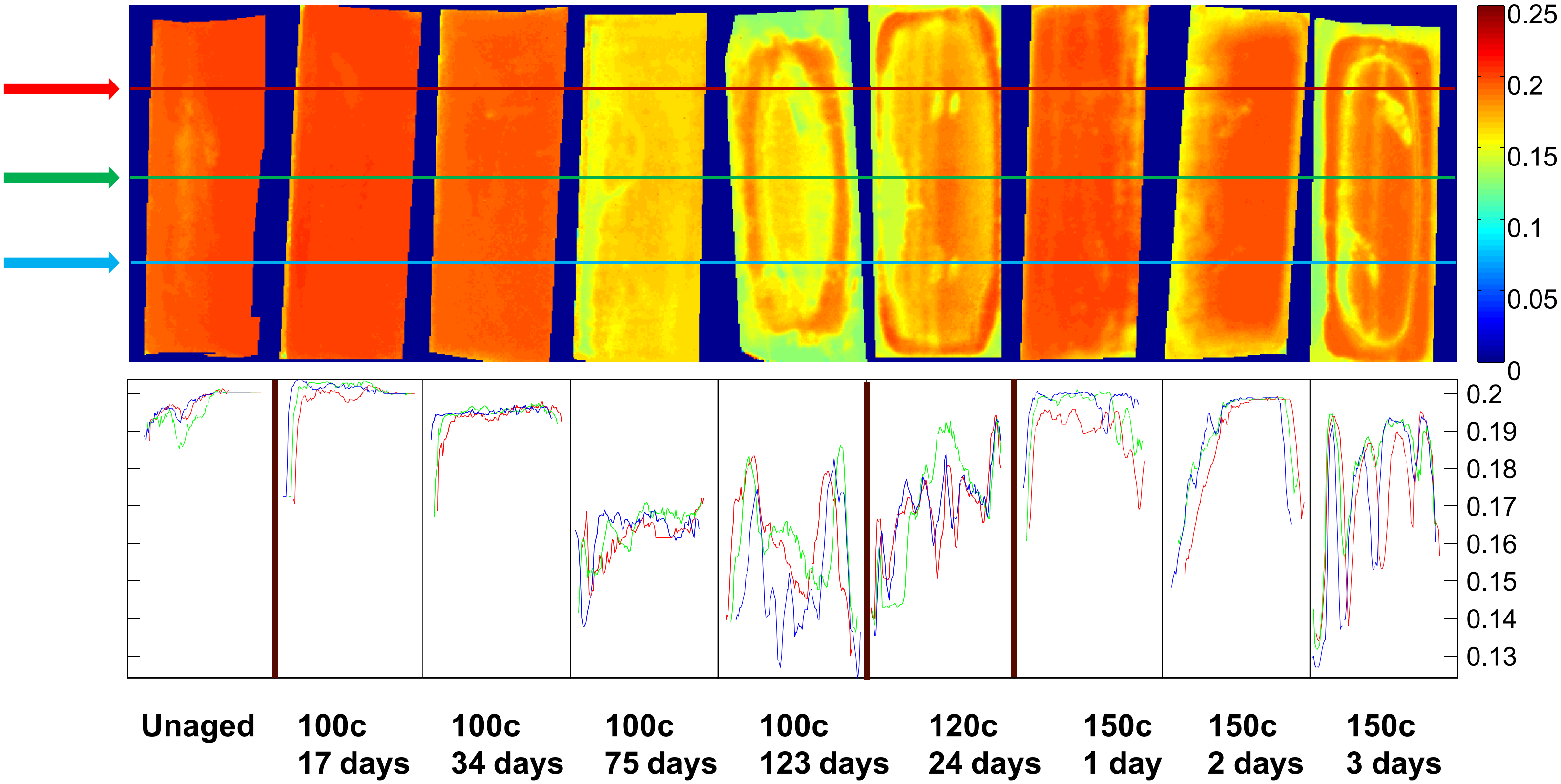
Post-Edge (E2) Region

Peak of Interest (P)

Pre-edge Region (E1)

