Assessing Redundancy of UV-Vis Microspectrophotometry, Scanning Electron Microscopy/Energy Dispersive Spectroscopy, Fourier Transform Infrared Spectroscopy, and Raman Spectroscopy to the Detection of Distinguishing Features of Colored Spray Paint

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Disclaimer

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Problem Statement + Research Question

Project Design + Implementation

Results + Discussion

Conclusions

Problem Statement + Research Question

Analytical Scheme

Analytical Scheme

- What if no exclusionary differences are noted?
  - Question of a common source
    - Rarity
  - Subjective process

Problem Statement

- Comparative analysis of pigments

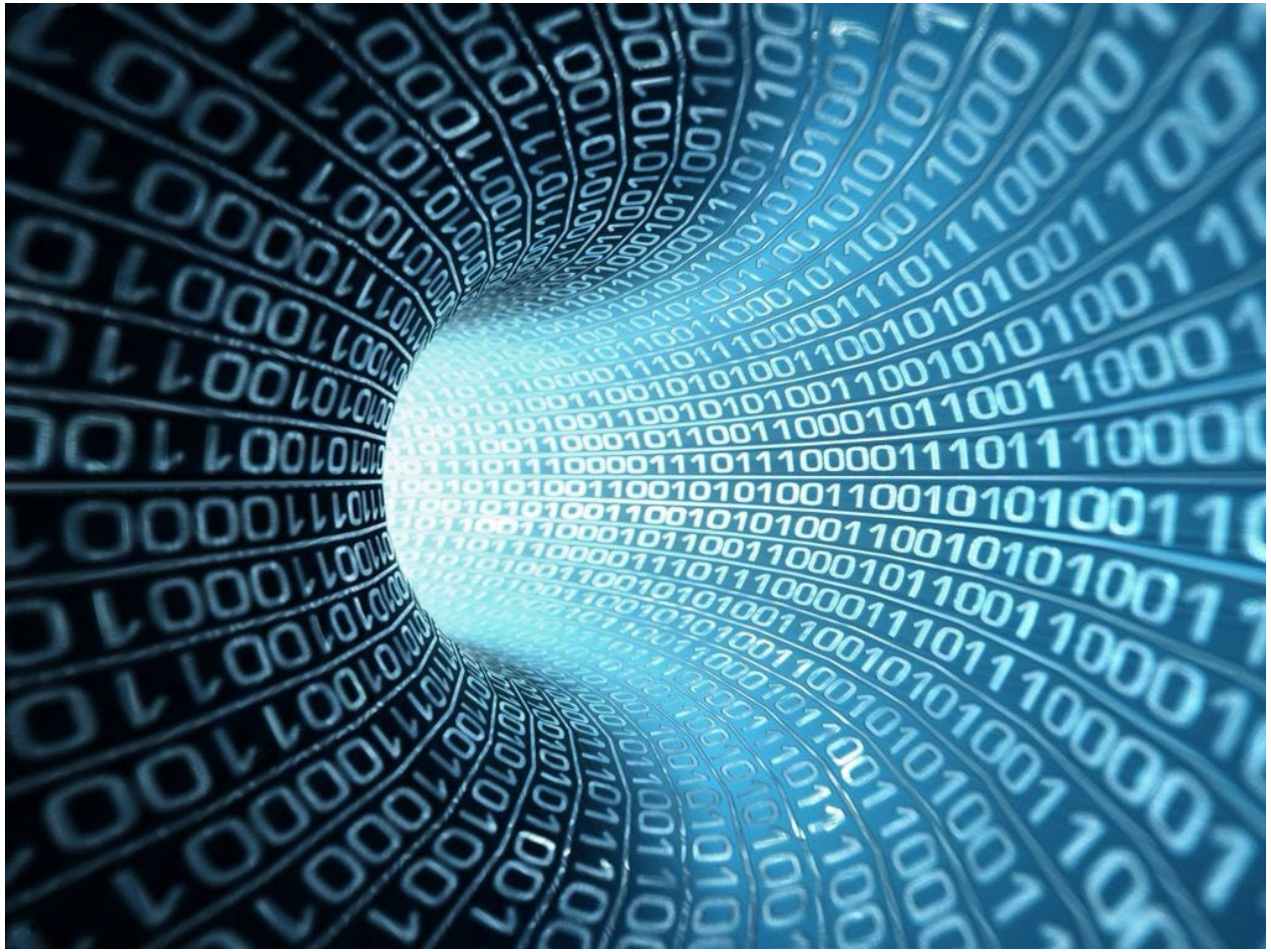
- Comparative analysis of possible pigments
- Comparative analysis of possible extenders

- Identification of binders and extenders
- Identification of some pigments

- Identification of pigments
- Identification of some extenders

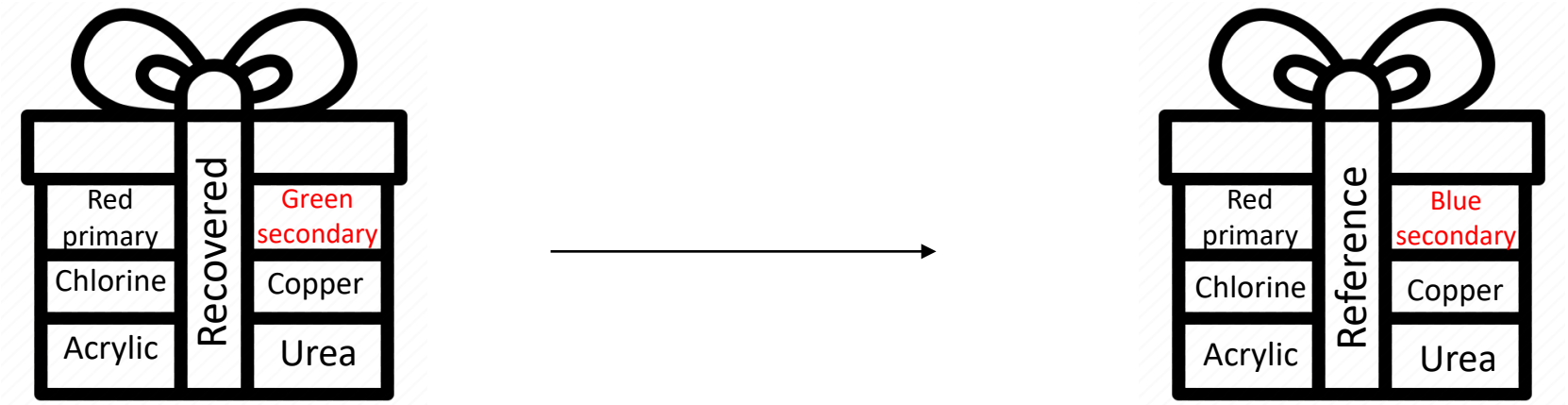
Problem Statement

- Huge amount of the same data
- Lost information
- Uncertainties in the results



Problem Statement

- Implementation of a holistic, objective, and verifiable comparison
  - Reliable data “packages”
  - Primary aim is the efficiency in building the packages



Research Goal

UV-Vis MSP data block containing the most selective features

SEM-EDS data block containing the most selective features

FTIR data block containing the most selective features

Raman data block containing the most selective features

VS.

UV-Vis MSP data

SEM-EDS data

FTIR data

Raman data

Research Objectives

- The goal will be met by:
  - **Defining the features of interest**
  - **Detection of minor components**
  - **Identifying dependencies or redundancies**
  - Evaluating the potential interferences of the adjacent layers
  - Compare variants of multi-block exploratory data analysis, feature selection, and predictive modeling methods

Redundancy Example

- UV-Vis MSP: indicative of blue color
- Micro-FTIR: Barium sulfate + alkyd orthophthalic
- Micro-Raman: C.I. Pigment Blue 15
- SEM/EDS: Ba, S, Cu

- What features from each analytical method are the most selective?
- Are any instruments offering solely redundant information?

Project Design and Implementation

Overall Strategy

- Collection of paint of different end use with a variety of relevant properties
- Analytical methods include:
  - Light microscopy methods
  - UV-Vis MSP
  - SEM/EDS
  - Micro-Raman spectroscopy (532 and 785 nm wavelength)
  - Micro-FTIR
- Qualitative and quantitative components

Samples

- Spray paint samples of commonly encountered colors
  - 20 spray paint samples plus 5 automotive refinishing paint samples
  - Major differences in regards to FTIR
    - Enable identification criteria to define chemical compositions
  - Additional information from pigment analysis

Sample Preparation

- Spray paint samples sprayed on glass slides
- UV-Vis MSP
  - Sample embedded using Kulzer Technovit ® blue light curing resin
  - Cross-sections at 8 µm thickness and mounted in 1:1 glycerin and water solution
- SEM/EDS
  - Sample removed from glass slide and fixed on double sided carbon tape for analysis
  - Currently not being carbon or gold coated
- Micro-Raman
  - Samples analyzed directly on glass slide
- Micro-FTIR
  - Sample removed from glass slide, micro-rolled and placed on NaCl pellet

Instrumentation

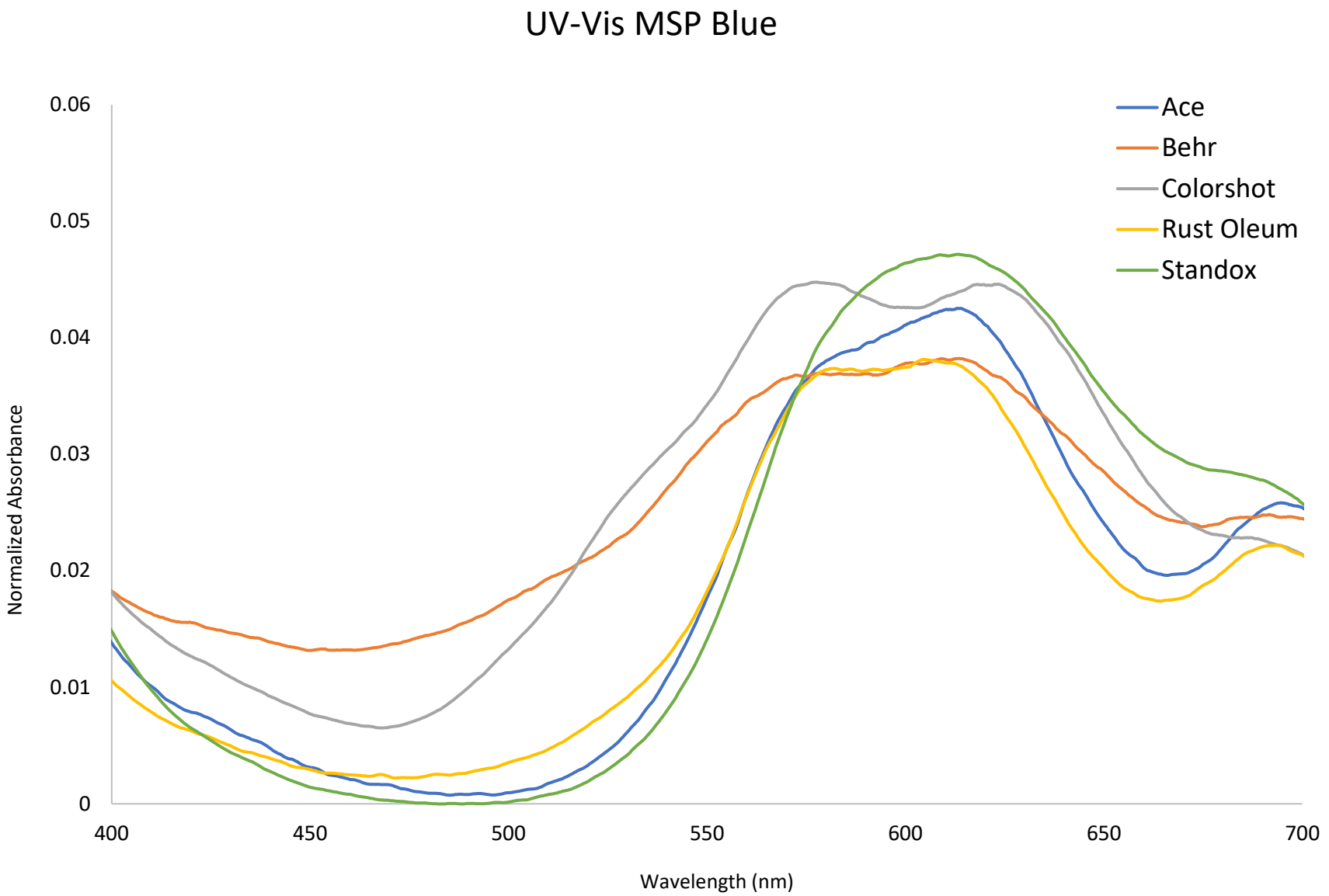
- CRAIC FLEX UV-Visible NIR microspectrophotometer (CRAIC Technologies, San Dimas, CA), coupled to a Zeiss AXIO research microscope (Carl Zeiss AG, Oberkochen, Germany)
- Hitachi SU3500S (Hitachi, Chiyoda, Tokyo, Japan) with secondary electron- and backscatter- detector SEM coupled to a Bruker SFlash 6|30 (Bruker, Billerica, MA) EDS microanalysis system
- Renishaw InViaTM Inspect confocal Raman microscope (Renishaw plc, Wotton-under-Edge, UK), equipped with laser lines at 532nm and 785nm attached to a confocal Leica DM 2700 M research microscope (Leica Microsystems GmbH, Wetzlar, Germany)
- Nicolet 6700 FT-IR spectrometer coupled to a FT-IR Nicolet Continuum microscope from Thermo Fisher Scientific Inc. (Madison, WI). The IR microscope has a 15x reflectance objective and a mercury-cadmium-telluride (MCT) detector

