Chemical Fingerprinting Program for RSRM Critical Materials

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September 16-18, 2002

ATK
THIOKOL PROPULSION
Presentation Outline

- Background
- Objectives and Approach
- Accomplishments
  - Description of Database Viewer
  - Success Stories
  - Direct and Additional Benefits
- Continuing Challenges
- Acknowledgements
Reusable Solid Rocket Motor (RSRM) Components Involving Critical Materials

- Segmented steel case
- Movable nozzle
- Case-bonded, composite solid propellant
- Elastomeric internal insulation
- Nozzle ablative liner
- Nozzle insulator and structural shell
- Clean bonding surfaces
- Effective adhesives
Background: Chemical Fingerprint Definition

Diagnostic Combination of Analytical Methods for Detailed Characterization of a Material

- Key importance is a chemical fingerprint that can be used to identify a material, to differentiate it from similar looking materials, or lead to its source.

- In the past, fingerprinting methods were used to characterize materials and processes:
  - Following a failure or noncompliance
  - Ad hoc, reactive, and incomplete generation and storage of data
  - Database scattered over dozens of file cabinets
  - Few techniques were adopted for receiving inspection/process control.

![Relative Response Graphs]

- Proton NMR
- FTIR
- HPLC
- GPC
- DSC
Objectives of Chemical Fingerprinting
(Recognize, Reduce, Resolve Problems)

- Detailed understanding of material composition
- Enhanced ability to detect changes in a material due to vendor changes or subtier supplier changes
  - Improved acceptance testing based on chemical composition
- Improved understanding of how a material works, ages, degrades, etc.
- Standardized approach to material fingerprinting
- Develop methods for monitoring all key ingredients
- Develop a comprehensive material database
- Reduced probability of unexpected and unrecognized changes to critical materials and processes
Approach: State of Art Facilities

- Chemical Characterization
  - NMR (300 and 400 MHz)
  - Surface analysis
    - ESCA/XPS
    - Auger
    - SIMS
    - ISS
  - RAMAN / FTIR / NIR
  - Metals analysis
    - ICP emission
    - AA/GFAA
    - ICP-MS
  - X-Ray Fluorescence
  - Chromatography
    - HPLC/HPLC-MS
    - GPC
    - GC (various detectors)
    - GC-MS
    - Ion chromatography
  - Flow injection auto analyzer
  - CHN O/S
  - Classical techniques
  - Asbestos identification
- Thermal Analysis
- Mechanical Properties
- Non Destructive Analysis
## Approach: Material Team

### Team Members

<table>
<thead>
<tr>
<th>Material Specialist</th>
<th>R&amp;D Analytical Laboratories</th>
</tr>
</thead>
<tbody>
<tr>
<td>M&amp;P Specialist</td>
<td>R&amp;D Materials and Process</td>
</tr>
<tr>
<td>Design Engineer</td>
<td>S&amp;E Engineering</td>
</tr>
<tr>
<td>Procurement Quality Engineer</td>
<td>Quality</td>
</tr>
<tr>
<td>Manufacturing Engineer</td>
<td>Operations</td>
</tr>
<tr>
<td>Process Control Lab</td>
<td>Quality Lab (material receipt)</td>
</tr>
</tbody>
</table>
Material Fingerprinting Approach

**Material Team**
- Review raw material
  - Review existing data
  - Contact supplier(s)
  - Select analytical instruments
  - Prepare test plans
  - Compile database reference data

**Fingerprinting Plan Phase I Development**
- Generate total signature
  - Develop analytical methods
  - Sampling
  - Sample preparation/separation
  - Instrument operation
  - Determine precision and accuracy
  - Establish quality controls
  - Document analytical test methods

**Laboratory Team**
- Generate total signature
  - Develop analytical methods
  - Sampling
  - Sample preparation/separation
  - Instrument operation
  - Determine precision and accuracy
  - Establish quality controls
  - Document analytical test methods

**Material Team**
- Inspect implementation
  - Train QA lab on "fingerprinting" methods
  - Perform current and "fingerprinting" acceptance testing
  - Collect sufficient "fingerprinting" data for statistics
  - Evaluate for specification change

