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

WP19-1040

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US Army – CCDC Soldier Center

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14. ABSTRACT
The objectives of this work were:
-Use a combination of pyrolysis – gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetric analysis (TGA) to develop a methodology to identify the hazardous pyrolysis/combustion products from FR fabrics and textiles.
-Use this method to establish a scoring system to assess the health and environmental impact of current FR materials used in Army clothing.

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Project Team

- Timothy Lawton, Ph.D. (PI) – Research chemist, CCDC Soldier Center
- Michael McPartlin – Research chemist, CCDC Soldier Center
- Brandon Italiano – Research chemist, CCDC Soldier Center
- Sarah Pilkenton, Ph.D. – Associate Professor, Dept. of Chemistry and Food Science, Framingham State University

Background

- The project was initiated in FY19

- The original Statement of Need (SoN) this project addressed was WPSON-19-C5: “To investigate multifunctional fibers, textiles and/or impregnated fabrics that utilize formulations with environmentally friendly insect repellants, insecticides and/or flame retardants (FR)”. Specifically our work sought “to advance the scientific understanding of such environmental and health risks [of FR treatments to military textiles]”.

Technical Objectives

- The objectives of this work were:
    - ♦ Use a combination of pyrolysis – gas chromatography/mass spectrometry (Py-GC/MS) and thermogravimetric analysis (TGA) to develop a methodology to identify the hazardous pyrolysis/combustion products from FR fabrics and textiles
    - ♦ Use this method to establish a scoring system to assess the health and environmental impact of current FR materials used in Army clothing

Technical Approach

Maintenance/Training on the Py-GC/MS → Obtain military textile/fiber samples → Determine elemental composition with EDS →

Assign pyrolysis compounds to fibers – Method 1 → Assign pyrolysis compounds to textiles – Method 1 → Develop Rating Score 1.0

Combustion in air or Score 2.0?

Determine % weight loss of each material with isothermal TGA → Identify temperatures of mass loss events

Include HCl, etc in compounds detected?

Sequential temperature runs in Py-GC/MS from TGA temperatures →

→ Develop Rating Score 2.0

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Technical Approach

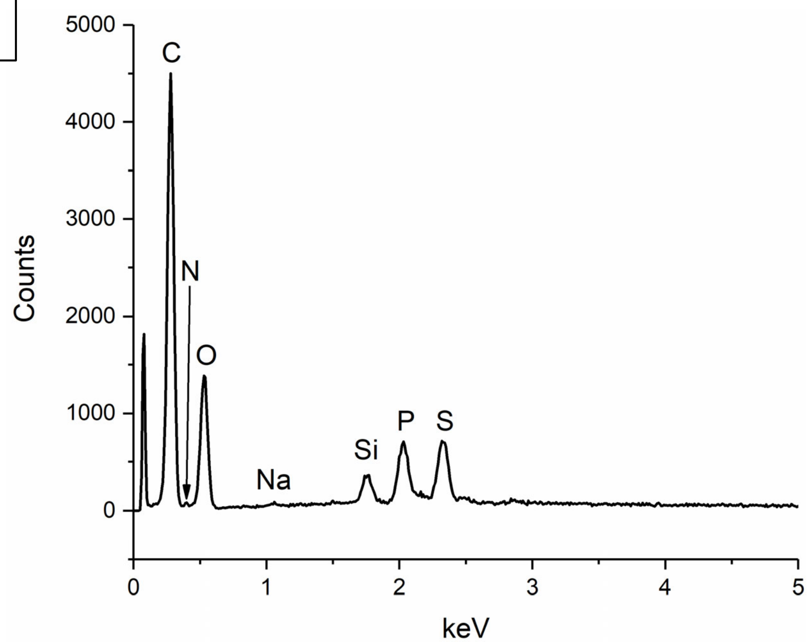
Blended Fabrics	Components
A	1
B	2
C	3
D	4
E	5
F	6
G	7

	Component 1	Component 2	Component 3	Component 4	Component 5	Component 6	Component 7
Fabric A	X	X					
Fabric B	X		X	X			
Fabric C					X		
Fabric D	X					X	X
Fabric E	X					X	X
Fabric F					X	X	X
Fabric G					X	X	X

- Due to the proprietary nature of the textiles investigated we are not disclosing what company they came from
  - They are currently fielded military textiles (blended fabrics A - G)
- Company could not provide us with exact composition but did indicate what fibers (1-7) make up each blended fabric. This aided in identifying compounds from the blended fabrics

