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>
</tr>
<tr>
<td>• Mass Spectrometry (MS)</td>
<td>• Micro-Raman</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Chromatography</th>
<th>Surface Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Gas Chromatography (GC)</td>
<td>• X-ray Photoelectron Spectroscopy (XPS)</td>
</tr>
<tr>
<td>• Gas Chromatography/Mass Spectrometry (GC/MS)</td>
<td>• Secondary Ion Mass Spectrometry (SIMS)</td>
</tr>
<tr>
<td>• High Performance Liquid Chromatography (HPLC)</td>
<td></td>
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<tr>
<td>• Gel Permeation Chromatography (GPC)</td>
<td></td>
</tr>
<tr>
<td>• Ion Chromatography (IC)</td>
<td>Therm al Analysis</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>• Thermal Gravimetric Analysis (TGA)</th>
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<tbody>
<tr>
<td></td>
<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

<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>Infrared Spectroscopy</th>
<th>• Molecular functional group identification</th>
<th>• Complements Raman spec.</th>
</tr>
</thead>
<tbody>
<tr>
<td></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>
</tbody>
</table>

- Raman Spectroscopy
  - • Molecular functional group identification
  - • Applicable to solids, liquids, aqueous
  - • Polarizability change required
  - • Not app. to colored or fluorescing samples

- Mass Spectrometry
  - • Organic compound identification
  - • Widely applicable to volatile samples
  - • Accessory required for non-volatile samples
  - • Extensive reference libraries
  - • Chromatographic detector
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>Characteristics</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 Chromatography (HPLC)</td>
<td>Separation of soluble components within mixtures</td>
</tr>
<tr>
<td></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 (GPC)</td>
<td>Separation of components based on molecular size</td>
</tr>
<tr>
<td></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

- **Simple Material**: One Method
- **Complex Material**: Multiple Methods

**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

**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>
</tr>
</thead>
<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

1. Supplier Material
2. Fingerprint Analysis
3. Fingerprint Database
4. Statistical Analysis
   - Control Charts
   - Trend Charts
   - Histograms
5. Process Capability
6. Numerical Data
   - Concentrations
   - Isomer Ratios
   - Peak Ratios
   - Molecular Wt's

- Fingerprints
  - Spectra
  - Chromatograms
  - Thermograms
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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