Data Curation

- UV-Vis MSP
  - Transmittance mode with 270 – 770 nm spectral range
  - 10x10 micron window
  - 7 replicates
- SEM/EDS
  - Parameters optimized to gain most information
    - 1000x magnification, 25.0 kV voltage, 10.0 working distance, 40.0 spot size
  - 7 replicates
- Micro-Raman
  - Both 532 nm and 785 nm laser
  - Parameters optimized for each sample (power, accumulations, accumulation time)
    - Spectral range of 2000 – 200 cm^{-1}
    - 100x objective
  - 7 replicates
- Micro-FTIR
  - Transmittance mode with spectral resolution of 4 cm^{-1} and 128 scans
  - 7 replicates

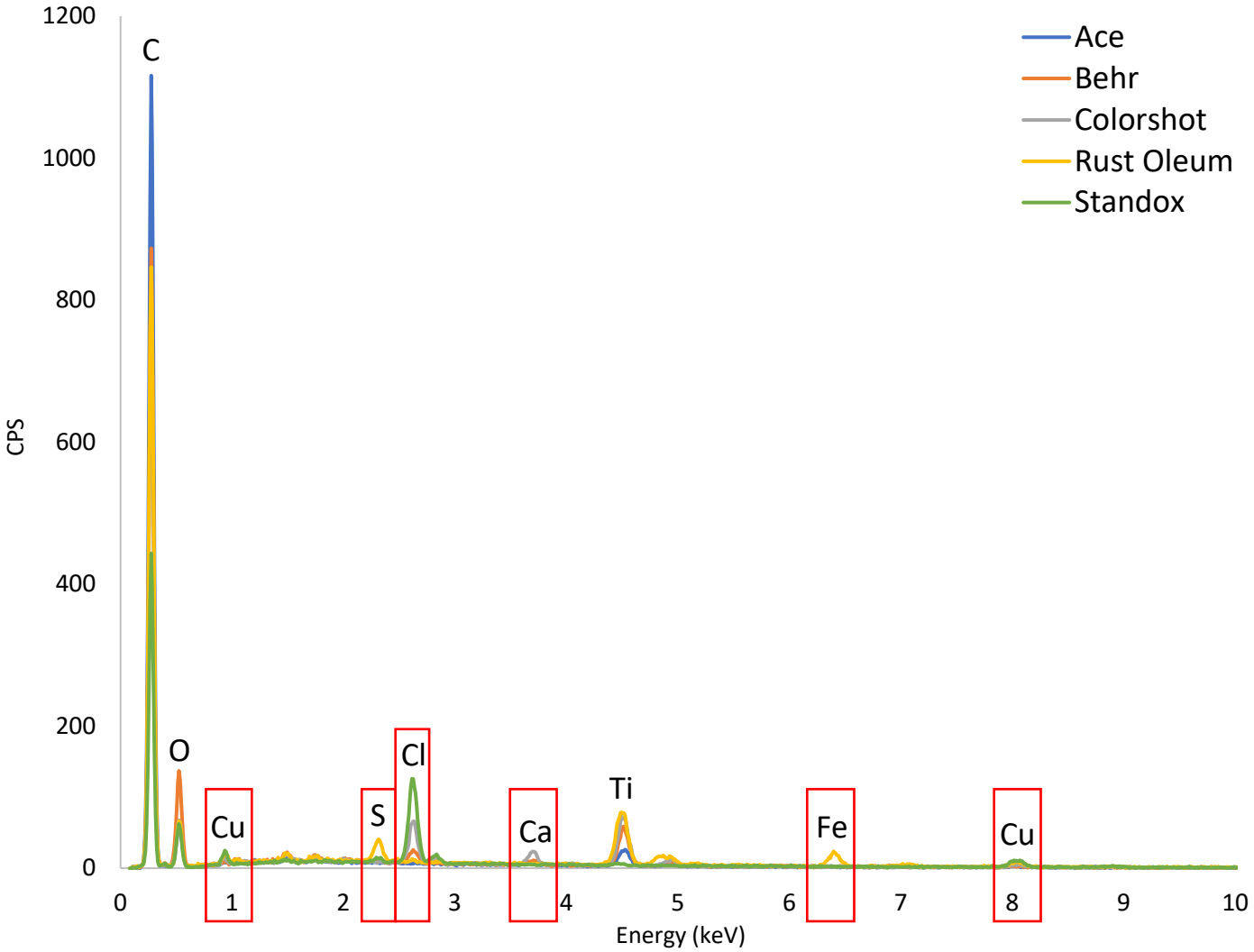
Results + Discussion

Blue Spray Paint

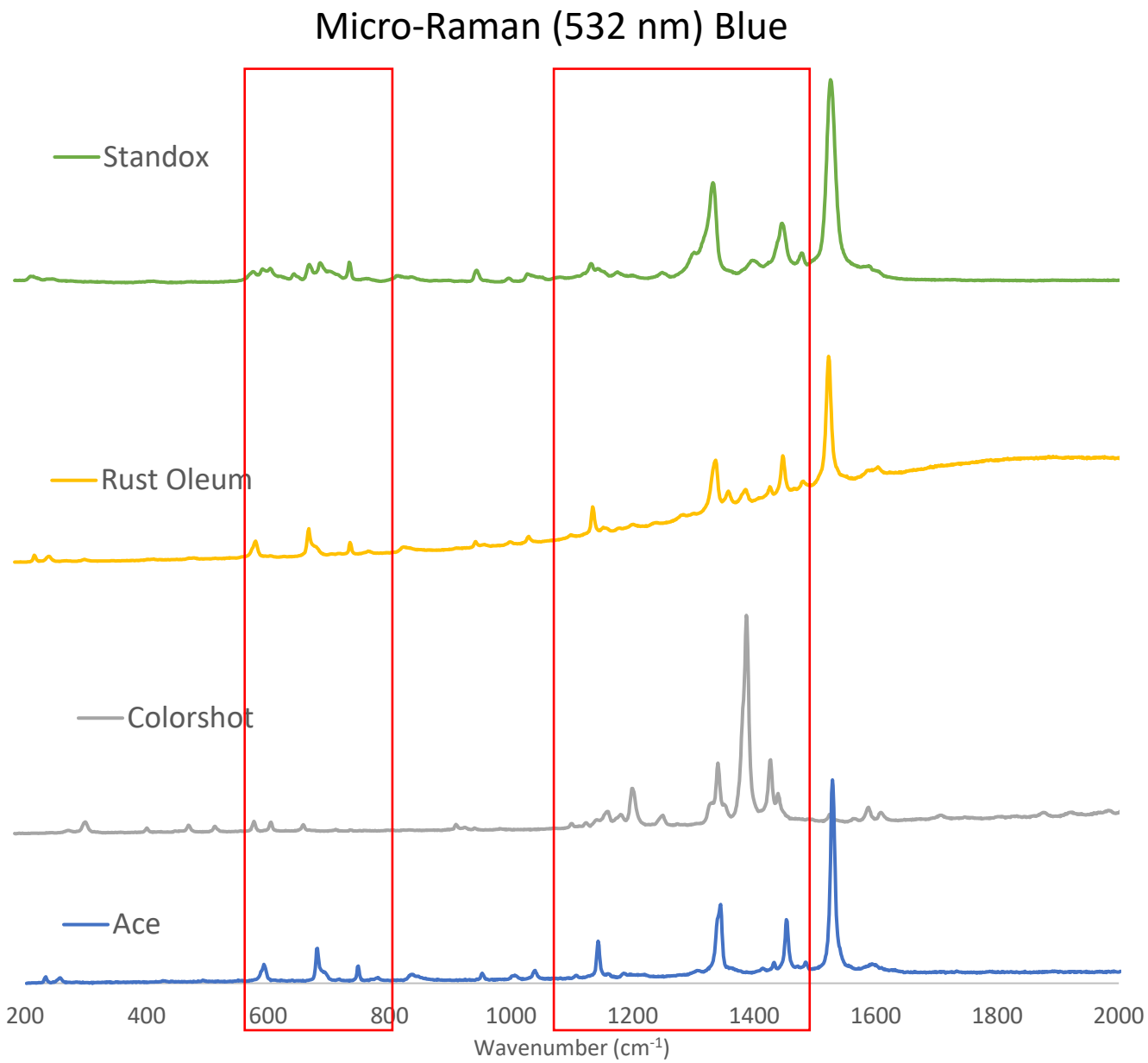


- Useful for quick differentiation
- Only beneficial for comparative analysis
- UV region to be investigated

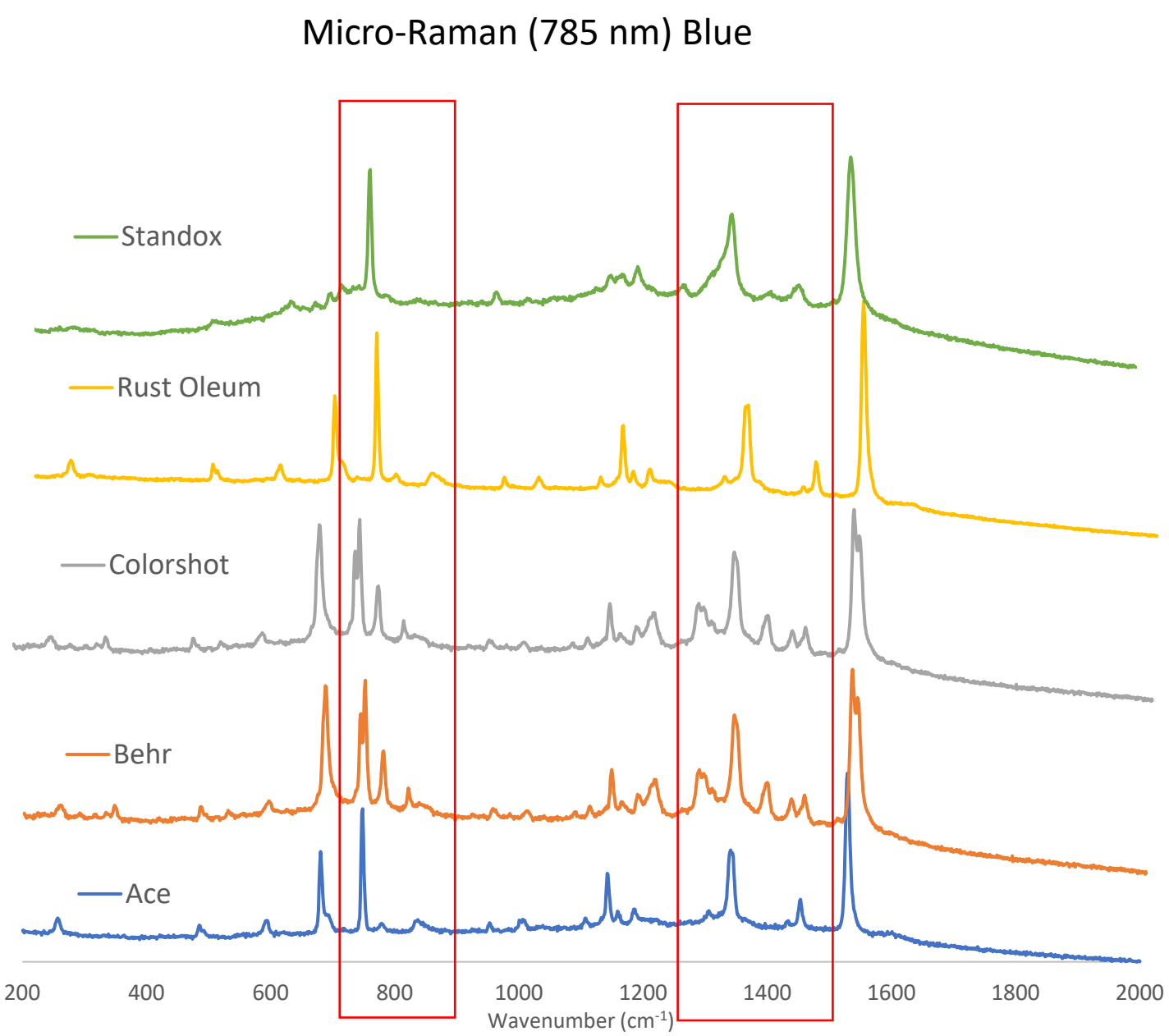
SEM/EDS Blue



- Hypothesized compounds present:
  - C.I. Pigment Blue 15 (copper)
  - C.I. Pigment Violet 21 (chlorine)
  - Barium sulfate
  - Calcium carbonate
- Compounds can be confirmed via Raman or FTIR
- S, Cl, Cu, Fe, and Ca could be more selective features
- Beneficial for comparative analysis



