

# **New Methodology to Assess Health and Environmental Impact of Flame Resistant (FR) Textiles**

**WP19-1040**

**Combat Capabilities Development Command Soldier Center**

**(CCDC – Soldier Center)**

**10 General Greene Ave**

**Natick, MA 01760**

**PI: Timothy Lawton, Ph.D.**

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## List of Acronyms

CCDC-Soldier Center - Combat Capabilities Development Command Soldier Center

CVC - Combat Vehicle Crewman Coverall

CWFS - Crashworthy Fuel Systems

EDS - Energy dispersive spectroscopy

EPA - Environmental Protection Agency

EPS - Environmental Protection System

FR - Flame resistant

FRACU - Flame Resistant Army Combat Uniforms

FREE - Flame Resistant Environmental Ensemble

FTIR - Fourier transform infrared spectroscopy

GEN III ECWCS - Generation III Extended Cold Weather Clothing System

GHS - Globally Harmonized System of Classification and Labeling of Chemicals

HCl - hydrogen chloride

IDLH - Immediately dangerous to life or health

IED - Improvised explosive devices

ISO - International Organization for Standardization

MRS - Material rating score

MS - Mass spectrometry

NBS - National Bureau of Standards

NIOSH - National Institute for Occupational Safety and Health

PBDE - Polybrominated Diphenyl Ethers

PFAS - Per- and polyfluoroalkyl substances

Py-GC/MS - Pyrolysis coupled with gas chromatography/mass spectrometry

RFI - Rapid Fielding Initiative

TCEP - Tris (2-chloroethyl) Phosphate

TDCIPP - Tris (1,3-dichloro-2-propyl) Phosphate

TGA-MS - Thermogravimetric analysis-mass spectrometry

TPHP - Triphenyl Phosphate

UPITT - University of Pittsburgh

## **Keywords**

Flame resistance; pyrolysis; gas chromatography; mass spectrometry; toxicity; thermogravimetric analysis

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## Abstract

**Introduction and Objectives:** In response to the increasing threat of flame events in conflicts over the last few decades there is increased demand for flame resistant (FR) uniforms to be fielded more quickly. While the FR uniforms have increased Soldier protection during a flame event, there is a question of the threat posed by the toxicity of the compounds evolved from those uniforms during and after a flame event. Of particular concern are the compounds released as a consequence of the flame event that the Soldier inhales.

**Technical Approach:** The aim of this project is to identify the compounds that are evolved from currently-fielded FR uniforms upon heating. To accomplish this, we use a combination of pyrolysis-gas chromatography/mass spectrometry and thermogravimetric analysis. Once the evolved compounds are identified, each compound is assigned a hazard score based on a modified version of the Globally Harmonized System for acute toxicity inhalation. These scores are weighted based on the relative amount of each compound detected. All the weighted scores for a material are summed to give a cumulative Material Rating Score. Multiple iterations of the Material Rating Score are discussed and further improvements for each are provided.

**Results:** From the work described here it was possible to determine a large portion of the compounds evolved from pyrolysis of currently-fielded FR uniforms. By identifying the compounds evolved two different ratings systems were developed using different pyrolysis profiles. It was possible to rate the fabrics on their relative toxicity. In both versions of the rating system Fabric B had the highest Material Rating Score, indicating the highest toxicity. In both rating systems Fabric C had the lowest Material Rating Score indicating the lowest toxicity. Fabric C was also the only fabric studied that had no chlorine present.

**Benefits:** We envision that these Material Rating Scores will serve as one metric, to serve alongside FR performance, when purchasing and fielding equipment in order to provide FR protection while minimizing negative health effects. While the focus of this work is on FR uniforms our methodology is translatable to other areas of concern including burn pits and the incineration of per- and polyfluoroalkyl substance-containing sorbent material. Further work is needed to refine this methodology to conduct the pyrolysis and thermogravimetric analysis in real-world atmospheres containing oxygen. Also, incorporation of another technique, such as thermogravimetric analysis coupled with infrared, may lead to the identification of small molecules not captured here.

## Objectives

The objectives of this work were to develop a methodology to identify the combustion products from FR fabrics and textiles, and use this to establish a scoring system to assess the health and environmental impact of current FR materials used in Army clothing. Successful completion of this objective resulted in a scoring system that can be used in conjunction with other performance metrics to allow for purchase of FR fabrics that protect the Soldier while minimizing negative health impacts.

## Background

Beginning during the Vietnam War, Nomex clothing was issued to flight and tank crews for mounted Soldiers to provide as much fire protection as possible. These new clothing systems, along with the introduction of Crashworthy Fuel Systems (CWFS), afforded crewmembers and passengers sufficient time to escape from crashed and/or damaged vehicles and resulted in a dramatic decrease in thermal injuries. Until 2007 uniforms with flame resistant (FR) properties, to include self-extinguishing and no melt/no drip when exposed to heat or flame, were only issued to Soldiers who performed high risk duties, such as mounted crewmen, airmen and fuel handlers. Uniforms supplied for these specialties were typically constructed from a fabric composed of a high percentage of “inherently flame resistant” fibers, such as *m*-aramids (Nomex) and *p*-aramids (Twaron and Kevlar), which have sufficient char yield to self-extinguish during burning.

In 2007 the Army began issuing Flame Resistant Army Combat Uniforms (FRACUs) to all Service members serving in contingency operations, such as Operation Iraqi Freedom, to reduce burn injuries when improvised explosive devices (IEDs) became a major threat. In addition to the FRACU, there has been development of a number of other FR uniform components incorporating FR including: Flame Resistant Environmental Ensemble (FREE), Generation III Extended Cold Weather Clothing System (GEN III ECWCS), Improved Combat Vehicle Crewman Coverall (CVC), and Environmental Protection System (EPS). Depending on the requirements these specific systems address, they can contain varying blends and components to render the material flame resistant. For example the fabric used in the FRACU consists of 65% FR rayon, 25% para-aramid, and 10% nylon 6,6 fiber. These different compositions will lead to different products evolved when the material is burned.

Fielding of the FRACU was done through a Rapid Fielding Initiative (RFI) that quickly got these uniforms out to the field to address the threat, but bypassed many of the standard acquisition processes more commonly performed when the Army fields equipment. Recently, Congress recommended that all uniforms have FR capabilities, and while this may or may not come to pass, it is important to fully understand the impact to the health of the Soldiers and the environment when these uniforms are actually subjected to a fire event.

## FR Materials Toxicology

Documented concern over the toxicity of smoke produced in fires dates at least as far back as the 1930s,<sup>2</sup> and in the 1980s an ISO subcommittee was established to study toxic hazards in fires. To

better understand hazards associated with smoke toxicity, assay methods and toxicology techniques based on laboratory animals were established. Smoke toxicity is tested using different furnace set-ups, such as the NBS Cup Furnace Test, the UPITT Test, and the U.S. Radiant Furnace Test. All of these tests utilized different experimental techniques to develop an index of potential hazards and were developed to assess exposure to large amounts of smoke in burning buildings.

In 2015 Mackay et. al. published a risk assessment of thermal and toxicological risks for commercial FR textiles including Protex Modacrylic Blends, FR Treated Cotton and Cotton/Nylon blend, and FR Treated Rayon.<sup>3</sup> The testing was performed in a full-scale system and utilized gas sampling followed by Fourier transform infrared spectroscopy (FTIR) to determine relative amounts of hydrogen chloride, hydrogen cyanide, nitrogen dioxide, sulfur dioxide and antimony trioxide (solid) evolved when the material was combusted. These results were then input into a model they developed to perform a risk characterization specifically to determine if exposure would have adverse effects, such as increased injury or impediment of escape. All of the textiles emitted all of the previously mentioned gases to some extent, while antimony was limited to the modacrylic containing materials. The results were modeled using IDLH (immediately dangerous to life or health) thresholds set by NIOSH. The results showed significant elevations in combustion gas concentrations lasting approximately 40 seconds past ignition. However, none of the respiratory exposures were found to exceed the threshold for these gases. Maximum exposure time was assumed to be 20 seconds post-ignition, and based on their model, the short duration of combustion in the flash fire did not permit for sufficient combustion gas production to represent a significant hazard. While this is one of the few studies we are aware of that analyzed the products evolved from FR uniforms during a flame event, it was focused on a small number of compounds. A more complete sampling of materials and the compounds emitted is required as there could be many more compounds released.

Little is known about the operational exposure risks for the Warfighter from off-gassing from FR uniforms during a fire event. It has been shown that Nomex, when heated to temperatures from 150 to 370°C in air, can evolve toxic chemicals such as benzene, aniline, diaminobenzene, benzoic acid, benzonitrile, dicyanobenzene, diphenylamine and cyanophenylbenzene. Kynol, another FR fiber, has been shown to evolve methane, phenol, methyl and dimethyl phenol.<sup>4</sup>

Under less stringent heating conditions Nomex degrades very slowly, releasing small quantities of organic compounds. These may include carbon dioxide, acetone, acetamide, acetaldehyde, benzene, butane, toluene and many other compounds (some possibly toxic or irritating) in trace amounts depending on exposure conditions.

Rayon is not an inherently FR material. In order for it to have FR properties, a flame retardant is incorporated into the fiber during processing. Traditionally the polymer industry incorporated halogenated, especially brominated, chemicals into their products to impart FR. Since 2004, industry has been shifting away from these chemicals in response to the Environmental Protection Agency's (EPA) phase out of PBDE (polybrominated diphenyl ethers)<sup>5</sup> due to their

carcinogenic effects<sup>6</sup> and moving to organophosphate flame retardants such as triphenyl phosphate (TPHP), tris (1,3-dichloro-2-propyl) phosphate (TDCIPP), and tris (2-chloroethyl)phosphate (TCEP). Specifically, FR Rayon incorporates an ammonium polyphosphate into the fiber to impart FR properties. According to the National Research Council, only one inhalation toxicity study was located for this material.<sup>7</sup> With the shift to these newer flame retardants, less is known about the possibly toxic compounds that could evolve during a flame event and therefore warrants investigation.

The need to investigate these newer flame resistant chemicals, such as organophosphate flame retardants, is especially great because the mechanism in which they provide FR protection is by producing gases and char which inhibit combustion. Flame resistant products alone or in combination with the fiber materials may represent a health and environmental hazard as the result of gaseous acidic combustion products - hydrogen chloride, hydrogen cyanide, nitric oxides, hydrogen sulfur oxides, and other combustion constituents being generated and released in the form of gases and/or particulates. Lab scale testing on materials that contain these flame retardants has identified the following emissions: hydrogen chloride and hydrogen cyanide released from modacrylic blends, nitrogen dioxide from flame-resistant cotton, hydrogen cyanide and sulfur dioxide from cotton/nylon blends, and sulfur dioxide emissions from rayon blends.

In an effort to get the FRACU to our Warfighters as quickly as possible, little research has been done on the environmental and health impacts resulting from the combustion of FR Rayon. It is known that carbon disulfide is used in the manufacturing and processing of rayon; a highly toxic compound that has occupational exposure associated with pain, distal sensory loss, neurophysiological impairment and cardiovascular disease. Because of EPA regulations (40 CFR Part 63 Subpart UUUU), rayon is no longer produced in the United States and a Berry Amendment Waiver has been granted to purchase the required FR rayon overseas. However, the environmental and health impact of the Defender M material used in the FRACU or its combustion products has not been characterized.

## **Materials and Methods**

For this project, commercially available flame retardant/resistant (FR) fabrics currently fielded by the military were obtained. For the privacy of the company, the acquired fabrics are coded from A-G. Due to proprietary restrictions the exact composition and potential additives are not known but it is known that the FR fabrics contain combinations of the component fibers nylon 6,6, lyocell, *p*-aramid, *m*-aramid, modacrylic and rayon. Samples of nylon 6,6 (Zytel 42A, DuPont), lyocell (Invodex Enterprises Inc.), *p*-aramid (Twaron, Warwick Mills), *m*-aramid (Nomex, Warwick Mills), modacrylic (Kaneka Corporation), and FR rayon (Lenzing FR, Invodex Enterprises Inc.) were obtained and used for comparison to the FR fabrics.

### **Energy dispersive spectroscopy (EDS)**

EDS data was collected with a Zeiss EVO 60 scanning electron microscope equipped with an EDAX Genesis system. Spectra were collected from 0-20 eV and averaged over 500 scans at 1 scan/second. EDS data was acquired in at least 3 separate areas for each material. Prior to collecting EDS data the fabric samples were sputter coated for 120 seconds with a gold/palladium source to render them conductive.