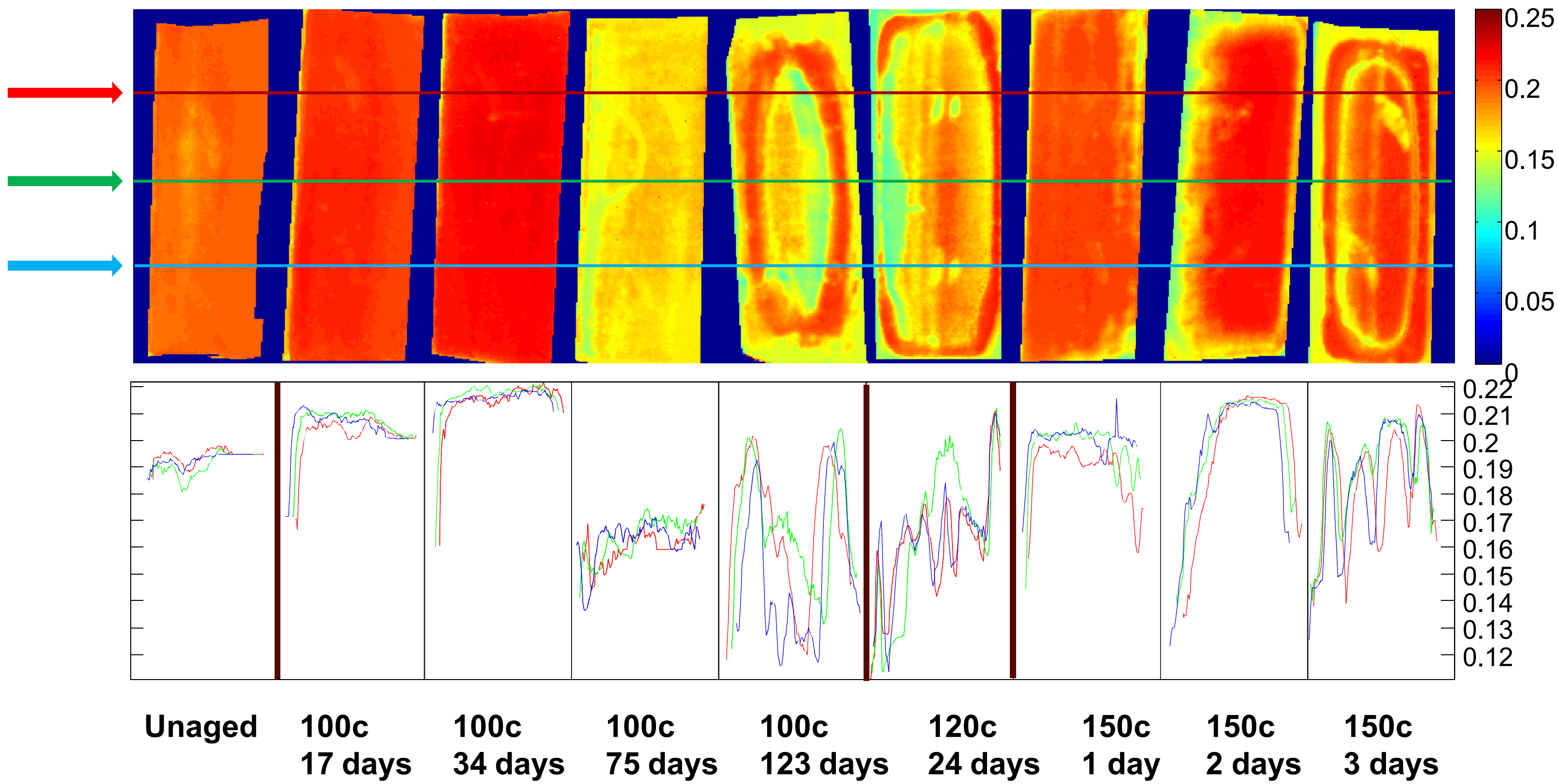
- Each peak image corrected for pre and post-edge intensities.
  - Normalizes for spectral intensity variations across the sample.

Filled Neoprene,
285.4eV, C-H ($1\pi^*_{C=C}$)



Generally decreases with aging.
Shows inverse DLO profile.

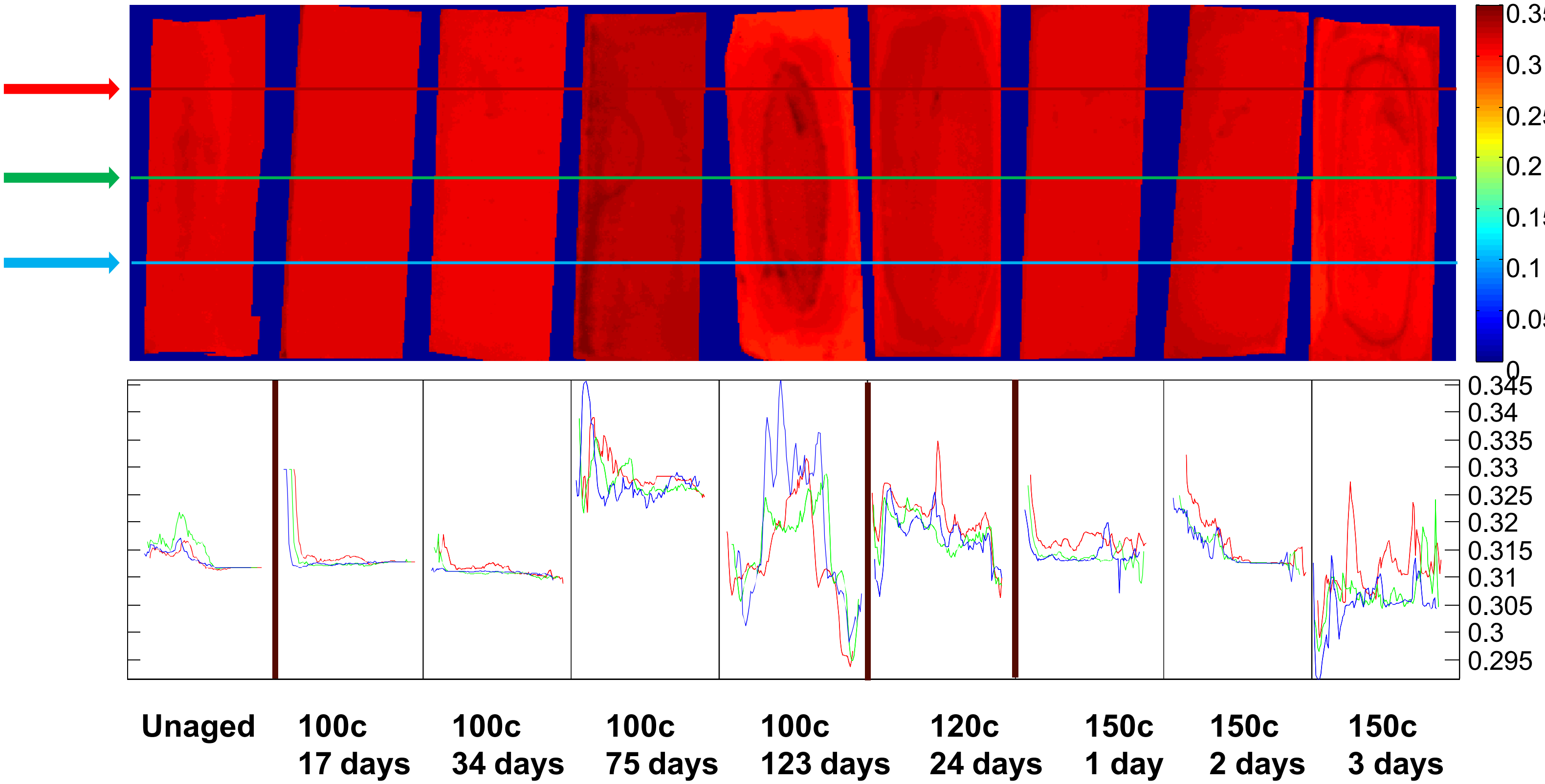
Filled Neoprene, 286.7eV, C=O ($1\pi^*_{C=O}$) and C-Cl ($1\pi^*_{C-C}$)



