Chemical Fingerprinting of Materials Developed Due to Environmental Issues

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Chemical Fingerprinting

- Aerospace Materials
  - Critical to performance
  - Replaced or modified due to environmental restrictions
  - Vary in composition from simple to complex; organic or inorganic; gas, liquid, or solid
  - Subject to variations in composition due to formulation changes, ingredient substitutions, degradation, contamination, and mislabeling
  - Must be adequately tested to detect variations
# Chemical Fingerprinting

- **Building Blocks of Capabilities**

<table>
<thead>
<tr>
<th>Spectroscopy</th>
<th>Micro-Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Fourier Transform Infrared Spectroscopy (FTIR)</td>
<td>- Scanning Electron Microscopy (SEM)</td>
</tr>
<tr>
<td>- Raman Spectroscopy</td>
<td>- Energy Dispersive Spectrometry (EDS)</td>
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<tr>
<td>- Inductively Coupled Plasma/Atomic Emission (ICP/AES)</td>
<td>- Micro-FTIR</td>
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<tr>
<td>- Mass Spectrometry (MS)</td>
<td>- Micro-Raman</td>
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<td></td>
<td>- Chemical Microscopy</td>
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<table>
<thead>
<tr>
<th>Chromatography</th>
<th>Surface Analysis</th>
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<tbody>
<tr>
<td>- Gas Chromatography (GC)</td>
<td>- X-ray Photoelectron Spectroscopy (XPS)</td>
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<tr>
<td>- Gas Chromatography/Mass Spectrometry (GC/MS)</td>
<td>- Secondary Ion Mass Spectrometry (SIMS)</td>
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<tr>
<td>- High Performance Liquid Chromatography (HPLC)</td>
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<tr>
<td>- Gel Permeation Chromatography (GPC)</td>
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<tr>
<td>- Ion Chromatography (IC)</td>
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<thead>
<tr>
<th>Thermal Analysis</th>
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<tbody>
<tr>
<td>- Thermal Gravimetric Analysis (TGA)</td>
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<tr>
<td>- Differential Scanning Calorimetry (DSC)</td>
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</tbody>
</table>
Chemical Fingerprinting

- **Spectroscopic Techniques: Atomic Spectroscopy**
  - Used to identify and quantify elements present in samples

  **X-Ray Fluorescence**
  - Rapid detection of elements of atomic number \( \geq 11 \)
  - Solid & liquid samples, minimal sample preparation
  - Quantification requires matrix matched standards

  **Atomic Absorption**
  - Rapid single-elemental quantitative analysis
  - Sample must be in solution (accessory required for solids)
  - Sample preparation may be time consuming
  - Small linear response range, high matrix interference
  - Not applicable to most non-metals

  **Inductively Coupled Plasma/Atomic Emission**
  - Multi-element qualitative and quantitative analysis
  - Sample must be in solution (accessory required for solids)
  - Sample preparation may be time consuming
  - Large linear response range
Chemical Fingerprinting

- **Spectroscopic Techniques:** Molecular Spectroscopy
  - Used to identify and quantify molecular compounds present in samples

<table>
<thead>
<tr>
<th>Technique</th>
<th>Molecular functional group identification</th>
<th>Complements Raman spec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infrared Spectroscopy</td>
<td>• Applicable to solids, liquids, gases</td>
<td>• Minimal sample preparation</td>
</tr>
<tr>
<td></td>
<td>• Not applicable to aqueous samples</td>
<td>• Extensive reference libraries</td>
</tr>
<tr>
<td></td>
<td>• Minor components masked by major</td>
<td>• Dipole moment change req.</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>• Molecular functional group identification</td>
<td>• Complements infrared spec.</td>
</tr>
<tr>
<td></td>
<td>• Applicable to solids, liquids, aqueous</td>
<td>• Minimal sample preparation</td>
</tr>
<tr>
<td></td>
<td>• Polarizability change required</td>
<td>• Limited reference libraries</td>
</tr>
<tr>
<td></td>
<td>• Not app. to colored or fluorescing samples</td>
<td></td>
</tr>
<tr>
<td>Mass Spectrometry</td>
<td>• Organic compound identification</td>
<td>• Extensive reference libraries</td>
</tr>
<tr>
<td></td>
<td>• Widely applicable to volatile samples</td>
<td>• Chromatographic detector</td>
</tr>
<tr>
<td></td>
<td>• Accessory required for non-volatile samples</td>
<td></td>
</tr>
</tbody>
</table>
## Chemical Fingerprinting

- **Chromatographic Techniques:**
  - Used to separate and quantify components in samples
  - Used in tandem with other techniques to identify components

<table>
<thead>
<tr>
<th>Technique</th>
<th>Description</th>
</tr>
</thead>
</table>
| Gas Chromatography (GC)    | • Separation of volatile components within mixtures  
                              • Quantitative or qualitative analysis  
                              • Not applicable to thermally unstable components  
                              • Not applicable to non-volatiles without derivatization |
| High Performance Liquid Chromatography (HPLC) | • Separation of soluble components within mixtures  
                              • Quantitative or qualitative analysis  
                              • Sample must be soluble in suitable solvent (many)  
                              • Method development time-consuming |
| Gel Permeation Chromatography (GPC) | • Separation of components based on molecular size  
                              • Determination of molecular weight distribution  
                              • Sample must be soluble in suitable solvent (few) |
| Ion Chromatography (IC)     | • Separation and quantification of ionic species  
                              • Applicable to organic and inorganic  
                              • Method development time-consuming |
Chemical Fingerprinting