### **Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS)**

To improve uniformity and reproducibility in the chromatograms collected, the fabric/fiber samples were first ground in a freezer mill by cooling below the glass transition temperature of the material with liquid nitrogen and pulverizing them using a solenoid driven impactor. For each spectra,  $85 \pm 5$   $\mu\text{g}$  of resulting powdered sample was loaded into a clean, quartz tube with quartz wool. The sample was pyrolyzed in a CDS Analytical Pyroprobe 5200 in a helium atmosphere. In Method 1 the pyroprobe was heated to 750 °C at 1,000 °C/second and held at 750 °C for 20 seconds. In Method 2 the pyroprobe was heated at 1,000 °C/second to the first temperature identified in the corresponding TGA for that material, held for 20 seconds and then allowed to cool back to ambient temperature. Once the GC/MS run had finished, the sample was heated to the next temperature identified with the TGA. This process was repeated until all temperatures identified in the TGA had been visited. Evolved compounds were collected in the trap containing 10XTA sorbent material where it was then desorbed for 5 minutes and transferred to the GC/MS via a heated transfer line at 300 °C. The GC used was a 7890A GC from Agilent Technologies equipped with a DB-5MS column, 30 m x 0.250 mm, 0.25  $\mu\text{m}$ . The column was heated from 40 – 300 °C at 20 °C/minute then held at 300 °C for 20 minutes with a 1.0 mL/min flow rate of helium. Mass spectra were collected using an Agilent 5975C MSD scanning from 30-400 m/z at 3.85 scans/second with a 1.5 minute solvent delay. While no solvent was used to apply the solid to the quartz tube, the solvent delay was still used to reduce the burden on the mass spectrometer and to ensure the signal of the evolved compounds was not washed out.

### **Thermogravimetric analysis-mass spectrometry (TGA-MS)**

TGA-MS was conducted at the University of Georgia using a TA Instruments Discovery TGA-MS benchtop system with high temperature platinum pans from TA Instruments. Samples were prepared by loading 5 – 8 mg of milled sample into the pan, and the sample was packed down such that no material sat above the edges of the pan. Argon was used as a carrier gas for all experiments, with a flow rate of 10 mL/min for the balance and 30 mL/min for the sample housing. A clean, unused platinum pan was used as a reference for the TGA balance.

In the TGA, the balance housing temperature was set to 40 °C. Samples were subjected to an isotherm at 50 °C for 5 minutes, then heated at a rate of 20 °C/minute to 700 °C, followed by a 5 minute isotherm at 700 °C. For the isothermal experiments when a 1% weight loss/minute or greater is detected, the TGA entered an isotherm at that temperature. This isotherm continued indefinitely until a weight loss of less than .05% is achieved. The linear ramp then continued until a temperature of 700 °C was obtained.

For the MS, a capillary transfer line from the TGA sample housing to the MS was used. The transfer line was held at 200 °C, and an evolved gas heater at 95% power was used on the front end of the transfer line. The mass spectrometer used high electron energy at a pressure of 30 torr to ionize gaseous products. A  $m/z$  range of 14-200 was used for each run with an accuracy of 5, which gave a cycle time of 11.25 seconds. Generally, a gain multiplier of 3 was used by the detector to boost signal.

TGA data collected at CCDC - Soldier Center was collected with a SDT Q600 from TA Instruments. In this set-up, 2-5 mg of milled sample was heated in a platinum pan to 755 °C at 20 °C/minute. To obtain the mass loss events, the system entered an isothermal mode when 6% weight loss/minute was detected. The isothermal mode was terminated when 0.01% weight loss/minute was detected and the 20 °C/minute linear heating rate was resumed. TGA experiments were carried out in a nitrogen atmosphere with a flow rate of 100 mL/minute.

## Results and Discussion

Table 1: Summary of EDS results indicating the elements present in each material.

| Material         | C | N | O | Na | Si | P | S | Cl | Sb |
|------------------|---|---|---|----|----|---|---|----|----|
| A                | X | X | X |    |    |   |   |    |    |
| B                | X | X | X | X  | X  | X | X |    |    |
| C                | X | X | X |    | X  | X |   | X  |    |
| D                | X | X | X |    |    |   |   | X  | X  |
| E                | X | X | X |    |    |   |   | X  | X  |
| F                | X | X | X |    | X  |   | X | X  | X  |
| G                | X | X | X |    |    |   | X | X  | X  |
| nylon 6,6        | X | X | X |    |    |   |   |    |    |
| raw cotton       | X |   | X |    |    |   |   |    |    |
| FR rayon         | X |   | X |    |    | X | X |    |    |
| <i>p</i> -aramid | X | X | X | X  |    |   | X |    |    |
| <i>m</i> -aramid | X | X | X |    |    |   |   |    |    |
| modacrylic       | X | X | X |    | X  | X |   | X  |    |
| lyocell          | X |   | X |    |    |   |   |    |    |

First, EDS was used to determine the elements present in each material. The qualitative identification of elements present in a given material are summarized in **Table 1**. The manufacturer of the materials can only provide limited information about the composition of the material and any coatings that may be present due to proprietary restrictions. Identification of the elements present by analysis of EDS spectra made subsequent chemical identification easier; potential compounds that were identified in the reference library searches could be eliminated if an element in that compound was not present in the EDS spectra.

Once the elements in all the fibers and fabrics were identified, the materials were analyzed with Py-GC/MS. The component fibers were analyzed first in

order to determine the compounds that were evolved from those materials before moving onto the more complex, blended fabrics. Once the materials were pyrolyzed in the pyroprobe and separated in the column of the GC, the resulting mass spectra were compared to reference spectra in the NIST library. Rather than analyzing every peak in the GC chromatogram, only peaks with at least 1% of the total area in the GC chromatogram were assigned. This threshold provided sufficient signal-to-noise to assign a compound to the peak with confidence. The steps taken to identify peaks from the Py-GC/MS spectra are highlighted in **Fig. 1**. For much of the subsequent

analysis and discussion, only data from one material is shown for clarity, but the identical steps were taken on the other 13 materials analyzed in this effort.

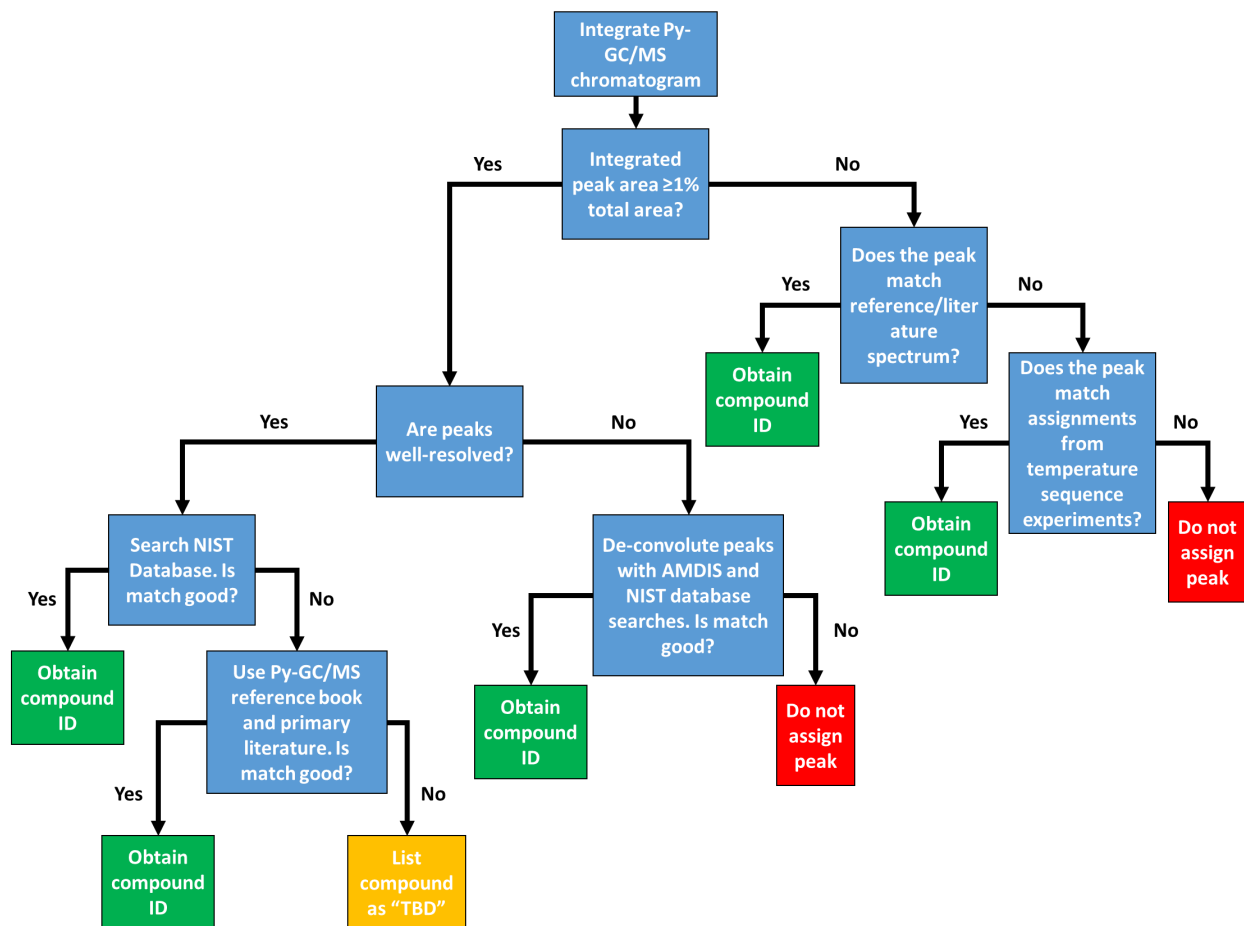


Figure 1: Decision tree for identifying peaks in the GC/MS chromatograms.

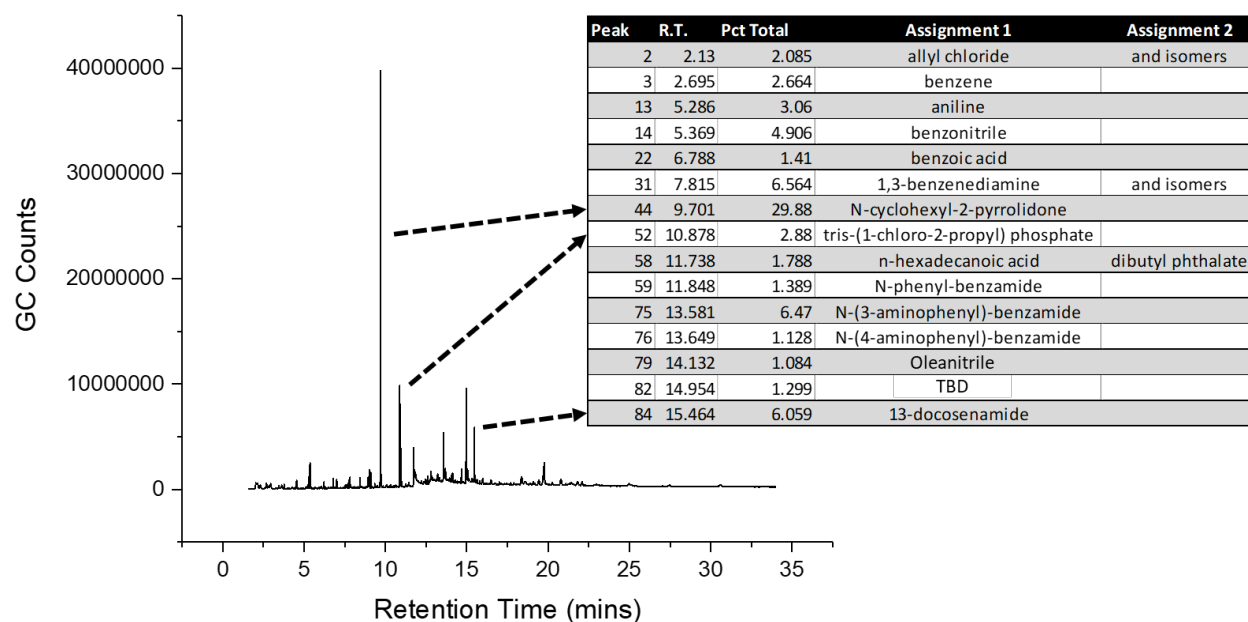


Figure 2: Representative GC/MS chromatogram with compound assignments in the inset. Example peak assignments are shown with the arrows.

Various steps were taken to attain the best identification possible including background subtraction, peak deconvolution using the AMDIS applet within the Agilent software and cross-referencing spectra with the NIST MS library and the “Pyrolysis-GC/MS Data Book of Synthetic Polymers”.<sup>8</sup> An example of a Py-GC/MS chromatogram with assignments for a single material is shown in **Fig. 2**. This same process was repeated for all 14 materials investigated. A representative Py-GC/MS chromatogram for all materials can be found in Appendix 1. After multiple reproducible Py-GC/MS chromatograms were acquired, the peaks were assigned. The list of compound assignments for each material can be found in Appendix 5.

