Use of Multivariate Analysis (MVA) for Failure Analysis: Application of MVA to ToF-SIMS Analysis of VIIRS On-Orbit Anomaly Investigation

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Outline

• ToF-SIMS

• Multivariate Analysis

• Application of MVA and ToF-SIMIS to VIIRS anomaly

• Imaging MVA
Time-of-Flight Secondary Ion Mass Spectrometry

A brief introduction

1. Primary Ion (Pulsed, 22 keV Au⁺)

2. Production of positive and negative secondary ions, electrons, and neutral species

3. Time-of-Flight analysis

mass/charge →
Time-of-Flight Secondary Ion Mass Spectrometry
A brief introduction

• Surface specific
  – 95% of detected ions originate from top two monolayers
• Positive or negative secondary ions can be analyzed
• A second ion beam may be used to remove material to provide depth profiling
• Primary ion beam is scanned over the surface providing simultaneous collection of spatial and chemical information
  – Each “pixel” represents a unique mass spectra
• Datasets can be large and information rich
  – More data does not necessarily lead to more useful information
What is Multivariate Analysis (MVA)?

More data does not necessarily lead to more useful information

• MVA provides a means of summarizing a large number of dependent variables into a smaller number of statistical variables.

• MVA is a general term that includes a number of statistical approaches that can be used for:
  – Identification: What species are present?
  – Classification: Does my data fit into a category or is it an outlier?
  – Quantification and Prediction: How does data relate to a library of known samples?

• Most systems are characterized by only a handful of processes or relationships.
  – Projecting high dimensional data into lower dimensional space can more efficiently summarize, simplify, and expose underlying trends.
ToF-SIMS Depth Profiling

Experiment and data

Data

Spectral variation as a function of depth
ToF-SIMS Depth Profile Analysis

One peak at a time

- In standard depth profile analysis, individual peaks are selected and plotted as a function of depth (time)
- Bias of analyst can influence the choice of peaks
- Small or unexpected spectral features may be missed
- Displaying multiple profiles can confuse interpretation
ToF-SIMS Depth Profiling

*Using multivariate analysis to simplify interpretation*

- With MVA, data is described using components.
- The spectral signature of each component is described by a "loading".
- The weight of each component as a function of sputter depth is described by a "score".
Visible/Infared Imager Radiometer Suite (VIIRS)

Suomi national polar-orbiting partnership (Suomi NPP)

- The Visible/infared imager radiometer suite (VIIRS) is the primary imaging instrument.
- Shortly after launch, VIIRS exhibited a marked decrease in optical throughput of near-infrared bands.
- Two mirrors supplied to Aerospace for analysis:
  - TWM (‘dirty’): affixed to VIIRS during payload assembly and testing.
  - FabWit (‘clean’): stored in pristine environment following fabrication.
- Use ToF-SIMS to determine the similarity of the mirrors.

![Image of VIIRS](https://npp.gsfc.nasa.gov)

![TWM layer diagram](https://npp.gsfc.nasa.gov)

Comparing FabWit and TWM

Taking advantage of MCR constraints

• To facilitate comparison, use MVA to treat layers as components
• Multivariate curve resolution (MCR) employed for analysis
• MCR requires a single input, the number of components to be modeled
• By considering the contamination on TWM to be a unique component, the remaining layers can be compared directly

![Diagram showing layers and contamination comparison between FabWit and TWM.](attachment:image.png)
FabWit and TWM Comparison

**Contamination layer on TWM detail**

- Surface contamination layer contains a number of commonly observed species
- No species observed that could be responsible for mirror darkening
FabWit and TWM Comparison

$WO_x$ layer score and loading detail
FabWit and TWM Comparison

$WO_x/SiO_2$ interface score and loading detail

![Graph 1](image1.png)  
![Graph 2](image2.png)

