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

WP19-1040

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US Army – CCDC Soldier Center

27 March 2020

SERDP
DOD ▪ EPA ▪ DOE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
03/27/2020	SERDP Project Out Brief	

4. TITLE AND SUBTITLE
New Methodology to Assess Health and Environmental Impact of Flame Resistant (FR) Textiles

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Timothy Lawton

5d. PROJECT NUMBER
WP19-1040

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
US Army Natick Soldier Research Development and Engineering Center (NSRDEC)
10 General Greene Ave, CCDC-SC
Natick, MA 01760

8. PERFORMING ORGANIZATION REPORT NUMBER
WP19-1040

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Strategic Environmental Research and Development Program
4800 Mark Center Drive, Suite 17D03
Alexandria, VA 22350-3605

10. SPONSOR/MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
WP19-1040

12. DISTRIBUTION/AVAILABILITY STATEMENT
DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.

13. SUPPLEMENTARY NOTES

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.

15. SUBJECT TERMS
Methodology, Health and Environmental Impact of Flame Resistant (FR) Textiles

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Timothy Lawton
					19b. TELEPHONE NUMBER *(Include area code)*
UNCLASS	UNCLASS	UNCLASS	UNCLASS	29	508-233-6056

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

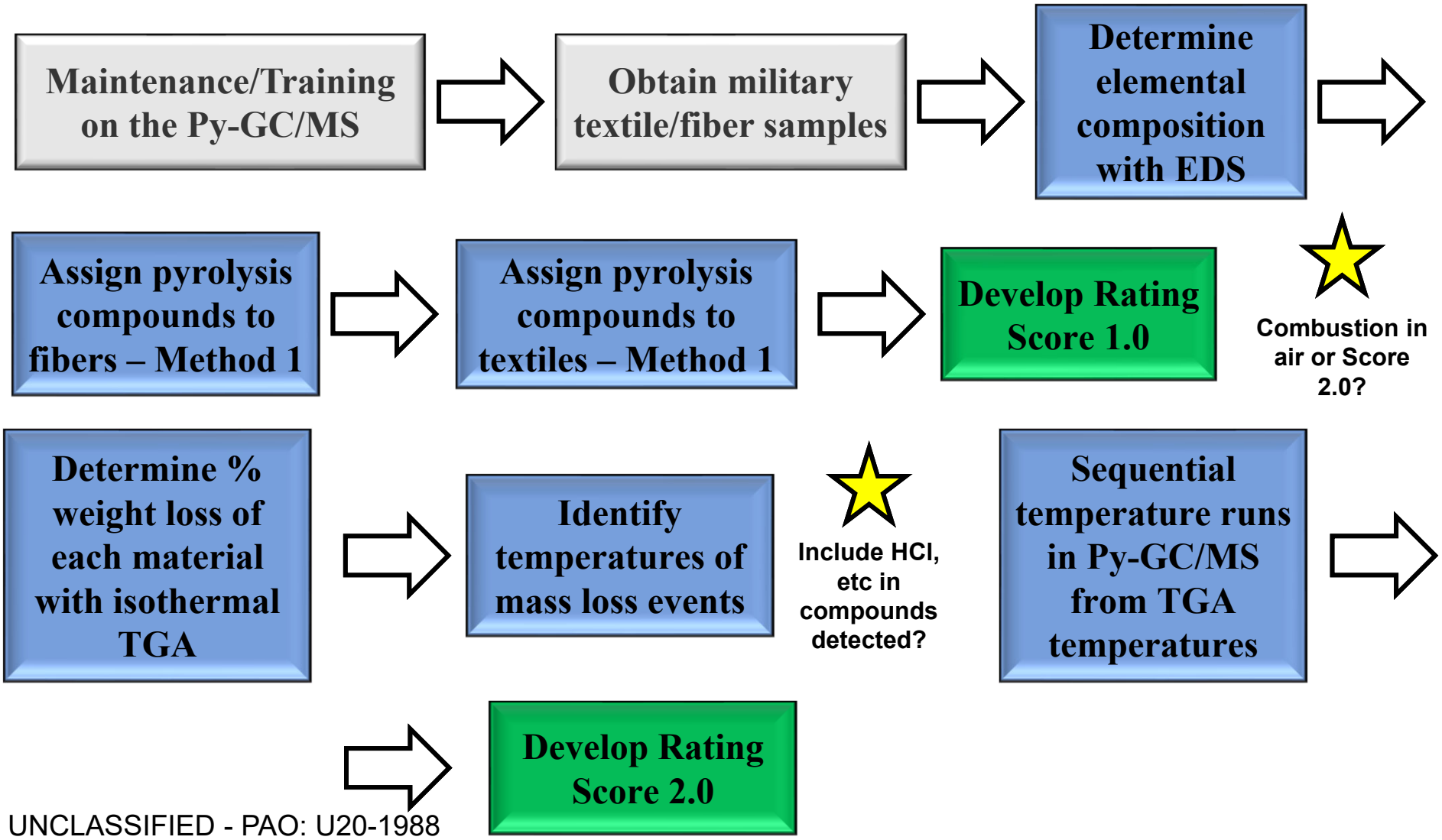
- The project was initiated in FY19

- 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



Technical Approach

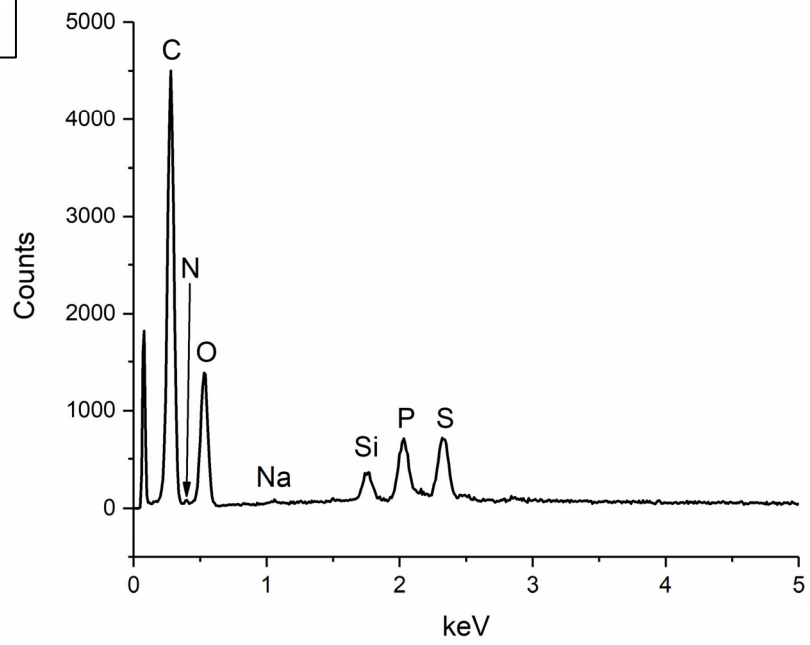
Blended Fabrics	Components
A	1
B	2
C	3
D	4
E	5
F	6
G	7