Once the assignment list of compounds for all 14 materials investigated was completed, each compound was assigned a hazard score related to the acute inhalation toxicity for (H330-H333) based on the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). These scores can be found in the Safety Data Sheet for a given chemical. The GHS system scores are inversely proportional to their toxicity (e.g. lower numbers correspond to more toxic compounds). In the present rating system, the GHS system was reversed so that low scores now represent low toxicity and high scores represent high toxicity. Whenever an assigned compound did not have a GHS score for acute inhalation toxicity it was scored “0”. Next, the modified GHS score for each compound was weighted ( $Compound_i^*$ ) by the relative amount of each compound present in the GC/MS chromatogram:

$$Compound_i^* = \frac{Compound_i \text{ peak area}}{Total \text{ integrated area}} \times Modified \text{ GHS score (0 – 4)} \quad \text{Equation 1}$$

To obtain the Material Rating Score (MRS) all the weighted scores for all compounds evolved from that material were summed:

$$MRS = \sum_{n=1}^i Compound_1^* + Compound_2^* + \dots + Compound_i^* \quad \text{Equation 2}$$

Table 2: Table of Material Rating Scores (MRS) 1.0 for all materials

| Material         | MRS 1.0 |
|------------------|---------|
| C                | 108     |
| <i>m</i> -aramid | 75.4    |
| <i>p</i> -aramid | 61.5    |
| modacrylic       | 38.3    |
| G                | 31.9    |
| E                | 29.3    |
| D                | 29      |
| F                | 23.1    |
| nylon 6,6        | 11.8    |
| A                | 10.8    |
| lyocell          | 6.3     |
| B                | 6.3     |
| FR rayon         | 4.6     |
| raw cotton       | 2.1     |

The compiled MRS 1.0 scores for all 14 materials investigated are found in **Table 2** in descending order. As mentioned above, the higher the MRS score, the more toxic compounds are off-gassed from that material during pyrolysis. Based on this methodology fabric C had the most toxic products evolved while fibers *m*-aramid, *p*-aramid and modacrylic were most hazardous, so caution should be taken with materials containing those fibers.

However during this process, we identified several shortcomings of this approach; 1) it was not possible to identify small molecules, such as hydrogen chloride (HCl), with this approach so the scores associated with these species are not accounted for and could dramatically alter the MRS, 2) the scores here reflect the relative ratio of the compounds in the GC/MS chromatogram rather than a physical amount of that material, 3) a material that was 100% assigned would have a higher score than another material with less total area assigned even if more toxic compounds were released, and 4) many compounds did not have a score for acute inhalation toxicity and where therefore scored 0. In an attempt to improve the validity of the MRS reported, TGA was incorporated to develop MRS 2.0 scores.

A collaboration with the University of Georgia was developed with the intent of supplementing the Py-GC/MS data with TGA-MS in order to quantify the amount of each compound that was released and to capture smaller molecules like HCl. An example of a TGA-MS is shown in Appendix 2. Unfortunately, these efforts did not obtain the desired results, so efforts were refocused to acquire TGA data at CCDC - Soldier Center. The TGA-MS system had too low sensitivity to measure many compounds identified with Py-GC/MS, it was not able to determine the originating compound based on *m/z* values and had no chromatography to separate the potentially dozens of compounds evolved at a single temperature. In the future, operating the Py-GC/MS in direct mode versus trap mode would enable relative concentrations of small molecules like HCl to be quantified but caution must be taken as HCl is extremely corrosive to GC columns. Generally, TGA data are acquired with a linear heating ramp but it is also possible to acquire data with an isothermal temperature program. In this mode the temperature is held constant when a certain mass loss threshold is detected. Once mass loss has finished the linear heating rate resumes until the next mass loss event. Through trial and error, a 6% weight loss per minute threshold was established to enter the isothermal mode as that provided discrete and well-separated mass loss events. Using the TGA in this manner, plots like **Fig. 3A** were acquired. From this TGA data, temperature ranges were identified with significant mass loss. Those same temperatures were visited in the Py-GC/MS for subsequent pyrolysis runs to identify the compounds evolved during the mass loss events in the TGA, shown in **Fig. 3B**. For example, the

black arrow in **Fig. 3A** corresponds to a mass loss of 6% at 230 °C. The black Py-GC/MS plot in **Fig. 3B** is the corresponding chromatogram that can be used to identify the compounds released in that 6% mass loss.

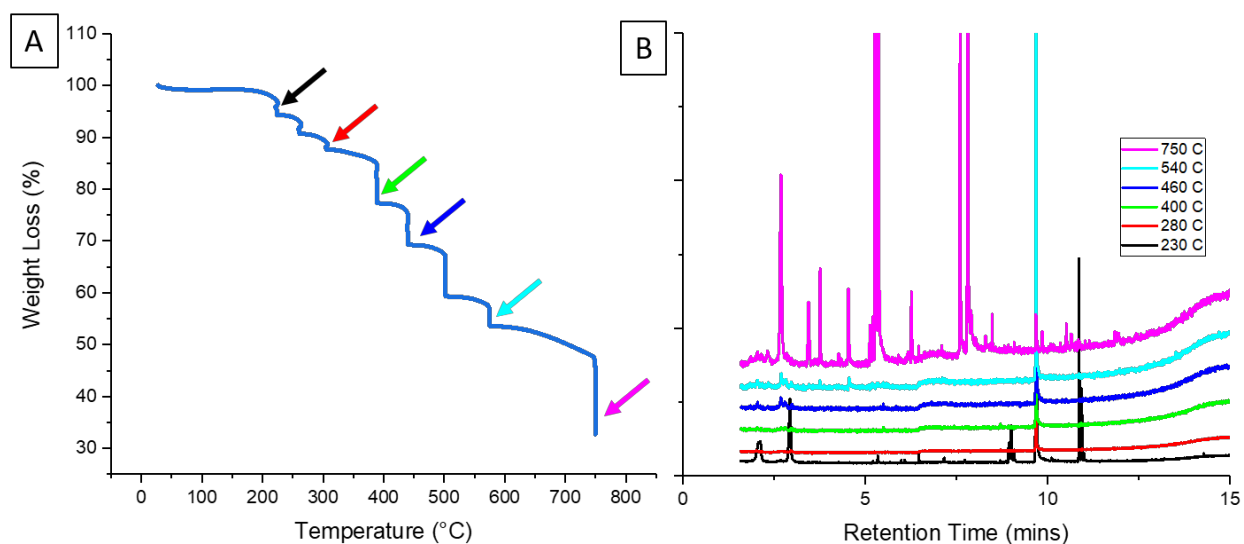


Figure 3: A) Representative TGA trace with significant mass loss events indicated with arrows. B) The corresponding GC/MS chromatograms taken sequentially for each mass loss temperature identified in A.

Table 3: Summary of TGA data collected. Each mass loss event for each material has shown the temperature at which the event occurs and the % weight loss for that step.

| Material         | Mass Loss Event 1 | Mass Loss Event 2 | Mass Loss Event 3 | Mass Loss Event 4 |
|------------------|-------------------|-------------------|-------------------|-------------------|
| A                | -                 | -                 | -                 | -                 |
| B                | 250 °C<br>8%      | 550 °C<br>56%     | 750 °C<br>15%     | -                 |
| C                | 230 °C<br>6%      | 280 °C<br>4%      | 400 °C<br>13%     | 750 °C<br>30      |
| D                | 250 °C<br>27%     | 375 °C<br>23%     | 750 °C<br>22%     | -                 |
| E                | 250 °C<br>24%     | 375 °C<br>26%     | 750 °C<br>23%     | -                 |
| F                | 240 °C<br>27%     | 500 °C<br>26%     | 750 °C<br>12%     | -                 |
| G                | 240 °C<br>23%     | 500 °C<br>29%     | 750 °C<br>9%      | -                 |
| nylon 6,6        | 410 °C<br>82%     | 750 °C<br>10%     | -                 | -                 |
| raw cotton       | -                 | -                 | -                 | -                 |
| FR rayon         | 280 °C<br>54%     | 750 °C<br>16%     | -                 | -                 |
| <i>p</i> -aramid | 550 °C<br>46%     | 750 °C<br>6%      | -                 | -                 |
| <i>m</i> -aramid | 430 °C<br>20%     | 560 °C<br>22%     | 750 °C<br>12      | -                 |
| modacrylic       | 220 °C<br>38%     | 710 °C<br>26%     | 750 °C<br>1%      | -                 |
| lyocell          | 280 °C<br>25%     | 320 °C<br>44%     | 750 °C<br>14%     | -                 |

With the same materials tested to develop MRS 1.0, TGA data were collected on each one to determine temperatures with mass loss events. The full TGA runs for each material can be found in Appendix 3. The vertical portions of the TGA plots indicate a mass loss event resulting in the temperature being held constant. Many of the materials have different numbers of mass loss events occurring at different temperatures with different % weight losses at each step. For each material, three reproducible TGA runs were collected and averaged to find average mass loss temperatures and % weight losses. Shown in **Table 3** is a summary of the averaged TGA data collected for each different material. Each cell has a temperature for the mass loss event identified along with the average % weight loss listed below for that temperature. In several instances mass loss

temperatures identified in the TGA were combined into one step if they were too tightly spaced to accurately visit with the Py-GC/MS.

After the TGA data was acquired, Method 2 was developed with the Py-GC/MS to sequentially heat to each temperature identified with the TGA. An example of the correlation between temperatures identified in TGA and the Py-GC/MS chromatograms can be seen in **Fig. 3**. Acquiring this Py-GC/MS data it became apparent that some of the temperature runs had no visible peaks in the GC/MS chromatogram; see Appendix 4 and Appendix 3 for the TGA and Py-GC/MS chromatograms respectively for material C. It is clear that even though the TGA data suggests significant mass loss between 300 – 500 °C there are no visible peaks for those corresponding temperatures in the Py-GC/MS. This discrepancy is assigned to the loss of small molecules that are too small to be trapped by the sorbent material in the Py-GC/MS and differences in the heating profile and absolute temperature between the TGA and Py-GC/MS instruments. From

Table 4: Material Rating Score (MRS) 2.0 using the modified GHS scores normalized to the weight of each compound off-gassed by comparing TGA and Py-GC/MS.

| Material | MRS 2.0 |
|----------|---------|
| C        | 144.1   |
| F        | 78      |
| E        | 50.6    |
| D        | 48.2    |
| G        | 39.5    |
| B        | 31.5    |

the resulting GC/MS chromatograms, compounds were identified at each temperature visited. In many instances the compounds identified at a retention time in a specific temperature run were the same compound identified at the same retention time for the direct heating to 750 °C. Interestingly, in several temperature runs new compounds were identified not previously seen in the direct 750 °C runs. The new identifications were likely due to the relative abundance increasing above the 1% threshold in the sequential temperature runs compared to the direct 750 °C heating. In many cases this was confirmed by going back to the direct 750 °C chromatogram and identifying the same compound at the same retention time. After identifying all the compounds, they were weighted using the average % weight loss values identified in **Table 3** with the TGA, assuming 100 g of material was pyrolyzed, instead

of the relative GC peak areas as done in Equation 1, before being multiplied by the modified GHS score for that compound. If a compound was evolved at multiple temperatures the total weight of that compound evolved across all temperatures was used. Once all weighted scores were obtained for that material they were summed, as in Equation 2, to obtain MRS 2.0 values. The summary of MRS 2.0 scores can be found in **Table 4**.

Unfortunately, due to the constraints of the experimental timeline it was only possible to compute MRS 2.0 scores for six of the seven blended fabrics but these are the most relevant samples to analyze compared to the component fibers. These were the most relevant samples because they are the actual FR fabrics being currently fielded. The seventh fabric, A, without a MRS 2.0 value was not a FR fabric. Rather than comparing the absolute values from either of these scoring systems, the more important metric is the relative trend of material scores within a particular system, either 1.0 or 2.0. When comparing the trends in the two scoring systems Fabric C has the highest score, thereby off-gassing more hazardous compounds, in both systems. In both scoring systems, Fabric B has the lowest score meaning it evolves the least amount of hazardous compounds. Of the fabrics analyzed in both scoring systems, the general trend is the same except for Fabrics F and G being swapped. During the process of assigning scores for MRS 2.0 we did observe compounds identified in the temperature runs that were not previously identified in the direct 750 °C heating runs. As a result, the MRS 2.0 scores arise from a more complete assignment of compounds from a given material compared to MRS 1.0. Unfortunately, it was not possible to determine the quantities of small molecules evolved, like HCl with either approach. Have a method to quantify molecules like HCl, potentially operating the Py-GC/MS in a different mode, may have a significant impact on the trends observed in each scoring system outlined in this work.

