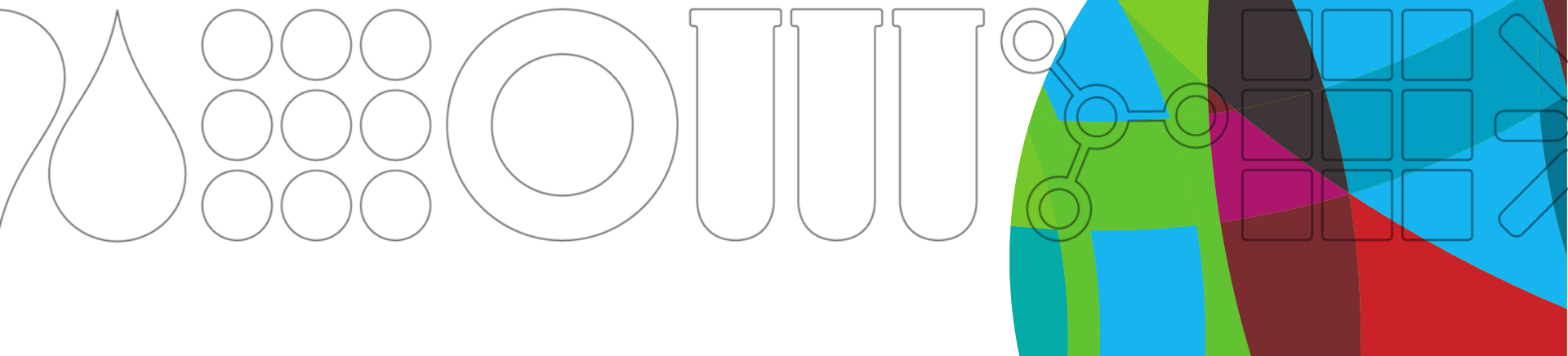# Chemical Analysis and Databases in the Paint Industry

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Global Analytical Network

July 19th, 2016

Agenda

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- Overview of Valspar and Analytical/Materials Science