- Behr not included due to fluorescence
- Ace, Rust Oleum, and Standox identified as PB15
- Colorshot identified as PV23
- ~1150 – 1550 cm^{-1} contains possible selective features
  - Key peak at 1390 cm^{-1} and 1430 cm^{-1} for PV23
- ~600 – 800 cm^{-1} could be additional selective region for PB15
- Reduces number of variables by half
  - Possible to reduce further by focusing on key peaks



- Behr was able to be analyzed
  - PB15
- No additional new information gained
- Possible selective region from 800 – 900 cm^{-1} and 1200 – 1400 cm^{-1}

Micro-FTIR Blue

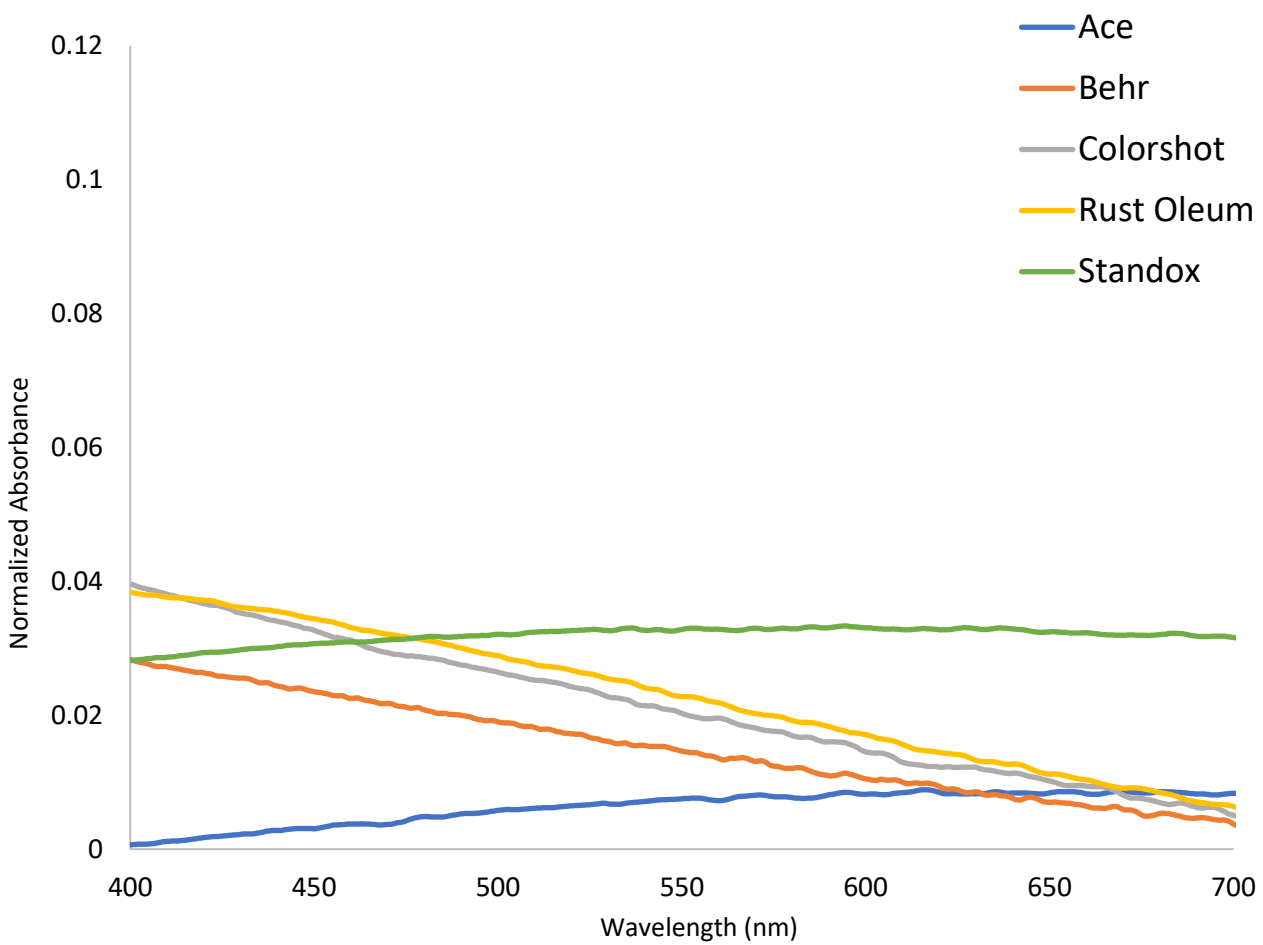
Brand	Binder(s)	Extender(s)
Ace	Alkyd orthophthalic	Styrene
Behr	Alkyd orthophthalic	Urea
Colorshot	Mixed polyester	Styrene
Rust Oleum	Alkyd orthophthalic	Styrene, barium sulfate
Standox	Mixed polyester	Inconclusive

Discussion

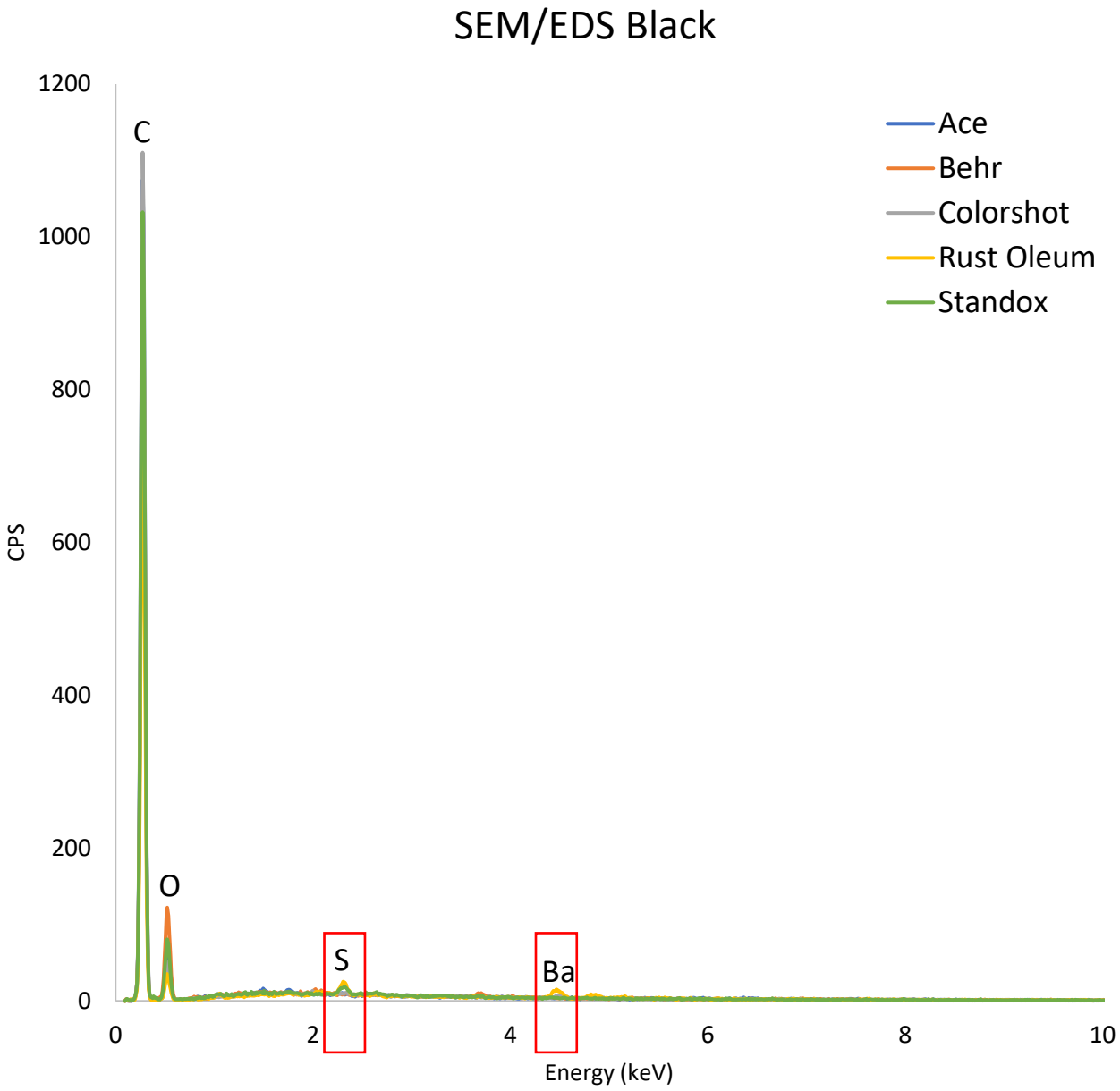
- Micro-FTIR offers the greatest differentiation
  - SEM/EDS yields redundant information
- Micro-Raman analysis using the 532 nm laser yielded varying pigments but was not able to analyze all samples
  - SEM/EDS yields redundant information
- By focusing on certain elements (Fe, Ca) that were unexplained by FTIR/Raman SEM/EDS offers selective features
- UV-Vis MSP does not yield any identification capabilities
  - Could be useful for the data fusion approach though