## Conclusions and Implications for Future Research and Benefits

Within this 1 year effort, we identified compounds evolved from seven different fabrics that are currently fielded by the U.S. Military during a pyrolysis event. Also, by compiling the hazard scores it was possible to develop a ratings system for these fabrics based on acute inhalation toxicity. We envision such a rating system complementing another metric, such as FR performance, to allow purchasing authorities to choose the fabric that provides the required FR protection with minimal health/environmental impact. Further refinement of our rating system is still needed to address the shortcomings mentioned of not being able to quantify the small molecules evolved (like HCl) and doing the pyrolysis in conditions analogous to what would be encountered in the field.



Figure 4: Figure of an open air burn pit found in CENTCOM.1

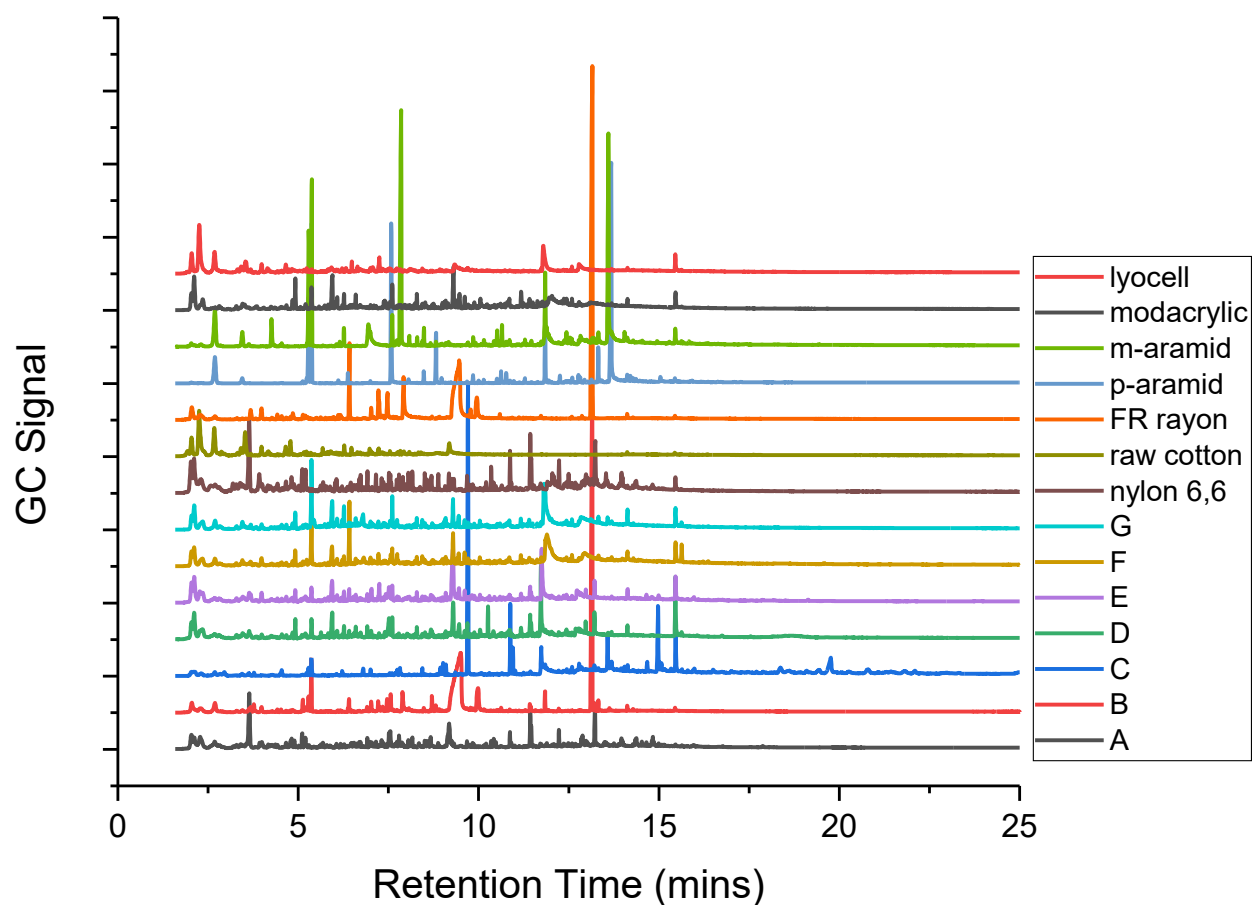
Beyond FR uniforms, our methodology and ratings system could be applied to many other materials. Burn pits, like the one shown in **Fig. 4**, stand out as a significant concern for causing Soldier illness and injury due to the hazardous compounds being off-gassed from burning a range of materials including plastics, fuels, batteries, human waste, etc.<sup>9</sup> Not only could our method developed here be applied to analyzing

the compounds emitted from a burn pit to help better understand the hazards facing Soldiers but our rating system could help identify materials that should not be burned.

In addition to burn pits, the incineration of per- and polyfluoroalkyl substances (PFAS) containing sorbent material is a growing concern. In order to dispose of or regenerate PFAS sorbent material, it is often heated to temperatures  $> 900\text{ }^{\circ}\text{C}$ .<sup>10</sup> Our methodology defined here could be applied to identifying the potentially hazardous compounds that are released upon heating of PFAS in sorbet material.

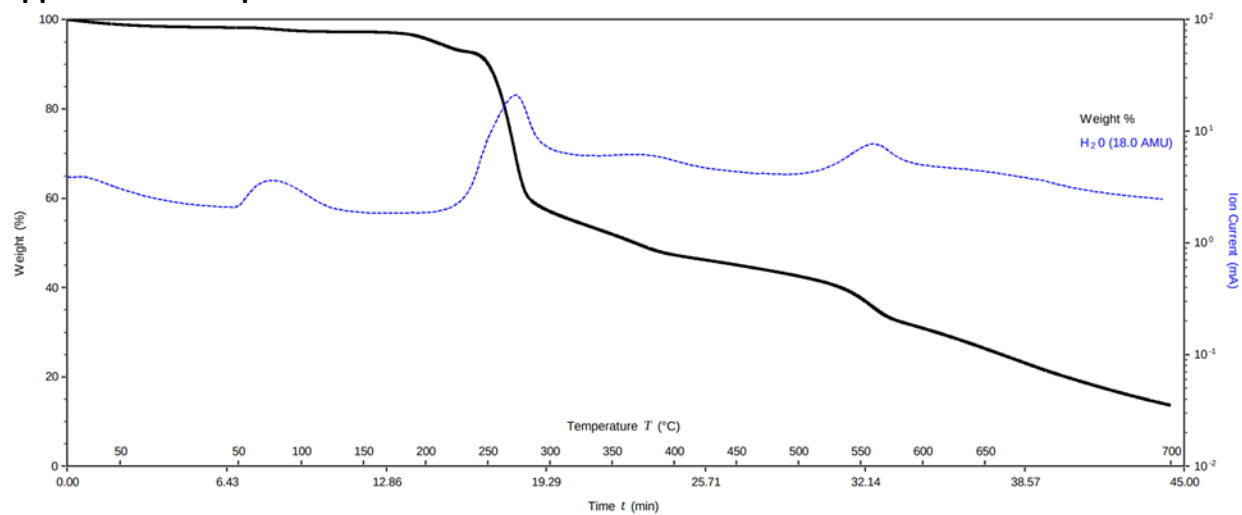
## Appendix

### Appendix 1. Representative Py-GC/MS of all materials heating to 750 °C



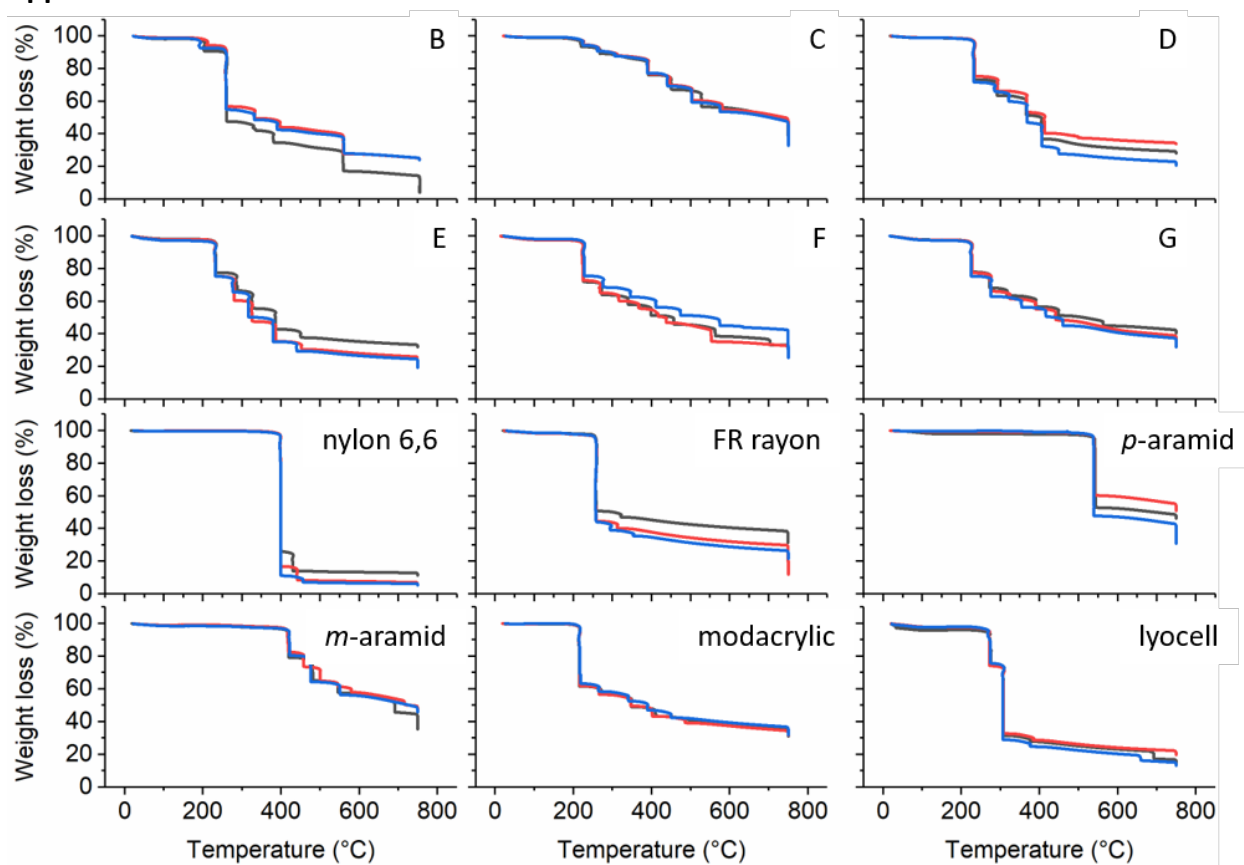
Supplemental Figure 1: Representative Py-GC/MS chromatogram for each material investigated. Material was pyrolyzed to 750 °C at 1,000 °C/second and held for 20 seconds. After desorbing from the trap the compounds passed through the column before entering the mass spectrometer. A 1.5 minute solvent delay was used before data was recorded by the mass spectrometer.