Results – Energy Dispersive Spectroscopy (EDS)

A



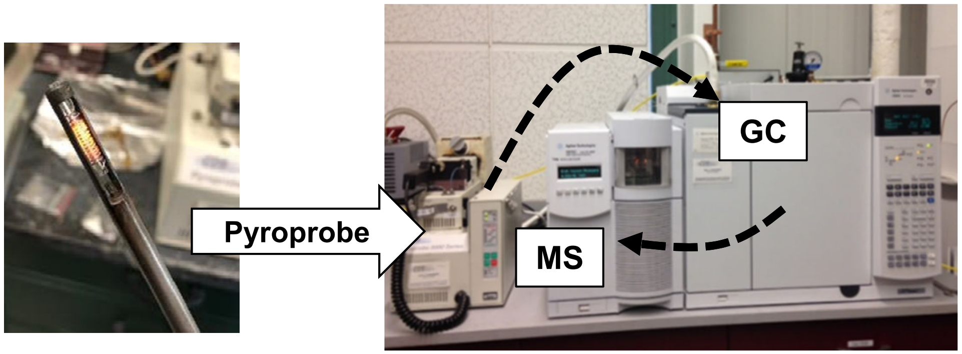
B

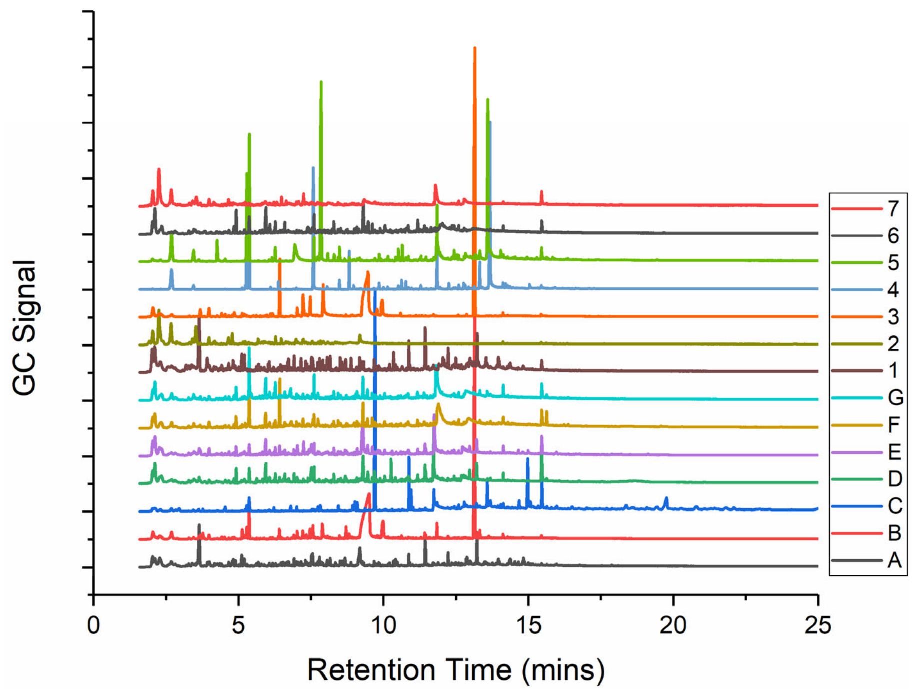
Elements

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
1	X	X	X						
2	X		X						
3	X		X			X	X		
4	X	X	X	X			X		
5	X	X	X						
6	X	X	X		X	X		X	
7	X		X						

- A) Representative EDS spectra from material B.
- B) Summary of EDS results indicating what elements are present for each material
- These results let us to know what elements were present in the materials so we could exclude possible matches if the match contained an element not present