- Paint Analysis in the Industry

- Example Analysis—Pyrolysis GC/MS of Latex Paint

- New Databases

- Color Databases

- Questions and Contact Information
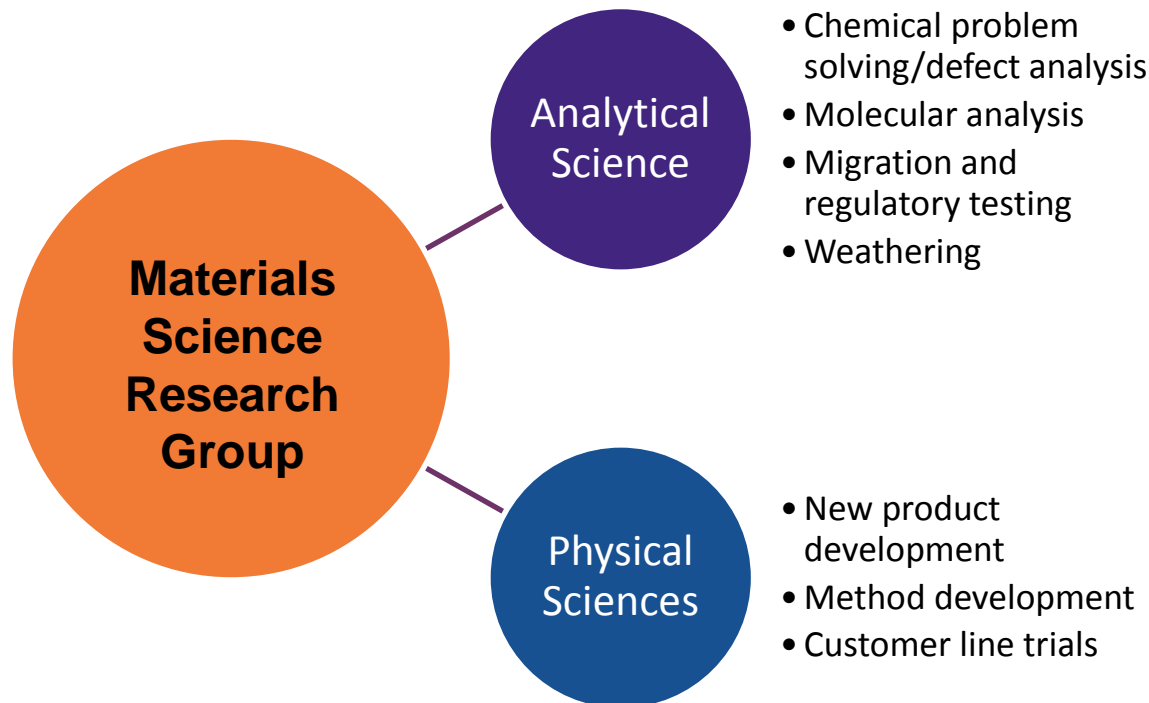
Valspar Coatings
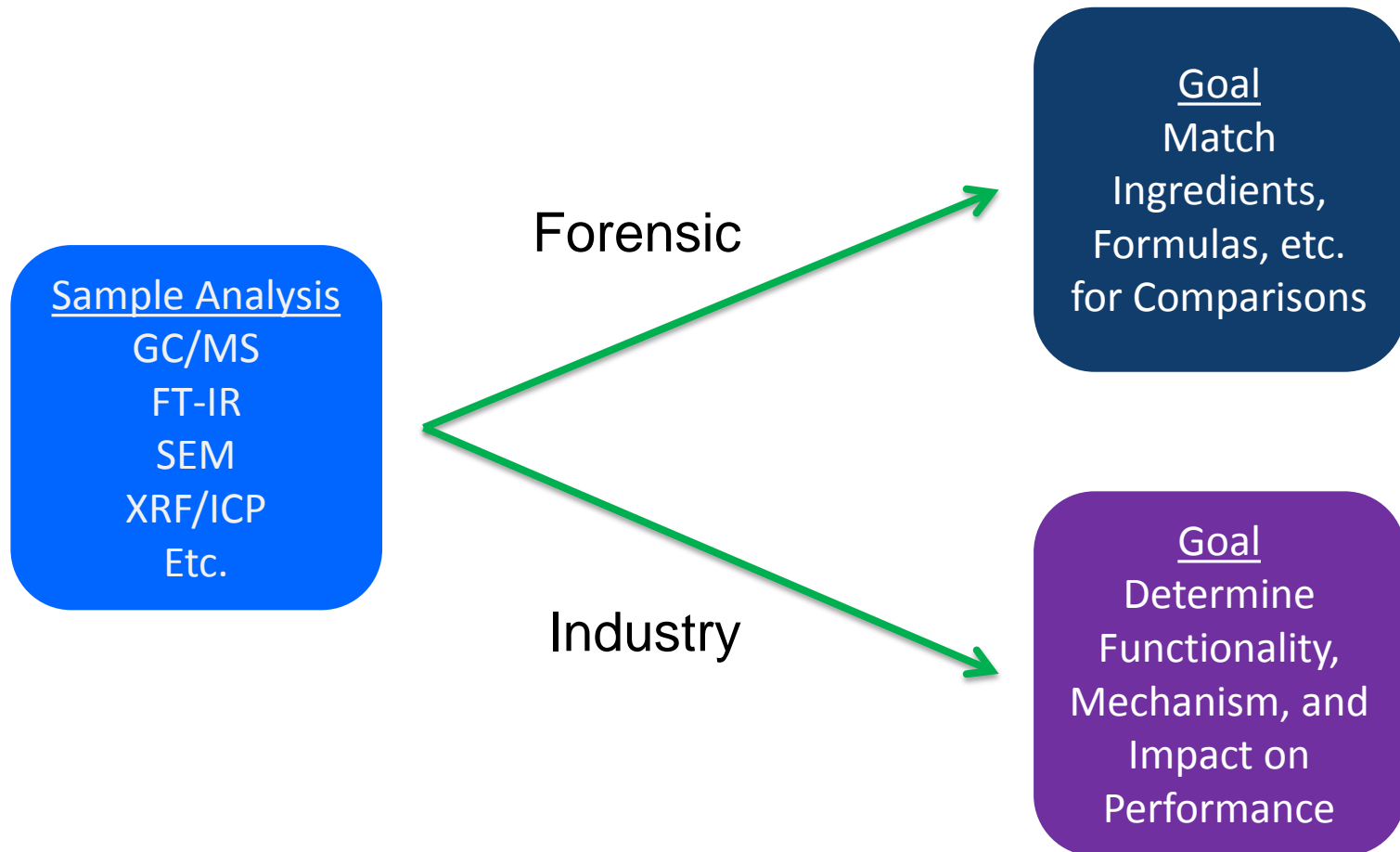
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Materials Science/Analytical

Objectives: Clarify working mechanisms of coatings' performance that provides:

- Design guidelines for continuous product improvements,
- Better performance protocols, and
- Root cause solutions of issues.

