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Sandia National Laboratories

Sandia National Laboratories / NIST Collaboration at NSLS / NSLS II

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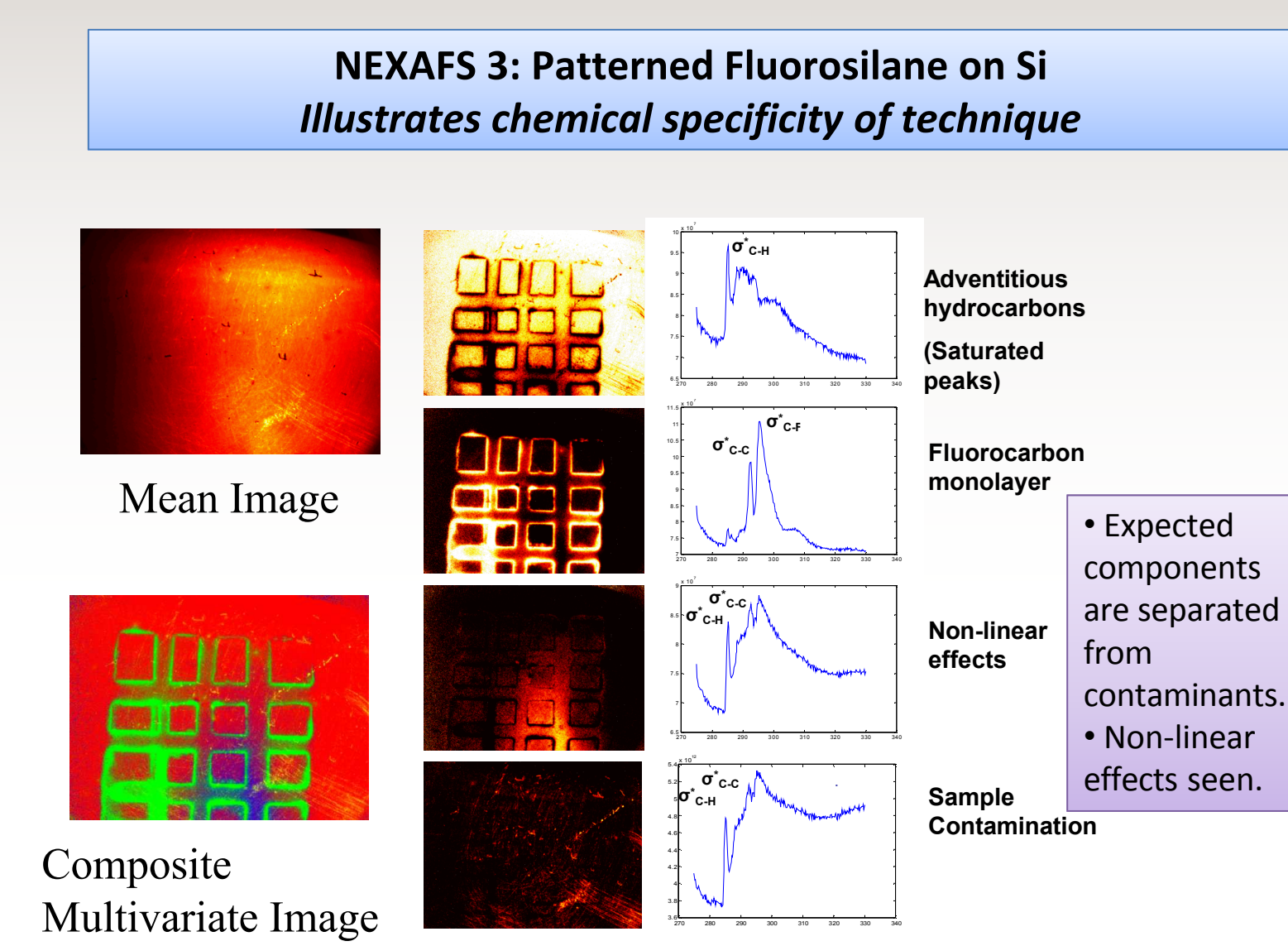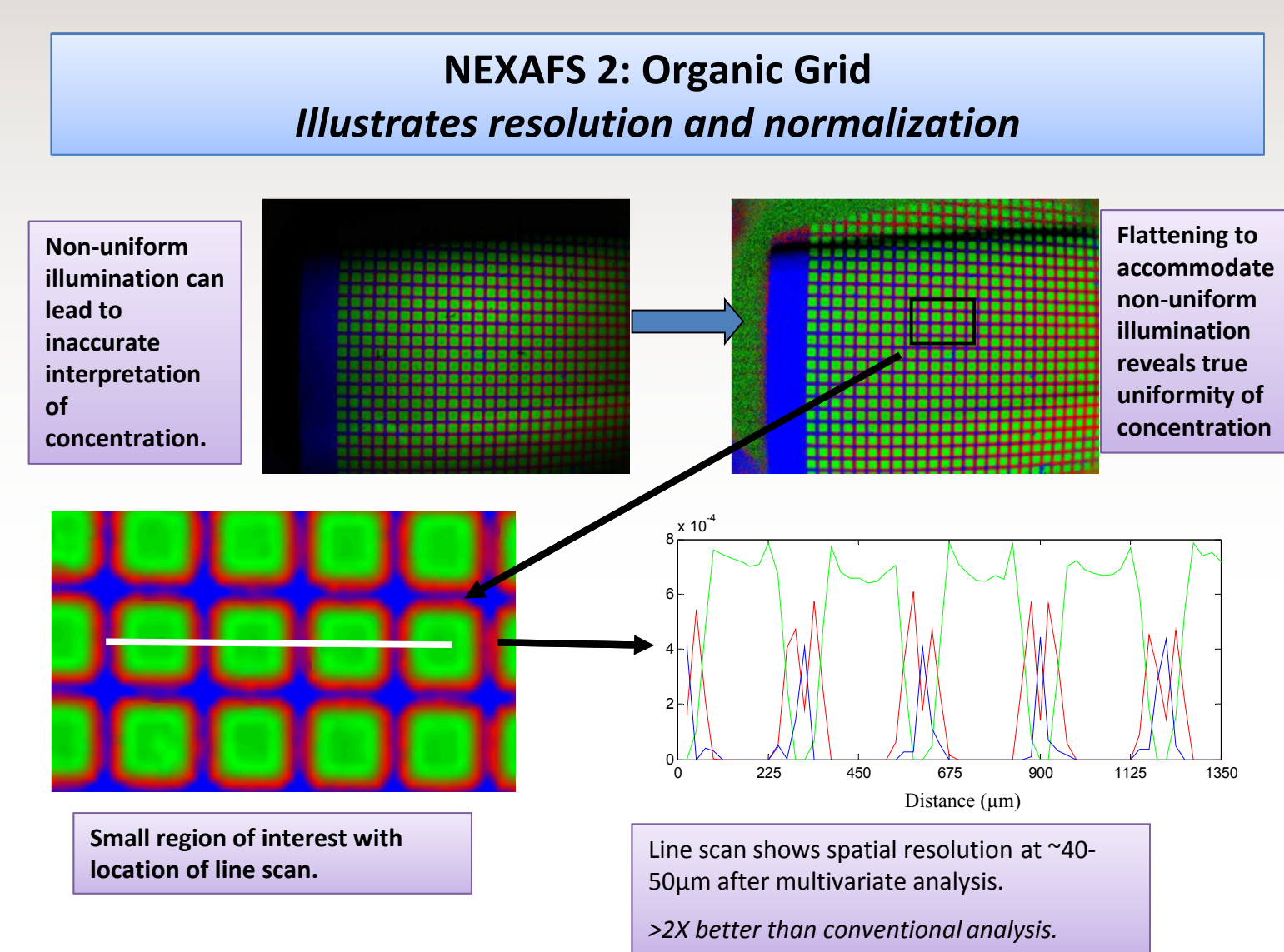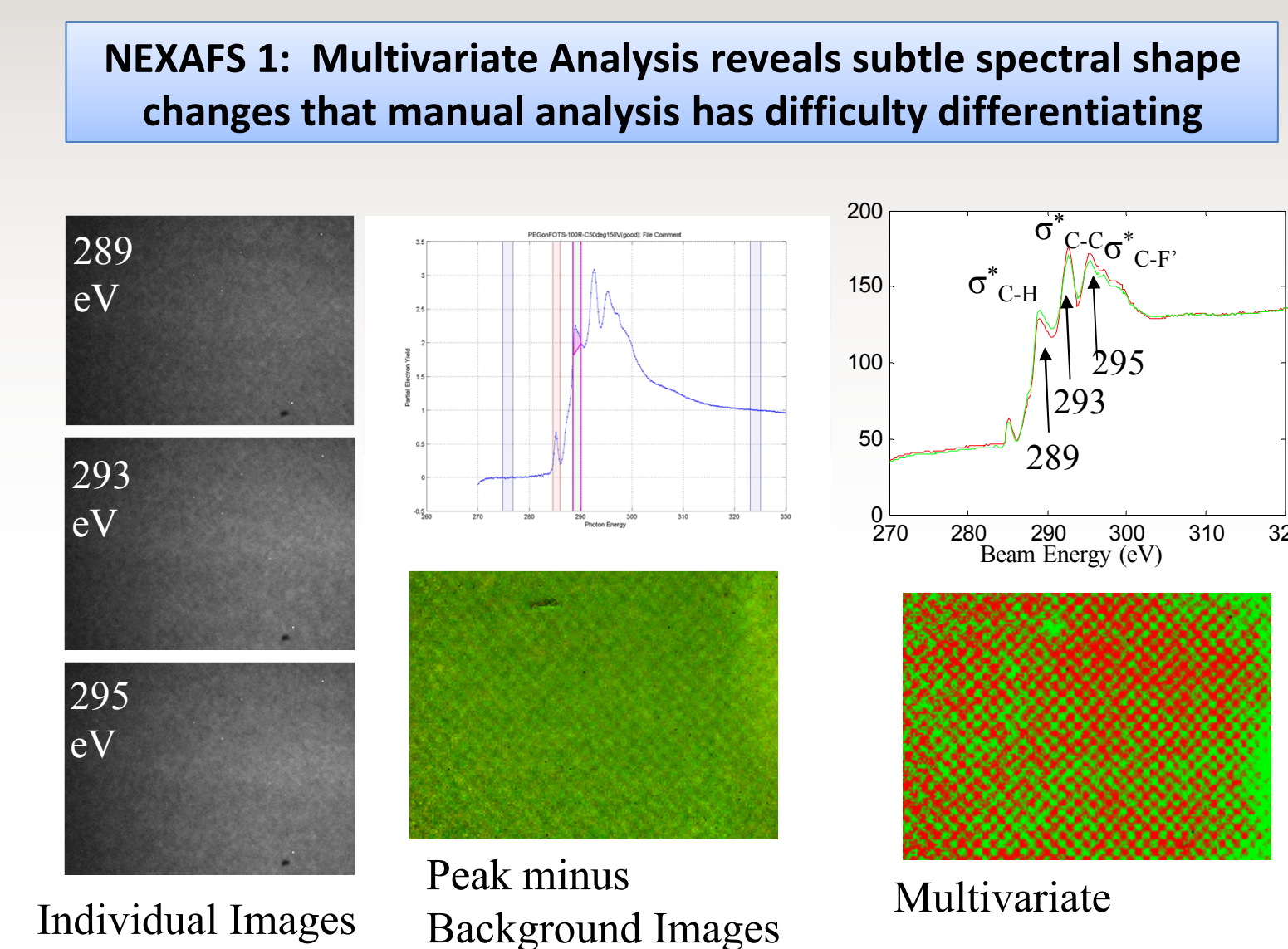
Accomplishments:
- Transferred AXSIA to NIST
  - See inset top middle
- AXSIA has been commercialized with Thermo-Noran for use in EDS (Energy Dispersive X-ray Spectroscopy)
- Implemented variance estimation acquisition protocol for proper handling of noise and other variances in multivariate analysis procedures.
- Development of new NEXAFS-specific multivariate analysis code that utilizes optimal variance procedure (above), to scale data prior to data analysis.
- Optimization of NEXAFS imaging beamline (U7a) for imaging:
  - Determining optimal mirror oscillation waveform, period and offset
  - Optimized I_0 timing (real time beamline intensity measurement) for proper quantification
- Developed a novel multivariate approach to NEXAFS peak fitting (Global Analysis).
  - See inset on right for example using aged O-rings
  - Fits entire spectrum for every pixel at the same time.
  - Uses peak shapes as defined by Stohr.