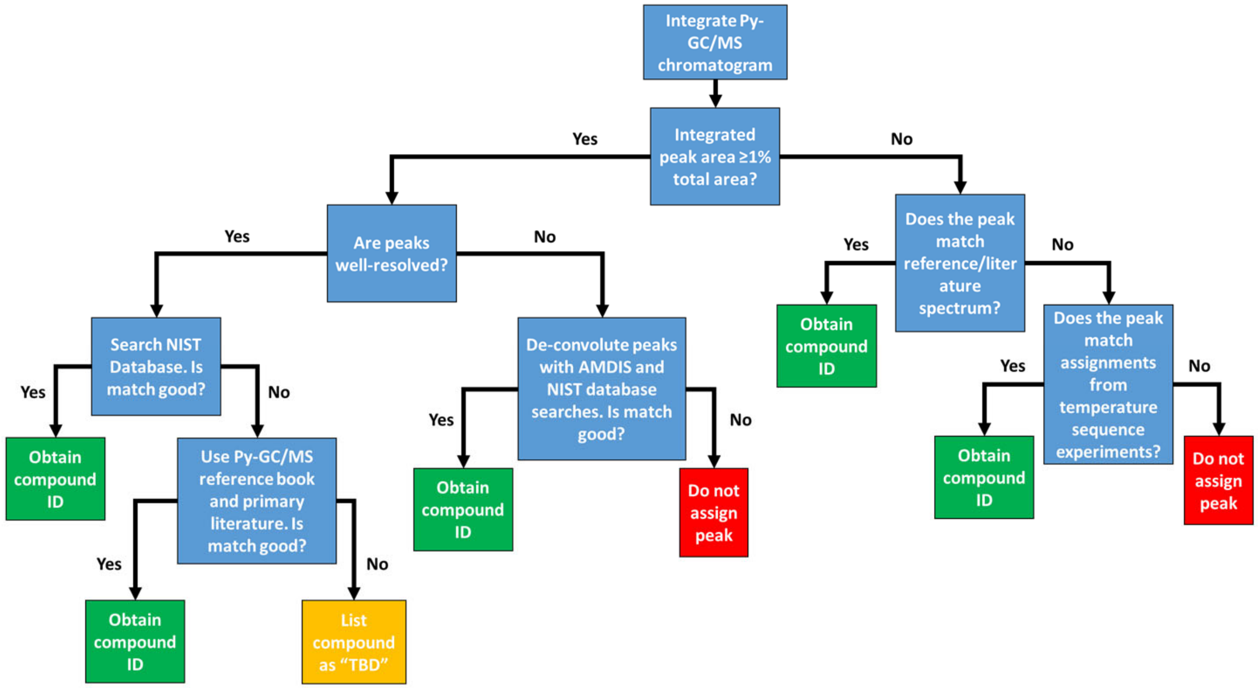
Results – Py-GC/MS – Method 1





- Pyrolysis occurs in the pryoprobe – released compounds collected in a trap transferred to the GC where they're separated and then identified in the MS.
- Representative Py-GC/MS chromatogram for all materials investigated in this study

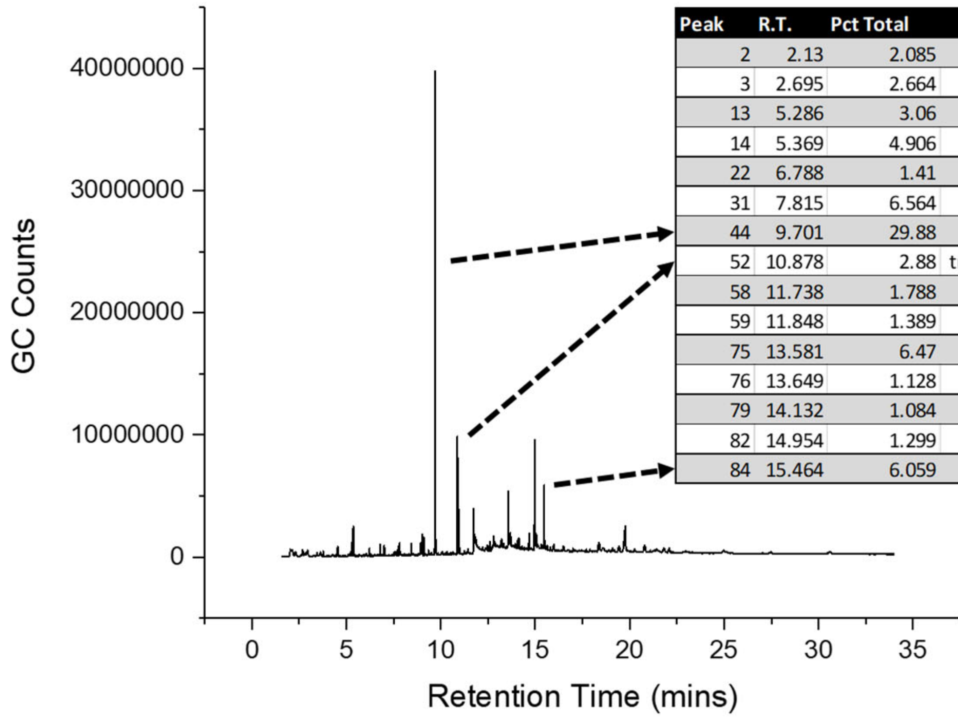
Results – Compound Assignment



- Decision tree used to assign a peak to a specific compound
- 1% total chromatogram cut-off
- Used peak deconvolution when needed for overlapping peaks
- NIST08 database and Py-GC/MS data book* for reference spectra