Materials Science Research Group
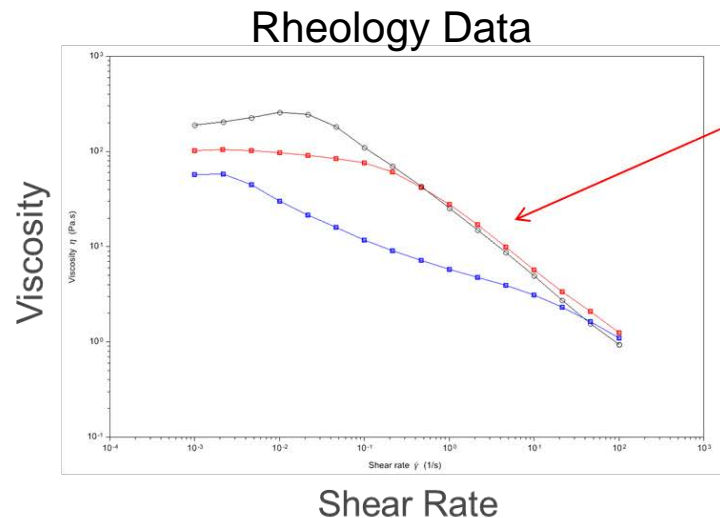
Analytical Science
- Chemical problem solving/defect analysis
- Molecular analysis
- Migration and regulatory testing
- Weathering

Physical Sciences
- New product development
- Method development
- Customer line trials

Paint Analysis in the Industry

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- We do the same tests but for different reasons.
- Therefore databases are built for different goals.

Sample Analysis
GC/MS
FT-IR
SEM
XRF/ICP
Etc.

Forensic

Goal
Match Ingredients, Formulas, etc. for Comparisons

Industry

Goal
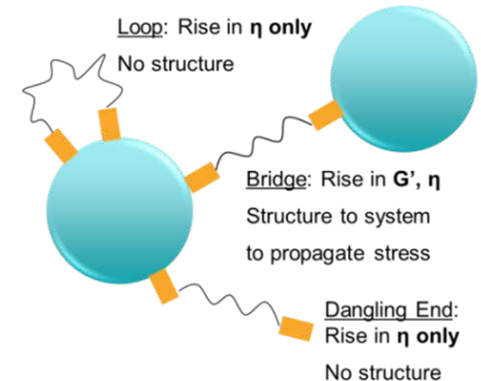Determine Functionality, Mechanism, and Impact on Performance
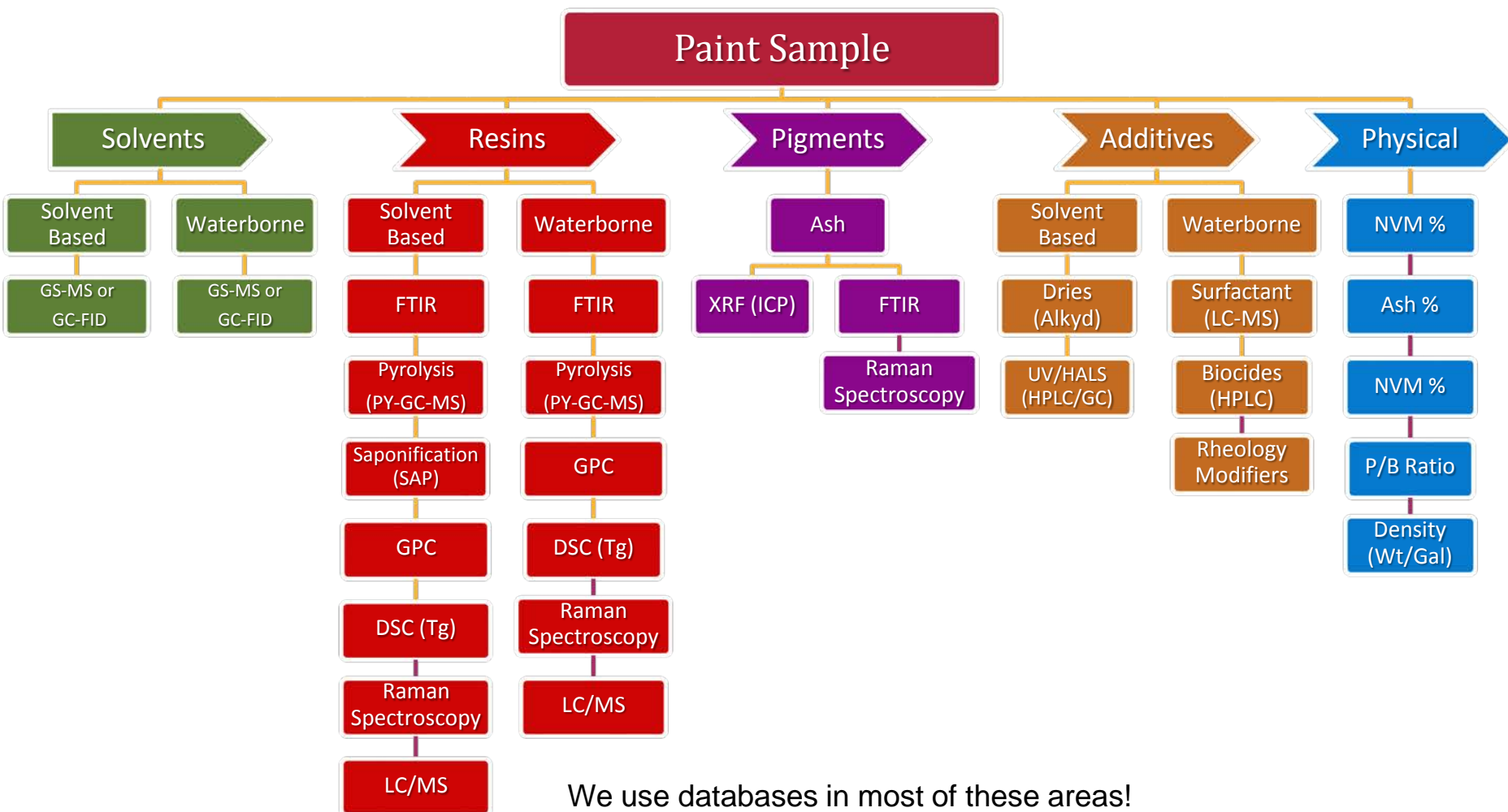
Mechanisms of Interaction