**Graph 1**:
- TWM Sputter Time (s) vs. Scores TWM
- FabWit (solid) vs. TWM (dashed)

**Graph 2**:
- $WO_x$/SiO$_2$ Interface
- m/z values: O, SiO$_2$, SiO$_3$, WO, WO$_2$, WO$_3$, WO$_4$

**Surface Contamination/WO$_x$**

**WO$_x$/SiO$_2$ Interface**

**SiO$_2$**
FabWit and TWM Comparison

SiO₂ interface score and loading detail
FabWit and TWM Comparison

Comparison of all modeled data

- Despite different storage environments, a high degree of chemical and spatial similarity is observed over 3 distinct layers ($\text{WO}_x$, $\text{SiO}_2$ and Layer 2) and two interfaces.
Origin of tungsten oxide and root cause of anomaly

Oxygen ion source with electron neutralizer

- It was discovered that an oxygen ion source was used by the vendor to “treat” the final mirror surface.
- Electron emission from tungsten provides charge neutralization during oxygen ion treatment. Volatile tungsten oxide forms on hot W-filaments and transfers to the mirror.
- Amorphous tungsten oxide contains color centers which when excited produce a broad band having a maximum at 910 nm.
ToF-SIMS analysis background

Image processing with multivariate analysis (MVA)

- In a ToF-SIMS depth profile, the collected mass spectral data is analyzed as a function of sputter time (depth).
- In a ToF-SIMS ion image, the collected mass spectral data is analyzed as a function of (x,y) pixel location.
Using MVA to Provide Context

Seeing the forest from the trees

Presence of tetraethyl ammonia (TEA) easily confirmed

Total Positive Ion

MCR Scores Plots

C₄H₁₂N 74.096974
C₅H₁₂N 86.096974
C₆H₁₄N 100.112624
C₈H₂₀N 130.159574
MVA on Tape Lift

Separating multiple organic components

Here an 8 x 8 grid, each 100 x 100 μm scan, is stitched together to form an 800 x 800 μm image area.

MVA analysis reveals 4 distinct components in the above mosaic scan region.
Deconvolution of two similar signatures using PCA

Using positive and negative correlations to separate components

- The top image and PCA correlation/anti-correlation plot is a thumb print from a male scientist whose hand had been inside a glove thus increasing the relative amount of potassium on the skin
- Positive and negative correlations can be used to distinguish regions
- Both prints overlap but are clearly resolvable with different spectral signatures
MVA Applications
Getting more from your data

- Spectral imaging
  - TEM
  - SEM
  - Auger/XPS
  - ToF-SIMS
  - TGA/FT-IR

- Calibration
  - Using MVA to predict multiple concentrations from a single spectra

- Classification
  - Searching for similarities in samples with multiple measurements
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Reflectance Measurements  
Optical Coatings  
Space Environmental Effects  
Time of Flight Secondary Ion Mass Spectrometry  
Optical Coatings  
Space Environmental Effects  
Optical Coatings  
Space Environmental Effects  
Time of Flight Secondary Ion Mass Spectrometry  
Reflectance Measurements
Backup Charts

Details on ToF-SIMS and MVA analysis
ToF-SIMS Depth Profiling

Challenges due to spectral convolution

- In reality, layered samples are rarely discrete in nature
- Mixing of layers is further enhanced by the sputtering process
- This can make it difficult to ascertain which spectral signatures are associated with each layer
- Overlap of spectral features between layers further complicates assignment

Areas at interfaces may contain mixtures of multiple components.

“Pure” spectra for each layer

Mixture of Components
Wavelength reflectance after 24 hours of UV exposure

Simulated orbital solarization

• TWM exposed to 24 hours of UV at air mass zero (space vacuum)
  – *VIIRS telescope only exposed to Earth albedo, and*
  – *24 hour laboratory dose simulates 5 days of full-sun irradiation*

• TWM has ~97% reflectance prior to solarization

• Wavelength response after UV dose approaches that of VIIRS

• Identical results observed for FabWit
As received TWM initial surface analysis by ToF-SIMS

Mosaic imaging raw positive ion data

- 0.8 x 0.8 mm\(^2\) mosaic image with 64 cells each
- Surface exhibited defects and numerous contaminants
  - Scratches expose underlying layers
  - Some subsurface layer material deposited on surface
- Spectral analysis showed
  - Na and numerous low mass hydrocarbon peaks
  - Small tungsten oxide signature in raw data
General Data Processing

