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**

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

Infrared Spectroscopy
- Molecular functional group identification
- Applicable to solids, liquids, gases
- Not applicable to aqueous samples
- Minor components masked by major
- Complements Raman spec.
  - Minimal sample preparation
  - Extensive reference libraries
  - Dipole moment change req.

Raman Spectroscopy
- Molecular functional group identification
- Applicable to solids, liquids, aqueous
- Polarizability change required
- Not app. to colored or fluorescing samples
- Complements infrared spec.
  - Minimal sample preparation
  - Limited reference libraries

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>Details</th>
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</thead>
<tbody>
<tr>
<td><strong>Gas Chromatography (GC)</strong></td>
<td>- Separation of volatile components within mixtures</td>
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<td>- Quantitative or qualitative analysis</td>
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<tr>
<td></td>
<td>- Not applicable to thermally unstable components</td>
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<td></td>
<td>- Not applicable to non-volatiles without derivatization</td>
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<tr>
<td><strong>High Performance Liquid Chromatography (HPLC)</strong></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><strong>Gel Permeation Chromatography (GPC)</strong></td>
<td>- Separation of components based on molecular size</td>
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<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><strong>Ion Chromatography (IC)</strong></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>
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</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

![Diagram showing the process of fingerprinting for simple and complex materials with the required characterization 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, polyl type
    - GC: Polyl conc. based on volatile portion
    - HPLC: Detectable polyl 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 polyl 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

![Diagram showing the flow of information from Supplier Material to Fingerprints through Statistical Analysis and back to Supplier Material.](image-url)
Chemical Fingerprinting

- Evolving Role of Fingerprinting in Aerospace Industry

Supplier Support

Trending

Failure Analysis

Monitoring

Past

Future
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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