Chemical Fingerprinting of Materials
Developed Due to Environmental Issues

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Doris A. Smith, Ph.D.
Technology Laboratories
Lockheed Martin Space Systems
Michoud Operations, New Orleans, LA
(504) 257-0228  doris.smith@maf.nasa.gov
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  • Micro-Raman</td>
</tr>
<tr>
<td>• Mass Spectrometry (MS)</td>
<td>• Chemical Microscopy</td>
</tr>
</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>
<td></td>
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<tr>
<td>• Gel Permeation Chromatography (GPC)</td>
<td></td>
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<tr>
<td>• Ion Chromatography (IC)</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Analysis</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Thermal Gravimetric Analysis (TGA)</td>
<td></td>
</tr>
<tr>
<td>• Differential Scanning Calorimetry (DSC)</td>
<td></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 ≥ 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</td>
<td>Applicable to solids, liquids, gases</td>
<td>Minimal sample preparation</td>
</tr>
<tr>
<td>Spectroscopy</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</td>
<td>Molecular functional group identification</td>
<td>Complements infrared spec.</td>
</tr>
<tr>
<td>Spectroscopy</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</td>
<td>Organic compound identification</td>
<td>Extensive reference libraries</td>
</tr>
<tr>
<td>Spectrometry</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

```
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

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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
Titration: 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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