## Appendix 2. Example TGA-MS of Fabric B



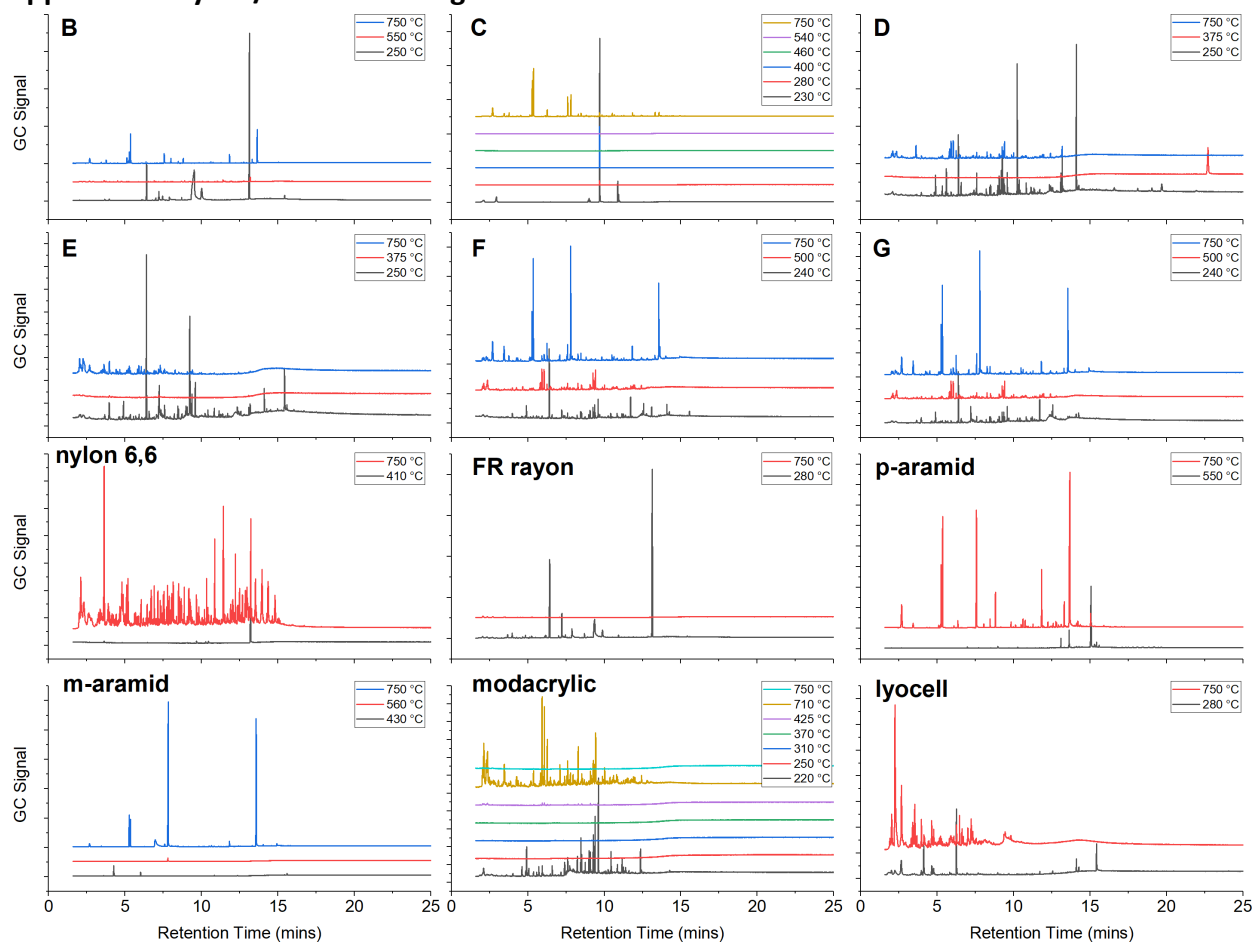
Supplemental Figure 2: Example of TGA-MS plot from UGA. The weight loss % from the TGA is plotted in black on the left y-axis. The ion current detected by the mass spectrometer for 18.0 m/z is plotted in the dashed blue line on the right y-axis. Both data are plotted as a function of time. Note the temperature scale is non-linear with respect to time owing to the isothermal program run.

### Appendix 3. Isothermal TGA of FR Materials



Supplemental Figure 3: Isothermal TGA data collected at CCDC - Soldier Center. Weight loss % is plotted on the y-axis as a function of temperature. The overlapping black, red and blue lines in each plot are repeated measurements for each material. The material is indicated in the top right corner of each plot.

## Appendix 4. Py-GC/MS Chromatograms of Mass Loss Events from TGA



Supplemental Figure 4: Py-GC/MS chromatograms for each material taken at each temperature identified by the TGA. Within a given plot for each material, each temperature run is vertically off-set for clarity.

**Appendix 5. Compound assignments from materials for MRS 1.0 and 2.0**

*Compound assignment from Py-GC/MS for nylon 6,6 for compounds with at least 1% of the total chromatogram area*

| Retention Time (min) | Compound Assignment                      | CAS Number   | Py-GC/MS Method 1 (Yes/No) | Py-GC/MS Method 2 (°C) |
|----------------------|------------------------------------------|--------------|----------------------------|------------------------|
| 2.029                | Acetonitrile                             | 75-05-8      | Yes                        |                        |
| 2.113                | 2-Propenenitrile                         | 107-13-1     | Yes                        | 750                    |
| 2.296                | 1-Hexene                                 | 592-41-6     | Yes                        | 750                    |
| 3.378                | Methallyl cyanide                        | 4786-19-0    | Yes                        | 750                    |
| 3.642                | Cyclopentanone                           | 120-92-3     | Yes                        | 750                    |
| 5.115                | <i>N</i> -Methyl-2-propenamide           | 1187-59-3    | Yes                        | ---                    |
| 7.556                | Caprolactam                              | 105-60-2     | Yes                        | 750                    |
| 8.672                | Butanamide                               | 541-35-5     | No                         | 750                    |
| 10.874               | <i>N</i> -(6-Aminohexyl)pent-4-enamide   | 1997102-57-4 | Yes                        | 750                    |
| 11.435               | 5-Cyano- <i>N</i> -(hex-5-enyl)pentamide | ---          | Yes                        | 750                    |
| 11.463               | 5-Cyano- <i>N</i> -hexylpentamide        | ---          | Yes                        | ---                    |
| 13.237               | 1,8-Diazacyclotetradecane-2,7-dione      | 4266-66-4    | Yes                        | 410, 750               |

*Compound assignment from Py-GC/MS for FR rayon for compounds with at least 1% of the total chromatogram area*

| Retention Time (min) | Compound Assignment                                                  | CAS Number   | Py-GC/MS Method 1 (Yes/No) | Py-GC/MS Method 2 (°C) |
|----------------------|----------------------------------------------------------------------|--------------|----------------------------|------------------------|
| 2.052                | Pyruvic aldehyde                                                     | 78-98-8      | Yes                        | 280, 750               |
|                      | Furan                                                                | 110-00-9     |                            |                        |
| 2.065                | 1,3-Pentadiene                                                       | 504-60-9     | No                         | 750                    |
| 2.368                | 2-Methylfuran                                                        | 534-22-5     | No                         | 750                    |
| 2.697                | Acetone alcohol                                                      | 116-09-6     | Yes                        | ---                    |
| 2.697                | 2-Methylbutanal                                                      | 96-17-3      | No                         | 750                    |
| 3.444                | Toluene                                                              | 108-88-3     | No                         | 750                    |
| 3.682                | (S)-5-Hydroxymethyl-2(5H)-furanone                                   | 78508-96-0   | Yes                        | ---                    |
| 3.984                | 2-Furfural                                                           | 98-01-1      | Yes                        | 280                    |
| 6.172                | 5,5-dimethyl-1,3,2-Dioxaphosphorinane                                | 25236-29-7   | No                         | 750                    |
| 6.424                | Levogluosenone                                                       | 37112-31-5   | Yes                        | 280                    |
| 7.226                | 3,6-Dianhydro- $\alpha$ -glucopyranose                               | 4451-30-3    | Yes                        | 280                    |
| 7.244                | 5-(Hydroxymethyl)-2-furfural                                         | 67-47-0      | Yes                        | ---                    |
| 7.922                | 2-Hydroxy-6,8-dioxabicyclo[3.2.1]octan-4-one                         | 2241885-40-3 | Yes                        | 280                    |
| 9.465                | Levoglucozan                                                         | 498-07-7     | Yes                        | 280                    |
| 9.955                | 1,6-Anhydro- $\beta$ -D-glucofuranose                                | 7425-74-3    | Yes                        | 280                    |
| 13.156               | 1,3,2-Dioxaphosphorinane, 2,2'-oxybis[5, 5-dimethyl-, 2,2'-disulfide | 4090-51-1    | Yes                        | 280                    |

Compound assignment from Py-GC/MS for p-aramid for compounds with at least 1% of the total chromatogram area

| Retention Time (min) | Compound Assignment                         | CAS Number  | Py-GC/MS Method 1 (Yes/No) | Py-GC/MS Method 2 (°C) |
|----------------------|---------------------------------------------|-------------|----------------------------|------------------------|
| 2.693                | Benzene                                     | 71-43-2     | Yes                        | 750                    |
| 5.287                | Aniline                                     | 62-53-3     | Yes                        | 750                    |
| 5.376                | Benzonitrile                                | 100-47-0    | Yes                        | 750                    |
| 6.378                | 4-Methylbenzonitrile                        | 104-85-8    | Yes                        | ---                    |
| 6.985                | 1-Dodecene                                  | 112-41-4    | No                         | 550                    |
| 7.585                | 1,4-Benzenediamine                          | 106-50-3    | Yes                        | 750                    |
|                      | <i>p</i> -Dicyanobenzene                    | 623-26-7    |                            |                        |
| 8.481                | Biphenyl                                    | 92-52-4     | Yes                        | ---                    |
| 8.827                | 4-Aminobenzonitrile                         | 873-74-5    | Yes                        | ---                    |
| 8.973                | Dodecanol                                   | 112-53-8    | No                         | 550                    |
| 11.849               | <i>N</i> -Phenyl-benzamide                  | 93-98-1     | Yes                        | 750                    |
| 13.323               | 4-Cyano- <i>N</i> -phenyl benzamide         | 17922-96-2  | Yes                        | 550, 750               |
| 13.684               | <i>N</i> -(4-Aminophenyl)benzamide          | 17625-83-1  | Yes                        | 550, 750               |
| 15.06                | 4-Cyano-4'-aminobenzanilide                 | 953740-53-9 | Yes                        | 550, 750               |
| 15.291               | 4-Cyano- <i>N</i> -(4-cyanophenyl)benzamide | 132640-25-6 | No                         | 550                    |

*Compound assignment from Py-GC/MS for m-aramid for compounds with at least 1% of the total chromatogram area*

| Retention Time (min) | Compound Assignment                | CAS Number   | Py-GC/MS Method 1 (Yes/No) | Py-GC/MS Method 2 (°C) |
|----------------------|------------------------------------|--------------|----------------------------|------------------------|
| 2.689                | Benzene                            | 71-43-2      | Yes                        | 750                    |
| 3.449                | Toluene                            | 108-88-3     | Yes                        | 750                    |
| 4.259                | <i>N,N</i> -Dimethyl acetamide     | 127-19-5     | Yes                        | 430                    |
|                      | <i>N</i> -Ethyl acetamide          | 625-50-3     |                            |                        |
| 5.285                | Aniline                            | 62-53-3      | Yes                        | 560, 750               |
| 5.37                 | Benzonitrile                       | 100-47-0     | Yes                        | 750                    |
| 6.017                | 1-Octanol                          | 111-87-5     | No                         | 430                    |
| 6.265                | 3-Methylbenzonitrile               | 620-22-4     | Yes                        | 750                    |
| 6.888                | Benzoic acid                       | 65-85-0      | Yes                        | ---                    |
| 7.605                | 1,3-Benzenedicarbonitrile          | 626-17-5     | Yes                        | 750                    |
| 7.843                | 1,3-Benzenediamine                 | 108-45-2     | Yes                        | 560, 750               |
| 8.488                | Biphenyl                           | 92-52-4      | Yes                        | 750                    |
| 10.647               | [1,1'-Biphenyl]-3-amine            | 2243-47-2    | Yes                        | ---                    |
| 11.842               | <i>N</i> -Phenyl-benzamide         | 93-98-1      | Yes                        | 430, 750               |
| 13.559               | 3'-Aminobenzanilide                | 14315-16-3   | No                         | 430, 560, 750          |
| 13.603               | <i>N</i> -(3-Aminophenyl)benzamide | 16091-26-2   | Yes                        | ---                    |
| 13.651               | <i>N</i> -(4-Aminophenyl)benzamide | 17625-83-1   | Yes                        | ---                    |
| 14.947               | 3-Cyano-3'-aminobenzanilide        | 1016512-51-8 | Yes                        | 430, 560, 750          |