Results + Discussion

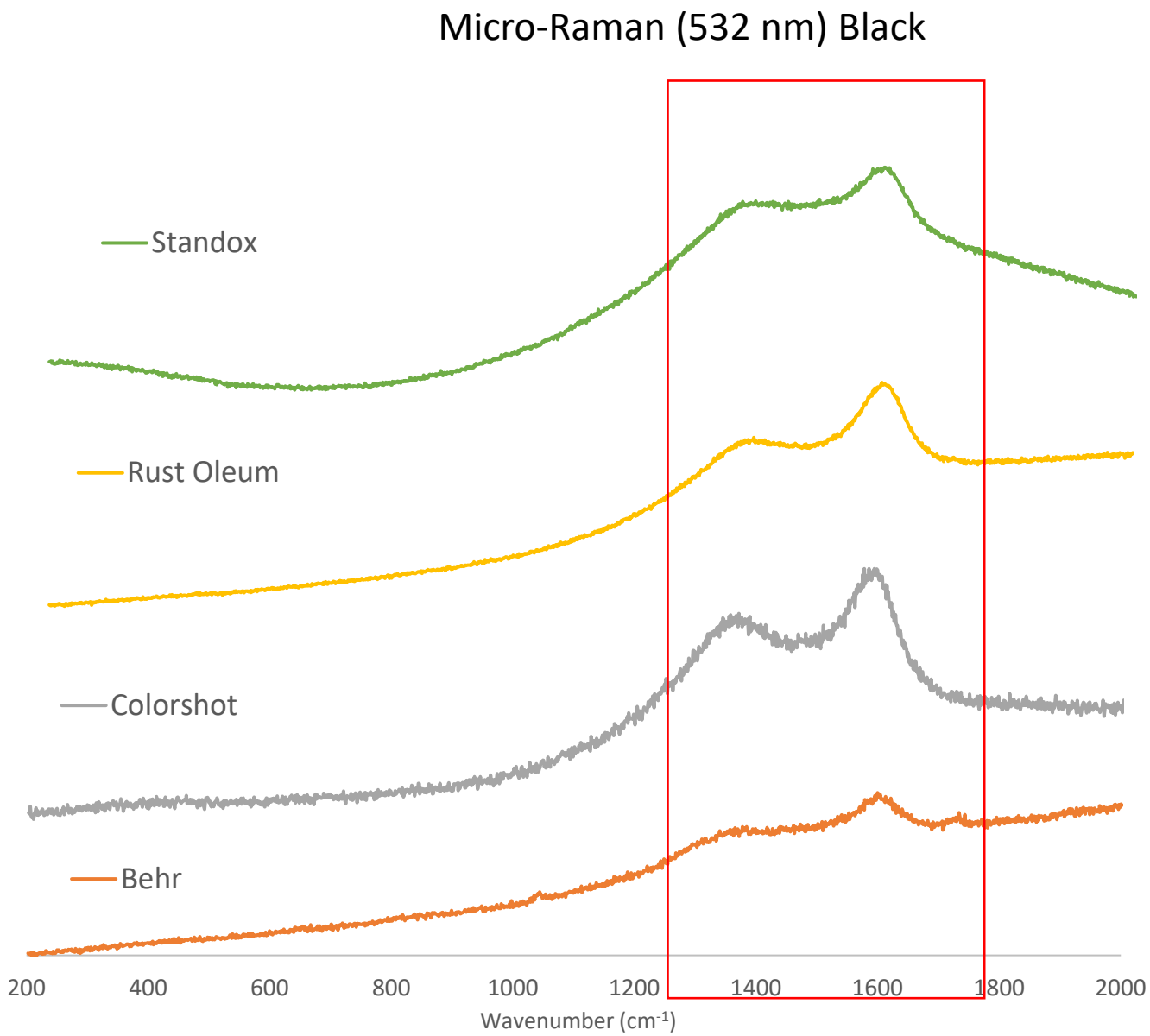
Black Spray Paint



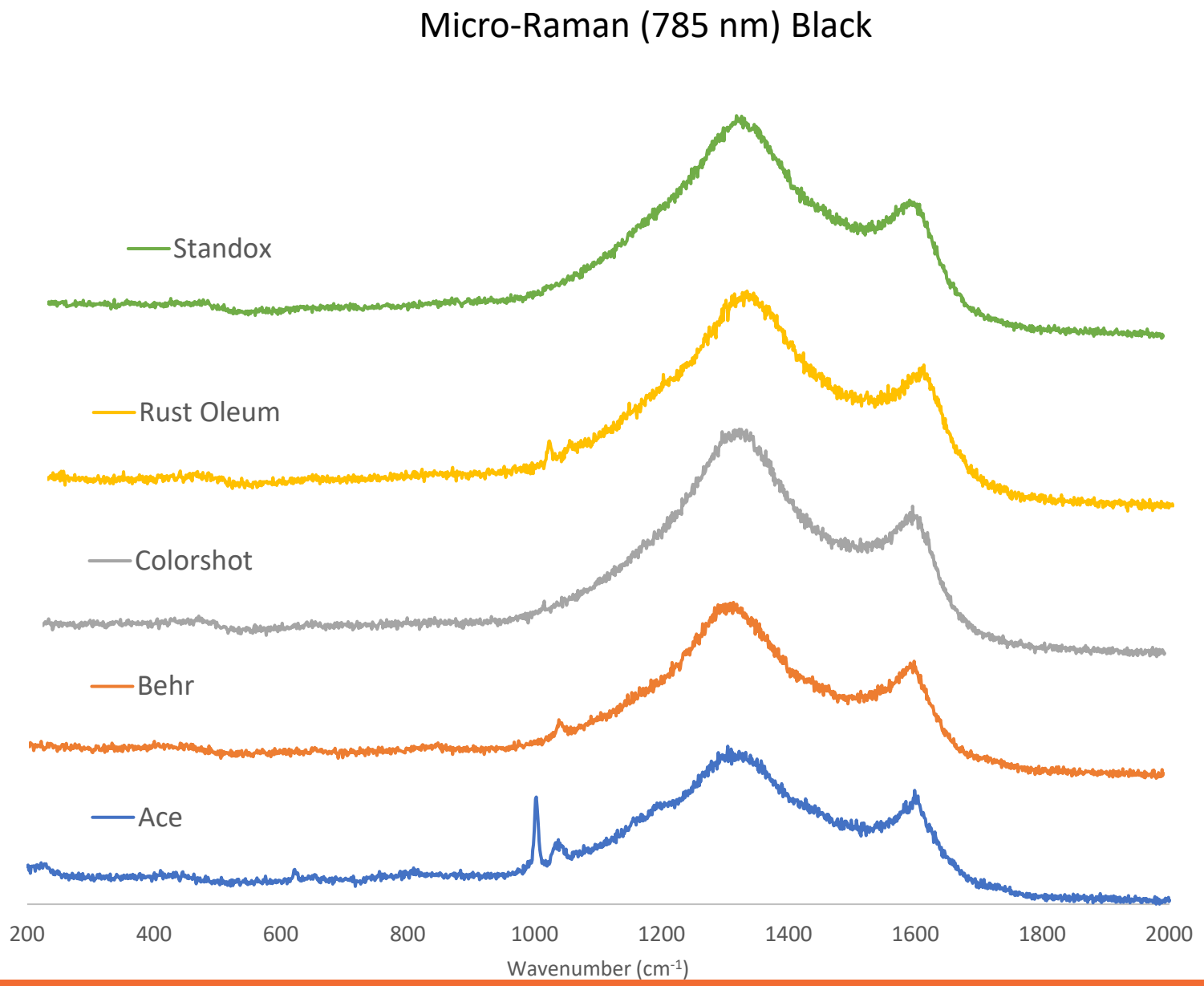
- No information gained from visible region
- UV region could offer information but needs to be investigated further



- Hypothesized barium sulfate present in Rust Oleum and possibly Standox
- Possible selective features that can be confirmed via micro-FTIR

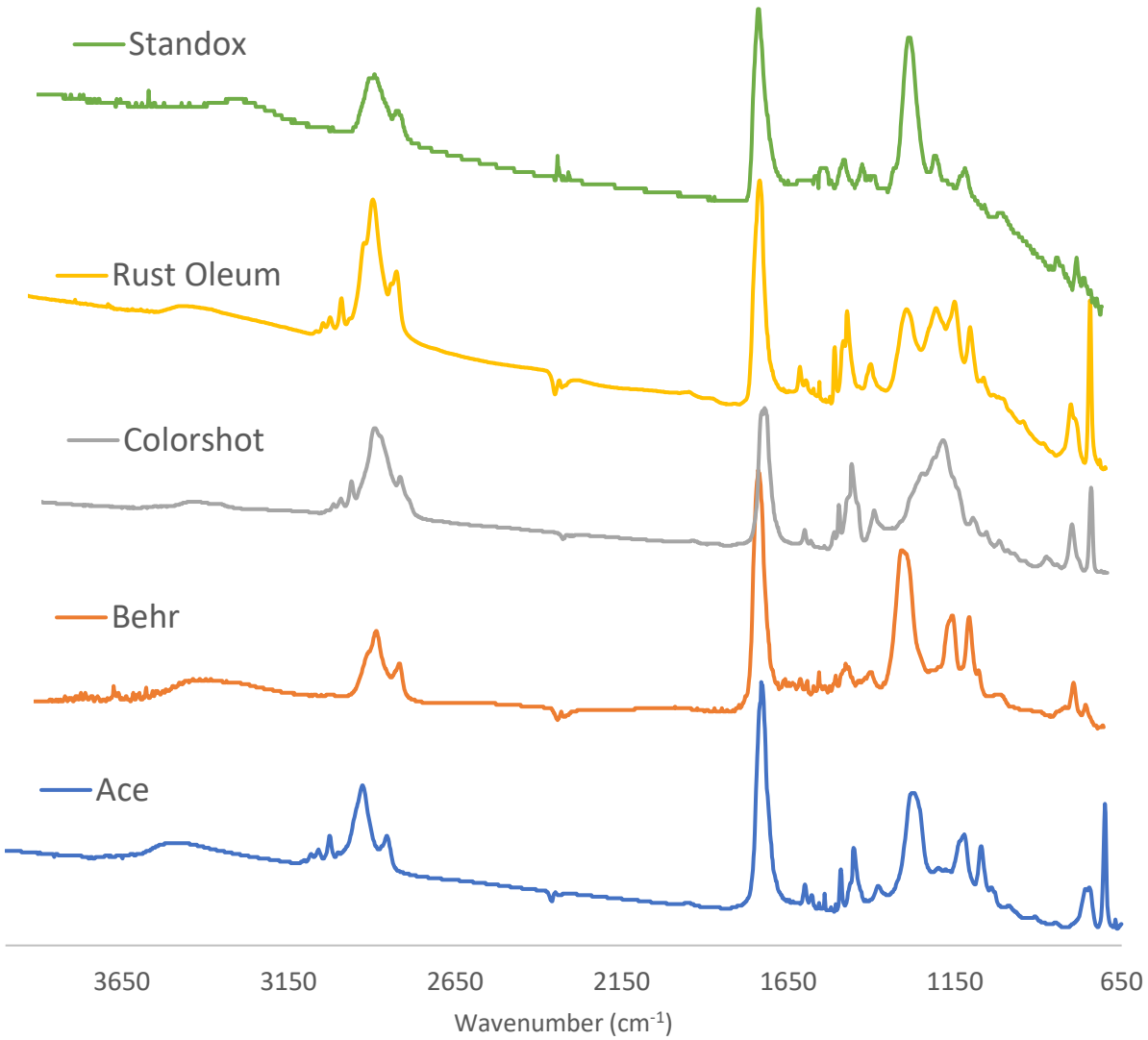


- Ace not able to be analyzed due to fluorescence
- All samples had pigment of carbon black
- Region from 1300 – 1600 cm^{-1} as useful region but does not give differentiation information



- All samples able to be analyzed
- All identified as carbon black
- 785 nm laser does allow for Ace peaks not accounted for with 532 nm laser

Micro-FTIR Black



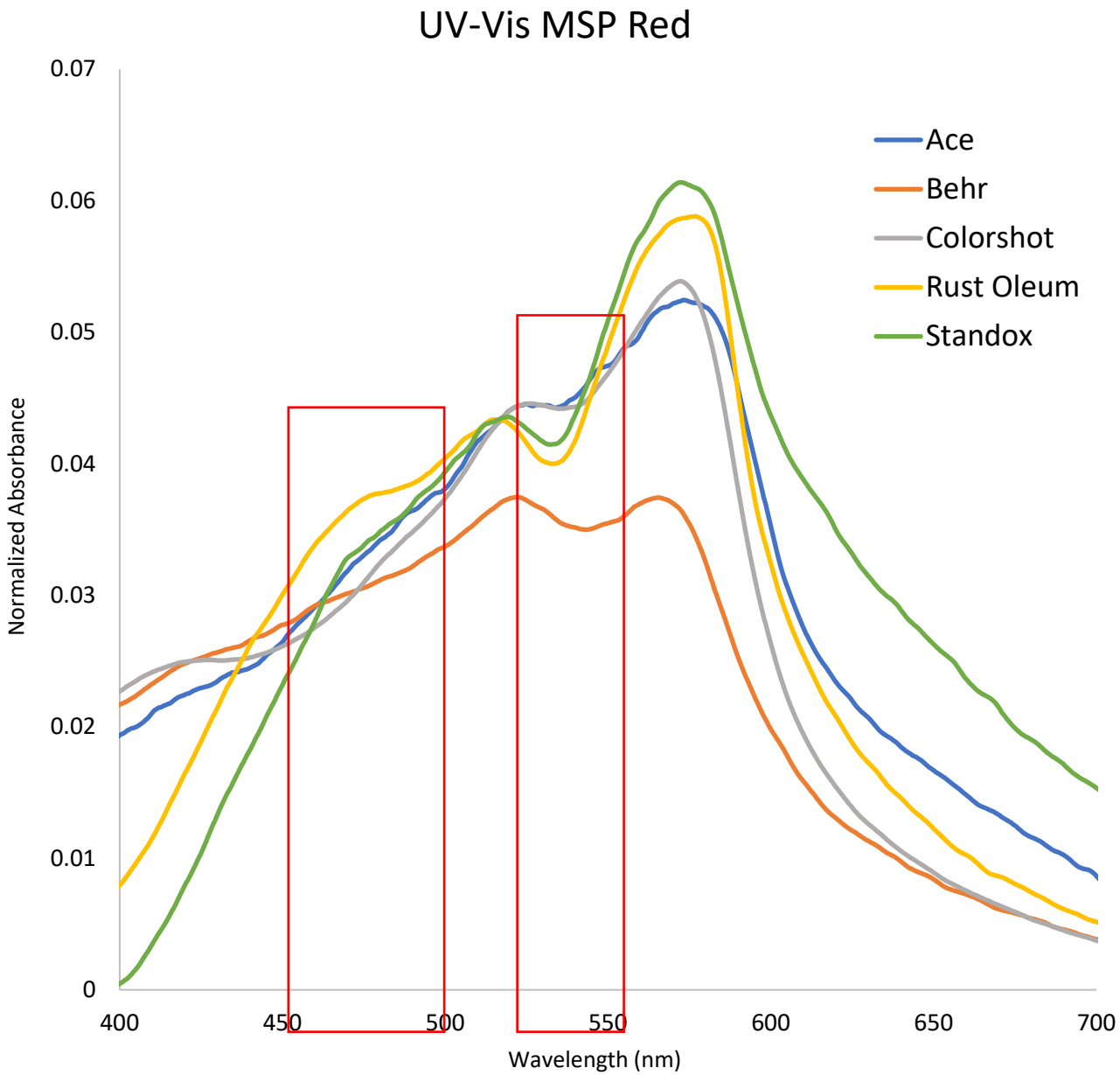
Brand	Binder(s)	Extender(s)
Ace	Alkyd orthophthalic	Styrene
Behr	Alkyd orthophthalic	Styrene
Colorshot	Mixed polyester	Inconclusive
Rust Oleum	Alkyd orthophthalic	Styrene, barium sulfate
Standox	Mixed polyester	Inconclusive