• For all ToF-SIMS data, the high resolution data is binned into 1 amu width bins
  – Why? simple to implement computationally
  – Python has fairly fast data structures (called dictionaries or hash tables) to deal with this type of data and make sorting, slicing, etc. pretty simple
  – Avoids most issues pertaining to calibration (If a peak shifts during a depth profile, is it really shifting or is a new peak growing in? How much does it need to shift before you call it a “new” feature instead of a continuation of a previous peak)
  – Even with the loss of resolution, these methods consistently provide a great deal of insight
  – Working on implementing some smarter peak picking algorithms to preserve the high resolution mass spectra coming from the TRIFT II

• For the 0.8 x 0.8 mm mosaic image
  – Each mosaic tile is 100 x 100 \( \mu m \) @ 256 x 256 pixels
  – Each tile is re-pixelated (?) to 8 x 8 pixels (giving 256/8 = 32x increase per pixel)
  – Images are unfolded for MVA, refolded following to make scores plots

• For the depth profile
  – Depth profile data is “binned” into 30 or 60 second time bins (The actual time is arbitrary, these are just round numbers tend to get used)
  – All spatial data is discarded, time slices are integrated across spatial
Multivariate Analysis (MVA) and ToF-SIMS

Systematically generating spectral variation

- Depth profiling
  - Variance as a function of sample depth
- Ion image analysis
  - Spatial variation
- PCA, MCR

- Ionization matrix
  - Use O$_2$ flood to selectively modify signal

- External measurement
  - Find spectral correlations between sample and secondary measurement

- ToF-SIMS library
- PLS, cluster analysis
Multivariate Analysis (MVA) in ToF-SIMS

Simplifying data interpretation

- MVA provides a means of summarizing a large number of dependent variables into a smaller number of statistical variables.
- MVA extracts information from data with multiple variables, such as a ToF-SIMS spectra, by using all variables simultaneously.
  - *This leads to more efficient analysis of large and high dimensional datasets*
  - *Because data is correlated across multiple variables, signal to noise can be improved*
- In a ToF-SIMS ion image, the collected mass spectral data is analyzed as a function of (x,y) pixel location.
  - *This shows how spectral components vary spatially*
- In a ToF-SIMS depth profile, the collected mass spectral data is analyzed as a function of sputter time (depth).
  - *Each unique layer and the interface between layers are described by separate components*
- **Scores plots** show the relative weight of each component as a function of sputter depth.
- **Loadings plots** show the mass spectral signature of each score.
Multivariate Analysis Methods Employed

More about Multivariate Curve Resolution

• Multivariate Curve Resolution (MCR) extracts “pure” component spectra from a multi-component mixture
• Only the number of components to be modeled is provided prior to analysis, no other a priori information is necessary
• MCR is similar to Principle Component Analysis (PCA), but has a some key differences
  – In PCA, the loadings (eigenvectors) can have positive or negative values. In MCR, loadings are constrained to positive values, this results in MCR results looking like ToF-SIMS spectra.
  – In PCA, the loadings (eigenvectors) are mutually orthorgonal. In MCR, the loadings are have no such restraint.
  – MCR results are dependent on the number of factors to be modeled as well as the convergence criteria selected
• MCR assumes that the data can be described as a linear sum of contributors (scores) associated with a given spectra (loading)
Observed on-orbit anomaly on VIIRS

UV photodarkening of telescope mirror

- Loss of near-infrared throughput on VIIRS associated with UV degradation of the optics observed November 2011. Testing of Suomi NPP suspended pending anomaly resolution outcome

- Ultraviolet induced degradation may arise from,
  - Decomposition of an organic/polymeric contamination layer, or
  - Excitation of a metallic ad-layer which would block certain IR bands

- If the anomaly was due to an adventitious coating, then
  - Where did the coating originate?
  - Were other NPP missions and instruments at risk?

- Two witness samples coated simultaneously and structurally identical to VIIRS telescope mirror were analyzed
  - Telescope witness mirror (TWM) from VIIRS integration and test
  - Fabrication witness mirror (FabWit) from the coating run