Compound assignment from Py-GC/MS for modacrylic for compounds with at least 1% of the total chromatogram area

| Retention Time (min) | Compound Assignment                          | CAS Number | Py-GC/MS Method 1 (Yes/No) | Py-GC/MS Method 2 (°C) |
|----------------------|----------------------------------------------|------------|----------------------------|------------------------|
| 2.039                | Acetonitrile                                 | 75-05-8    | Yes                        | 710                    |
| 2.116                | 2-Propenenitrile                             | 107-13-1   | Yes                        | 220, 710               |
| 2.272                | Propanenitrile                               | 107-12-0   | No                         | 710                    |
| 2.354                | 2-Methyl-2-propenenitrile                    | 126-98-7   | Yes                        | 710                    |
| 2.476                | Isobutyronitrile                             | 78-82-0    | No                         | 710                    |
| 3.065                | 2-Methyl-2-butenenitrile                     | 30574-97-1 | No                         | 710                    |
| 3.451                | 2-Methylene butanenitrile                    | 1647-11-6  | No                         | 710                    |
| 3.459                | Toluene                                      | 108-88-3   | Yes                        | 710                    |
| 3.519                | 2,4-Pentadienenitrile                        | 1615-70-9  | Yes                        | ---                    |
| 3.859                | 3-Methylpyridine                             | 108-99-6   | No                         | 710                    |
| 4.262                | Ethylbenzene                                 | 100-41-4   | No                         | 710                    |
|                      | <i>o</i> -Xylene                             | 95-47-6    |                            |                        |
| 4.348                | <i>m</i> -Xylene                             | 108-38-3   | No                         | 710                    |
|                      | <i>p</i> -Xylene                             | 106-42-3   |                            |                        |
| 4.608                | 1,2,3,4-Tetrachlorobutane                    | 3405-32-1  | No                         | 220                    |
| 4.838                | 3-Chloropyridine                             | 626-60-8   | No                         | 220                    |
| 4.922                | 2-Chloropyridine                             | 109-09-1   | Yes                        | 220                    |
| 5.37                 | Benzonitrile                                 | 100-47-0   | Yes                        | 220, 710               |
| 5.918                | Pentanedinitrile                             | 544-13-8   | No                         | 710                    |
| 5.949                | 2-Methylene pentanedinitrile                 | 1572-52-7  | Yes                        | 220, 710               |
| 6.07                 | 2-Methylpentanedinitrile                     | 4553-62-2  | No                         | 220, 710               |
| 6.272                | 2-Methylbenzonitrile                         | 529-19-1   | Yes                        | 710                    |
| 6.596                | 3-Chlorobenzonitrile                         | 766-84-7   | Yes                        | 220                    |
| 7.097                | 3,5-Dimethylbenzonitrile                     | 22445-42-7 | No                         | 710                    |
| 7.422                | 2,4-Dichlorobenzonitrile                     | 6574-98-7  | No                         | 220                    |
| 7.61                 | 1,3-Benzenedicarbonitrile                    | 626-17-5   | Yes                        | 220, 710               |
| 7.782                | Heptanedinitrile                             | 646-20-8   | No                         | 710                    |
| 8.228                | 2-Chloronaphthalene                          | 91-58-7    | No                         | 220                    |
| 8.29                 | 4-Cyanobenzeneacetonitrile                   | 876-31-3   | Yes                        | 710                    |
| 8.515                | (2Z, 4Z)-3,4-Dimethyl-2,4-hexadienedinitrile | 1557-61-5  | No                         | 220                    |
| 9.078                | Benzene-1,2,4-tricarbonitrile                | 10347-14-5 | No                         | 220, 710               |
| 9.308                | Hexane-1,3,5-tricarbonitrile (trimer)        | 1572-50-5  | Yes                        | 220, 710               |
| 9.473                | Pentane-1,3,5-tricarbonitrile (trimer)       | 4379-04-08 | Yes                        | 710                    |
| 10.052               | (Z)-Hex-1-ene-1,3,5-tricarbonitrile (trimer) | ---        | Yes                        | 710                    |

|        |                                                         |            |     |     |
|--------|---------------------------------------------------------|------------|-----|-----|
| 10.843 | Tricyclo[3.3.1.0(2,8)]nona-3,6-diene-2,6-dicarbonitrile | ---        | No  | 220 |
| 11.869 | Oct-7-ene-1,3,5,7-tetracarbonitrile (tetramer)          | 64918-32-7 | Yes | --- |
| 12.356 | 1-Chlorohexadecane                                      | 4860-03-1  | No  | 220 |
| 15.462 | 13-Docosenamide                                         | 112-84-5   | Yes | --- |

*Compound assignment from Py-GC/MS for lyocell for compounds with at least 1% of the total chromatogram area*

| Retention Time (min) | Compound Assignment                          | CAS Number   | Py-GC/MS Method 1 (Yes/No) | Py-GC/MS Method 2 (°C) |
|----------------------|----------------------------------------------|--------------|----------------------------|------------------------|
| 2.047                | Pyruvic aldehyde                             | 78-98-8      | Yes                        | 280, 750               |
| 2.258                | Hydroxyacetaldehyde                          | 141-46-8     | Yes                        | 280, 750               |
| 2.679                | Acetone alcohol                              | 116-09-6     | Yes                        | 280, 750               |
| 3.538                | 1,4-Butanediol                               | 110-63-4     | Yes                        | ---                    |
| 3.549                | 2-Oxo-propanoic acid methyl ester            | 600-22-6     | No                         | 750                    |
| 3.976                | 2-Cyclopenten-1-one                          | 930-30-3     | No                         | 750                    |
| 3.986                | 2-Furfural                                   | 98-01-1      | Yes                        | 280, 750               |
| 4.148                | 2-Furanmethanol                              | 98-00-0      | Yes                        | 280, 750               |
| 4.658                | 2(5H)-Furanone                               | 497-23-4     | Yes                        | 280, 750               |
|                      | 2(3H)-furanone                               | 20825-71-2   |                            |                        |
| 4.773                | Butyrolactone                                | 96-48-0      | No                         | 280                    |
| 4.799                | 5-Methylfuran-2(3H)-one                      | 591-12-8     | Yes                        | 750                    |
| 6.097                | 2,5-Furandicarboxaldehyde                    | 823-82-5     | No                         | 750                    |
| 6.264                | Pentanal                                     | 110-62-3     | No                         | 280, 750               |
| 6.485                | 5-(Hydroxymethyl)dihydro-2(3H)-furanone      | 10374-51-3   | Yes                        | 750                    |
| 7.034                | 3,6-Dianhydro- $\alpha$ -glucopyranose       | 4451-30-3    | Yes                        | 750                    |
| 7.247                | 5-(Hydroxymethyl)-2-furfural                 | 67-47-0      | Yes                        | 750                    |
| 7.981                | 2-Hydroxy-6,8-dioxabicyclo[3.2.1]octan-4-one | 2241885-40-3 | Yes                        | ---                    |
| 9.344                | Levoglucosan                                 | 498-07-7     | Yes                        | 750                    |
| 11.796               | Hexadecanoic acid                            | 57-10-3      | Yes                        | ---                    |
| 12.787               | Octadecanoic acid                            | 57-11-4      | Yes                        | ---                    |

Compound assignment and parent fiber identification from Py-GC/MS for Fabric B for compounds with at least 1% of the total chromatogram area.

| Retention Time (min) | Compound Assignment                                                 | CAS Number   | Origin                 | Method 1 Py-GC/MS (Yes/No) | Method 2 Py-GC/MS (°C) |
|----------------------|---------------------------------------------------------------------|--------------|------------------------|----------------------------|------------------------|
| 2.05                 | Pyruvic aldehyde                                                    | 78-98-8      | FR rayon               | Yes                        | 550                    |
| 2.678                | 1-Butanol                                                           | 71-36-3      | ---                    | No                         | 550                    |
| 2.693                | Benzene                                                             | 71-43-2      | <i>p</i> -aramid       | Yes                        | 750                    |
| 2.883                | 2-Propenoic acid, ethyl ester                                       | 140-88-5     | ---                    | No                         | 550                    |
| 3.446                | Toluene                                                             | 108-88-3     | FR rayon               | No                         | 750                    |
| 3.685                | Cyclopentanone                                                      | 120-92-3     | nylon 6,6              | Yes                        | 550                    |
| 4.518                | 2-Propenoic acid, butyl ester                                       | 141-32-2     | ---                    | No                         | 550                    |
| 5.121                | Isocyanatobenzene                                                   | 103-71-9     | ---                    | No                         | 750                    |
| 5.287                | Aniline                                                             | 62-53-3      | <i>p</i> -aramid       | Yes                        | 750                    |
| 5.367                | Benzonitrile                                                        | 100-47-0     | <i>p</i> -aramid       | Yes                        | 750                    |
| 6.413                | Levogluosenone                                                      | 37112-31-5   | FR rayon               | No                         | 250                    |
| 6.901                | Hexanedinitrile                                                     | 111-69-3     | ---                    | No                         | 550                    |
| 7.22                 | 1,4:3,6-Dianhydro- $\alpha$ -d-glucopyranose                        | 4451-30-3    | FR rayon               | Yes                        | 250, 550               |
| 7.566                | 1,4-Benzenedicarbonitrile                                           | 623-26-7     | <i>p</i> -aramid       | Yes                        | 750                    |
| 7.891                | 2-Hydroxy-6,8-dioxabicyclo[3.2.1]octan-4-one                        | 2241885-40-3 | FR rayon               | Yes                        | ---                    |
| 8.473                | Biphenyl                                                            | 92-52-4      | <i>p</i> -aramid       | No                         | 750                    |
| 8.806                | 4-Aminobenzonitrile                                                 | 873-74-5     | <i>p</i> -aramid       | No                         | 750                    |
| 9.485                | Levogluconan                                                        | 498-07-7     | FR rayon               | Yes                        | 250                    |
| 9.969                | 1,6-Anhydro- $\beta$ -d-gluofuranose                                | ---          | FR rayon               | Yes                        | 250                    |
| 10.618               | <i>p</i> -Phenylbenzonitrile                                        | 2920-38-9    | ---                    | No                         | 750                    |
| 11.027               | Triethyl hex-5-ene-1,3,5-tricarboxylate (trimer)                    | 10080-58-7   | ---                    | No                         | 550                    |
| 11.843               | <i>N</i> -Phenylbenzamide                                           | 93-98-1      | <i>p</i> -aramid       | Yes                        | 750                    |
| 13.147               | 1,3,2-Dioxaphosphorinane, 2,2'-oxybis[5,5-dimethyl-, 2,2'-disulfide | 4090-51-1    | FR rayon (FR additive) | Yes                        | 250                    |
| 13.211               | 1,8-Diazacyclotetradecane-2,7-dione                                 | 4266-66-4    | nylon 6,6              | Yes                        | 550                    |
| 13.31                | 4-Cyano- <i>N</i> -phenyl- Benzamide                                | 17922-96-2   | <i>p</i> -aramid       | No                         | 750                    |
| 13.64                | 4'-Aminobenzanilide                                                 | 17625-83-1   | <i>p</i> -aramid       | No                         | 750                    |

Compound assignment and parent fiber identification from Py-GC/MS for Fabric C for compounds with at least 1% of the total chromatogram area.

| Retention Time (min) | Compound Assignment                | CAS Number            | Origin           | Method 1 Py-GC/MS (Yes/No) | Method 2 Py-GC/MS (°C) |
|----------------------|------------------------------------|-----------------------|------------------|----------------------------|------------------------|
| 2.13                 | Allyl chloride                     | 107-05-1              | FR additive      | Yes                        | 230                    |
| 2.119                | 1-Chloro-1-propene                 | 590-21-6              | <i>m</i> -aramid | No                         | 230                    |
| 2.695                | Benzene                            | 71-43-2               | <i>m</i> -aramid | Yes                        | 750                    |
| 2.94                 | 1,2-Dichloropropene                | 7069-38-7<br>563-54-2 | <i>m</i> -aramid | No                         | 230                    |
| 3.448                | Toluene                            | 108-88-3              | <i>m</i> -aramid | No                         | 750                    |
| 4.545                | Styrene                            | 100-42-5              | <i>m</i> -aramid | Yes                        | 750                    |
| 5.286                | Aniline                            | 62-53-3               | <i>m</i> -aramid | Yes                        | 750                    |
| 5.369                | Benzonitrile                       | 100-47-0              | <i>m</i> -aramid | Yes                        | 750                    |
| 6.268                | 4-Methylbenzonitrile               | 104-85-8              | <i>m</i> -aramid | Yes                        | 750                    |
| 6.788                | Benzoic acid                       | 65-85-0               | <i>m</i> -aramid | Yes                        | ---                    |
| 7.606                | 1,3-Benzenedicarbonitrile          | 626-17-5              | <i>m</i> -aramid | Yes                        | 750                    |
| 7.815                | 1,3-Benzenediamine                 | 108-45-2              | <i>m</i> -aramid | Yes                        | 750                    |
| 8.298                | <i>m</i> -Aminobenzonitrile        | 2237-30-1             | <i>m</i> -aramid | Yes                        | 750                    |
| 8.488                | Biphenyl                           | 92-52-4               | <i>m</i> -aramid | Yes                        | 750                    |
| 9.701                | <i>N</i> -Cyclohexyl-2-pyrrolidone | 6837-24-7             | dye carrier      | Yes                        | 230, 280, 400, 750     |
| 10.518               | <i>p</i> -Phenylbenzonitrile       | 2920-38-9             | <i>m</i> -aramid | Yes                        | 750                    |
| 10.878               | Tris(1-chlor-2-propyl)phosphate    | 13674-84-5            | FR additive      | Yes                        | 230                    |
| 11.738               | <i>N</i> -Hexadecanoic acid        | 57-10-3               | lubricant        | Yes                        | ---                    |
| 11.848               | <i>N</i> -Phenylbenzamide          | 93-98-1               | <i>m</i> -aramid | Yes                        | 750                    |
| 13.324               | 3-Cyano- <i>N</i> -phenylbenzamide | 143330-38-5           | <i>m</i> -aramid | Yes                        | 750                    |
| 13.581               | <i>N</i> -(3-Aminophenyl)benzamide | 16091-26-2            | <i>m</i> -aramid | Yes                        | 750                    |
| 13.649               | <i>N</i> -(4-Aminophenyl)benzamide | 17625-83-1            | <i>m</i> -aramid | Yes                        | ---                    |
| 14.132               | Oleanitrile                        | 112-91-4              | lubricant        | Yes                        | ---                    |
| 15.464               | 13-Docosenamide                    | 112-84-5              | lubricant        | Yes                        | ---                    |