Discussion

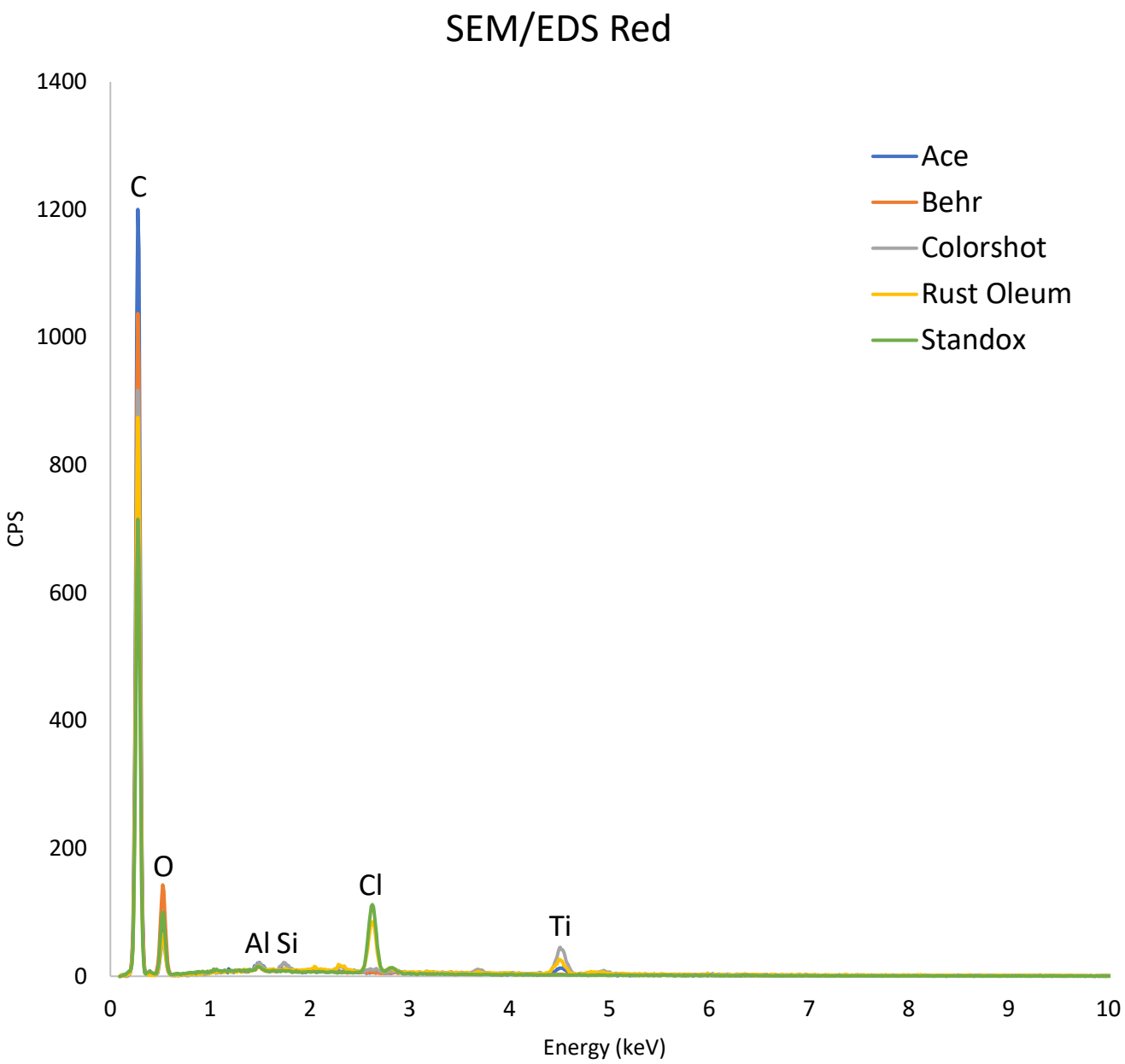
- Micro-FTIR offers the greatest variation
- Micro-Raman with 532 nm laser is redundant
  - 785 nm could offer more information
- Barium and sulfur offer selective features in SEM/EDS
- UV-Vis MSP does not help in visible region but could be valuable if UV region is researched further

Results + Discussion

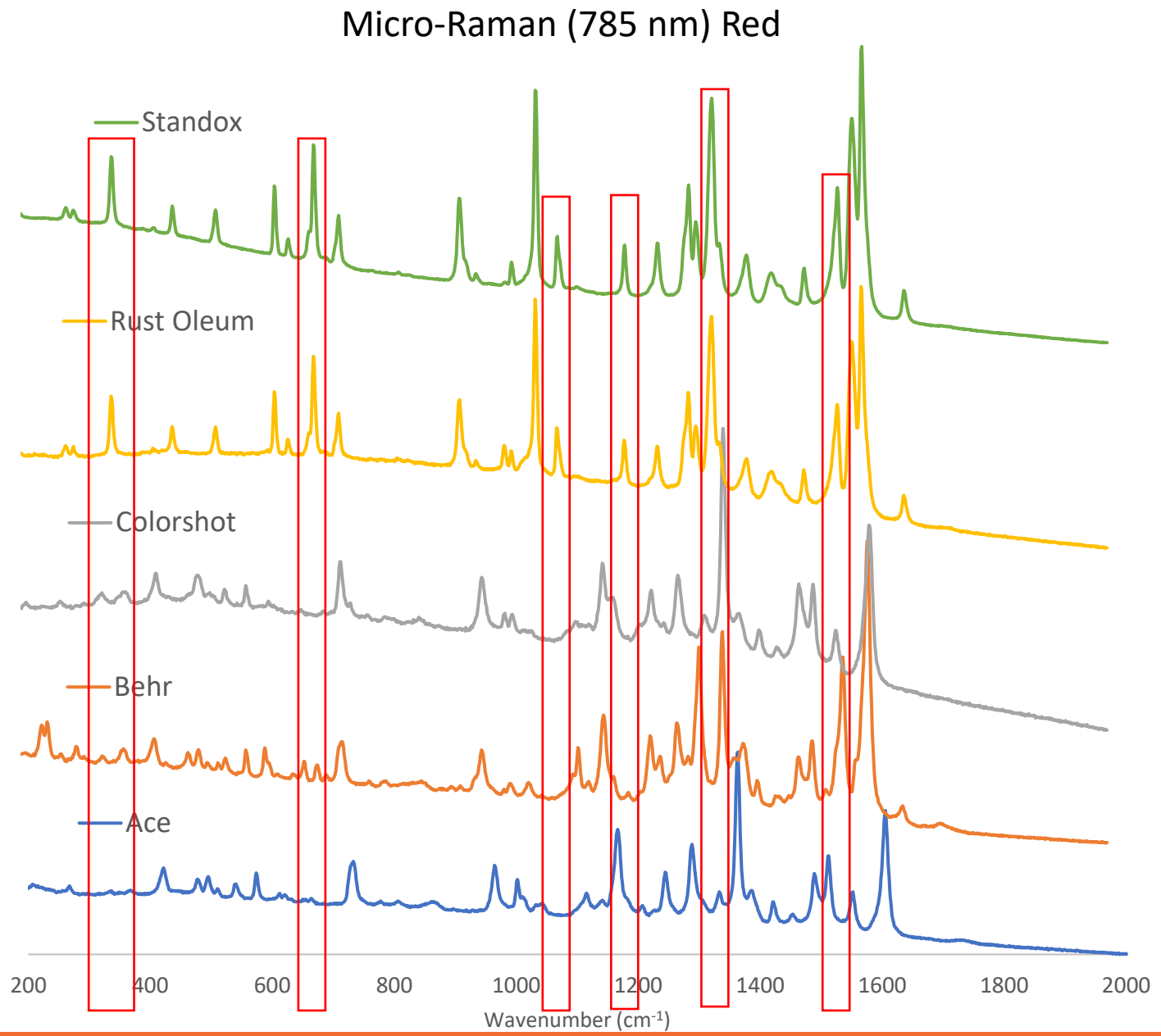
Red Spray Paint



- Some variation at ~475 nm and 525 – 550 nm
- Variation could offer useful information as selective regions

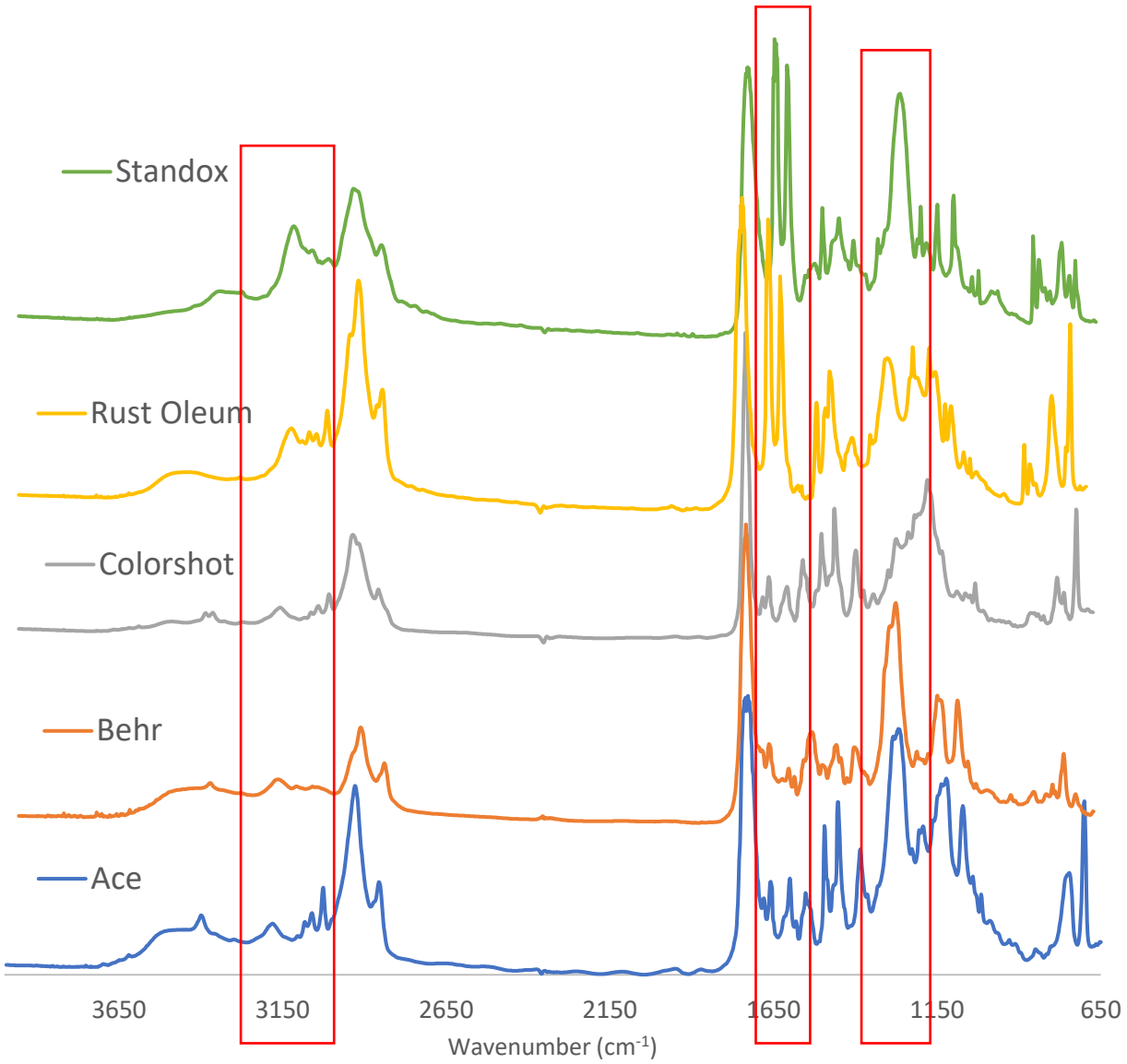


- Hypothesized titanium dioxide and aluminum silicate present
  - Chlorine could come from pigment
- Due to only some samples displaying the hypothesized binders and extenders present, these could be chosen as selective features



- Only 785 nm laser produced identifiable information
- Ace, Behr, and Colorshot identified as PR 170
- Rust Oleum and Standox identified as PR 254
  - Chlorine
- Peaks at 350, 685, 1055, 1165, 1345, and 1510 cm^{-1} as selective features

Micro-FTIR Red



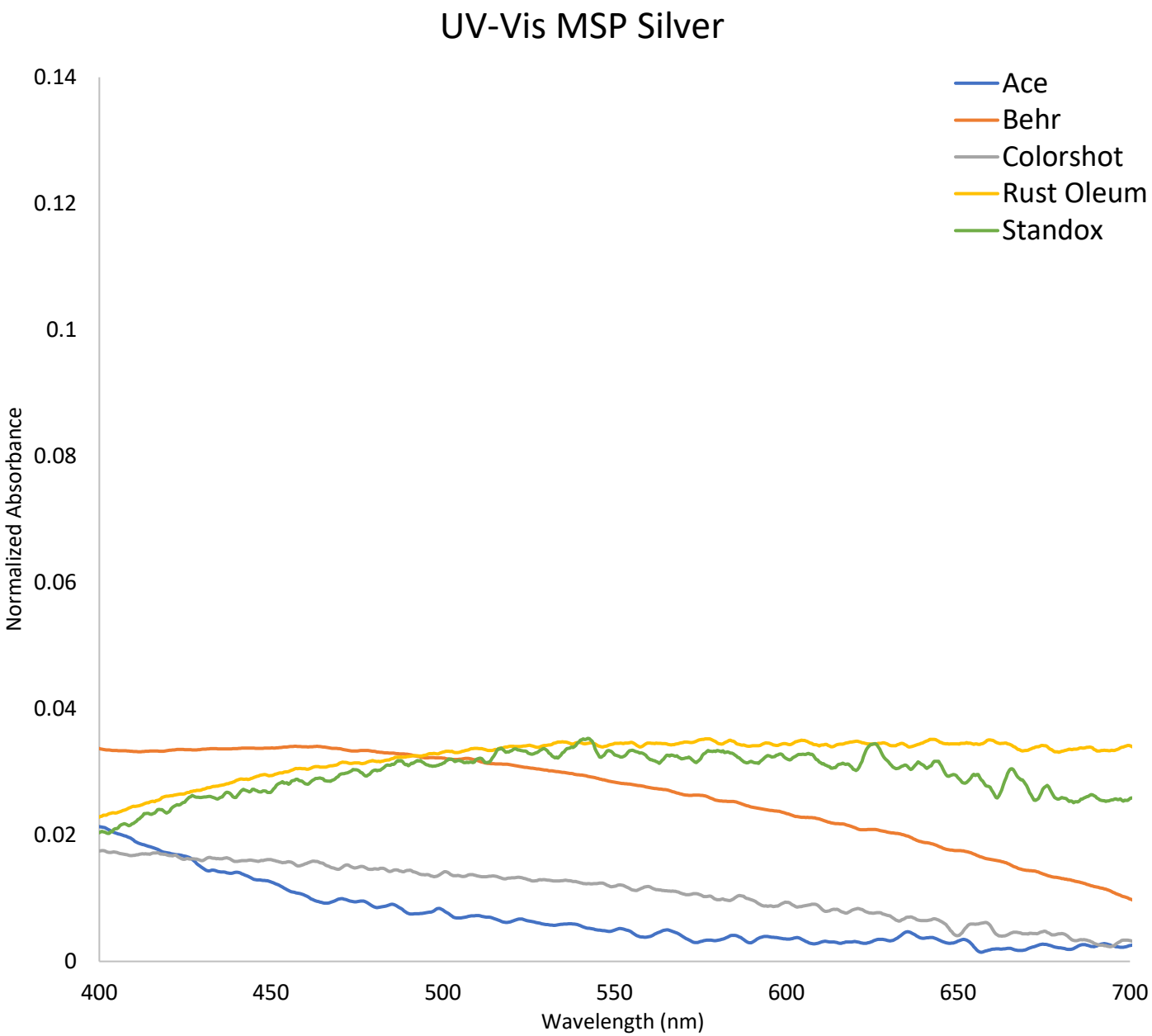
Brand	Binder(s)	Extender(s)
Ace	Alkyd orthophthalic	Styrene
Behr	Alkyd orthophthalic	Urea
Colorshot	Polyurethane	Styrene, aluminum silicate
Rust Oleum	Alkyd orthophthalic	Styrene
Standox	Acrylic	Inconclusive