	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



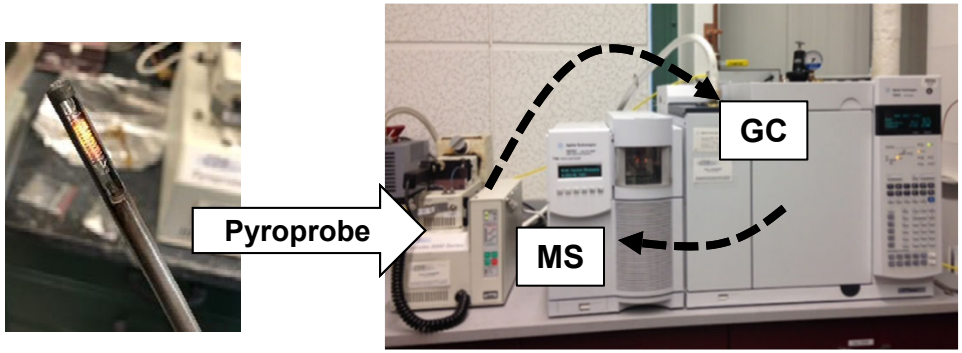
B

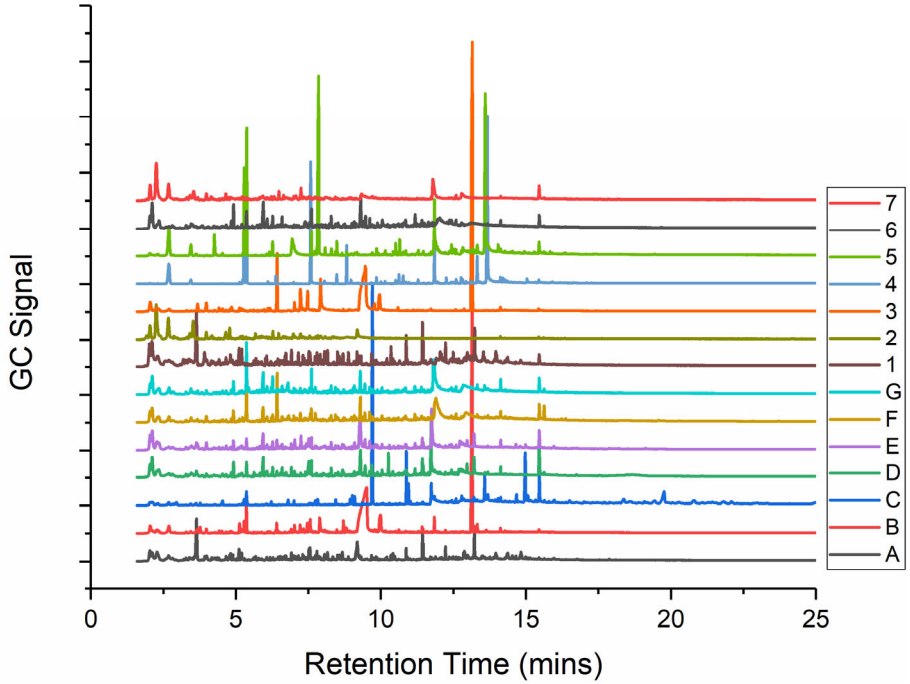
Elements

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

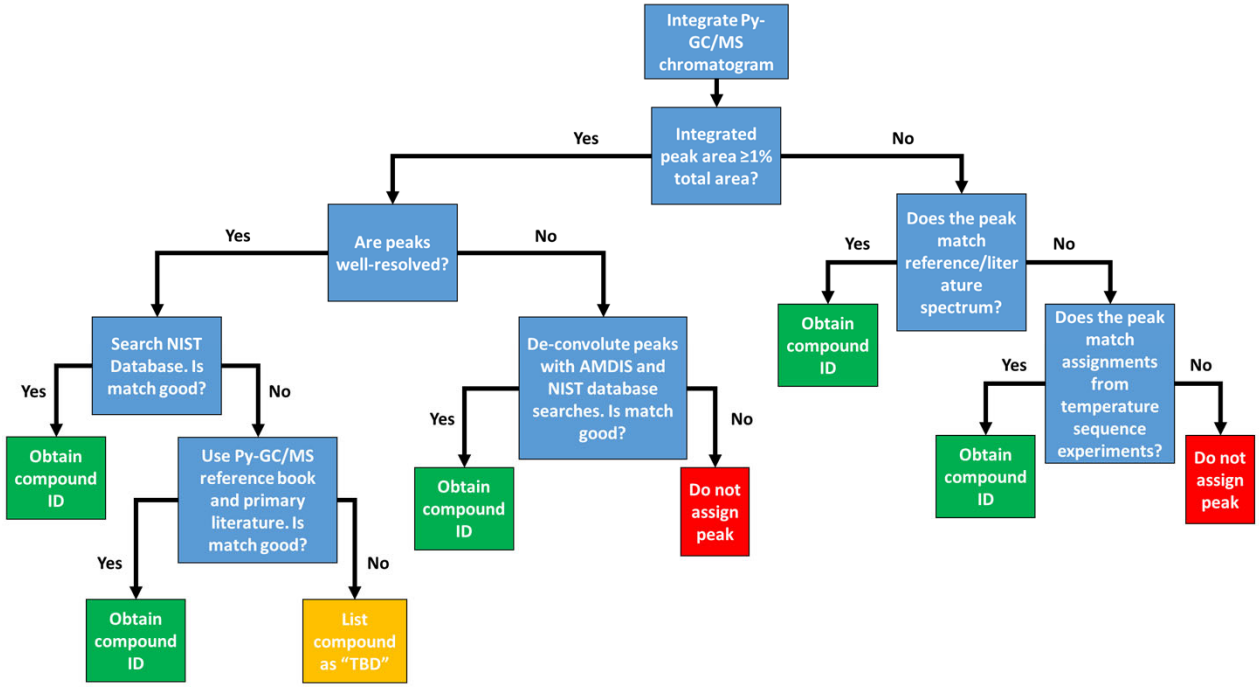
Results – Py-GC/MS – Method 1





- 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