- Factors that Determine Fingerprinting Approach
  - Physical State: Solid, liquid, or gas? Homogeneous or distinct phases? Sample size?
  - Chemical Properties: Single ingredient or complex mixture? Major, minor, or trace components? Organic, inorganic, or combination? Masking of one component by another? Separation of components required?
  - Information Required: Qualitative or quantitative data? Bulk or surface composition?
Chemical Fingerprinting

- Fingerprinting: Combination of instrumental analysis methods that diagnostically characterize a material

Simple Material  \[\xrightarrow{\text{One Method}}\]  Needed Characterization
- Identify Ingredients
- Quantify Ingredients
- Determine Material Purity
- Identify Contaminant
- Determine Material Stability
- Detect Degradation
- Differentiate Products
- Component Mix Ratio
- Identify Reaction Products

Complex Material  \[\xrightarrow{\text{Multiple Methods}}\]
Chemical Fingerprinting

- Simple Materials and Approach: HCFC-225 and HCFC-225G

**HCFC-225G**
- Single Isomer
- Trace Impurities

**HCFC-225**
- Two isomers
- Trace Impurities

**FTIR:**
- Rapid Differentiation

**GC:**
- Isomer Ratio, % Purity
Chemical Fingerprinting

- Complex Material Example: Urethane Foam Component

  - **Polyol**: One or several polyols
    - Aromatic and/or non-aromatic
    - Polyesters and/or polyethers
    - Concentration ~5 - 65%

  - **Blowing Agent**: CFC, HCFC, third generation
    - Concentration ~15-35%

  - **Flame Retardant**: One or several flame retardants
    - Phosphorus- and/or halogen-based
    - Concentration ~1-20%

  - **Catalyst**: One or several catalysts
    - Organic amine and/or organometallic
    - Concentration ~0.5-4%

  - **Surfactant**: Silicone copolymer
    - Concentration ~1-2%
Chemical Fingerprinting

- **Complex Material Approach: Urethane Foam Component**

  - **Polyol**
    - FTIR: Functional groups, polyol type
    - GC: Polyol conc. based on volatile portion
    - HPLC: Detectable polyol concentration
    - GPC: Molecular weight distribution

  - **Blowing Agent**
    - GC: Blowing agent concentration
    - GC/MS: Blowing agent degradation
    - FTIR: Rapid blowing agent identification

  - **Flame Retardant**
    - ICP/AES: Phosphorus concentration
    - GC: Phosphorus-based flame ret. conc.
    - HPLC: Halogen-based flame retardant conc.
    - GC: Concentration of polyol diluent

  - **Catalyst**
    - ICP/AES: Tin, lead concentration (organometallic)
    - GC: Volatile amine catalyst concentration

  - **Surfactant**
    - ICP/AES: Silicon concentration
Chemical Fingerprinting

- Complex Material and Approach: Phenolic Resin

<table>
<thead>
<tr>
<th>Starting Materials</th>
<th>Phenolic Resin</th>
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<tbody>
<tr>
<td>Phenol</td>
<td>Methylol Phenols</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Dimethylol Phenols</td>
</tr>
<tr>
<td>Solvent</td>
<td>Trimethylol Phenol</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Dinuclear Phenols</td>
</tr>
<tr>
<td>Water</td>
<td>Polynuclear Phenols</td>
</tr>
</tbody>
</table>

HPLC: Phenol and methylol phenol concentrations
GC: Solvent concentrations
GPC: Molecular weight distribution (resin advancement)
FTIR: Functional groups (resin advancement)
ICP/AES: Concentration of metal due to metal hydroxide catalysts
IC: Ammonium hydroxide catalyst concentration
Titrations: Formaldehyde and water concentrations
Chemical Fingerprinting

- Supplier Partnership is Vital Element in Fingerprint Program

Material Suppliers:
- Provide information on formulation and chemistry
- Supply samples of formulation ingredients
- Avoid changes to material formulation when possible
- Notify us of necessary changes to material

Fingerprinting Program:
- Use information to understand material’s chemistry and threats to availability
- Use information and samples to develop fingerprint methods
- Supply fingerprint data
- Safeguard proprietary information
Chemical Fingerprinting

- Fingerprint Databases & Trending to Detect Material Variations

**Supplier Material** ➔ **Fingerprint Analysis** ➔ **Fingerprints**
- Spectra
- Chromatograms
- Thermograms

**Statistical Analysis**
- Control Charts
- Trend Charts
- Histograms
- Process Capability

**Fingerprint Database**

**Numerical Data**
- Concentrations
- Isomer Ratios
- Peak Ratios
- Molecular Wts
Chemical Fingerprinting

- Evolving Role of Fingerprinting in Aerospace Industry

Supplier Support

Trending

Failure Analysis

Monitoring
Chemical Fingerprinting

• Benefits: Fingerprinting provides benefits in the areas of receiving acceptance, failure investigations, new material development, and alternate material qualification
  – Multipurpose methods with diagnostic capability
  – Quantitative databases and reference libraries
  – Increased material reliability
  – Ensured future replication of successful materials
  – Expeditious problem resolution
  – Automated sample analysis
  – Reduced cost of material requalifications
  – Increased supplier communication
Chemical Fingerprinting

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  - Lockheed Martin Space Systems, Michoud Operations, Laboratory Operations: Tammy Bourgeois, Todd Bologna, Mary Capezza, Emile Evans, Roger May, Don Melton, Debra Pierce, Laurie Rando, and Lance Spiers contributed to method and database development.
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