Generally increases with aging. Shows inverse DLO profile.

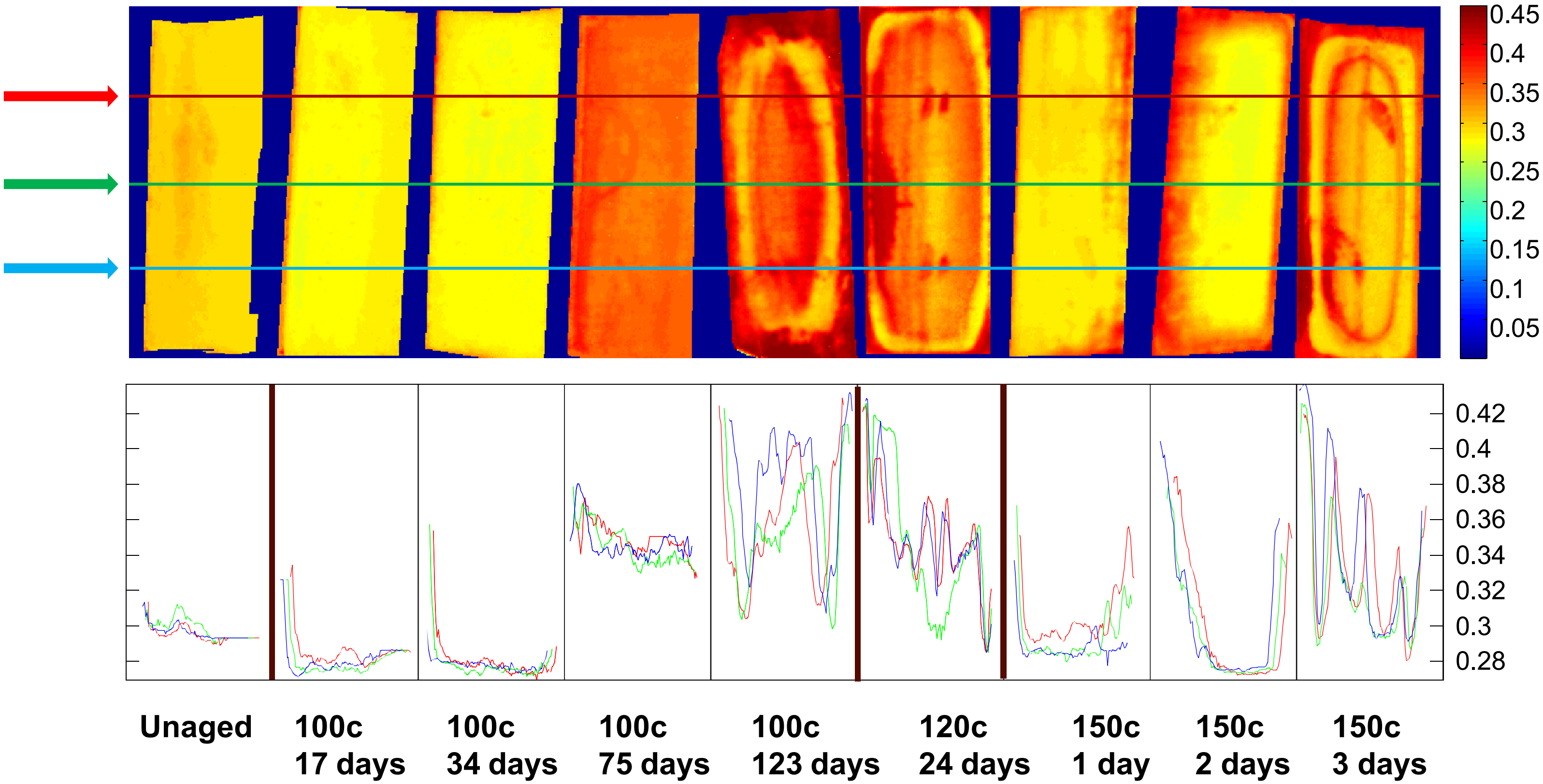
Banding due to the overlapping contributions of the loss of Cl and addition of OH.