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- Ultimately our goal is to get here!
- Determining mechanisms which impact performance
- Need to ID materials before you can do this.

Rheology Data

Viscosity

Shear Rate

Flow, Leveling, and Sag profiles can be identified in a rheometer experiment

Loop: Rise in η only
No structure

Bridge: Rise in G', η
Structure to system
to propagate stress

Dangling End:
Rise in η only
No structure

Paint Analysis Overview

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Paint Sample

- **Solvents**
  - Solvent Based
    - GS-MS or GC-FID
  - Waterborne
    - GS-MS or GC-FID

- **Resins**
  - Solvent Based
    - FTIR
    - Pyrolysis (PY-GC-MS)
    - Saponification (SAP)
    - GPC
    - DSC (Tg)
    - Raman Spectroscopy
    - LC/MS
  - Waterborne
    - FTIR
    - Pyrolysis (PY-GC-MS)
    - GPC
    - DSC (Tg)
    - Raman Spectroscopy
    - LC/MS

- **Pigments**
  - Ash
    - XRF (ICP)
    - FTIR
      - Raman Spectroscopy

- **Additives**
  - Solvent Based
    - Dries (Alkyd)
    - UV/HALS (HPLC/GC)
  - Waterborne
    - Surfactant (LC-MS)
    - Biocides (HPLC)
    - Rheology Modifiers

- **Physical**
  - NVM %
  - Ash %
  - NVM %
  - P/B Ratio
  - Density (Wt/Gal)

We use databases in most of these areas!
Areas are further subdivided from raw material for more details
(i.e. resin monomers, surfactant/rheology modifier end groups, etc.)

Databases at Valspar

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- Numerous types of databases are used:
  - Some commercially available
    - Coatings Technology Library—FSCT* (FT-IR)
    - NIST GC/MSD Library
  - Many custom developed in-house
  - Also use color databases
- Focus on functionality and not formulations (i.e. paints)
  - Reverse Engineering/Competitive
    - Cost Information
    - IP/Patent infringement
  - Problem Solving/Customer/Internal R&D
    - General Technology
    - Failure mechanisms for coatings
  - Regulatory
    - VOC
    - Packaging Oligomers

*Federation of Societies for Coatings Technology
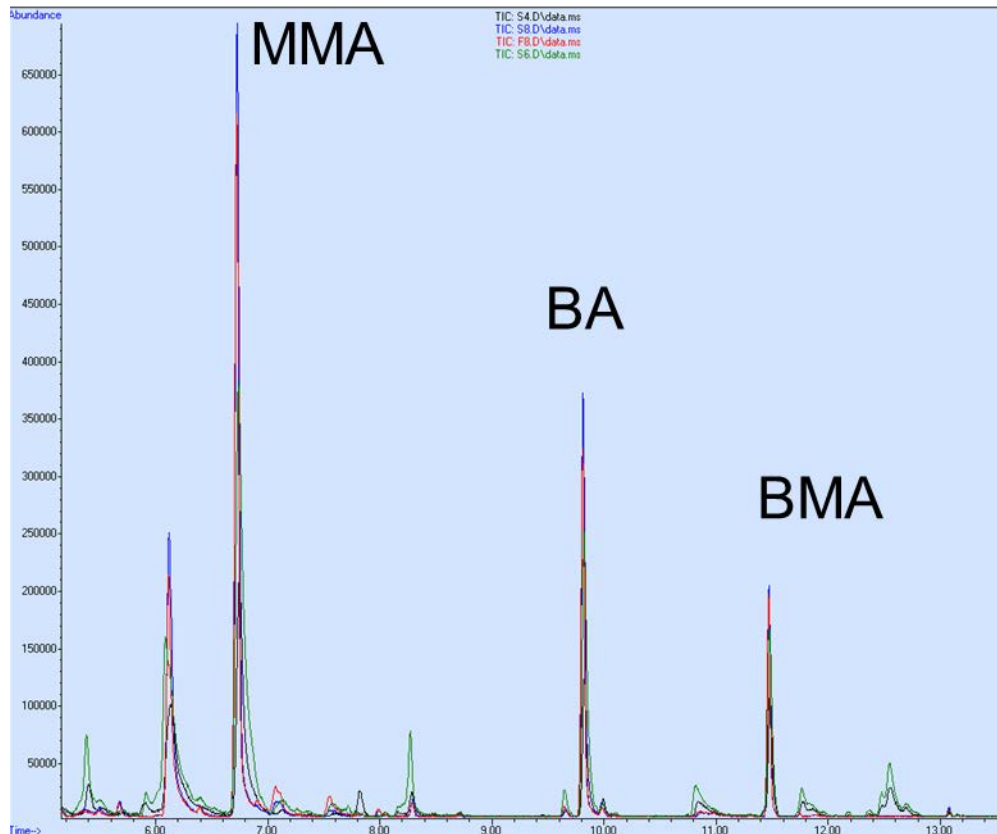
Competitive Latex Paint Analysis