Impacts at Sandia National Labs:
At Sandia, we need more detailed understanding of materials aging. This collaboration has allowed us to probe complex materials that have been difficult to measure otherwise.

AXSIA (Automated eXpert Spectrum Image Analysis)
- Transferred to NIST at NSLS/U7a

NEXAFS 1: Multivariate Analysis reveals subtle spectral shape changes that manual analysis has difficulty differentiating

289 eV
293 eV
295 eV

Individual Images
Peak minus Background Images
Multivariate

NEXAFS 2: Organic Grid
Illustrates resolution and normalization

Non-uniform illumination can lead to inaccurate interpretation of concentration.

Flattening to accommodate non-uniform illumination reveals true uniformity of concentration

Small region of interest with location of line scan.

Line scan shows spatial resolution at ~40-50µm after multivariate analysis.
>2X better than conventional analysis.

NEXAFS 3: Patterned Fluorosilane on Si
Illustrates chemical specificity of technique

Mean Image

Composite Multivariate Image

Adventitious hydrocarbons (Saturated peaks)

Fluorocarbon monolayer

Non-linear effects

Sample Contamination

- Expected components are separated from contaminants.
- Non-linear effects seen.

Collaboration History at NSLS:
- Began with Joe Lenhart (currently at Army Research Labs)
- Many purchases for X24a beamline including: high energy hemispherical analyzer, fast closing valve, turbo pump.

Collaboration Future (NSLS II):
- Optimization of Imaging NEXAFS (LARIAT II) System
- Implement multivariate analysis on LARIAT II
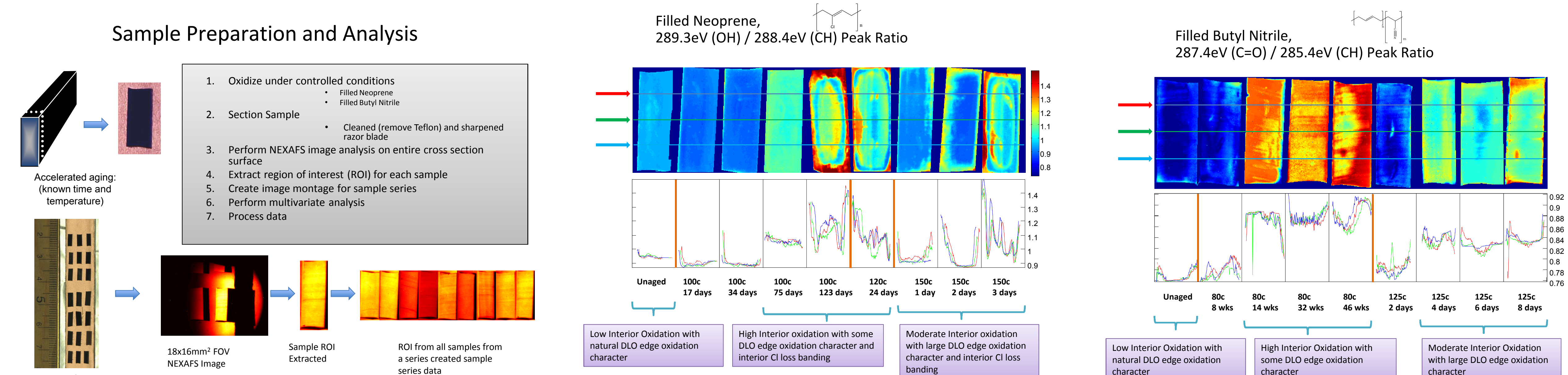- Consultation regarding optimal acquisition protocols for multivariate analysis.

- Using Sandia's multivariate analysis toolkit (AXSIA), complex NEXAFS datasets have become more manageable.
- We have devised custom data processing methods do reduce the effects of artifacts seen in this technique.

- Measurement of Diffusion Limited Oxidation (DLO) of filled elastomer systems demonstrates the ability of NEXAFS to provide needed aging related chemical information at appropriate length scales.