Filled Neoprene, 288.4eV, C-H ($\sigma^*_{C\text{-}H}$)



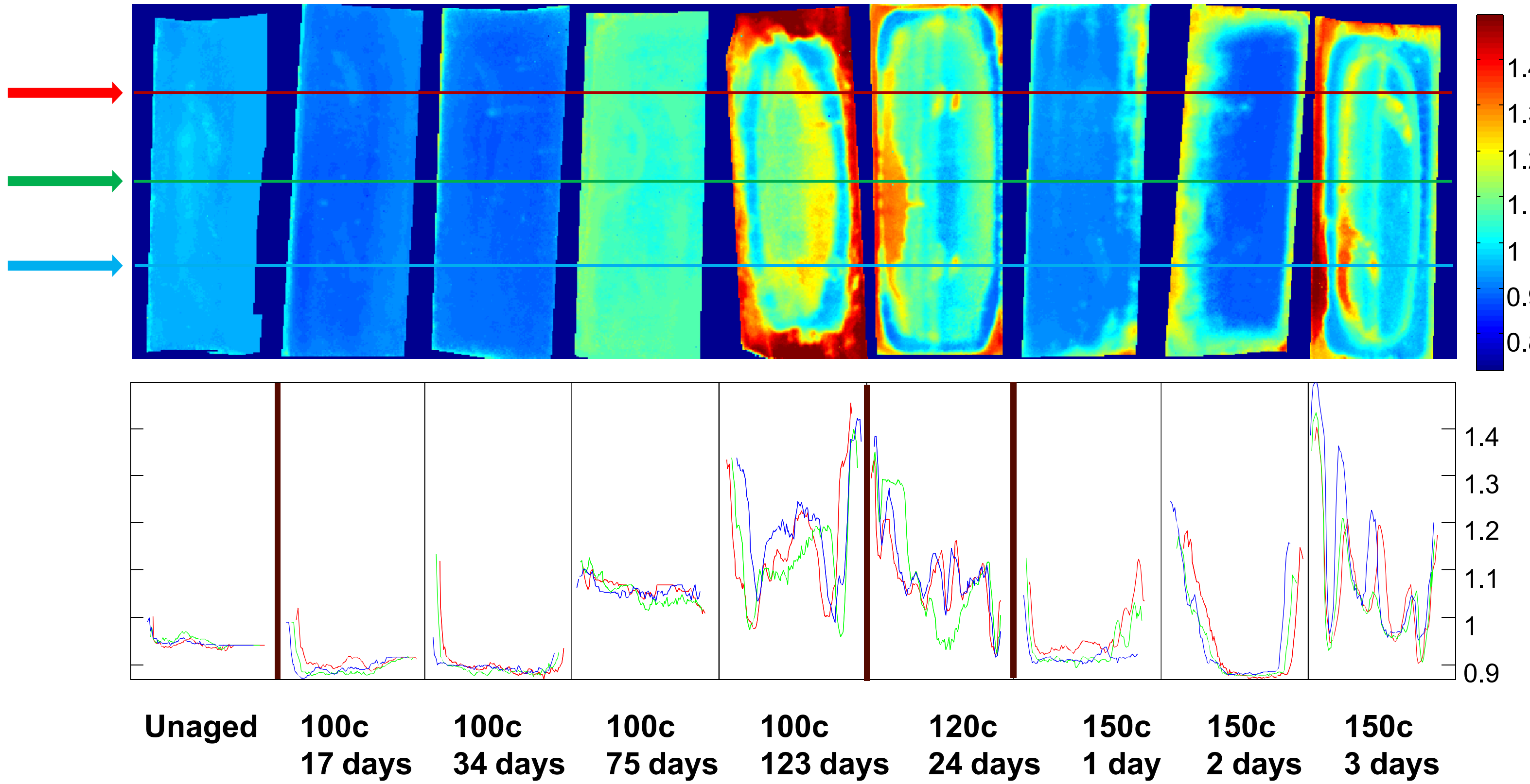
No general trend with aging.
Shows inverse DLO profile.

Filled Neoprene, 289.3eV, CH_2 ($\sigma^*_{C\text{-}OH}$)



Generally increases with aging.
Shows DLO profile.