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- 4 Different Competitive Latex Paints Analyzed
- What is Valspar interested in?
  - Cost
  - Performance
  - IP protection

Pyrolysis GC/MS

Acrylic Monomers

Additives and larger fragments

Latex Paint Analysis

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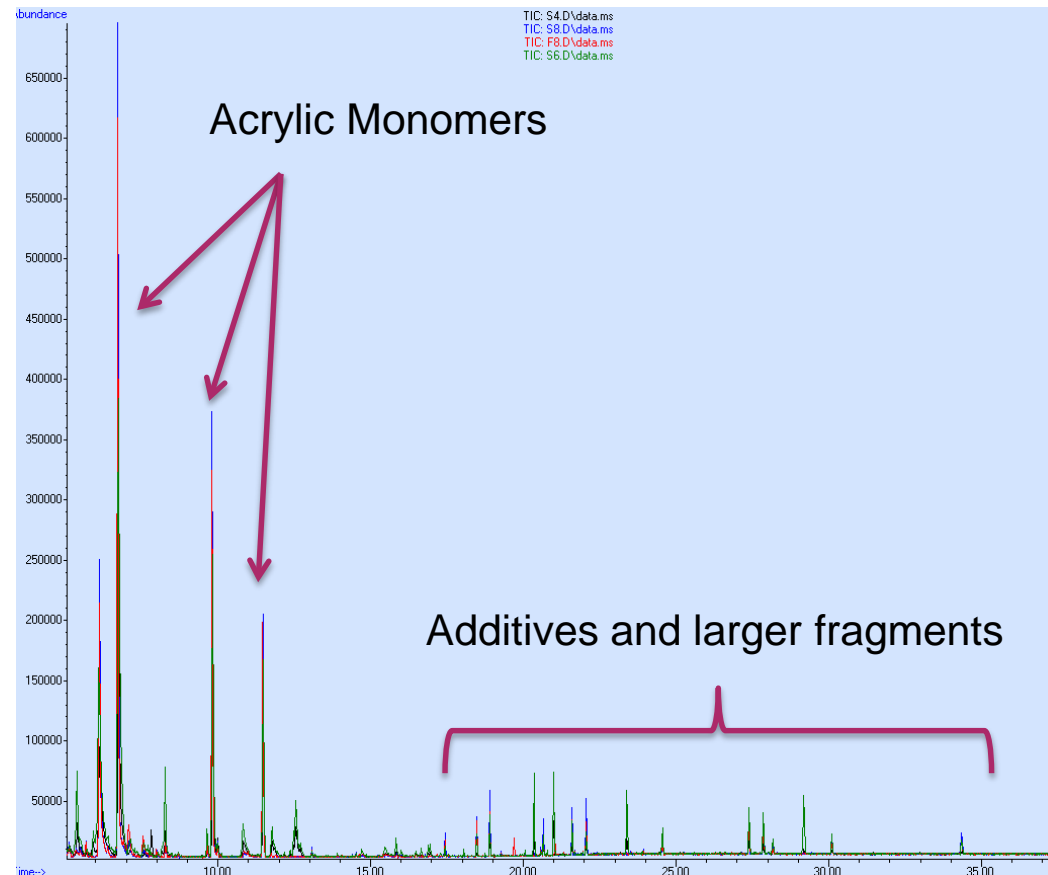
- Same Acrylic Monomers in the same ratio
- Paint manufacturers use commodity acrylics

- **Database used for the following:**
  - **Acrylic Monomer ID (EI MSD)**
  - **Latex type**
    - **Based on ratio of monomers**
    - **Link back to manufacturers**
    - **~300 Latex types in database**