Discussion

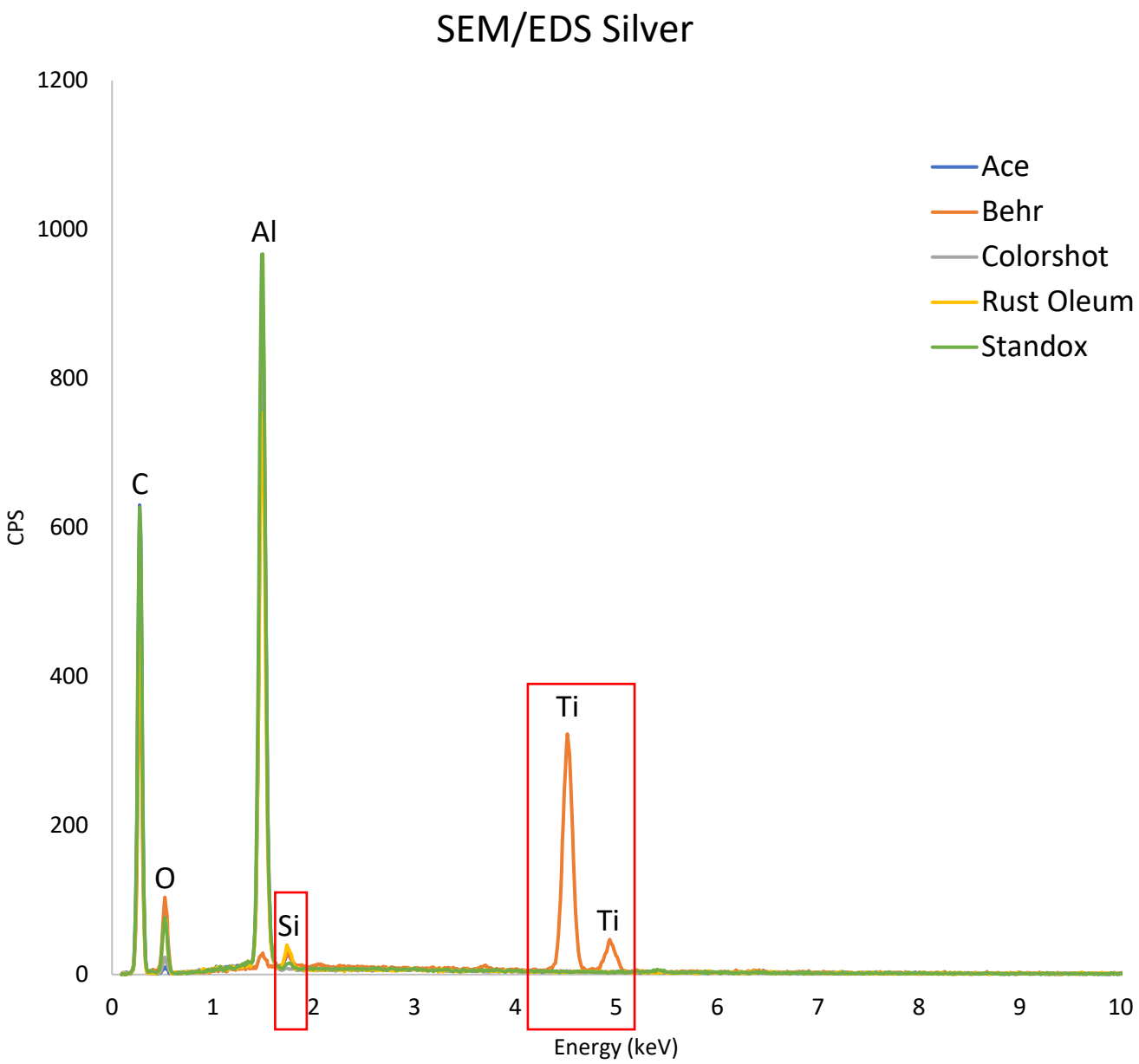
- Both micro-Raman and micro-FTIR offer selective features for differentiation
  - 532 nm laser does not yield any useful information
- Titanium appears in SEM/EDS but is not explained elsewhere but other elemental information is redundant
  - Supportive information but redundant
- UV-Vis MSP gives selective regions that can lead to further differentiation

Results + Discussion

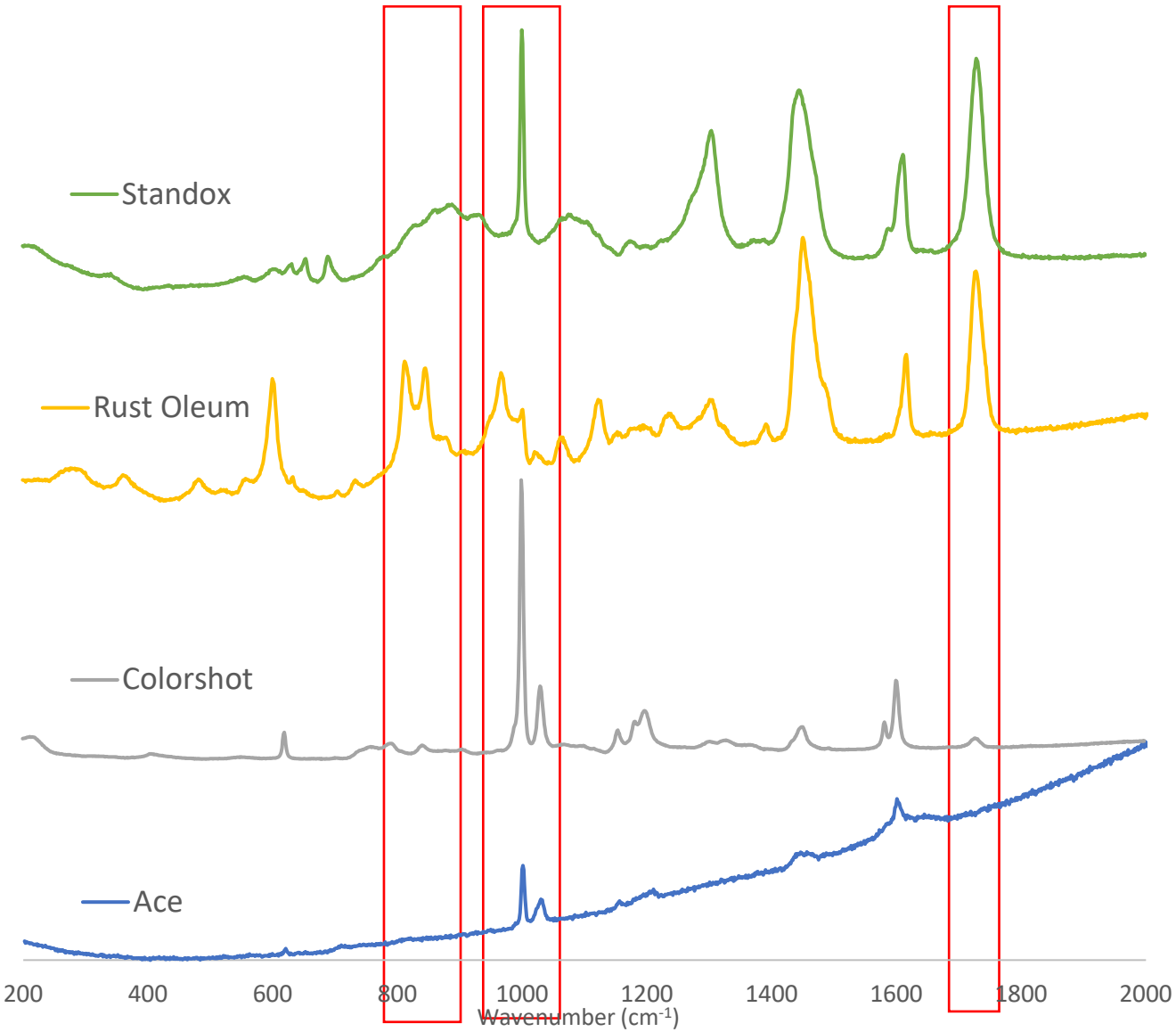
Silver Spray Paint



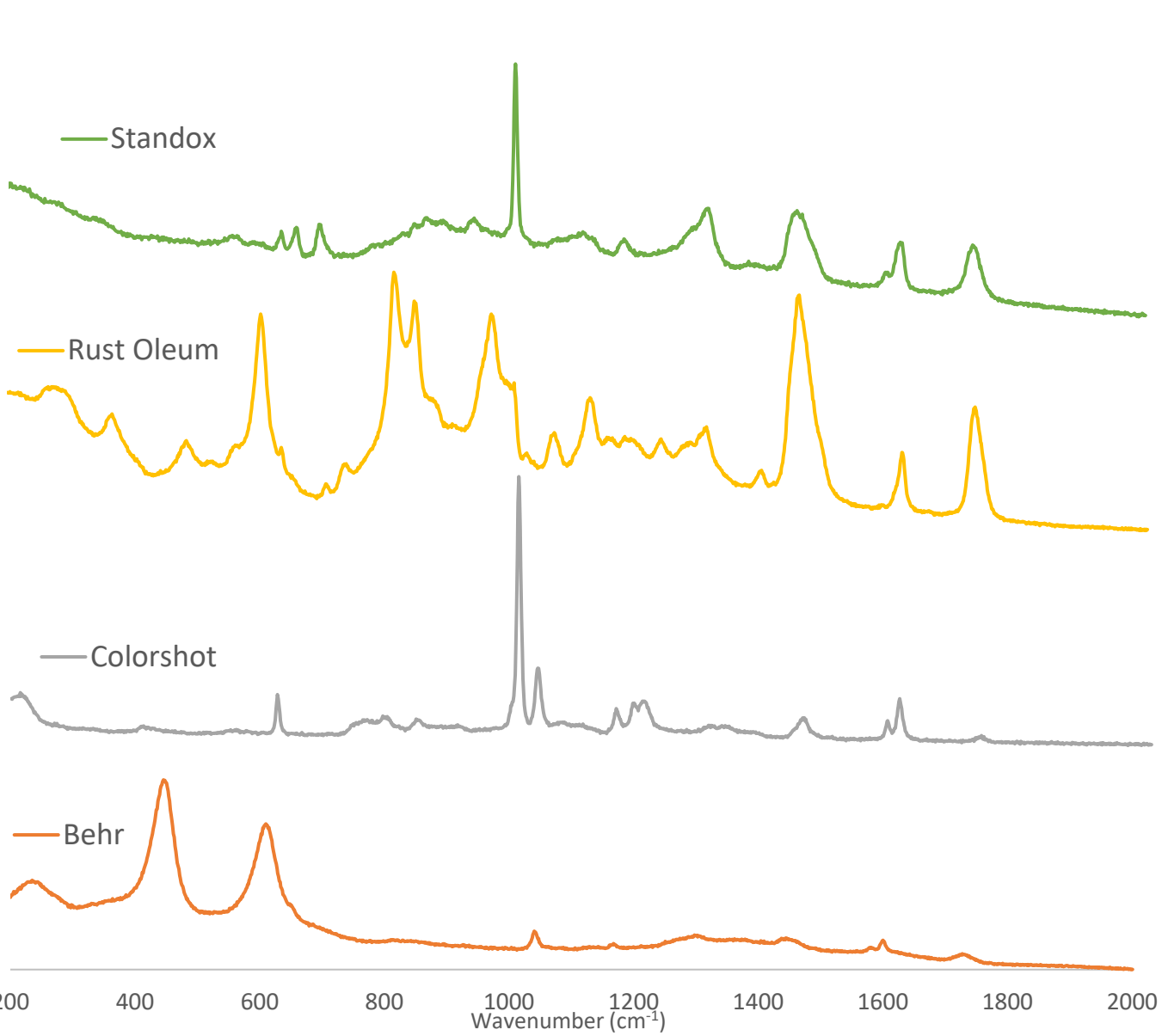
- Due to metallic particle, UV-Vis MSP is not suitable for analysis