*Tsuge, S.; Ohtani, H.; Watanabe, C., *Pyrolysis-GC/MS Data Book of Synthetic Polymers*. First ed.; Elsevier: 2011.

Results – Compound Assignment



Peak	R.T.	Pct Total	Assignment 1	Assignment 2
2	2.13	2.085	allyl chloride	and isomers
3	2.695	2.664	benzene	
13	5.286	3.06	aniline	
14	5.369	4.906	benzonitrile	
22	6.788	1.41	benzoic acid	
31	7.815	6.564	1,3-benzenediamine	and isomers
44	9.701	29.88	N-cyclohexyl-2-pyrrolidone	
52	10.878	2.88	tris-(1-chloro-2-propyl) phosphate	
58	11.738	1.788	n-hexadecanoic acid	dibutyl phthalate
59	11.848	1.389	N-phenyl-benzamide	
75	13.581	6.47	N-(3-aminophenyl)-benzamide	
76	13.649	1.128	N-(4-aminophenyl)-benzamide	
79	14.132	1.084	Oleanitrile	
82	14.954	1.299	TBD	
84	15.464	6.059	13-docosenamide	

- Representative GC/MS chromatogram from material C with compound assignments in the inset. Example peak assignments are shown with the arrows.
- Similar assignment carried out for all 14 materials; blended fabrics and fibers
- Some peaks were combination of >1 compounds
- Can't resolve between stereoisomers, *cis* vs. *trans*, *meta* vs. *ortho* vs. *para*

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Results – Material Rating Score 1.0

$$(1)\ Compound_i^* = \frac{Compound_i\ peak\ area}{Total\ integrated\ area} \times Modified\ GHS\ score\ (0-5)$$

$$(2)\ MRS = \sum_{n=1}^{i} Compound_1^* + Compound_2^* + \cdots + Compound_i^*$$

- Equation 1 – relative area of total chromatogram multiplied by modified GHS score for each identified compound
  - GHS scores based on acute inhalation toxicity (H330 – H333)
  - GHS scores – low = high toxicity, our modified score is high = high toxicity
  - Any compound without a GHS score H330-H333 was scored 0

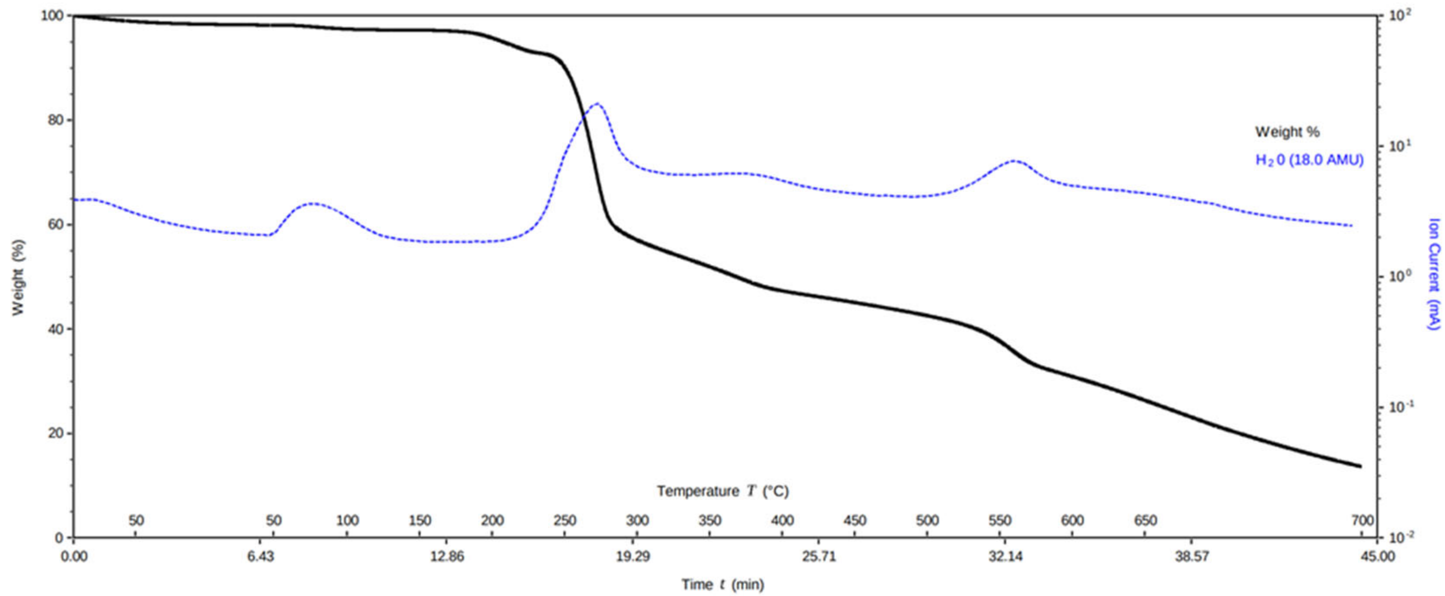
- Equation 2 – sum all weighted scores of all compounds in a material to get the Material Rating Score 1.0

