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>
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<tr>
<td>- Mass Spectrometry (MS)</td>
<td>- Micro-Raman</td>
</tr>
<tr>
<td></td>
<td>- Chemical Microscopy</td>
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</tbody>
</table>

<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>
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<tr>
<td>- Gel Permeation Chromatography (GPC)</td>
<td></td>
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<tr>
<td>- Ion Chromatography (IC)</td>
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</tbody>
</table>

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<thead>
<tr>
<th>Thermal Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Thermal Gravimetric Analysis (TGA)</td>
</tr>
<tr>
<td>- Differential Scanning Calorimetry (DSC)</td>
</tr>
</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>Spectroscopy</th>
<th>Molecular functional group identification</th>
<th>Complements Raman spec.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Infrared</strong></td>
<td>Applicable to solids, liquids, gases</td>
<td>Minimal sample preparation</td>
</tr>
<tr>
<td><strong>Raman</strong></td>
<td>Not applicable to aqueous samples</td>
<td>Extensive reference libraries</td>
</tr>
<tr>
<td><strong>Mass Spectrometry</strong></td>
<td>Minor components masked by major</td>
<td>Dipole moment change req.</td>
</tr>
<tr>
<td></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>
</tbody>
</table>

- **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</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

- 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

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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

Phenolic Resin
- Methylyol Phenols
- Dimethylol Phenols
- Trimethylol Phenol
- Dinuclear Phenols
- Polynuclear Phenols

Phenol and methylphenol concentrations
Solvent concentrations
Molecular weight distribution (resin advancement)
Functional groups (resin advancement)
Concentration of metal due to metal hydroxide catalysts
Formaldehyde and water concentrations

Starting Materials
- Phenol
- Formaldehyde
- Solvent
- Catalyst

HPLC:
GC:
GPC:
FTIR:
ICP/AES:
FID:
GDS:
NMR:

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

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- 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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