- Behr is a non-metallic sample so lack of aluminum is expected
- Hypothesized titanium dioxide and aluminum silicate present
- Silicon and titanium can be considered a selective feature

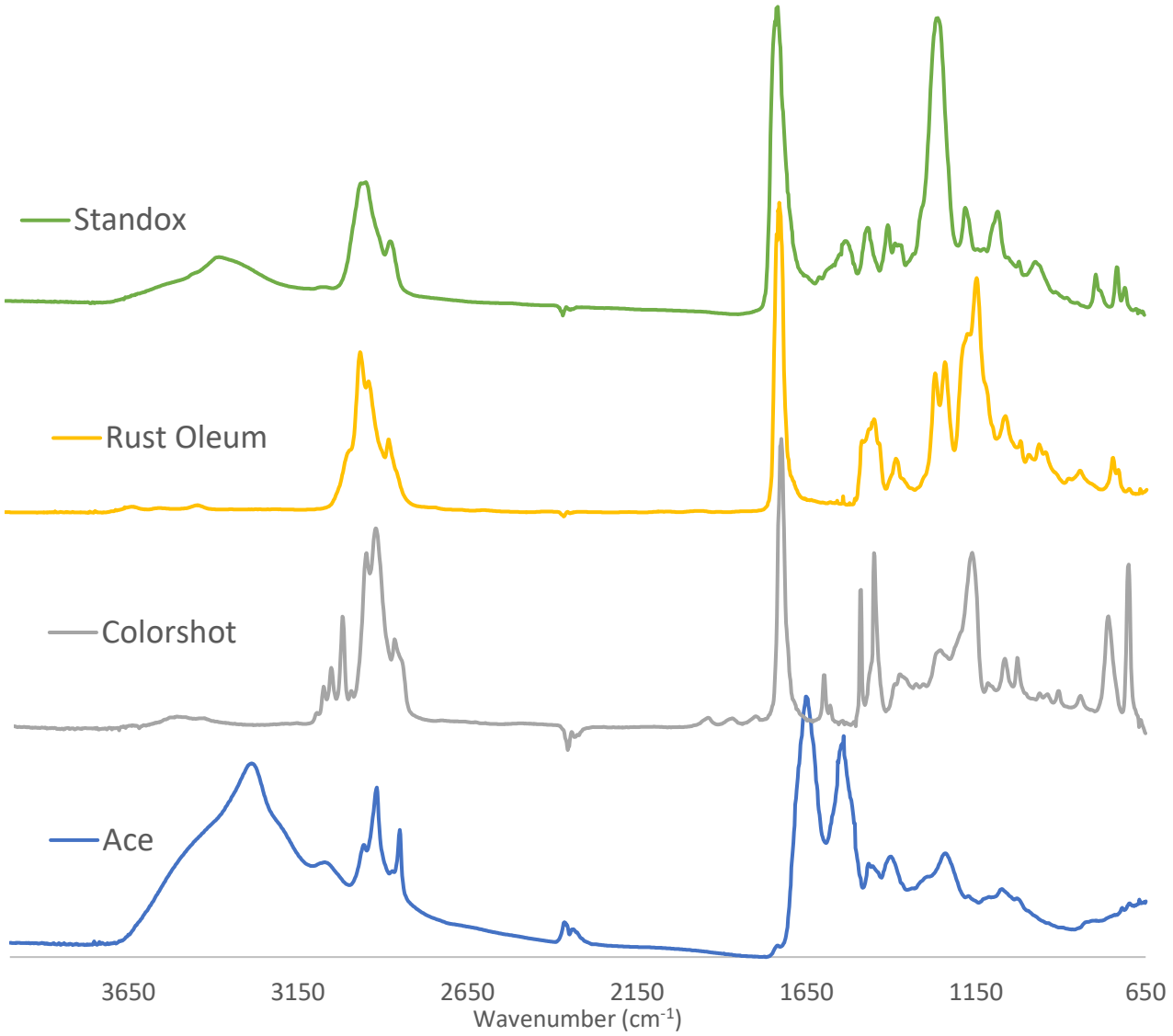


- No pigments identified
  - Further research to determine what peaks are
- Due to unknown composition, whole spectra can be used as selective features
  - Key peaks 800 – 900, 1000 – 1050, 1700 – 1750 cm^{-1}
- Large overall variation between samples
- Behr not included due to fluorescence



- Rutile form of titanium dioxide identified in Behr sample
- Large overall display of variation
- Ace not included due to fluorescence
- Both lasers necessary to gain information on all samples

Micro-FTIR Silver



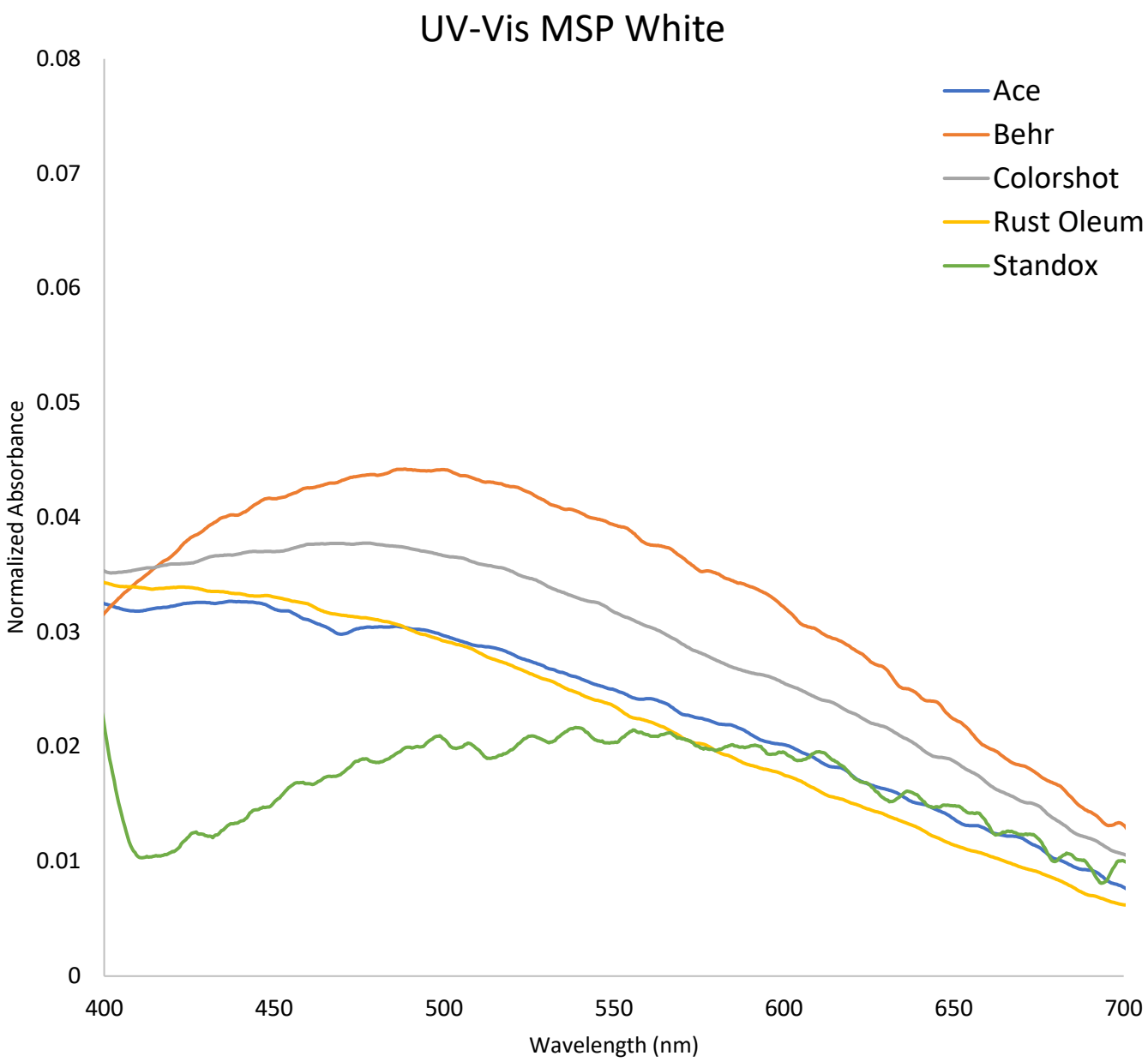
Brand	Binder(s)	Extender(s)
Ace	Mixed polyester	Melamine
Colorshot	Polyurethane	Styrene
Rust Oleum	Alkyd orthophthalic	Styrene
Standox	Alkyd orthophthalic	Inconclusive

Discussion

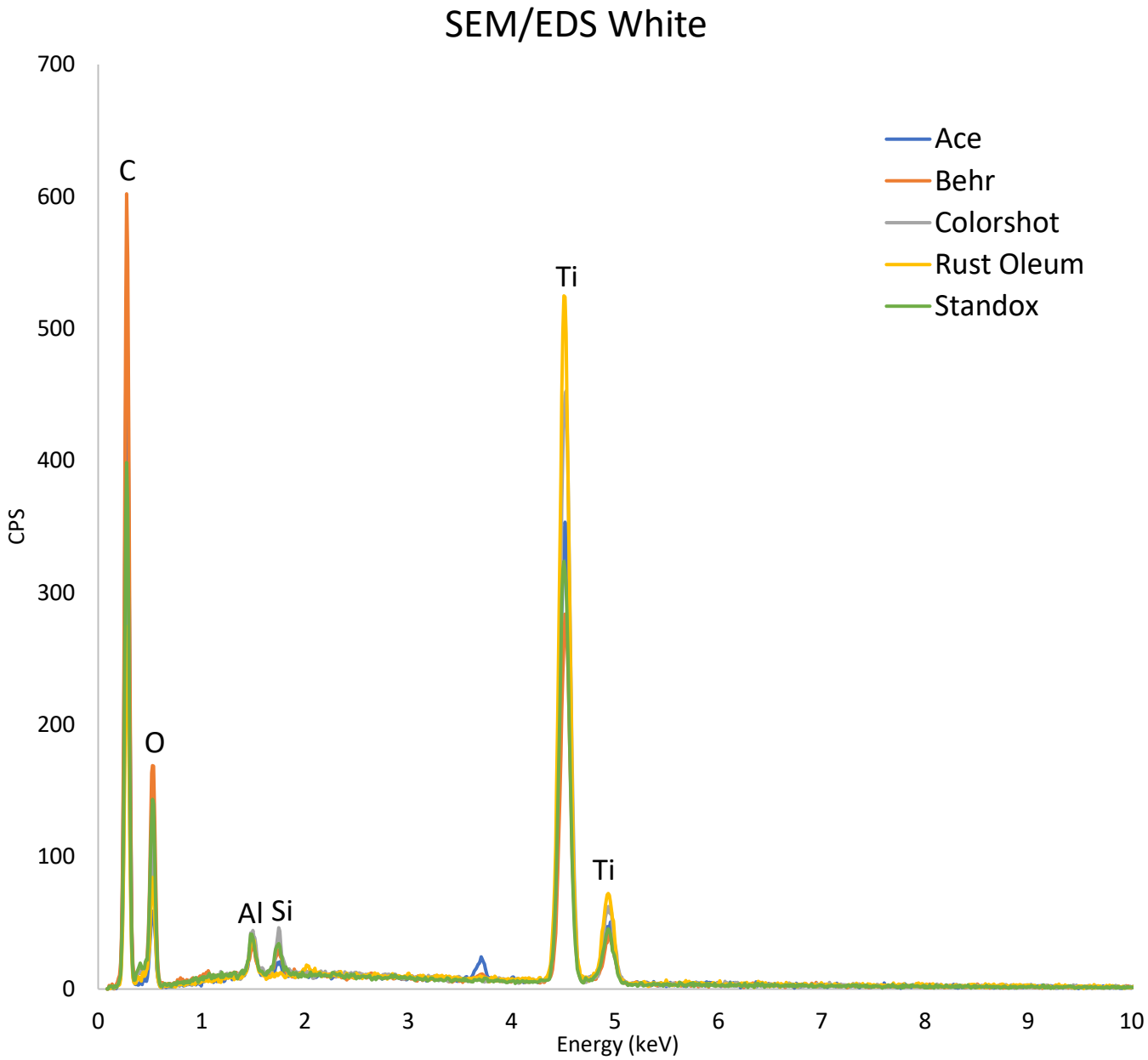
- Both micro-Raman and micro-FTIR offer selective features for differentiation
  - Both lasers are necessary to extract the most information
- SEM/EDS can offer selective features based on binder and extender type
- UV-Vis MSP is not suitable for this type of sample