Results – Material Rating Score 1.0

Material	MRS 1.0
C	**108.0**
5	**75.4**
4	**61.5**
6	**38.3**
G	**31.9**
E	**29.3**
D	**29.0**
F	**23.1**
1	**11.8**
A	**10.8**
7	**6.3**
B	**6.3**
3	**4.6**
2	**2.1**

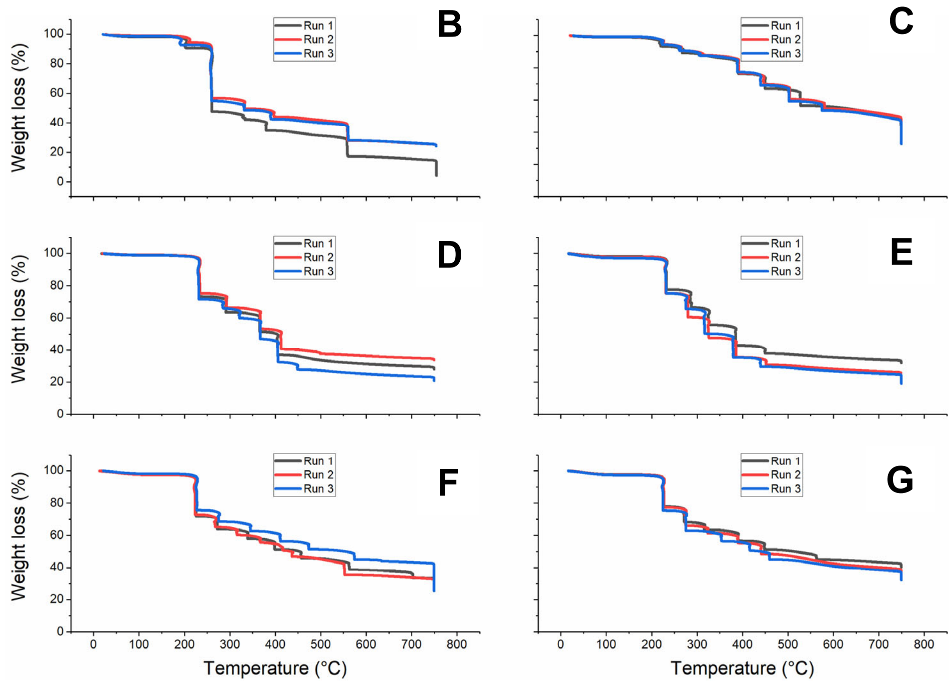
- MRS 1.0 scores organized to the left
  - Higher numbers indicated more toxic compounds off-gassed.
  - The overall number is less important than the trend in the material
- Material C released most toxic pyrolysis products. Material 2 released the least
- Developing this score we learned:
  - It was not possible to identify small molecules, such as hydrogen chloride (HCl)
  - 1.0 scores based on relative ratios in GC chromatogram rather than an amount. Ignores char left behind in the quartz tube
  - A material with a higher fraction assigned would have a higher score than a material with a smaller fraction assigned
  - Many compounds do not have a GHS score for acute inhalation toxicity and were scored 0.

