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>
</tr>
<tr>
<td>- Inductively Coupled Plasma/Atomic Emission (ICP/AES)</td>
<td>- Micro-FTIR</td>
</tr>
<tr>
<td>- Mass Spectrometry (MS)</td>
<td>- Micro-Raman</td>
</tr>
<tr>
<td>- Chemical Microscopy</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Chromatography</th>
<th>Surface Analysis</th>
<th>Thermal Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Gas Chromatography (GC)</td>
<td>- X-ray Photoelectron Spectroscopy (XPS)</td>
<td>- Thermal Gravimetric Analysis (TGA)</td>
</tr>
<tr>
<td>- Gas Chromatography/Mass Spectrometry (GC/MS)</td>
<td>- Secondary Ion Mass Spectrometry (SIMS)</td>
<td>- Differential Scanning Calorimetry (DSC)</td>
</tr>
<tr>
<td>- High Performance Liquid Chromatography (HPLC)</td>
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<tr>
<td>- Gel Permeation Chromatography (GPC)</td>
<td></td>
<td></td>
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<tr>
<td>- Ion Chromatography (IC)</td>
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</tr>
</tbody>
</table>
Chemical Fingerprinting

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

<table>
<thead>
<tr>
<th>Technique</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-Ray Fluorescence</td>
<td>- Rapid detection of elements of atomic number $\geq 11$</td>
</tr>
<tr>
<td></td>
<td>- Solid &amp; liquid samples, minimal sample preparation</td>
</tr>
<tr>
<td></td>
<td>- Quantification requires matrix matched standards</td>
</tr>
<tr>
<td>Atomic Absorption</td>
<td>- Rapid single-elemental quantitative analysis</td>
</tr>
<tr>
<td></td>
<td>- Sample must be in solution (accessory required for solids)</td>
</tr>
<tr>
<td></td>
<td>- Sample preparation may be time consuming</td>
</tr>
<tr>
<td></td>
<td>- Small linear response range, high matrix interference</td>
</tr>
<tr>
<td></td>
<td>- Not applicable to most non-metals</td>
</tr>
<tr>
<td>Inductively Coupled Plasma/Atomic Emission</td>
<td>- Multi-element qualitative and quantitative analysis</td>
</tr>
<tr>
<td></td>
<td>- Sample must be in solution (accessory required for solids)</td>
</tr>
<tr>
<td></td>
<td>- Sample preparation may be time consuming</td>
</tr>
<tr>
<td></td>
<td>- Large linear response range</td>
</tr>
</tbody>
</table>
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>• Applicable to solids, liquids, aqueous</td>
<td>• Complements infrared spec.</td>
</tr>
<tr>
<td></td>
<td>• Polarizability change required</td>
<td>• Minimal sample preparation</td>
</tr>
<tr>
<td></td>
<td>• Not applicable to colored or fluorescing samples</td>
<td>• Limited reference libraries</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>Method</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Chromatography (GC)</td>
<td>• Separation of volatile components within mixtures</td>
</tr>
<tr>
<td></td>
<td>• Quantitative or qualitative analysis</td>
</tr>
<tr>
<td></td>
<td>• Not applicable to thermally unstable components</td>
</tr>
<tr>
<td></td>
<td>• Not applicable to non-volatiles without derivatization</td>
</tr>
<tr>
<td>High Performance Liquid</td>
<td>• Separation of soluble components within mixtures</td>
</tr>
<tr>
<td>Chromatography (HPLC)</td>
<td>• Quantitative or qualitative analysis</td>
</tr>
<tr>
<td></td>
<td>• Sample must be soluble in suitable solvent (many)</td>
</tr>
<tr>
<td></td>
<td>• Method development time-consuming</td>
</tr>
<tr>
<td>Gel Permeation Chromatography</td>
<td>• Separation of components based on molecular size</td>
</tr>
<tr>
<td>(GPC)</td>
<td>• Determination of molecular weight distribution</td>
</tr>
<tr>
<td></td>
<td>• Sample must be soluble in suitable solvent (few)</td>
</tr>
<tr>
<td>Ion Chromatography (IC)</td>
<td>• Separation and quantification of ionic species</td>
</tr>
<tr>
<td></td>
<td>• Applicable to organic and inorganic</td>
</tr>
<tr>
<td></td>
<td>• Method development time-consuming</td>
</tr>
</tbody>
</table>
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

Needed Characterization
- Identify Ingredients
- Quantify Ingredients
- Determine Material Purity
- Identify Contaminant
- Determine Material Stability
- Detect Degradation
- Differentiate Products
- Component Mix Ratio
- Identify Reaction Products
Chemical Fingerprinting

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

FTIR: Rapid Differentiation

GC: Isomer Ratio, % Purity

<table>
<thead>
<tr>
<th>HCFC-225G</th>
<th>Two Isomers Trace Impurities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single Isomer Trace Impurities</td>
<td></td>
</tr>
</tbody>
</table>

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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

**Starting Materials**
- Phenol
- Formaldehyde
- Solvent
- Catalyst

**Phenolic Resin**
- Phenol
- Formaldehyde
- Solvent
- Catalyst
- Water
- Methylol Phenols
- Dimethylol Phenols
- Trimethylol Phenol
- Dinuclear Phenols
- Polynuclear Phenols

**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
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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