Latex Paint Analysis

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- Additives area shows bigger differences
- Databases used for identification of additive fragments (EI MS)
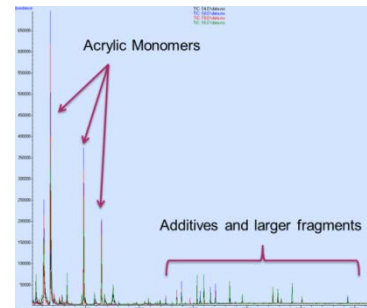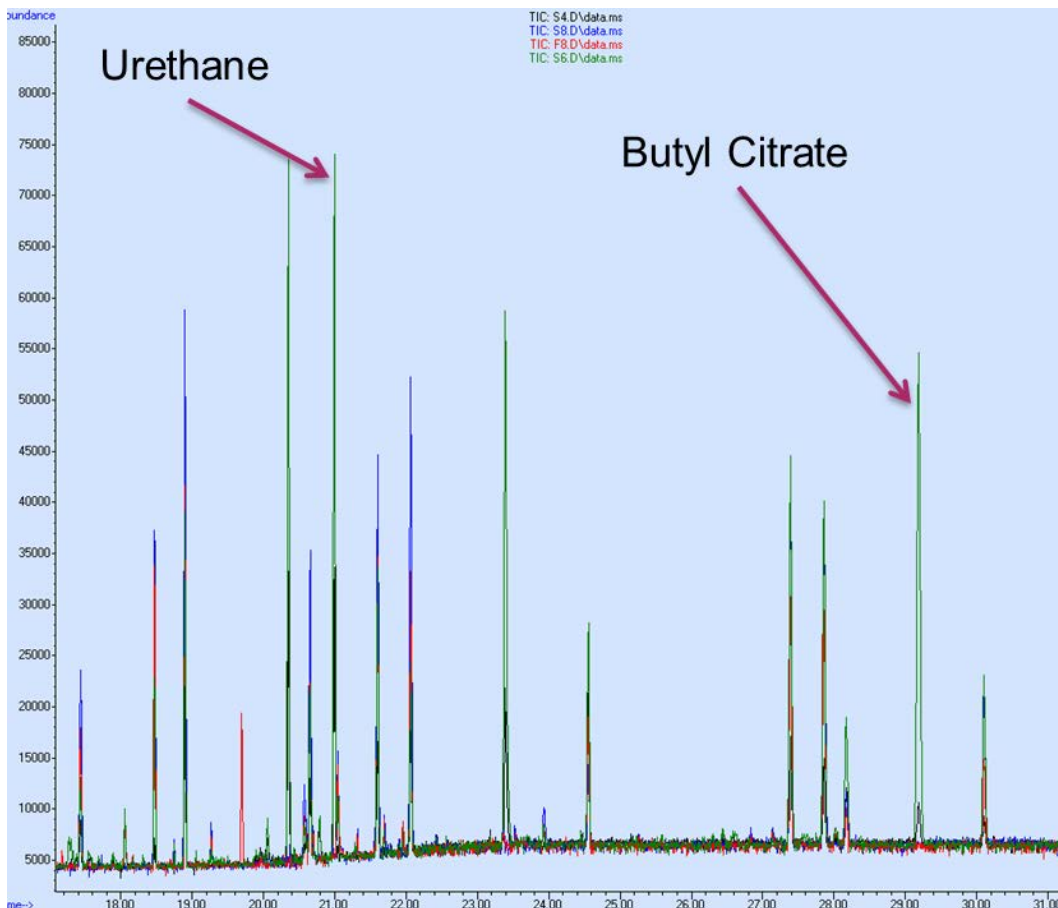
o **Urethane**
  a. **Indicates presence of HEUR***
  b. **Added for flow and application performance**
  c. **Lack of HEUR means HASE** or Cellulosic most likely present**

o **Butyl Citrate**
  a. **Coalescing agent**
  b. **Helps polymer diffusion**

*Hydrophobically Modified Ethylene Oxide
Urethane Rheology Modifier (HEUR)
**Hydrophobically Modified Alkali Swellable Emulsions (HASE)