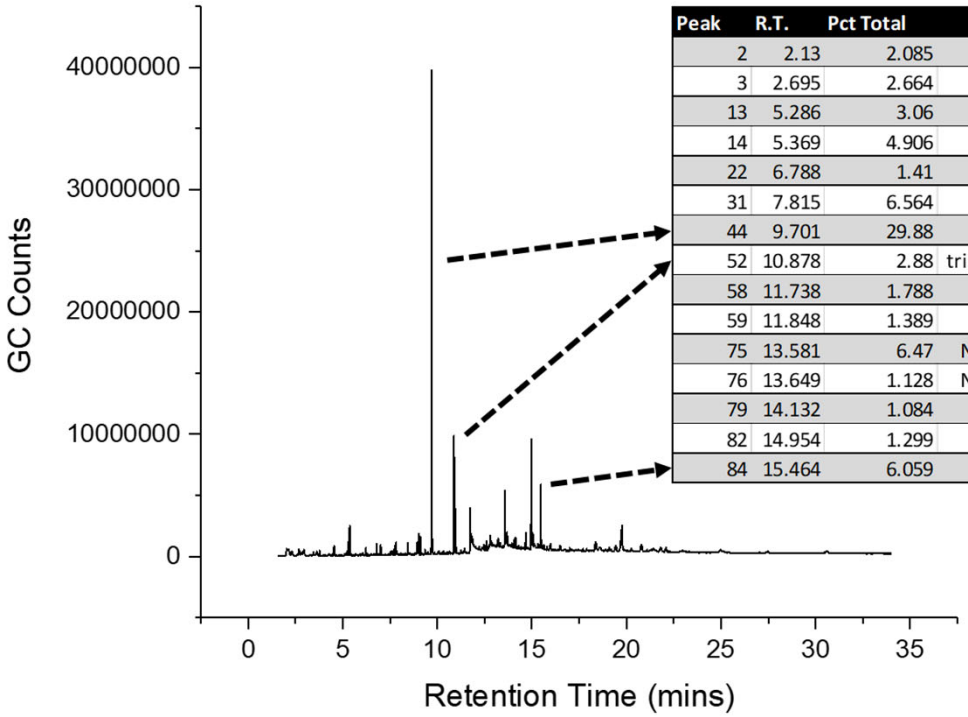
Results – Compound Assignment



- 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*

Results – Material Rating Score 1.0

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

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

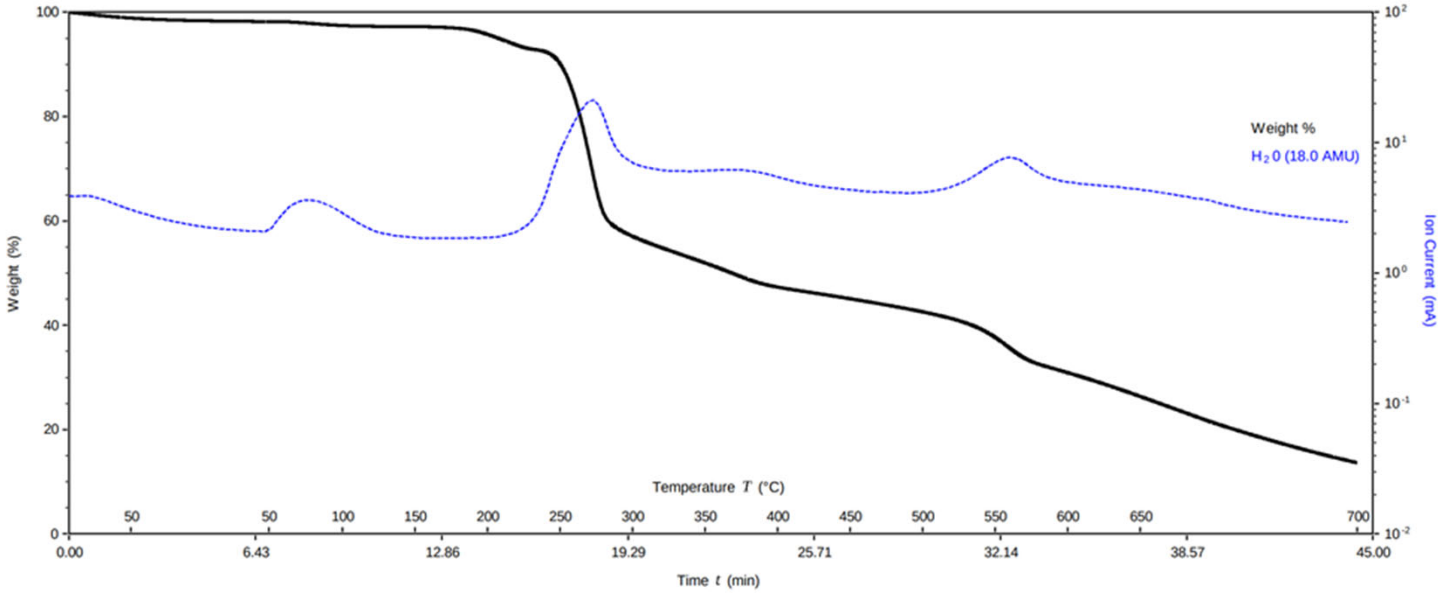
- Equation 1 – relative area of total chromatogram multiplied by modified GHS score for each identified compound
  - GHS scores based on acute inhalation toxicity (H330 – H333)
  - GHS scores – low = high toxicity, our modified score is high = high toxicity
  - Any compound without a GHS score H330-H333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

