Chemical Fingerprinting Program for RSRM Critical Materials

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ATK
THIOKOL PROPULSION
Presentation Outline

- Background
- Objectives and Approach
- Accomplishments
  - Description of Database Viewer
  - Success Stories
  - Direct and Additional Benefits
- Continuing Challenges
- Acknowledgements
Reusuable 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

![Graph showing relative response of various analytical methods: Proton NMR, FTIR, HPLC, GPC, DSC.](image)
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>
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<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

**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

**Phase II**
- Implementation

**Material Team**
- Evaluate signature
  - Downselect applicable techniques
  - Establish method/material variations
  - Set preliminary fingerprinting limits

**Inspection Implementation**
- Train QA lab on "fingerprinting" methods
- Perform current and "fingerprinting" acceptance testing
- Collect sufficient "fingerprinting" data for statistics
- Evaluate for specification change

**Specification**
- Select fingerprint limits
- Update specification
Data Management
Fingerprinting Data Manipulation and Storage

Manual Data Storage
- Manual GRAMS Conversion

MS Word or Powerpoint
Excel Spreadsheets
ChemDraw
Merck Index
Scanned Images

Automated Data Storage
- Fingerprinting Data Loader

Lab Equipment
- Automated GRAMS Conversion

Data Storage
- Quantitative Data
- Nautilus Lims System

File Storage
Lan Server
- Raw Data, converted GRAMS, and other files are stored on the server. Quantitative data and material definition information is stored in Nautilus.

Presentation Manager
- Fingerprinting Viewer
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
for Neoprene FB
Presentation Module: Executive Screen

THIOLK PROPELLATION
Material Example: Neoprene FB in EPDM

EPDM Usage in Booster Motor
### Method Information Screen

**THIOLK PROPELLION**

<table>
<thead>
<tr>
<th>Test</th>
<th>Description</th>
<th>Method No.</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>Analog</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>GPC</td>
<td>Gel Permeation Chromatography</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>LC</td>
<td>Liquid Chromatography</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>ME</td>
<td>Mass Spectrometry</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>MT</td>
<td>Mass Spectrometry</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
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<tr>
<td>NV</td>
<td>Nuclear Magnetic Resonance</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>Thermal Conductivity</td>
<td>LCP 0790</td>
<td></td>
</tr>
<tr>
<td>TQ</td>
<td>Thermal Conductivity</td>
<td>LCP 0790</td>
<td></td>
</tr>
</tbody>
</table>

**Equipment View**

1. Portable Instruments
2. Portable Instruments
3. Portable Instruments
4. Portable Instruments
5. Portable Instruments
6. Portable Instruments
7. Portable Instruments
8. Portable Instruments
9. Portable Instruments
10. Portable Instruments

**Method Information**

- **Name:** Method Information
- **Type:** Lab Notebook
- **Date:** 01/01/2023
- **Version:** 1.0

**Additional Notes:**

- [Method Information](#)
- [View Method](#)
- [Method Info](#)
- [Method Info](#)
- [Method Info](#)
- [Method Info](#)
- [Method Info](#)
- [Method Info](#)
- [Method Info](#)
- [Method Info](#)
Component Info: Analyte Trends

Material Fingerprinting for Neoprene

Executive View | Method Information | Component Info | Method QC | View Comparisons | Lab Notes |
--- | --- | --- | --- | --- | --- |
Project: R&D, Acceptable
Test Methods: Neoprene - Brookfield Viscosity
Analyte: Brookfield Viscosity (50C)
Material Lot: (optional)

Sort By
- Sort By Date
- Sort By Lot and Date

Display Values
Print Values & Graph

Measured Date (in sequence)

+2 sigma -2 sigma +3 sigma -3 sigma average ○ sample data

Project: R&D, Acceptable  Test Method: Neoprene - Brookfield Viscosity
Analyte: Brookfield Viscosity (50C)  Avg: 786000  Sigma: 77400  Max: 956000  Min: 613000
Method QC: Duplicate GPC Analysis Trends

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

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

Measured Date (In sequence)
View Comparison: FTIR Data

![FTIR Data Chart]

**Neoprene Overview Spectra**

**Neoprene Reference Spectrum**

| L130_5 | NEOPRENE FB LOT 8262 60X MONTH TEST-L130_5.SPC |

**File Path:** 

- File Name: `NEOPRENE.fb LOT 8262 60X MONTH TEST--L130.5.SPC`
- File Location: `C:\WPRM19\PDATA\FIINGERPRINTING\DB\NEOPRENE\DATA\L130_5.SPC`

**Wavenumber (cm⁻¹):**

- 3500
- 3000
- 2500
- 2000
- 1500
- 1000

**Absorbance:**

- 0.8
- 0.6
- 0.4
- 0.2
- 0.0
- -0.2
- -0.4
- -0.6
- -0.8
Analysis Details: FTIR Spectra From Aging Study
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