Results – Incorporating TGA



- 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 amu 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.
- Unfortunately TGA-MS throughput was too slow so TGA data was collected internally at CCDC Soldier Center

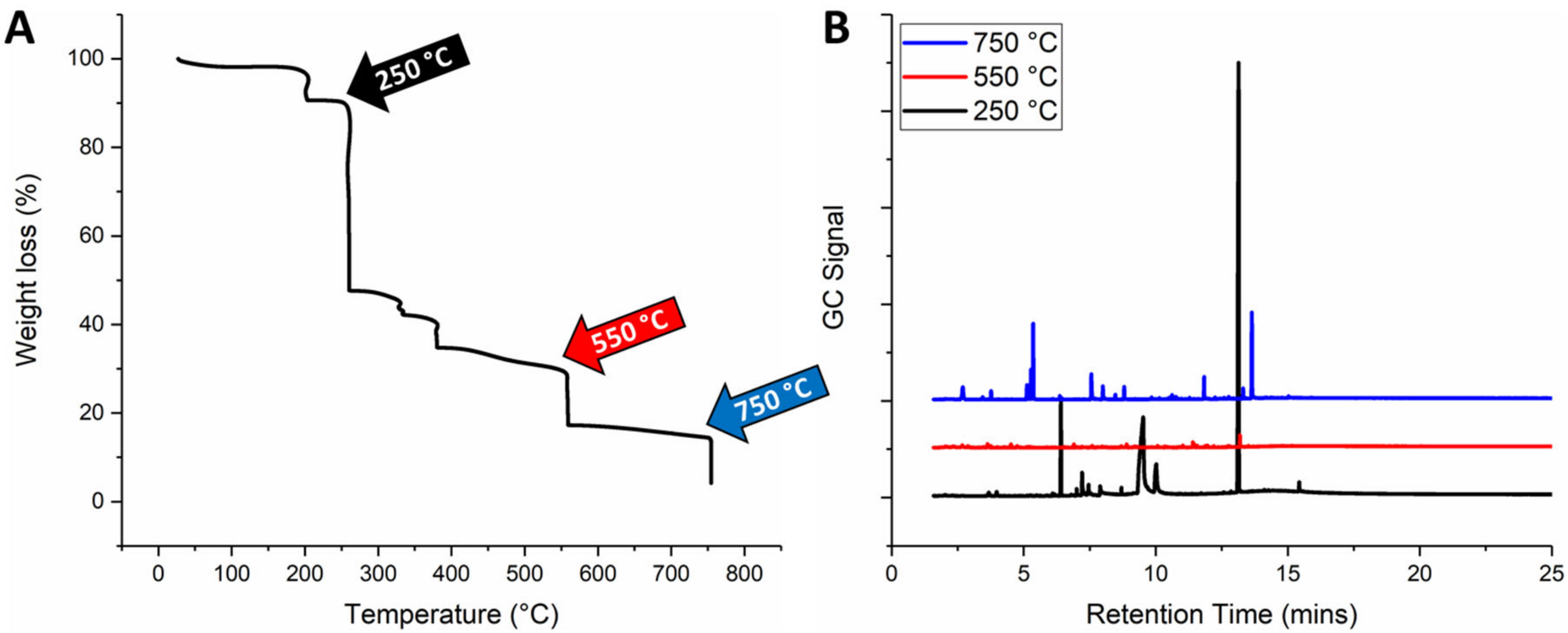
Results – Isothermal TGA



Material	Mass Loss Event 1	Mass Loss Event 2	Mass Loss Event 3	Mass Loss Event 4
B	250 °C 8%	550 °C 56%	750 °C 15%	-
C	230 °C 6%	280 °C 4%	400 °C 13%	750 °C 30%
D	250 °C 27%	375 °C 23%	750 °c 22%	-
E	250 °C 24%	375 °C 26%	750 °C 23%	-
F	240 °C 27%	500 °C 26%	750 °C 12%	-
G	240 °C 23%	500 °C 29%	750 °C 9%	-