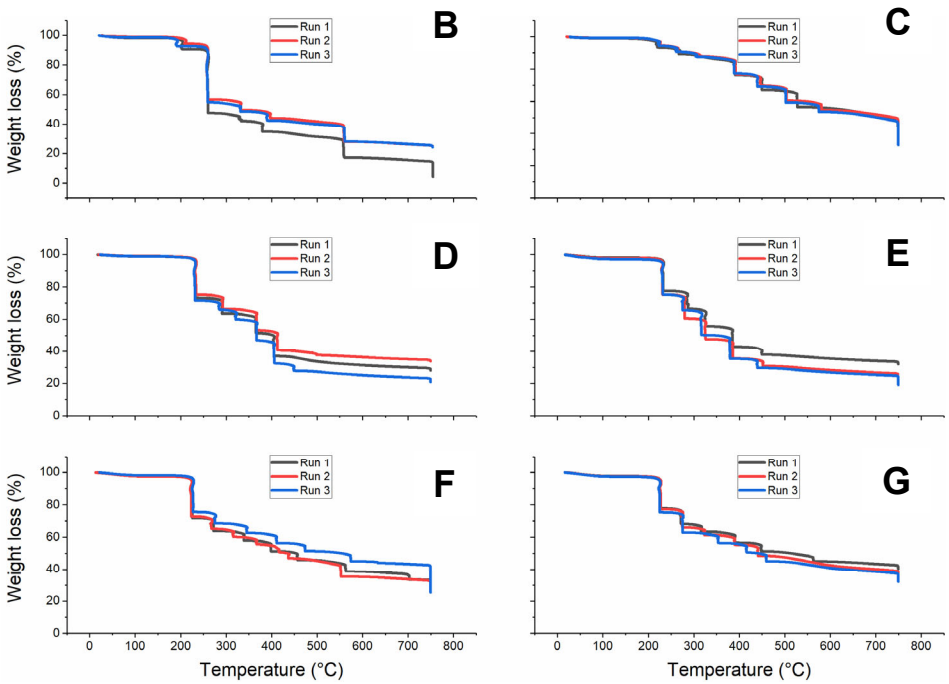
- MRS 1.0 scores organized to the left
  - Higher numbers indicated more toxic compounds off-gassed.
  - The overall number is less important than the trend in the material
- Material C released most toxic pyrolysis products. Material 2 released the least
- Developing this score we learned:
  - It was 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