Results + Discussion

White Spray Paint

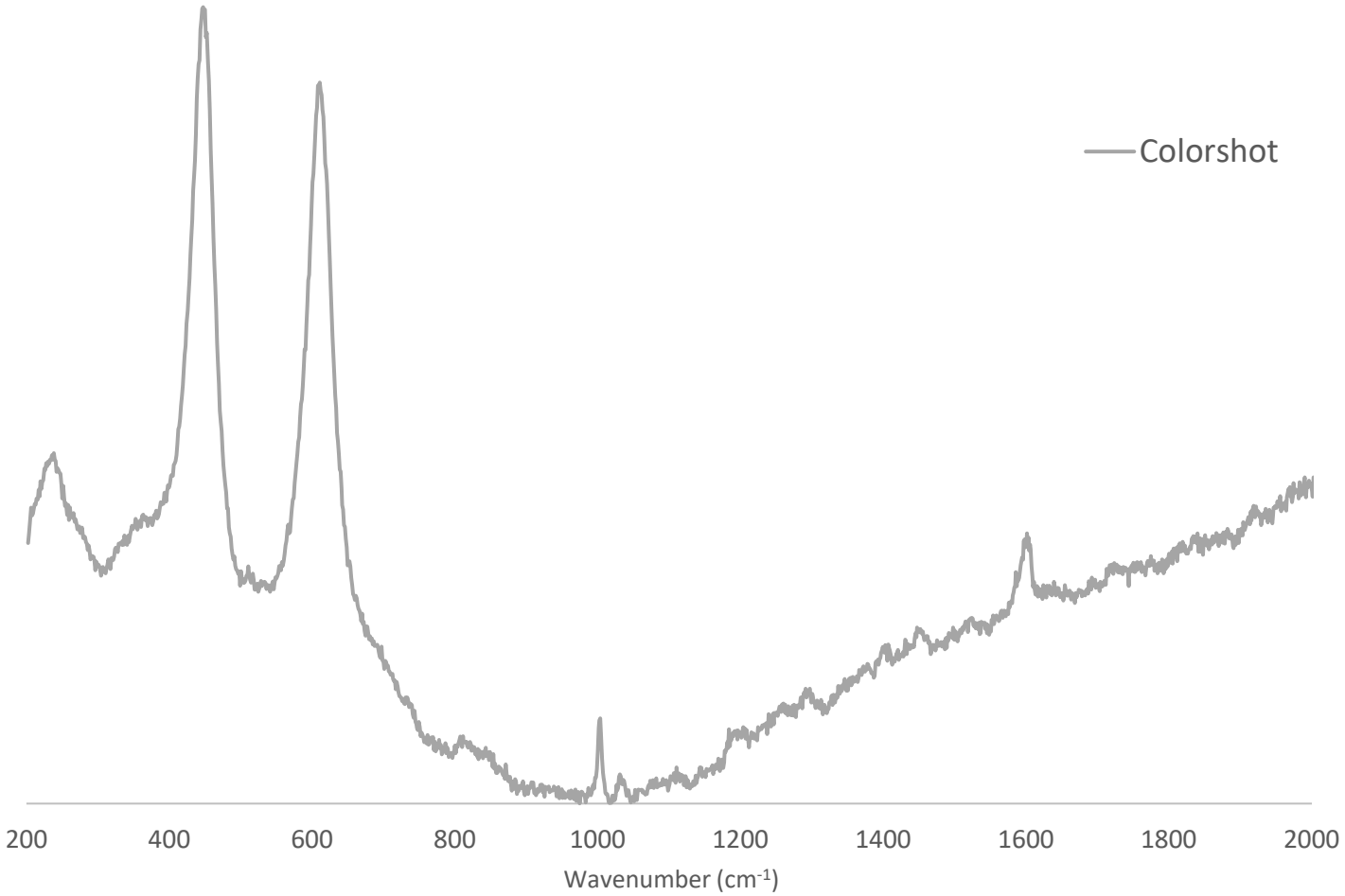


- UV-Vis MSP not suitable for analysis
  - UV region could offer selective information but needs to be further researched

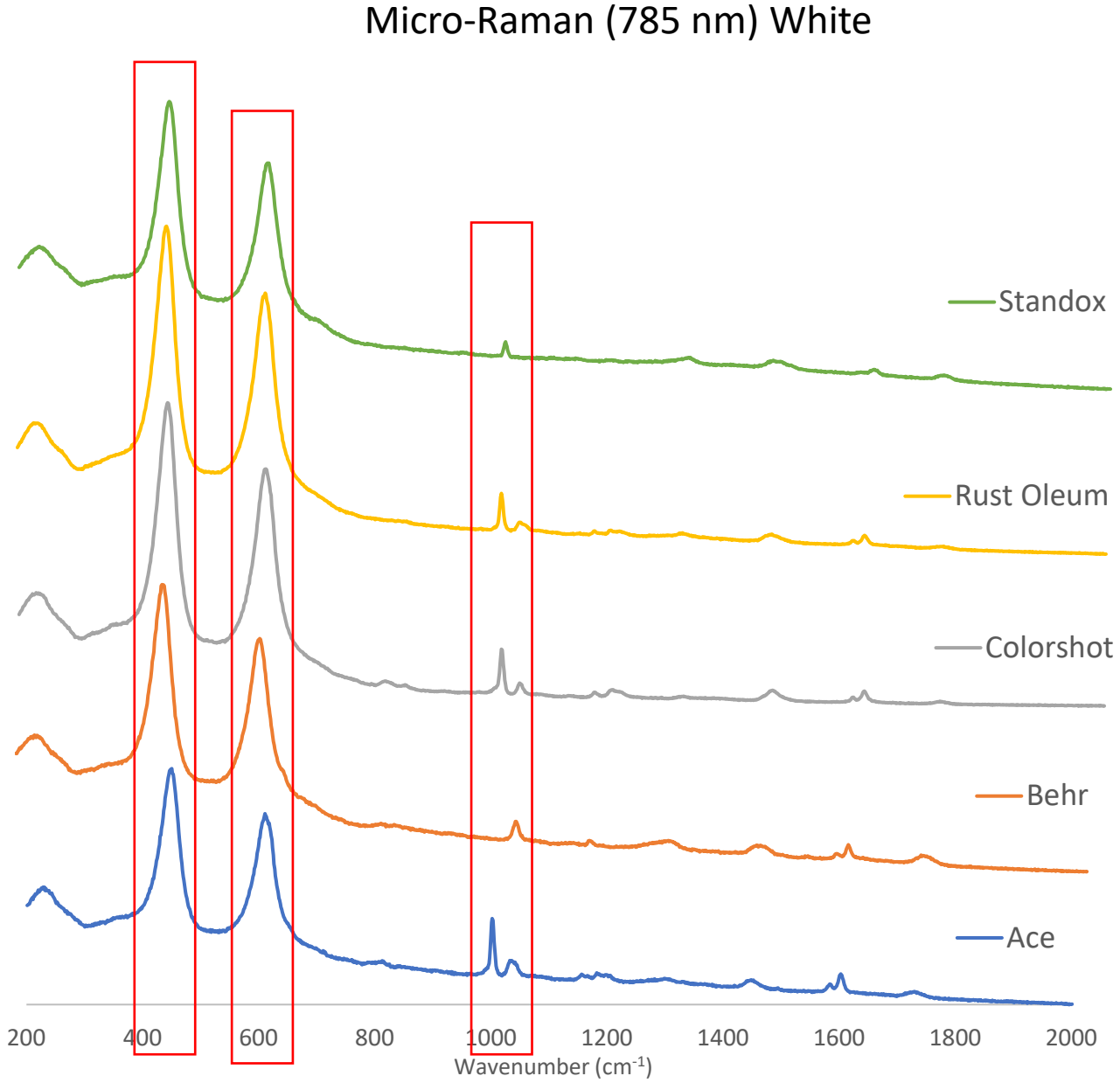


- Extra Ace peak likely not a real elemental peak
- Due to very little variation in white paint pigments, the SEM/EDS data is redundant
  - All elements can be confirmed with identification analysis

Micro-Raman (532 nm) White

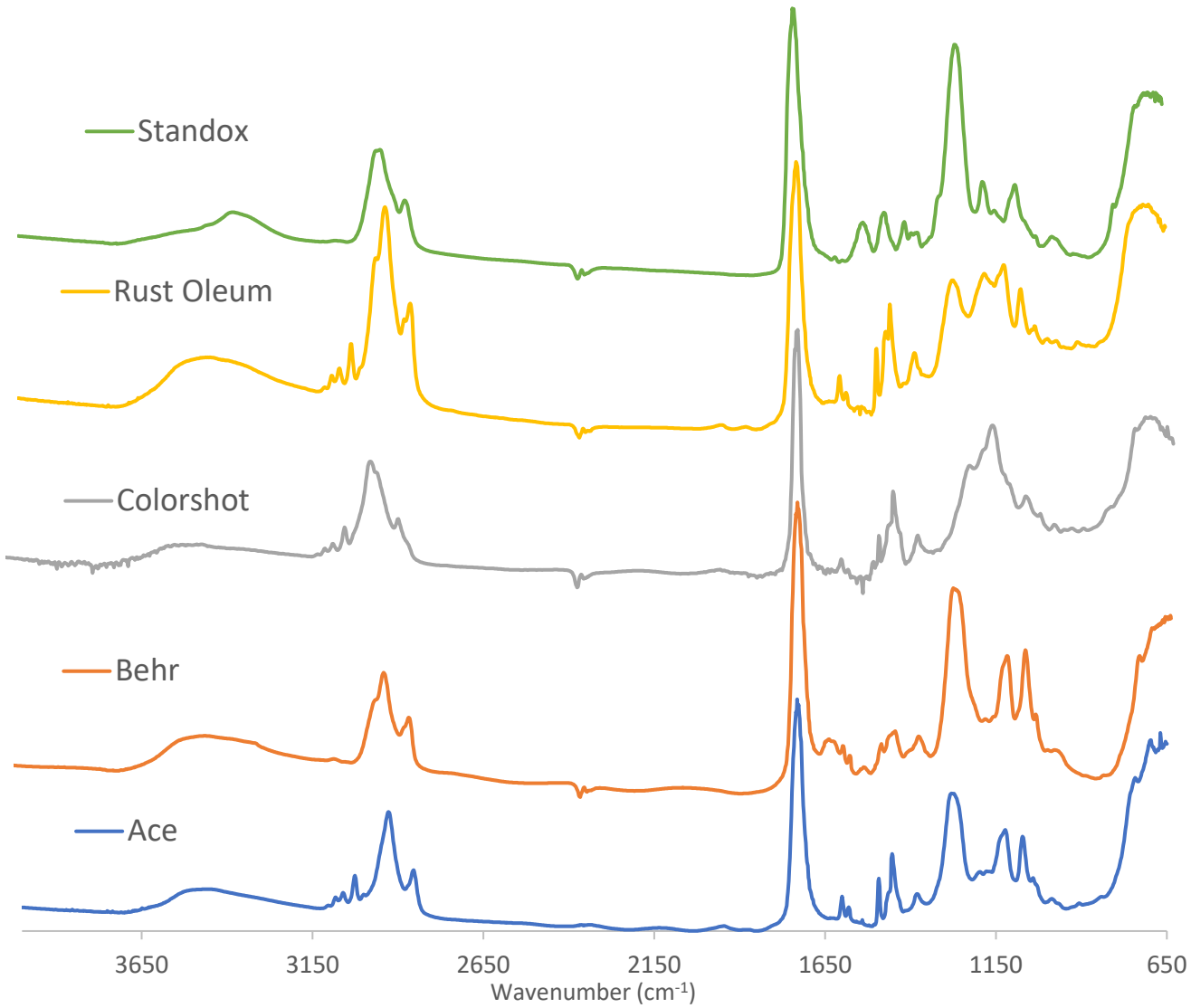


- Only Colorshot yielded identifiable peaks
  - Rutile form of titanium dioxide
- Lack of information deems this laser as not suitable



- All samples give the same spectra with the pigment being identified as the rutile form of titanium oxide
- Selective regions include 380 – 480, 550 – 660, and 980 – 1060 cm^{-1}

Micro-FTIR White



Brand	Binder(s)	Extender(s)
Ace	Alkyd orthophthalic	Styrene
Behr	Alkyd orthophthalic	Styrene
Colorshot	Acrylic	Inconclusive
Rust Oleum	Alkyd orthophthalic	Styrene
Standox	Alkyd orthophthalic	Styrene

Discussion

- Due to the lack of pigment in white paint, all features present can be used as selective features
  - Exception of UV-Vis MSP and micro-Raman with 532 nm laser
- Discarding irrelevant data and focusing on regions with selective peaks is key to ensure the signal is not overcome by noise in data analysis

Conclusions

Conclusions

- The purpose of discarding redundant information and focusing on selective features is to reduce the risk of noise overcoming signal when using a data fusion approach
  - Reduction of variables
  - More signal focused approach

Conclusions

- Overall, micro-FTIR and micro-Raman offer the most selective features but SEM/EDS and UV-Vis MSP can assist in further differentiating samples when extenders or pigments differ
- Depending on the type of pigment and binder present, SEM/EDS does not always offer selective features
  - Carbon black
  - Organic binders
- UV-Vis MSP gives the most information when analyzing colored samples versus relying on secondary pigments from black and white samples

Questions?

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