Filled Neoprene, 289.3eV (OH) / 288.4eV (CH) Peak Ratio

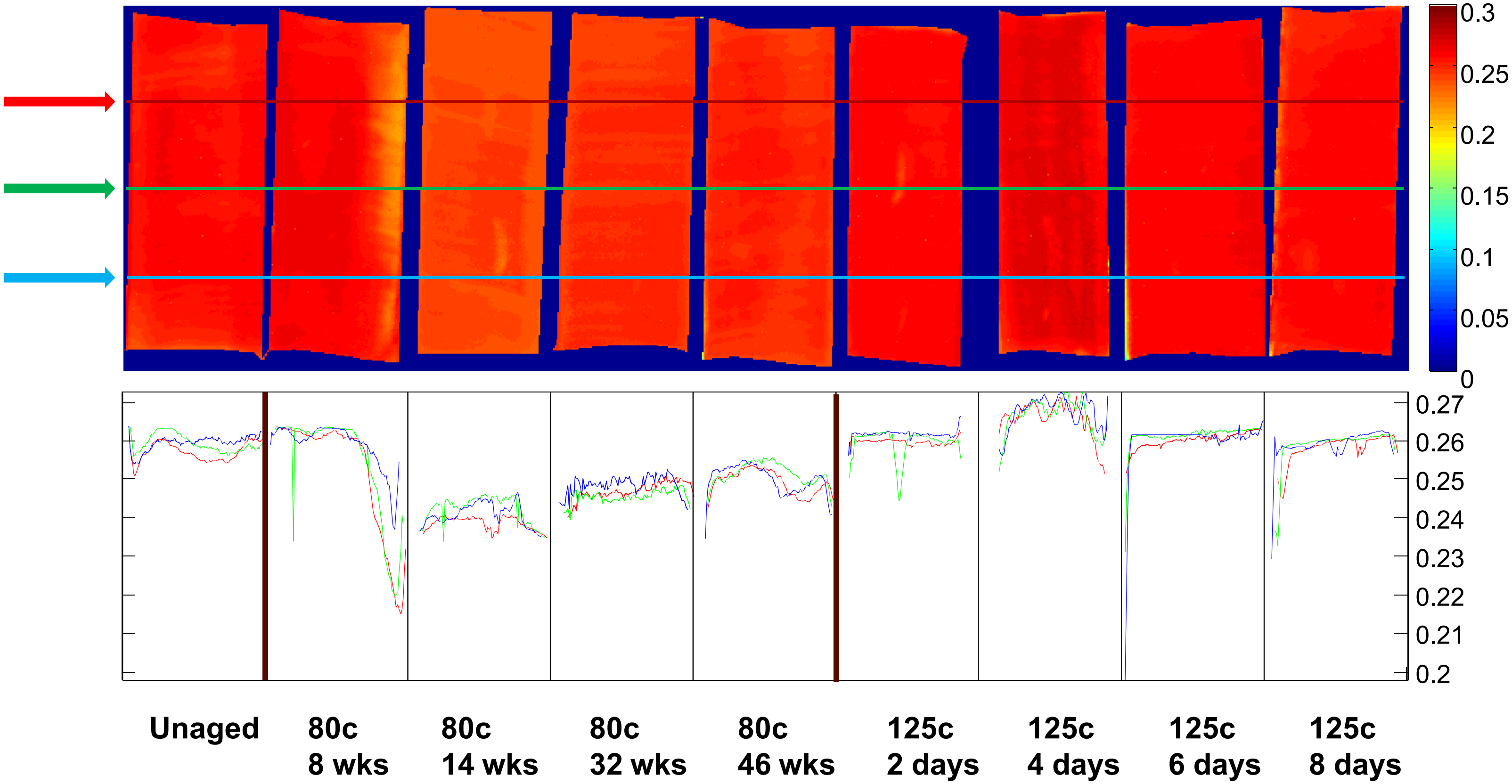


Low Interior Oxidation with natural DLO edge oxidation character

High Interior oxidation with some DLO edge oxidation character and interior Cl loss banding