New Databases

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- LC/MS/MS (RT, Mass, Fragmentation)
    - Surfactants
    - Organic Pigments/Colorants
    - Additives
    - Oligomers
    - Packaging Regulatory (<1000 daltons)
- Raman
    - Organic Pigments
    - Additives
- Solubility Parameters
    - Compatibility of materials
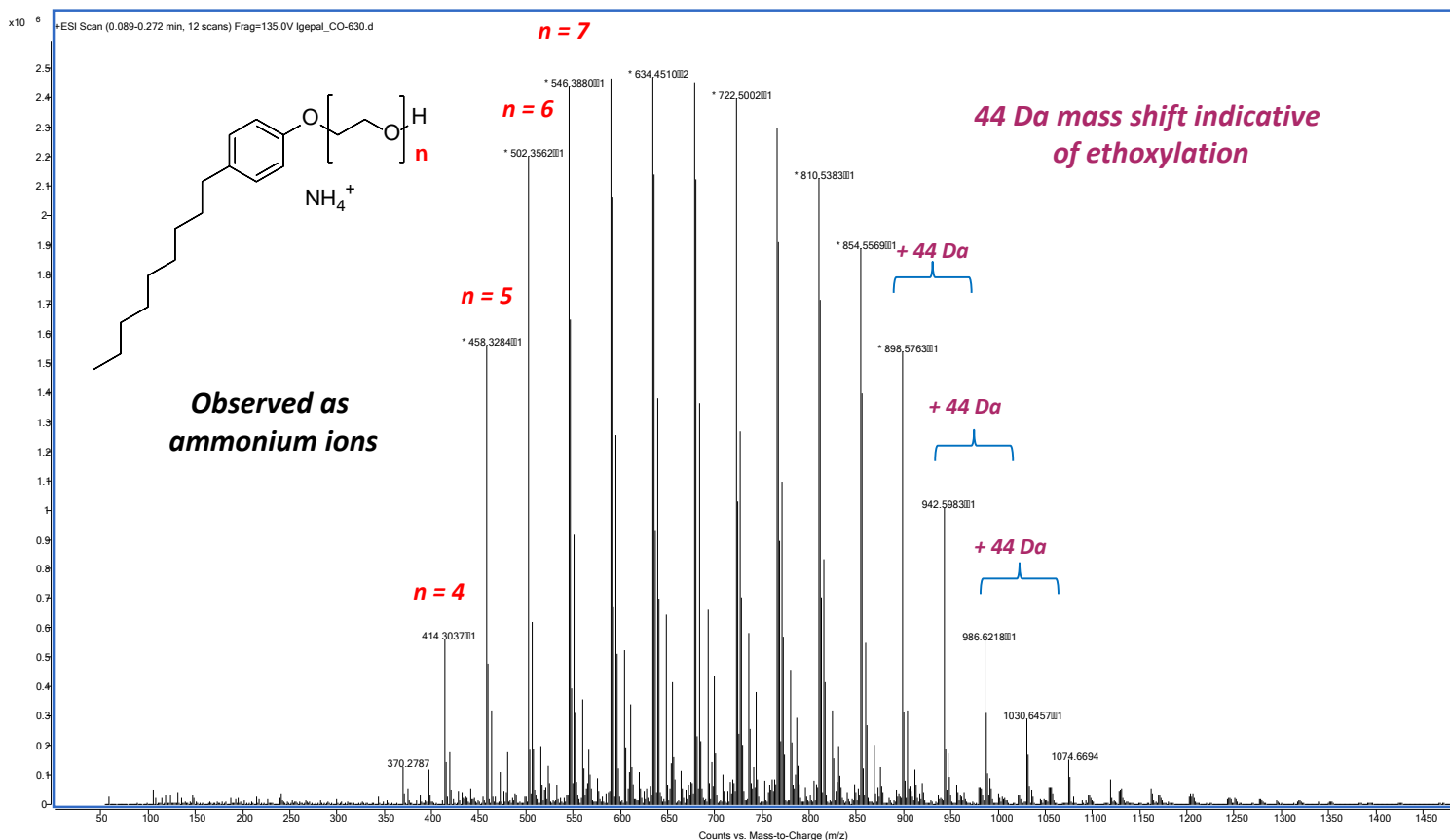- Continuous updates to existing