**Phase II Implementation**
- Evaluate signature
  - Downselect applicable techniques
  - Establish method/material variations
  - Set preliminary fingerprinting limits

**Specification**
- Select fingerprint limits
- Update specification
Data Management

Fingerprinting Data Manipulation and Storage

Manual Data Storage
- Manual GRAMS Conversion

Automated Data Storage
- Fingerprinting Data Loader

Data Storage
- Quantitative Data
- File Storage
- Nautilus Lims System

Presentation Manager
- Fingerprinting Viewer

Lab Equipment

MS Word or Powerpoint
Excel Spreadsheets
ChemDraw
Merck Index
Scanned Images

Data is manually or automatically loaded into the appropriate storage area.

Raw Data, converted GRAMS, and other files are stored on the server. Quantitative data and material definition information is stored in Nautilus.
Database Components and Software
(No Commercially Available Integrated System: Integration and Data Parsing Developed Internally)

- Server-based PC Network: Novell®
- Data loader and Viewer: developed software programs internally using PowerBuilder®
- Oracle® database
- LIMS (Lab Information Management System) software: Nautilus® R2B2, LabSystems
- Spectroscopic/Chromatographic Data Viewer: Grams/32® v. 7.0, LabSystems, Galactic Industries
Accomplishments: RSRM Fingerprinting Materials

- 55 Materials completed or in process
  - 11 Solvents or cleaning solutions
  - Phenolic resin and 3 phenolic composites
  - 4 Compounded rubber insulations
  - 2 Propellant systems
  - 10 Polymeric components
  - 3 Sealants and ablative compounds
  - 5 Rubber adhesives
  - 3 Epoxy based adhesives
  - 5 Paints and primers
  - 7 Inorganic fillers, abrasives and reactive components
  - 1 Corrosion inhibiting grease
Accomplishments: Database Viewer Features

• Executive view
  • Material overview, reference documents, data examples

• Method information
  • Chemical characterization methods

• Component information
  • Trend analysis and visualization of key analytes

• Method quality control
  • Trend analysis of QC parameters

• View comparison
  • Direct graphical overlay of raw spectroscopic and chromatographic data

• Lab notes
Material Fingerprinting Success Example

- Neoprene FB
  - Secondary polymer used as a component in case insulation EPDM formulations
  - Material no longer produced
  - Fingerprinting showed that under proper storage conditions: Neoprene FB could be stored over 10 years and still meet specification
    - Storage at 40°F, low humidity, and minimal light
    - Stockpiled 100,000 lb till new EPDM formulation can be qualified
  - Test methods developed to ensure material is well within specification
    - Viscosity measurement performed as a check at the vendor's storage site, while the GPC and FTIR analyses confirm the molecular weight distribution and the chemical composition
- Defense program experienced solvating problem with gum stock for carbon fiber EPDM
  - Fingerprinting knowledge allowed immediate identification of the problem
  - Corrective action given on controlling Neoprene FB
<table>
<thead>
<tr>
<th>Stock #</th>
<th>Usage</th>
<th>Model Name</th>
<th>Material Number</th>
<th>NEOPRENE FB</th>
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</thead>
<tbody>
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</table>

**Presentation Module: Executive Screen**

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Material Example: Neoprene FB in EPDM

EPDM Usage in Booster Motor
<table>
<thead>
<tr>
<th>Method</th>
<th>File Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC</td>
<td>F1600</td>
<td>Differential Scanning Calorimetry (DSC)</td>
</tr>
<tr>
<td>AL</td>
<td>F1800</td>
<td>Alpha Analyzer</td>
</tr>
<tr>
<td>NMR</td>
<td>F800</td>
<td>Nuclear Magnetic Resonance (NMR)</td>
</tr>
<tr>
<td>FTIR</td>
<td>F2000</td>
<td>Fourier Transform Infrared Spectroscopy (FTIR)</td>
</tr>
<tr>
<td>GC</td>
<td>F2000</td>
<td>Gas Chromatography (GC)</td>
</tr>
<tr>
<td>HPLC</td>
<td>F2000</td>
<td>High-Performance Liquid Chromatography (HPLC)</td>
</tr>
<tr>
<td>AFS</td>
<td>F700</td>
<td>Atomic Absorption Spectroscopy (AFS)</td>
</tr>
<tr>
<td>CHN</td>
<td>F1800</td>
<td>CHN Analyzer</td>
</tr>
<tr>
<td>Raman</td>
<td>F1800</td>
<td>Raman Spectroscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>F2000</td>
<td>Thermogravimetric Analyzer (TGA)</td>
</tr>
<tr>
<td>ICP</td>
<td>F2000</td>
<td>Inductively Coupled Plasma (ICP)</td>
</tr>
</tbody>
</table>