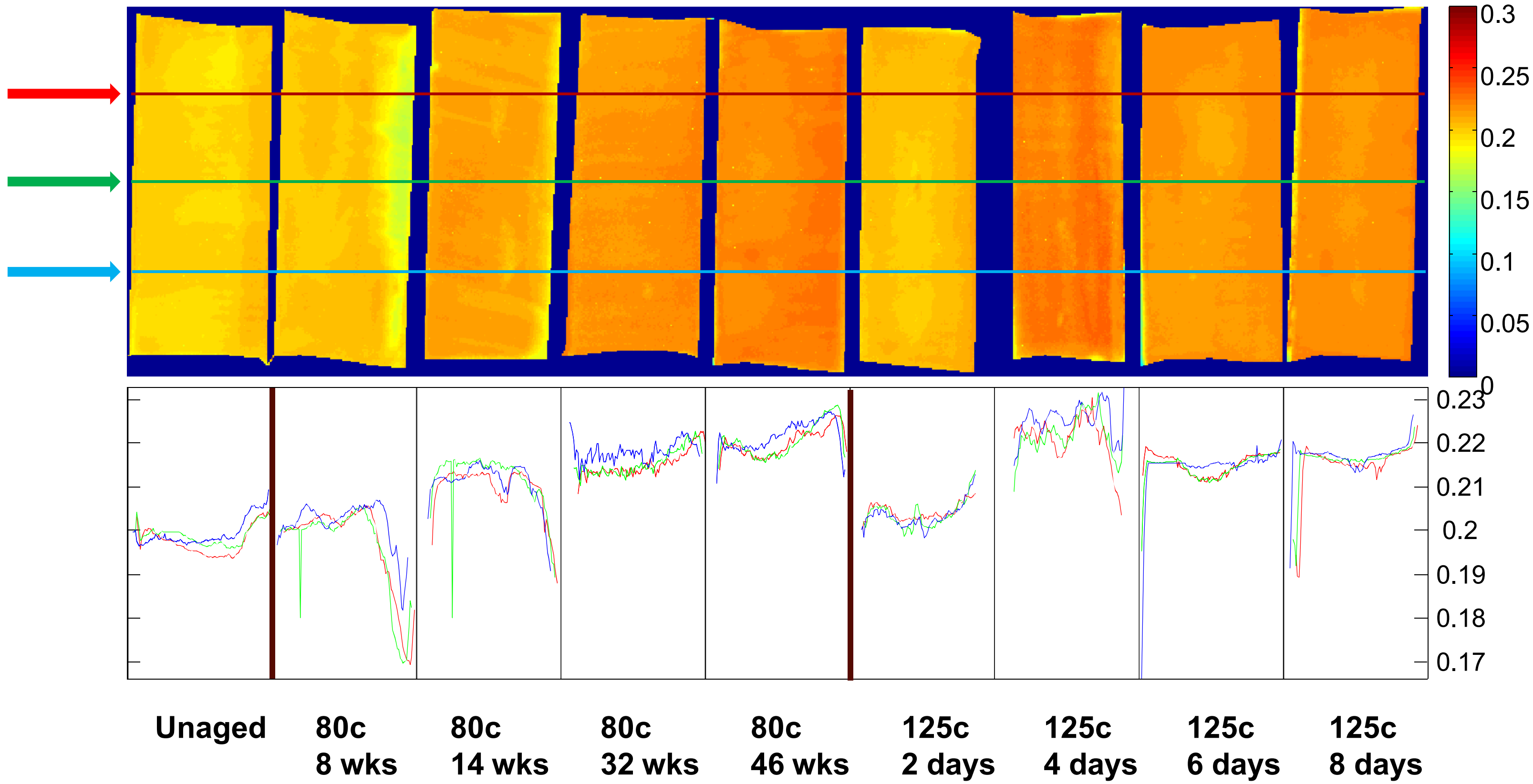
Moderate Interior oxidation with large DLO edge oxidation character and interior Cl loss banding

Filled Butyl Nitrile, 285.4eV, C-H ($1\pi^*_{C=C}$)



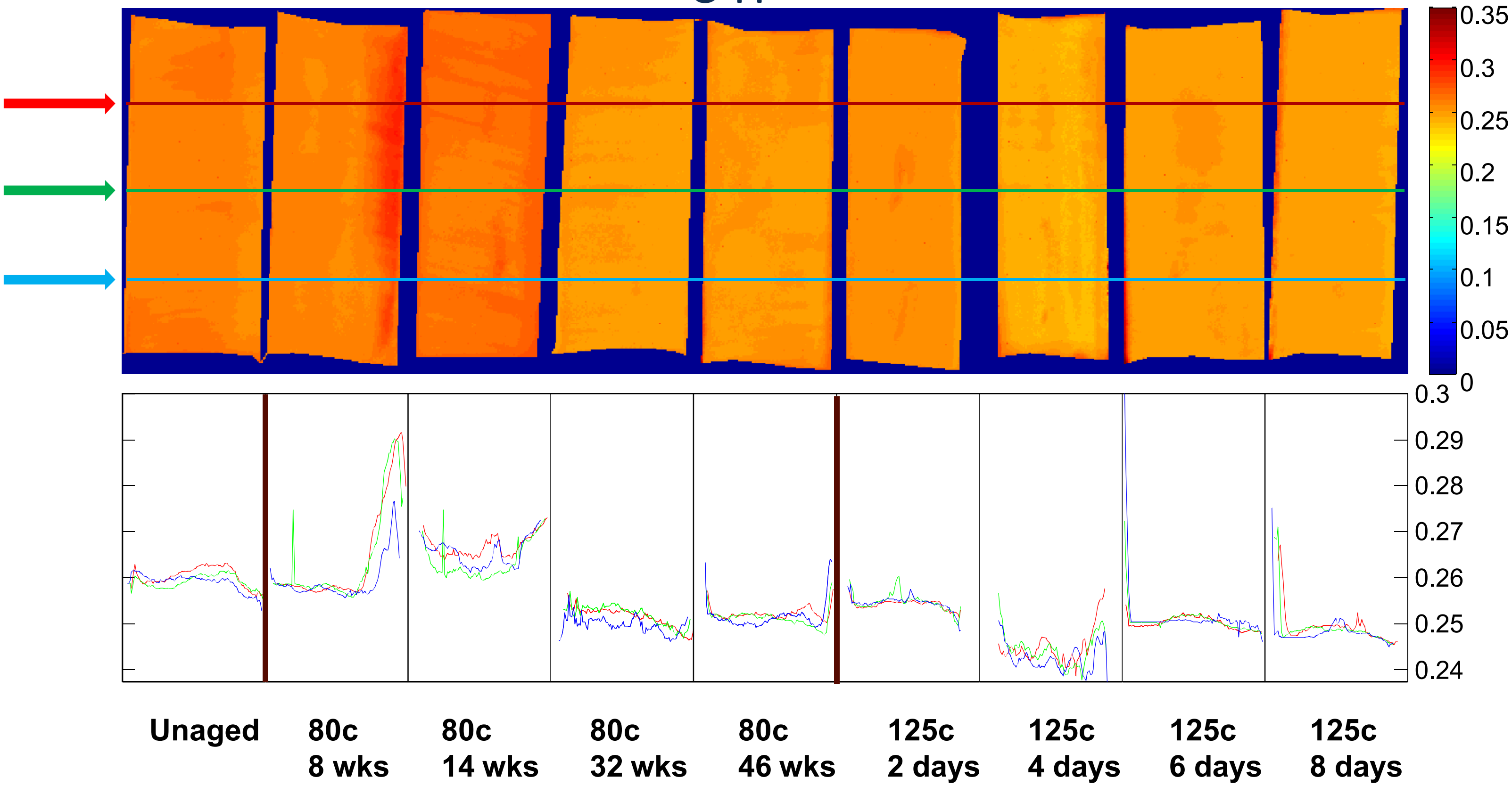
Generally increases with aging.
Shows inverse DLO profile.