- **Global Analysis**, a multivariate analysis technique, provides simultaneous peak shape fitting of the entire image data set, where each pixel contains a unique spectrum.
- Results reveal chemical detail that cannot be found using traditional data analysis methods.
- A patent has been filed for this technique.
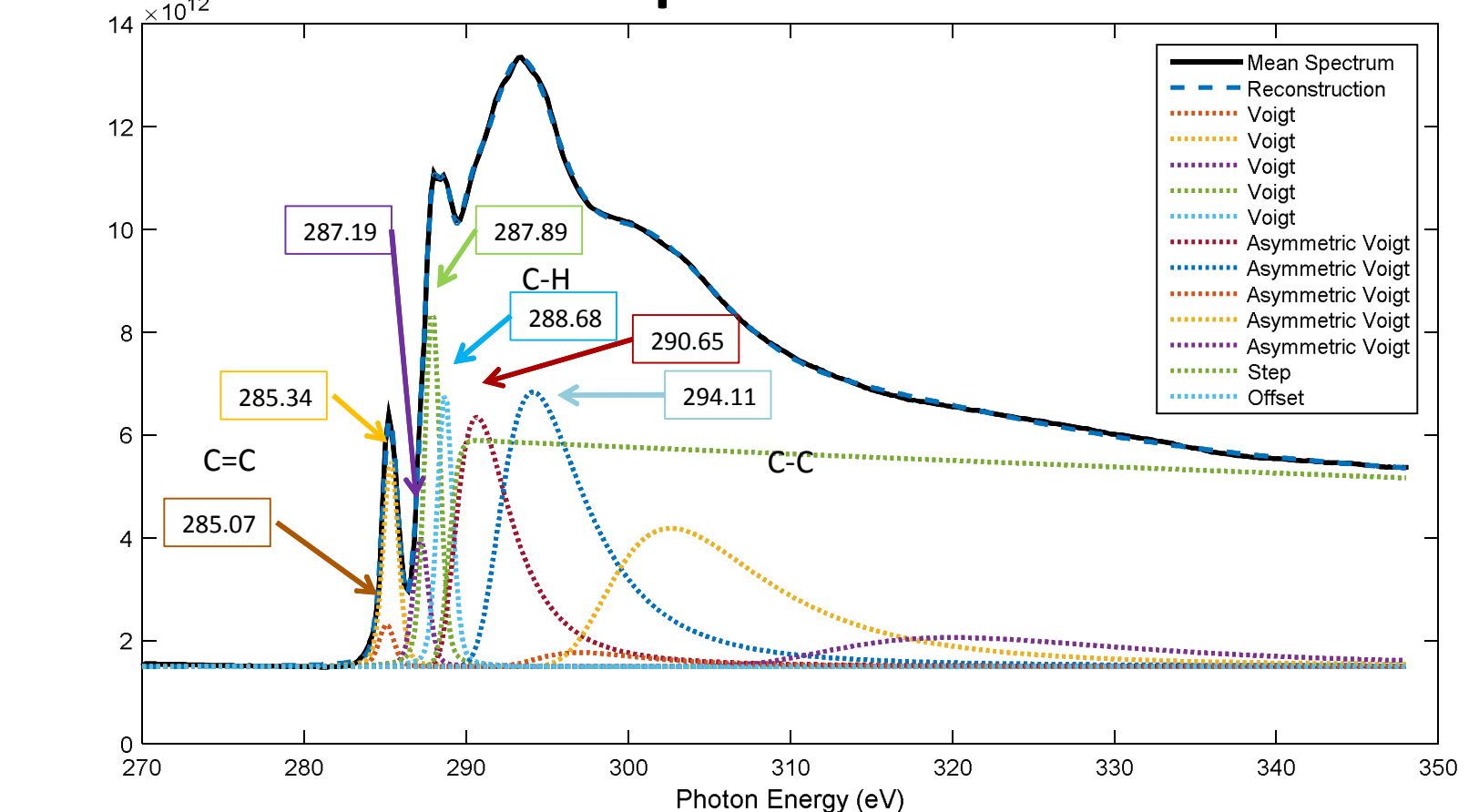
Novel Multivariate Data Analysis Technique: Global Analysis
Provisional Patent Application: SNL SD-13122, April 2015

Samples Analyzed

12Mar14-25-BI-07-0 Native
12Mar14-25-BI-07-k 125°C, 10 days
12Mar14-25-BI-07-l 125°C, 21 days