Note: The TGA and NMR analyzers are primary tools used in the analysis of the material properties.
Component Info: Analyte Trends

Material Fingerprinting for Neoprene

Project: R&D, Acceptable
Test Method: Neoprene - Brookfield Viscosity
Analyte: Brookfield Viscosity (50°C)

Graph showing data values over time with ±σ limits and average sample data.

<table>
<thead>
<tr>
<th>Measured Date (in sequence)</th>
<th>Data Values CP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  3  5  7  9  11  13  15  17  19  21  23  25  27  29  31  33  35  37  39  41  43  45  47  49  51  53</td>
<td></td>
</tr>
<tr>
<td>500000  600000  700000  800000  900000  1000000  1100000</td>
<td></td>
</tr>
</tbody>
</table>

+2 sigma  -2 sigma  -3 sigma  +3 sigma  average  ○ sample data
Method QC: Duplicate GPC Analysis Trends

- **Lab**: R&D Lab
- **Test Methods**: Neoprene FB - GPC Analysis
- **Analyte**: RPD - MWw (RI)
- **QC Parameter**: IDUP
- **Units**: RPD

QC Parameter: IDUP  Units: RPD  Avg: 1.1  Sigma: 0.498  Max: 1.8  Min: 0.6

Data Values, RPD

Measured Date (In sequence)

+2 sigma  -2 sigma  - +3 sigma  - -3 sigma  - average  ○ sample data
View Comparison: FTIR Data

[Graph showing FTIR data comparison]
Analysis Details: FTIR Spectra From Aging Study

The graph shows the absorbance of FTIR spectra over time, with different aging times indicated. The x-axis represents the wavenumber in cm⁻¹, ranging from 1540 to 1480 cm⁻¹, and the y-axis shows absorbance values from 0.010 to 0.085.
Material Fingerprinting
Successes/Improvements (cont’d)

• **HC polymer, carboxy terminated polybutadiene (CTPB)**
  - This liquid polymer is used in the liner that bonds the propellant to the case insulation.
  - Understanding the details of the polymer and the manufacturing process enabled analysts to identify a noxious byproduct at increased levels that was making operators sick.
    - The bad lot was taken out of production and a corrective action was developed to improve the vendor’s manufacturing process.
    - A detection and quantification method with new limits for the byproduct is in place for acceptance of future lots.

• **In-depth fingerprinting knowledge has also been invaluable for the development of the replacement after current vendor announced the closure of their HC polymer plant.**
  - Initial carboxy terminated polybutadiene (CTPB) received from a new vendor showed distinct differences from HC polymer in small acids and molecular weights.
  - Recommendations to improve reaction mixture ratios as well as process washing and drying have enabled new vendor to produce acceptable polymer, now being tested for use on RSRM.
  - Also developing acceptance testing and spec limits for both commercial and defense programs with this new material.
Material Fingerprinting Successes/Improvements (cont’d)

• BRULIN 1990 GD-T
  • ODC replacement for methyl chloroform vapor degreasing
  • Water-based solvent used with spray-in-air technology
  • Several issues developed with material during certification
    • Material received with insoluble material in drums
    • Material received with lower than expected pH
  • Vendor asked for site visit from Thiokol’s chemist
    • Knowledge from fingerprinting provided information to stabilize product through small changes in use of de-ionized water, mixing steps, and cycles
    • Use of hydrated silicates
  • Recommendation for KOH add back to spray-in-air baths
    • Increased useable bath life from 8 to 90 days
  • Knowledge from fingerprinting effort provided suggestion for corrosion inhibitor rinse cycle (new inhibitor currently qualified)
Material Fingerprinting
Successes/Improvements (cont’d)