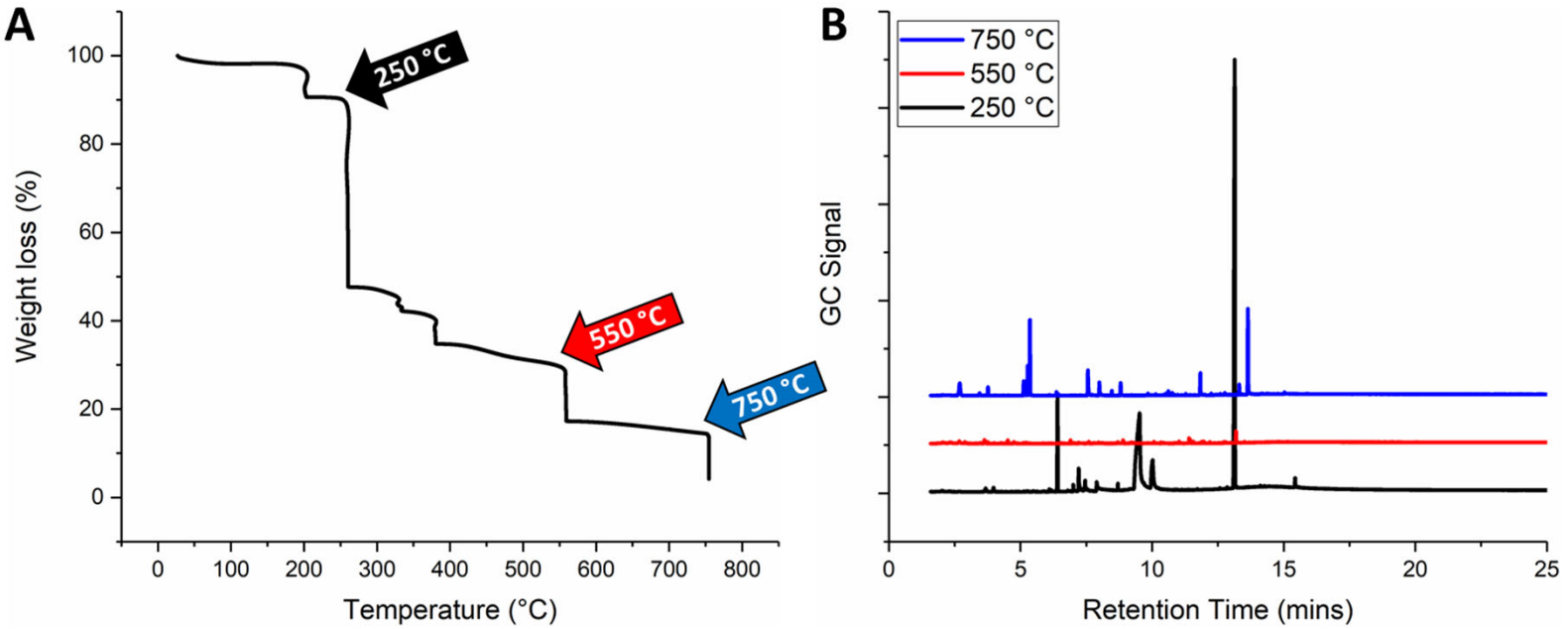
Results – Isothermal TGA



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%	-

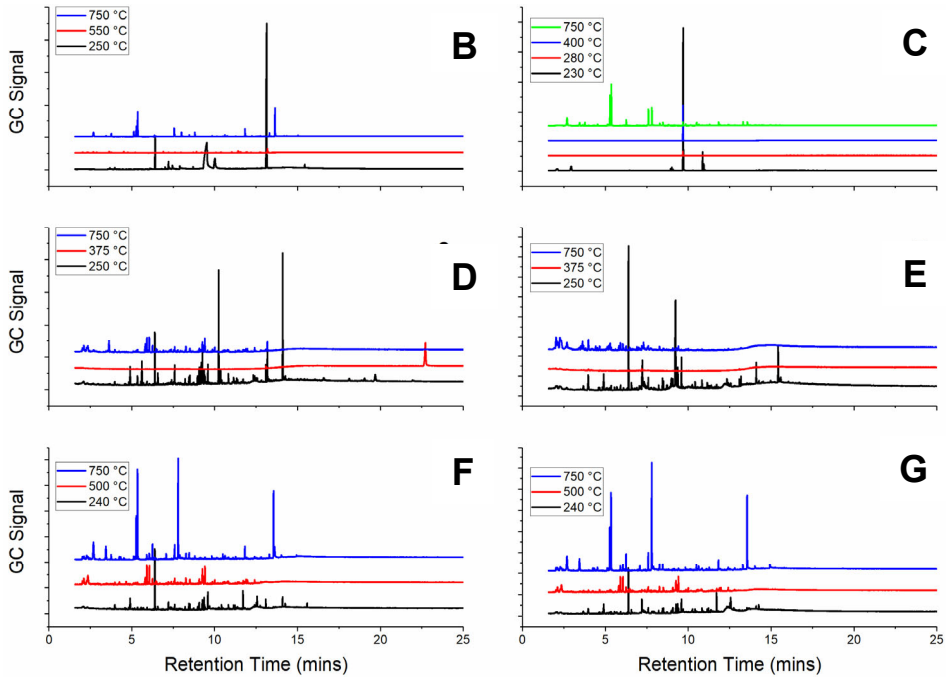
- Had to trim down the number of samples to acquire data in the remaining time
- Instead of linear temperature ramp, isothermal mode entered when 6% weight loss/min detected. Returned to linear heating when 0.05% weight loss/min detected
- Temperatures identified for mass loss events and average % loss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