*Compound assignment and parent fiber identification from Py-GC/MS for Fabric D for compounds with at least 1% of the total chromatogram area.*

| Retention Time (min) | Compound Assignment                          | CAS Number | Origin                  | Method 1 Py-GC/MS (Yes/No) | Method 2 Py-GC/MS (°C) |
|----------------------|----------------------------------------------|------------|-------------------------|----------------------------|------------------------|
| 2.04                 | Acetonitrile                                 | 75-05-8    | nylon 6,6<br>modacrylic | Yes                        | ---                    |
| 2.117                | 2-Propenenitrile                             | 107-13-1   | nylon 6,6<br>modacrylic | Yes                        | 750                    |
| 2.276                | Propanenitrile                               | 107-12-0   | modacrylic              | Yes                        | 750                    |
|                      | Hydroxyacetaldehyde                          | 141-46-8   | lyocell                 |                            |                        |
| 2.348                | 2-Methyl-2-propenenitrile                    | 126-98-7   | modacrylic              | Yes                        | 750                    |
| 2.691                | Acetone alcohol                              | 116-09-6   | lyocell                 | Yes                        | ---                    |
|                      | Benzene                                      | 71-43-2    | ---                     |                            |                        |
| 3.464                | Toluene                                      | 108-88-3   | modacrylic              | Yes                        | 750                    |
| 3.641                | Cyclopentanone                               | 120-92-3   | nylon 6,6               | Yes                        | 750                    |
| 3.971                | 2-Furfural                                   | 98-01-1    | lyocell                 | No                         | 250                    |
| 4.845                | 3-Chloropyridine                             | 626-60-8   | modacrylic              | Yes                        | ---                    |
| 4.922                | 2-Chloropyridine                             | 109-09-1   | modacrylic              | Yes                        | 250                    |
| 5.194                | Butanedinitrile                              | 110-61-2   | ---                     | No                         | 750                    |
| 5.37                 | Benzonitrile                                 | 100-47-0   | modacrylic              | Yes                        | 250, 750               |
| 5.61                 | Benzoyl chloride                             | 98-88-4    | ---                     | No                         | 250                    |
|                      | 1-Chloro-4-methylbenzene                     | 106-43-4   |                         |                            |                        |
| 5.945                | 2-Methylene pentanedinitrile                 | 1572-52-7  | modacrylic              | Yes                        | 750                    |
| 6.061                | 2-Methylpentanedinitrile                     | 4553-62-2  | modacrylic              | No                         | 750                    |
| 6.39                 | Levogluosenone                               | 37112-31-5 | lyocell                 | No                         | 250                    |
| 6.507                | 3-Methylbenzonitrile                         | 620-22-4   | ---                     | No                         | 750                    |
| 6.572                | 3-Chlorobenzonitrile                         | 766-84-7   | modacrylic              | No                         | 250                    |
| 7.609                | 1,3-Benzenedicarbonitrile                    | 626-17-5   | modacrylic              | Yes                        | 250, 750               |
| 7.769                | Heptanedinitrile                             | 646-20-8   | modacrylic              | No                         | 750                    |
| 8.267                | 4-Cyanobenzeneacetonitrile                   | 876-31-3   | modacrylic              | No                         | 750                    |
| 8.445                | 1-Chloro-3-ethenylbenzene                    | 2039-85-2  | ---                     | No                         | 250                    |
| 8.502                | (2Z, 4Z)-3,4-Dimethyl-2,4-hexadienedinitrile | 1557-61-5  | modacrylic              | No                         | 250, 750               |
| 8.961                | 1-Chlorodecane                               | 1002-69-3  | ---                     | No                         | 250                    |
| 9.065                | Benzene-1,2,4-tricarbonitrile                | 10347-14-5 | modacrylic              | No                         | 250                    |
| 9.195                | N,N-Dimethyl-1-dodecanamine                  | 112-18-5   | ---                     | No                         | 250                    |
| 9.26                 | N-Isopropyl phthalimide                      | 304-17-6   | ---                     | No                         | 250                    |
| 9.297                | Hexane-1,3,5-tricarbonitrile (trimer)        | 1572-50-5  | modacrylic              | Yes                        | 250, 750               |
| 9.416                | 1,2,3-Trimethyl-1H-indole                    | 1971-46-6  | ---                     | No                         | 250                    |

|        |                                                         |            |            |     |          |
|--------|---------------------------------------------------------|------------|------------|-----|----------|
| 9.462  | Pentane-1,3,5-tricarbonitrile (trimer)                  | 4379-04-08 | modacrylic | Yes | 750      |
| 10.015 | (Z)-Hex-1-ene-1,3,5-tricarbonitrile (trimer)            | ---        | modacrylic | No  | 750      |
| 10.264 | N-Butylphthalimide                                      | 1515-72-6  | ---        | Yes | 250      |
| 10.366 | <i>N,N</i> -Dimethyl-1-tetradecanamine                  | 112-75-4   | ---        | No  | 250      |
| 10.83  | Tricyclo[3.3.1.0(2,8)]nona-3,6-diene-2,6-dicarbonitrile | ---        | modacrylic | No  | 250      |
| 11.431 | 5-Cyano- <i>N</i> -hexylpentamide                       | ---        | nylon 6,6  | Yes | 750      |
| 11.731 | <i>N</i> -Hexadecanoic acid                             | 57-10-3    |            | Yes | ---      |
| 13.214 | 1,8-Diazacyclotetradecane-2,7-dione                     | 4266-66-4  | nylon 6,6  | Yes | 250, 750 |
| 14.103 | <i>N</i> -Oleanitrile                                   | 112-91-4   | lubricant  | No  | 250      |
| 15.459 | 13-Docosenamide                                         | 112-84-5   | lubricant  | Yes | ---      |

*Compound assignment and parent fiber identification from Py-GC/MS for Fabric E for compounds with at least 1% of the total chromatogram area.*

| Retention Time (min) | Compound Assignment                          | CAS Number | Origin     | Method 1 Py-GC/MS (Yes/No) | Method 2 Py-GC/MS (°C) |
|----------------------|----------------------------------------------|------------|------------|----------------------------|------------------------|
| 2.044                | Acetonitrile and                             | 75-05-8    | nylon 6,6  | Yes                        | 750                    |
|                      | Pyruvic aldehyde                             | 78-98-8    | lyocell    |                            | 250,750                |
| 2.121                | 2-Propenenitrile                             | 107-13-1   | nylon 6,6  | Yes                        | 250, 750               |
| 2.275                | Propanenitrile                               | 107-12-0   | modacrylic | Yes                        | 250, 750               |
|                      | Hydroxyacetaldehyde                          | 141-46-8   | lyocell    |                            |                        |
| 2.353                | 2-Methyl-2-propenenitrile                    | 126-98-7   | modacrylic | Yes                        | 250, 750               |
| 2.684                | Acetone alcohol                              | 116-09-6   | lyocell    | No                         | 750                    |
| 2.696                | Benzene                                      | 71-43-2    | ---        | Yes                        | 750                    |
| 2.82                 | Pyridine                                     | 110-86-1   | ---        | Yes                        | ---                    |
| 3.293                | 2,4-Pentadienenitrile                        | 1615-70-9  | modacrylic | Yes                        | ---                    |
| 3.47                 | Toluene                                      | 108-88-3   | modacrylic | Yes                        | 750                    |
| 3.547                | 2-Oxopropanoic acid, methyl ester            | 600-22-6   | lyocell    | No                         | 750                    |
| 3.643                | Cyclopentanone                               | 120-92-3   | nylon 6,6  | Yes                        | 250, 750               |
| 3.668                | Carbonocyanidic acid, ethyl ester            | 623-49-4   | ---        | No                         | 250                    |
| 3.989                | 2-Furfural                                   | 98-01-1    | lyocell    | Yes                        | 250, 750               |
| 4.922                | 2-Chloropyridine                             | 109-09-1   | modacrylic | Yes                        | 250                    |
| 5.37                 | Benzonitrile                                 | 100-47-0   | modacrylic | Yes                        | 250, 750               |
| 5.81                 | (1-Methylethylidene)-propanedinitrile        | 13166-10-4 | ---        | No                         | 750                    |
| 5.909                | 2-Methylene pentanedinitrile                 | 1572-52-7  | modacrylic | No                         | 750                    |
|                      | Pentanedinitrile                             | 544-13-8   |            |                            |                        |
| 5.922                | 2-Methylpentanedinitrile                     | 4553-62-2  | modacrylic | No                         | 250, 750               |
| 6.247                | 4-Methylbenzonitrile                         | 104-85-8   | ---        | No                         | 250, 750               |
| 6.399                | Levogluosenone                               | 37112-31-5 | lyocell    | No                         | 250                    |
| 7.247                | 5-(Hydroxymethyl)-2-furfural                 | 67-47-0    | lyocell    | Yes                        | 250                    |
| 7.609                | 1,3-Benzenedicarbonitrile                    | 626-17-5   | modacrylic | Yes                        | 750                    |
| 7.765                | Heptanedinitrile                             | 646-20-8   | modacrylic | No                         | 750                    |
| 8.267                | 5-Methylisophthalonitrile                    | 39718-07-5 | ---        | No                         | 250                    |
| 8.268                | 4-Cyanobenzeneacetonitrile                   | 876-31-3   | modacrylic | No                         | 750                    |
| 8.502                | (2Z, 4Z)-3,4-Dimethyl-2,4-hexadienedinitrile | 1557-61-5  | modacrylic | No                         | 250                    |
| 9.234                | N,N-Dimethyl-1-dodecanamine                  | 112-18-5   | ---        | No                         | 250                    |
| 9.291                | Hexane-1,3,5-tricarbonitrile (trimer)        | 1572-50-5  | modacrylic | Yes                        | 250, 750               |
| 9.456                | Pentane-1,3,5-tricarbonitrile (trimer)       | 4379-04-08 | modacrylic | Yes                        | 250, 750               |

|        |                                                 |           |            |     |          |
|--------|-------------------------------------------------|-----------|------------|-----|----------|
| 10.015 | (Z)-Hex-1-ene-1,3,5-tricarbonitrile<br>(trimer) | ---       | modacrylic | No  | 250, 750 |
| 11.402 | 5-Cyano- <i>N</i> -(hex-5-enyl)pentamide        | ---       | nylon 6,6  | No  | 750      |
| 11.427 | 5-Cyano- <i>N</i> -hexylpentamide               | ---       | nylon 6,6  | Yes | 750      |
| 11.755 | <i>N</i> -Hexadecanoic acid                     | 57-10-3   | lubricant  | Yes | ---      |
| 12.733 | Octadecanoic acid                               | 57-11-4   | lyocell    | Yes | ---      |
| 13.213 | 1,8-Diazacyclotetradecane-2,7-<br>dione         | 4266-66-4 | nylon 6,6  | Yes | 250, 750 |
| 14.103 | <i>N</i> -Oleanitrile                           | 112-91-4  | lubricant  | No  | 250      |
| 15.416 | (Z)-9-Octadecenamide                            | 3322-62-1 | ---        | No  | 250      |
| 15.458 | 13-Docosenamide                                 | 112-84-5  | lubricant  | Yes | ---      |