- MAPO (Methyl Aziridinyl Phosphine Oxide)
  - Used as a curative for the liner between insulation and propellant
  - Recent Lot received with incomplete certification
  - Acceptance testing indicated material was out of specification for reactive imine, hydrolyzable chloride and total chloride
  - Additional tests were done per the fingerprinting SLP that supported the previous testing and included GPC data that began to suggest the nature of the problem
  - Further testing using more detailed techniques (HPLC/MS) developed through fingerprinting in R&D Labs identified the process by-product impurities and aided vendor in finding a resolution
  - Material returned to vendor for reprocessing
Material Fingerprinting
Successes/Improvements (cont’d)

- TCA – Methyl Chloroform
  - Ozone Depleting Chemical (ODC) TCA has limited availability due to restrictions for defined essential use.
  - A large amount of stored TCA had exceeded its shelf life and deteriorated out of specification.
    - Distillation was proposed as a recovery technique, but there was uncertainty on its effects on the stabilization components.
    - Fingerprinting analyses were able to prove the distilled material acceptable to NASA.
  - Basic understanding has also identified problems with long-term storage of the TCA from a second source due to incompatibility between two components in its stabilizer package.
  - Currently working with vendor, design and manufacturing engineers to assess new methods for storage to ensure this critical solvent will be available until a replacement solvent can be qualified or, if necessary, for the life of the RSRM program.
Material Fingerprinting
Successes/Improvements (cont’d)

- Corrosion inhibiting grease from new plant verified with FTIR
  - Vendor tried a new formulation but reverted to original catalyst after fingerprinting confirmed it gave most consistent result
- D-limonene containing solvents removed from use on uncured rubber after testing confirms degradation of cure system
- BHT identified as a minor additive to inhibit d-limonene degradation in solvents
- Detailed fingerprinting of rubber to metal adhesives has provided new insight into aging processes plus new ways to monitor aging
  - Aging studies indicate resin interaction as early step in degradation
  - Significant reduction in shelf life with certain environments
  - New methods provide early warning of potential problems
Direct Benefits of Fingerprinting

• Fundamental understanding of critical materials that often equals or exceeds vendor's knowledge
  • Provide baseline chemical profile of materials in use
  • Material changes can often be traced to their source

• Standardized approach including:
  • Material team for focus and relevance
  • Flexible test plan for method adaptation or development
  • Laboratory team for technical expertise
  • Final report and R&D procedures to document method development
  • SLP of key down-selected robust methods in standard format for routine use in Process Control Lab

• Material team technical ownership
  • Analytical chemist as material specialist
  • Improved communication between procurement, work centers, quality and labs
Additional Benefits of Fingerprinting

- Versatile database broadly available both for new lot comparison and problem solving
  - Available plant-wide and informative on many levels of detail
  - Trending of key parameters and QC data as well as detailed overlay
  - Lot-to-lot consistency monitored and changes flagged
  - Security functions provide protection for vendor proprietary information

- Improved vendor relationships through data and method sharing
  - New methods shared with vendors to enhance their capabilities
  - Vendors acknowledge our expertise and expand cooperation by timely reporting of planned changes

- Greater efficiency and confidence in requalification/qualification of materials due to obsolescence or changes in vendor or production site
Continuing Challenges

• Down selection for Process Control Lab
  • Basic chemical characterization
  • Methods robust and simple enough for routine analysis
  • Key component information – what is likely to go wrong next
    • History of materials and vendors
    • Dependable crystal ball

• Implementation in Process Control Lab
  • Training at higher level of technical expertise
  • Greater demands on LIMS and data entry
  • Setting limits for new acceptance criteria

• Data utilization
  • Continuing education of vendors and engineers
Acknowledgements

- Vision of NASA/MSFC and Thiokol management to see the benefits of a formal Fingerprinting Program
- NASA funding through Marshall Space Flight Center
- Data sharing cooperation of material vendors
- Analytical efforts of Thiokol material specialists, scientists, and engineers