NEXAFS Integrated Image before cropping
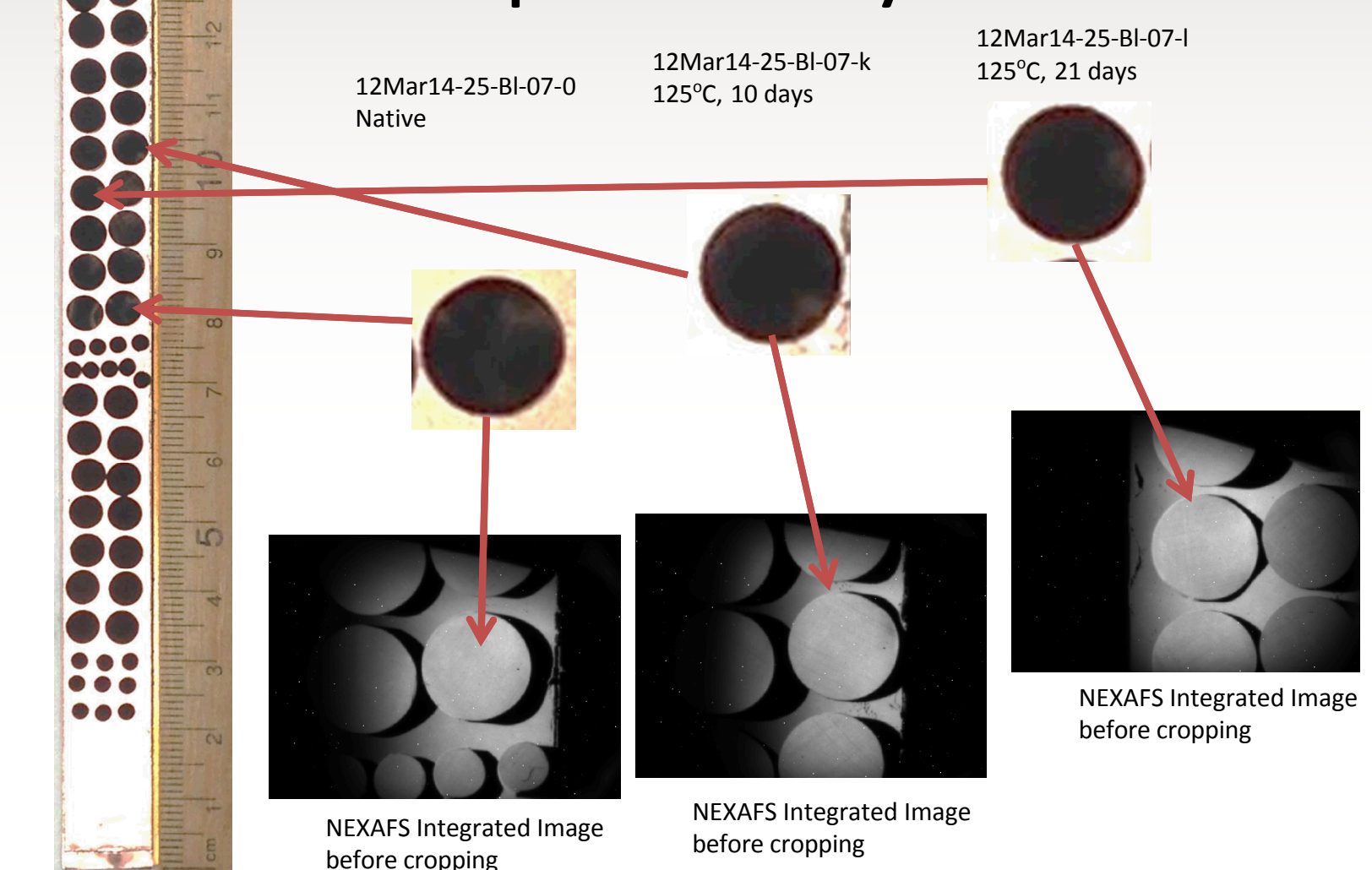
Total Spectrum Fit

Global Analysis Factors

1 Voigt	2 Voigt
3 Voigt	4 Voigt
5 Voigt	6 Asym. Voigt
7 Asym. Voigt	8 Asym. Voigt
9 Asym. Voigt	10 Asym. Voigt
11 Step	12 Offset

PE center 285.07eV C=C
PE center 285.34eV C=C
PE center 287.19eV C-H
PE center 287.89eV C-H
PE center 288.68eV C-H
PE center 290.65eV C-C
PE center 294.12eV C-C ?
PE center 297.04eV C-C
PE center 302.62eV
PE center 320.00eV
PE center 288.91eV

Measuring the Diffusion Limited Oxidation (DLO) of Filled Elastomers
--Challenging due to presence of carbon black filler--

Sample Preparation and Analysis

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

Accelerated aging: (known time and temperature)

NEXAFS Sample Bar

18x16mm² FOV NEXAFS Image

Sample ROI Extracted

ROI from all samples from a series created sample series data

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

Unaged	100c 17 days	100c 34 days	100c 75 days	100c 123 days	120c 24 days	150c 1 day	150c 2 days	150c 3 days

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

Unaged	80c 8 wks	80c 14 wks	80c 32 wks	80c 46 wks	125c 2 days	125c 4 days	125c 6 days	125c 8 days

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