Filled Butyl Nitrile, 287.4eV, C=O ($1\pi^*_{C=O}$) and C≡N ($\pi^*_{C\equiv N}$)



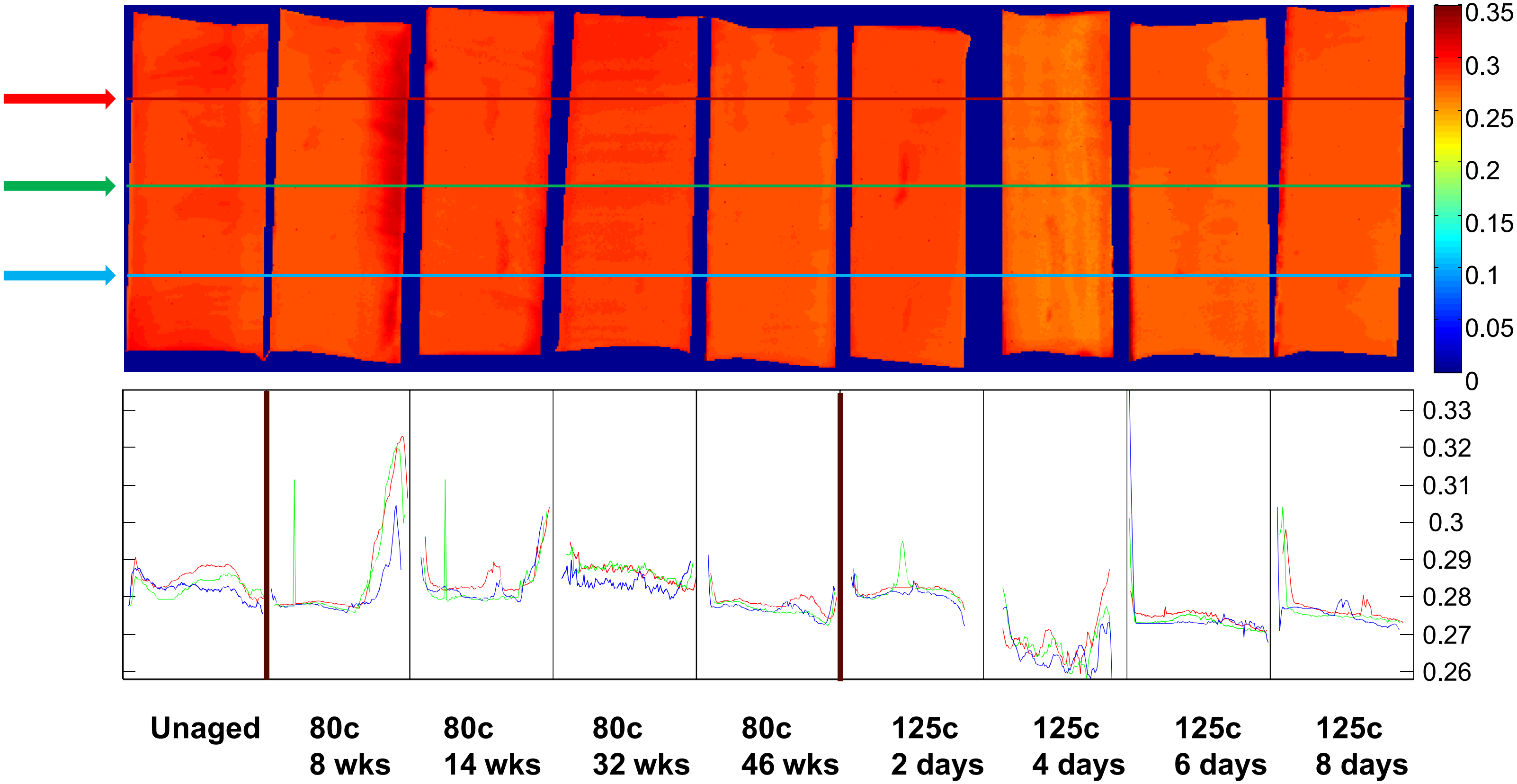
Generally increases with aging.
Shows some DLO sensitivity.