*Compound assignment and parent fiber identification from Py-GC/MS for Fabric F for compounds with at least 1% of the total chromatogram area.*

| Retention Time (min) | Compound Assignment                   | CAS Number | Origin           | Method 1 Py-GC/MS (Yes/No) | Method 2 Py-GC/MS (°C) |
|----------------------|---------------------------------------|------------|------------------|----------------------------|------------------------|
| 2.025                | Methyl isocyanide                     | 593-75-9   | ---              | No                         | 750                    |
| 2.033                | Pyruvic aldehyde                      | 78-98-8    | lyocell          | No                         | 240, 500, 750          |
|                      | Furan                                 | 110-00-9   |                  |                            |                        |
| 2.041                | Acetonitrile                          | 75-05-8    | modacrylic       | Yes                        | 750                    |
|                      | Acetone                               | 67-64-1    |                  |                            |                        |
| 2.115                | 2-Propenenitrile                      | 107-13-1   | modacrylic       | Yes                        | 500, 750               |
| 2.276                | Propanenitrile                        | 107-12-0   | modacrylic       | No                         | 750                    |
| 2.343                | 2-Methyl-2-propenenitrile             | 126-98-7   | modacrylic       | Yes                        | 500                    |
|                      | 1-Hexanol                             |            |                  |                            |                        |
| 2.35                 | 2-Methylfuran                         | 534-22-5   | ---              | No                         | 500                    |
| 2.694                | Benzene                               | 71-43-2    | ---              | Yes                        | 750                    |
| 3.455                | Toluene                               | 108-88-3   | modacrylic       | Yes                        | 750                    |
| 3.984                | 2-Furfural                            | 98-01-1    | lyocell          | Yes                        | 240, 500               |
| 3.98                 | 2-Cyclopenten-1-one                   | 930-30-3   | ---              | No                         | 500                    |
| 4.249                | Ethylbenzene                          | 100-41-4   | modacrylic       | No                         | 750                    |
|                      | <i>o</i> -Xylene                      | 95-47-6    |                  |                            |                        |
| 4.331                | <i>m</i> -Xylene                      | 108-38-3   | modacrylic       | No                         | 750                    |
|                      | <i>p</i> -Xylene                      | 106-42-3   |                  |                            |                        |
| 4.253                | 2-Propylfuran                         | 4229-91-8  | ---              | No                         | 500                    |
| 4.526                | Styrene                               | 100-42-5   | <i>m</i> -aramid | No                         | 750                    |
| 4.656                | 1-(2-Furanyl)ethanone                 | 1192-62-7  | ---              | No                         | 500                    |
| 4.919                | 2-Chloropyridine                      | 109-09-1   | modacrylic       | Yes                        | 240                    |
| 5.268                | Aniline                               | 62-53-3    | <i>m</i> -aramid | No                         | 750                    |
| 5.386                | Benzonitrile                          | 100-47-0   | modacrylic       | Yes                        | 750                    |
| 5.814                | (1-Methylethylidene)-propanedinitrile | 13166-10-4 | ---              | No                         | 500                    |
| 5.905                | Pentanedinitrile                      | 544-13-8   | modacrylic       | No                         | 500, 750               |
|                      | 2-Methylene pentanedinitrile          | 1572-52-7  |                  |                            |                        |
| 5.939                | 2-Methylenepentanedinitrile           | 1572-52-7  | modacrylic       | Yes                        | 500                    |
| 6.247                | 2-Methylbenzonitrile                  | 529-19-1   | modacrylic       | No                         | 500, 750               |
| 6.422                | Levogluosenone                        | 37112-31-5 | lyocell          | Yes                        | 240                    |
| 6.577                | 4-Chlorobenzonitrile                  | 623-03-0   | ---              | No                         | 240                    |
| 6.819                | Benzoic acid                          | 65-85-0    | <i>m</i> -aramid | Yes                        | ---                    |

|        |                                                         |            |                  |     |          |
|--------|---------------------------------------------------------|------------|------------------|-----|----------|
| 7.08   | 2,5-Dimethylbenzonitrile                                | 13730-09-1 | modacrylic       | No  | 750      |
| 7.227  | 3,6-Dianhydro- $\alpha$ -glucopyranose                  | 4451-30-3  | lyocell          | Yes | 240, 500 |
| 7.606  | 1,3-Benzenedicarbonitrile                               | 626-17-5   | modacrylic       | Yes | 240, 750 |
| 7.791  | 1,3-Benzenediamine                                      | 108-45-2   | <i>m</i> -aramid | No  | 750      |
| 8.216  | 2-Chloronaphthalene                                     | 91-58-7    | modacrylic       | No  | 240      |
| 8.267  | 4-Cyanobenzeneacetonitrile                              | 876-31-3   | modacrylic       | No  | 500      |
| 8.268  | 5-Methylisophthalonitrile                               | 39718-07-5 | ---              | No  | 750      |
| 8.463  | Biphenyl                                                | 92-52-4    | <i>m</i> -aramid | No  | 750      |
| 8.502  | (2Z, 4Z)-3,4-Dimethyl-2.4-hexadienedinitrile            | 1557-61-5  | modacrylic       | No  | 240, 500 |
| 9.07   | Benzene-1,2,4-tricarbonitrile                           | 10347-14-5 | modacrylic       | No  | 240, 500 |
| 9.294  | Hexane-1,3,5-tricarbonitrile (trimer)                   | 1572-50-5  | modacrylic       | Yes | 240, 500 |
| 9.408  | Pentane-1,3,5-tricarbonitrile (trimer)                  | 4379-04-08 | modacrylic       | No  | 500      |
| 10.002 | (Z)-Hex-1-ene-1,3,5-tricarbonitrile (trimer)            | ---        | modacrylic       | No  | 500      |
| 10.83  | Tricyclo[3.3.1.0(2,8)]nona-3,6-diene-2,6-dicarbonitrile | ---        | modacrylic       | No  | 240      |
| 11.552 | <i>N</i> -(3-Aminophenyl)benzamide                      | 16091-26-2 | <i>m</i> -aramid | No  | 750      |
| 11.71  | Dibutyl phthalate                                       | 84-74-2    | ---              | No  | 240      |
| 11.855 | <i>N</i> -Phenylbenzamide                               | 93-98-1    | <i>m</i> -aramid | Yes | ---      |
| 11.897 | <i>N</i> -Hexadecanoic acid                             | 57-10-3    | lubricant        | Yes | ---      |
| 12.564 | Bis(2-ethylhexyl) maleate                               | 142-16-5   | ---              | No  | 240      |
| 12.95  | Octadecanoic acid                                       | 57-11-4    | lyocell          | Yes | ---      |
| 14.099 | Oleanitrile                                             | 112-91-4   | <i>m</i> -aramid | No  | 240      |
| 14.259 | 1,2-Benzenedicarboxylic acid, diisooctyl ester          | 27554-26-3 | ---              | No  | 240      |
| 15.463 | 13-Docosenamide                                         | 112-84-5   | lubricant        | Yes | ---      |
| 15.632 | Squalene                                                | 111-02-4   | lubricant        | Yes | ---      |

*Compound assignment and parent fiber identification from Py-GC/MS for Fabric G for compounds with at least 1% of the total chromatogram area.*

| Retention Time (min) | Compound Assignment                    | CAS Number | Origin           | Method 1 Py-GC/MS (Yes/No) | Method 2 Py-GC/MS (°C) |
|----------------------|----------------------------------------|------------|------------------|----------------------------|------------------------|
| 2.02                 | Pyruvic aldehyde                       | 78-98-8    | lyocell          | No                         | 240, 500, 750          |
| 2.042                | Acetonitrile                           | 75-05-8    | modacrylic       | Yes                        | 500, 750               |
| 2.114                | 2-Propenenitrile                       | 107-13-1   | modacrylic       | Yes                        | 500                    |
| 2.272                | Propanenitrile                         | 107-12-0   | modacrylic       | No                         | 500, 750               |
| 2.275                | 1-Hexanol                              | 111-27-3   | ---              | Yes                        | ---                    |
| 2.35                 | 2-Methyl-2-propenenitrile              | 126-98-7   | modacrylic       | Yes                        | 500                    |
| 2.693                | Benzene                                | 71-43-2    | ---              | Yes                        | 750                    |
| 3.454                | Toluene                                | 108-88-3   | modacrylic       | Yes                        | 750                    |
| 3.682                | Carbocyanidic acid, methyl ester       | 17640-15-2 | ---              | Yes                        | ---                    |
| 3.985                | 2-Furfural                             | 98-01-1    | lyocell          | Yes                        | 240, 500               |
| 4.251                | Ethylbenzene                           | 100-41-4   | modacrylic       | No                         | 750                    |
|                      | <i>o</i> -xylene                       | 95-47-6    |                  |                            |                        |
| 4.255                | 2-Propylfuran                          | 4229-91-8  | ---              | No                         | 500                    |
| 4.526                | Styrene                                | 100-42-5   | <i>m</i> -aramid | No                         | 750                    |
| 4.652                | 1-(2-Furanyl)ethanone                  | 1192-62-7  | ---              | No                         | 240, 500               |
| 4.92                 | 2-Chloropyridine                       | 109-09-1   | modacrylic       | Yes                        | 240                    |
| 5.268                | Aniline                                | 62-53-3    | <i>m</i> -aramid | No                         | 750                    |
| 5.369                | Benzonitrile                           | 100-47-0   | modacrylic       | Yes                        | 750                    |
| 5.809                | (1-Methylethylidene)-propanedinitrile  | 13166-10-4 | ---              | No                         | 500                    |
| 5.901                | 2-Methylene pentanedinitrile           | 1572-52-7  | modacrylic       | No                         | 500                    |
| 5.941                | Pentanedinitrile                       | 544-13-8   | modacrylic       | Yes                        | 500, 750               |
| 6.507                | 2-Methylpentanedinitrile               | 4553-62-2  | modacrylic       | No                         | 500, 750               |
| 6.269                | 2-Methylbenzonitrile                   | 529-19-1   | modacrylic       | Yes                        | 500, 750               |
| 6.39                 | Levogluosenone                         | 37112-31-5 | lyocell          | No                         | 240                    |
| 6.572                | 4-Chlorobenzonitrile                   | 623-03-0   | ---              | No                         | 240                    |
| 6.783                | Benzoic acid                           | 65-85-0    | <i>m</i> -aramid | Yes                        | ---                    |
| 7.197                | 3,6-Dianhydro- $\alpha$ -glucopyranose | 4451-30-3  | lyocell          | No                         | 240, 500               |
| 7.607                | 1,3-Benzenedicarbonitrile              | 626-17-5   | modacrylic       | Yes                        | 240, 500, 750          |
| 7.794                | 1,3-Benzenediamine                     | 108-45-2   | <i>m</i> -aramid | No                         | 750                    |
| 8.211                | 2-Chloronaphthalene                    | 91-58-7    | modacrylic       | No                         | 240                    |
| 8.268                | 2-(3-Cyanophenyl)-acetonitrile         | 16532-78-8 | ---              | No                         | 500, 750               |

|        |                                                         |            |                  |     |          |
|--------|---------------------------------------------------------|------------|------------------|-----|----------|
| 8.273  | <i>m</i> -Amino-benzonitrile                            | 2237-30-1  | <i>m</i> -aramid | No  | 750      |
| 8.441  | 1-Chloro-4-ethenylbenzene                               | 1073-67-2  | ---              | No  | 240      |
| 8.482  | Biphenyl                                                | 92-52-4    | <i>m</i> -aramid | No  | 750      |
| 8.497  | (2Z, 4Z)-3,4-Dimethyl-2,4-hexadienedinitrile            | 1557-61-5  | modacrylic       | No  | 240, 500 |
| 9.065  | Benzene-1,2,4-tricarbonitrile                           | 10347-14-5 | modacrylic       | No  | 240, 500 |
| 9.287  | Hexane-1,3,5-tricarbonitrile (trimer)                   | 1572-50-5  | modacrylic       | Yes | 240, 500 |
| 9.408  | Pentane-1,3,5-tricarbonitrile (trimer)                  | 4379-04-08 | modacrylic       | No  | 500      |
| 9.445  | 1,2,3-Trimethyl-1H-indole                               | 1971-46-6  | ---              | Yes | 240      |
| 10.629 | [1,1'-Biphenyl]-4-amine                                 | 92-67-1    | <i>m</i> -aramid | No  | 750      |
| 10.825 | Tricyclo[3.3.1.0(2,8)]nona-3,6-diene-2,6-dicarbonitrile |            | modacrylic       | No  | 240      |
| 11.22  | 1,2-Benzenedicarboxylic acid, bis(2-methylpropyl) ester | 84-69-5    | ---              | No  | 240      |
| 11.705 | Dibutyl phthalate                                       | 84-74-2    | ---              | No  | 240      |
| 11.704 | Oct-7-ene-1,3,5,7-tetracarbonitrile (tetramer)          | 64918-32-7 | modacrylic       | No  | 500      |
| 11.82  | <i>N</i> -Phenylbenzamide                               | 93-98-1    | <i>m</i> -aramid | Yes | 750      |
| 11.844 | <i>N</i> -Hexadecanoic acid                             | 57-10-3    | lubricant        | Yes | ---      |
| 12.525 | Diisooctyl maleate                                      | 1330-76-3  | ---              | No  | 240      |
| 12.831 | Octadecanoic acid                                       | 57-11-4    | lyocell          | Yes | ---      |
| 13.551 | <i>N</i> -(3-aminophenyl)benzamide                      | 16091-26-2 | <i>m</i> -aramid | No  | 750      |
| 15.458 | 13-docosenamide                                         | 112-84-5   | lubricant        | Yes | ---      |

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