LC/MS/MS

Confocal Raman Microscope

Surfactant Analysis by LC/MS/MS:
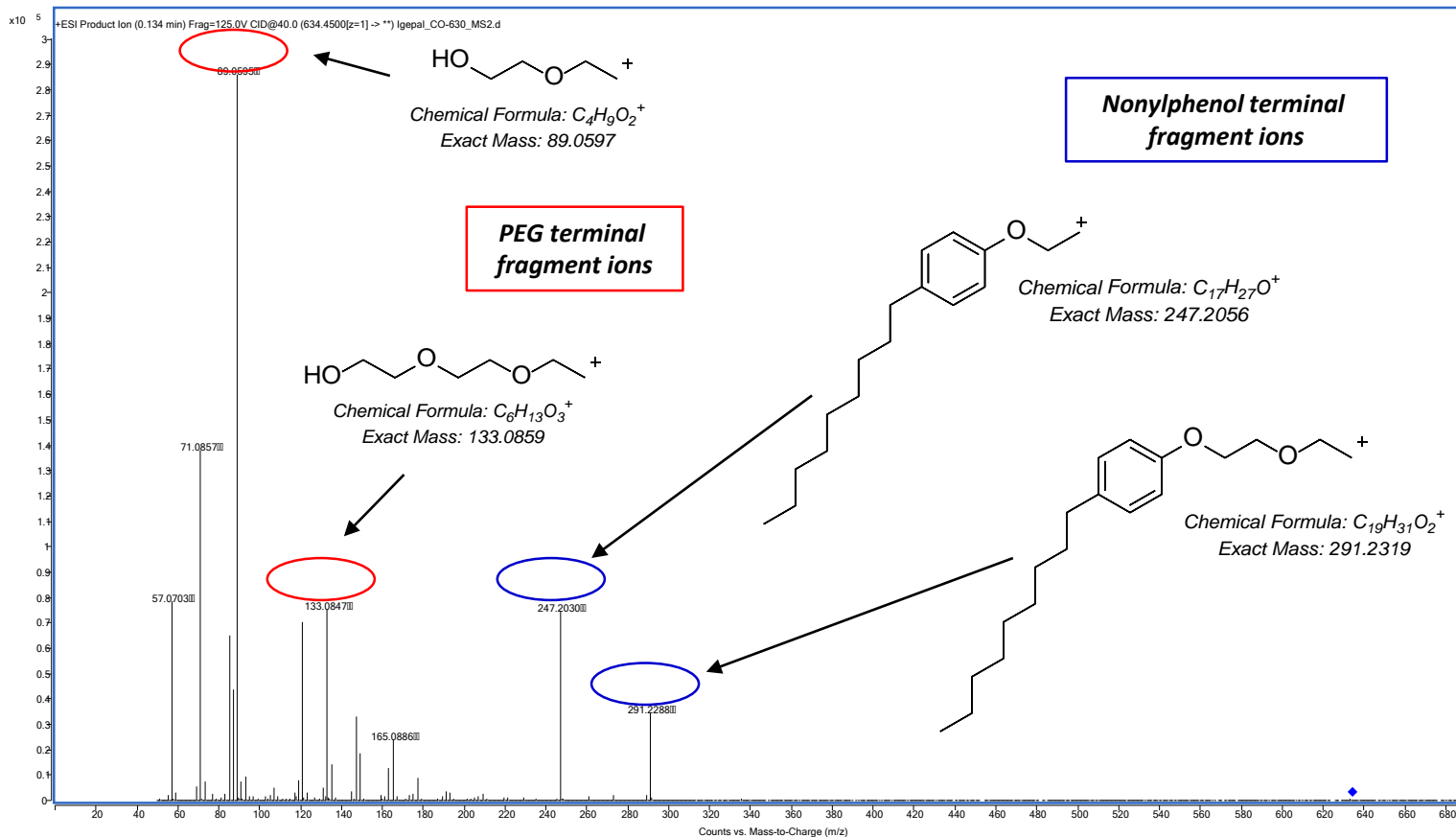## *Identification of Nonylphenol Ethoxylate*

Total Ion Mass Spectrum – Positive Ion Mode

Surfactant Analysis by LC/MS/MS:
## *Identification of Nonylphenol Ethoxylate*

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End group and ethoxylation chain size help understand interactions

Tandem Mass Spectrum – Fragmentation of Nonylphenol Ethoxylate, n = 9

Color Databases

- Color Databases are used for color matching (refinish)
  - Spectrophotometer (Visible Spectrum between 400 – 700 nm)
  - Multi-angle stored. ~15k Colors in database. Also stored as CIELAB.
  - Coarseness for effect pigments
  - Also gather make, model, year, part of car taken, etc.

- Variation can be significant and needs to be known
  - Different OEM manufacturers/Different chemistry/technology
  - Variations in raw materials
  - Age/environmental conditions of the vehicle
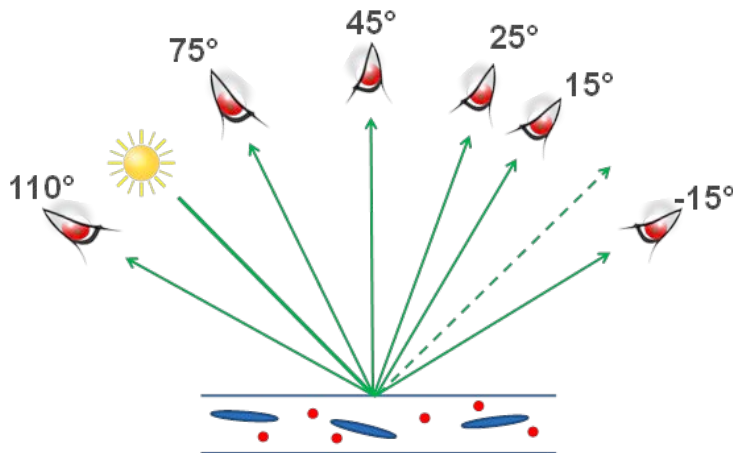
Questions

- How can we help?

- Contact Information:
  - Rich Simon   rsimon@valspar.com   612-375-7388