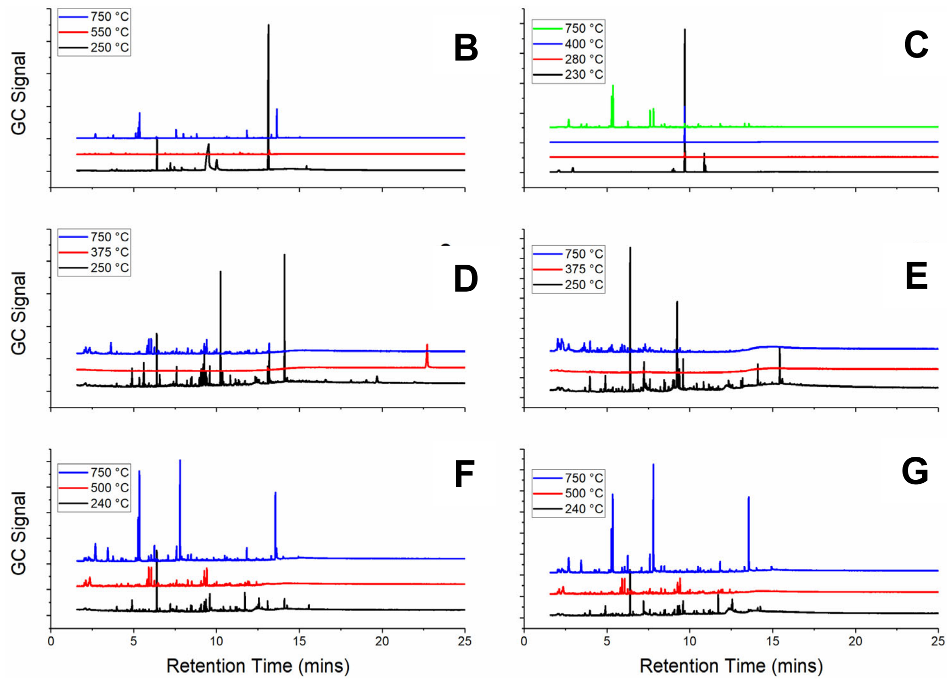
- Had to trim down the number of samples to acquire data in the remaining time
- Instead of linear temperature ramp, isothermal mode entered when 6% weight loss/min detected. Returned to linear heating when 0.05% weight loss/min detected
- Temperatures identified for mass loss events and average % loss at each temperature

Results – Isothermal TGA + Py-GC/MS



- A) Representative isothermal TGA of material B with mass loss events indicated with colored arrows.
- B) Corresponding Py-GC/MS of material B. Temperatures were visited sequentially in a single run.
- Each temperature plot is vertically offset in B for clarity. The colored plots in B were taken at the same temperature as the mass loss events indicated by the same color in A.

Results – Py-GC/MS



Temperature (°C)	Retention Time (mins)	Compound Assignment	CAS	Modified GHS Score
250	6.41	Levoglucosenone	37112-31-5	0
	7.22	1,4:3,6-Dianhydro-α-d-glucopyranose	4451-30-3	0
	9.49	Levoglucosan	498-07-7	0
	9.97	1,6-Anhydro-β-d-gluofuranose	-	0
	13.15	1,3,2-Dioxaphosphorinane, 2,2'-oxybis[5,5-dimethyl-,2,2'-disulfide	4090-51-1	0
550	2.05	Pyruvic aldehyde	78-98-8	0
	2.68	1-Butanol	71-36-3	2
	2.88	2-Propenoic acid, ethyl ester	140-88-5	2
	3.69	Cyclopentanone	120-92-3	0
	4.52	2-Propenoic acid, butyl ester	141-32-2	2
	6.90	Hexanedinitrile	111-69-3	2
	7.22	1,4:3,6-Dianhydro-α-d-glucopyranose	4451-30-3	0
	11.03	Triethyl hex-5-ene-1,3,5-tricarboxylate (trimer)	10080-58-7	0
	13.21	1,8-diazacyclotetradecane-2,7-dione	4266-66-4	0
750	2.69	Benzene	71-43-2	0
	3.45	Toluene	108-88-3	0
	5.12	Isocyanatobenzene	103-71-9	5
	5.29	Aniline	62-53-3	3
	5.37	Benzonitrile	100-47-0	2
	7.57	1,4-Benzenedicarbonitrile	623-26-7	2
	8.47	Biphenyl	92-52-4	0
	8.81	4-Aminobenzonitrile	873-74-5	0
	10.62	*p*-Phenylbenzonitrile	2920-38-9	2
	11.84	N-Phenylbenzamide	93-98-1	0
	13.31	4-Cyano-N-phenyl- Benzamide	17922-96-2	0
	13.64	4'-Aminobenzanilide	17625-83-1	0