Filled Butyl Nitrile, 288.4eV, C-H (σ^*_{C-H})



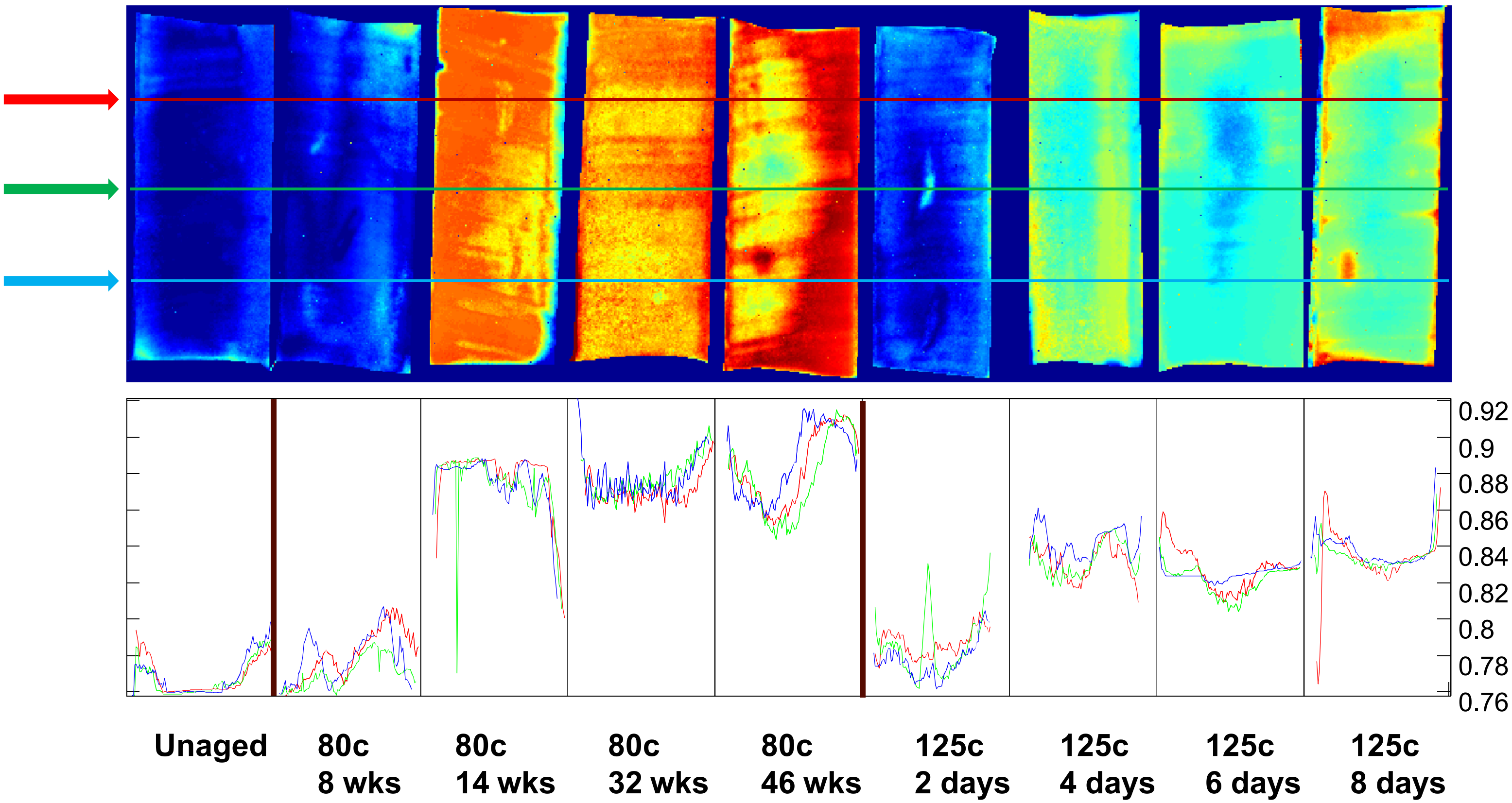
Generally decreases with aging.
Shows little DLO sensitivity.

Filled Butyl Nitrile, 293.6eV, CH_2 ($\sigma^*_{C\text{-}OH}$)



Little change with aging.
Shows little DLO sensitivity.

Filled Butyl Nitrile,
287.4eV (C=O) / 285.4eV (CH) Peak Ratio



Low Interior Oxidation with natural DLO edge oxidation character

High Interior Oxidation with some DLO edge oxidation character

Moderate Interior Oxidation with large DLO edge oxidation character

Conclusions

- We have developed a custom tool for multivariate analysis of NEXAFS imaged data
- We have analyzed 2 aged materials series
  - Filled Neoprene
  - Filled Butyl Nitrile
- We have successfully analyzed these aged materials series using Imaging NEXAFS
  - Measured increase in interior oxidation levels for long term aged samples
  - Measured diffusion limited oxidation profiles for short term high temperature samples
  - See evidence of Cl removal as banding in the OH peak for Filled Neoprene
- **Method looks promising for determining extent and profile of oxidation for samples of Neoprene and Butyl Nitrile based materials with unknown aging pedigrees.**

Acknowledgements

- This work could not be performed without our active collaboration with NIST and Synchrotron Research, Inc. at NSLS, BNL

  NIST
    - Dan Fischer
    - Cherno Jaye

  Synchrotron Research, Inc.
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    - Peter Sobol
    - Conan Weiland