- Left. Representative Py-GC/MS chromatograms collected for each material at each temperature identified in Slide 14
- The material that each chromatogram was collected from is indicated by the letter in the top right of each panel.
- For a given material the chromatograms collected at different temperatures are vertically offset for clarity.
- Right. Example of assignment list for Material B on the left

Results – MRS 2.0

$$(1)\ Compound_i^* = \%\ Mass\ Loss_{Temp\ i}\ (\mathrm{TGA}) \times \%\ Peak\ Area\ (GC)_{Temp\ i} \times Modified\ GHS\ score\ (0-5)$$

$$(2)\ MRS\ 2.0 = \sum_{n=1}^{i} Compound_1^* + Compound_2^* + \cdots + Compound_i^*$$

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

- % Mass loss for each temperature from the TGA
- Each % Mass loss was multiplied by the % Peak Area from the GC chromatogram
- The absolute numbers in 1.0 vs. 2.0 are less relevant than the trends in each system.

- Trends in 1.0 and 2.0 are very similar
- In both systems Material C has the highest score (most toxic) and Material B has the lowest score (least toxic).

- With MRS 2.0 we identified new compounds not previously identified in MRS 1.0
- Still not possible to determine affect of smaller molecules like HCl

Next Steps

- This 1 year SEED effort is complete but there are additional items we identified that are worth pursuing with possible follow-on effort

Technology Transfer

- Presentation at the 2019 SERDP/ESTCP Symposium
  - In-person discussions with other DoD and EPA researchers
- Planning to submit a manuscript for publication in a peer-reviewed journal

Key Points

- Developed a method to identify compounds emitted from pyrolyzed samples
- Coupled TGA data with Py-GC/MS to better quantitate the amount of each compound being emitted
- Assigned a hazard score for each compound to provide each fabric with a hazard score
- Identified the universality of our methodology which could be applied to other problem areas

Future Research

- Based on the universality of our methodology we see it being applied beyond environmental/health concerns with FR textiles
- Specifically, follow-on research would be aimed at evaluating materials commonly discarded into burn pits in forward operating bases.
- Combustion in more field-like atmospheres would be conducted
- Scope – 2 years
- Cost estimate – $300k / year

https://www.militarytimes.com/

Future Research

- The methodology we developed here could also be extended to understanding compounds emitted from remediation of sorbent material for per- and polyfluoroalkyl substances
  - ♦ SERDP SoN ERSON-21-C1
- Scope – 3 years
- Estimated cost - $300k / year

https://pfascentral.org/

BACKUP SLIDES

Publications

- Current manuscript in preparation for submission to a peer-reviewed journal

Supporting Material

- Provide any appropriate supporting material that could not be included in the brief, if necessary

Project Funding

	FY19	FYxx	FYxx
Funds received to date ($K)	$175k		
% Expended	100		
Funds Remaining ($K)	$0k		

Status of Funds for Federal Performers

- Report on the status of funds for each MIPR received by a directly funded Federal performer. Provide information on each fiscal year for which there has not been 100% expenditure of funds.

FY2014 Funds			
Directly Funded Federal Performer(s)	**Funds Received**	**Funds Obligated***	**Percent Funding Obligated**
Federal Performer A - Direct Cite MIPR			
Federal Performer A - Reimbursable MIPR			
Federal Performer B - Direct Cite MIPR			
Federal Performer B - Reimbursable MIPR			

* Funds put on contracts and/or purchase orders that have been issued, and funds associated with internal labor or travel expenses that have been incurred.

WP19-1040: New Methodology to Assess Health & Environmental Impact of Flame Resistant Textiles

Performers: Timothy Lawton, Ph.D., Michael McPartlin, Brandon Italiano, Sarah Pilkenton, Ph.D.

Technology Focus

- *Develop a methodology that assigns a toxicity score to currently-fielded flame resistant (FR) textiles.*

Research Objectives

- *Use a combination of analytical techniques to identify compounds emitted from FR textiles when pyrolyzed. Designate a toxicity score for each compound based on the Globally Harmonized System.*

Project Progress and Results

- *Successfully identified compounds emitted from pyrolyzed samples of currently-fielded FR textiles.*
- *Calculated 2 iterations of a Material Rating Score assigning each textile a toxicity score.*

Technology Transition

- *Incorporate additional techniques to identify small molecules*
- *We have regular discussions with textile manufacturers about the results from this work.*