SAND2010-2160P

Chem Forensics

Multicomponent Forensic Signature Development: Interactions with Common Textiles; Mustard Precursors and Simulants

Mark Van Benthem

Materials Characterization

Research Team: Theodore T. Borek III, Curtis D. Mowry, and Paul G. Kotula

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

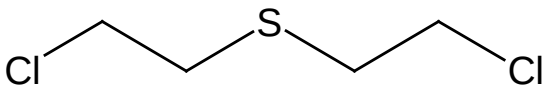
Project Objectives

- **Use TD/MS to develop methods for generating chemical attribution signatures (CAS) employing mustard simulants and surrogates**
  - No use of the actual chemical agent
- **Develop chemometric tools to facilitate data analysis and interpretation**
  - Examine noise in the data
  - Test techniques to quickly analyze data sets
- **Conduct aging studies for mustard simulants on fabrics**
  - Age samples of simulants on fabrics at various humidity levels
  - Examine signature of simulant at various time intervals

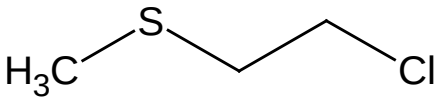
Technical Approach/Tasks

- **Task 1: Examine mustard surrogates on selected substrates to determine efficacy of TD/MS method for this class of agents.**
- **Task 2: Apply mustard surrogates to fabrics for aging studies and perform TD/MS analysis on these samples.**
- **Task 3: Develop and test chemometric algorithms and programs to rapidly analyze TD/MS data acquired in Tasks 1 and 2.**
- **Task 4: Final report**
- **Total Funding $230K**

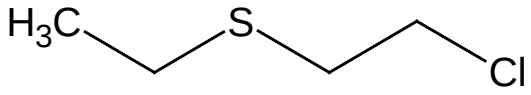
Sulfur Mustard and Simulants



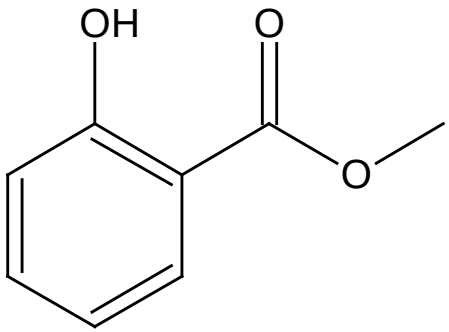
Sulfur mustard (HD)



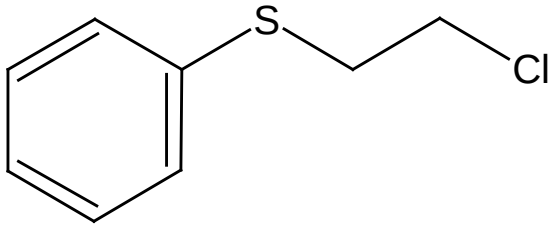
2-Chloroethyl methyl sulfide (CEMS)



Chloroethyl ethyl sulfide (CEES)



Methyl salicylate (MS)



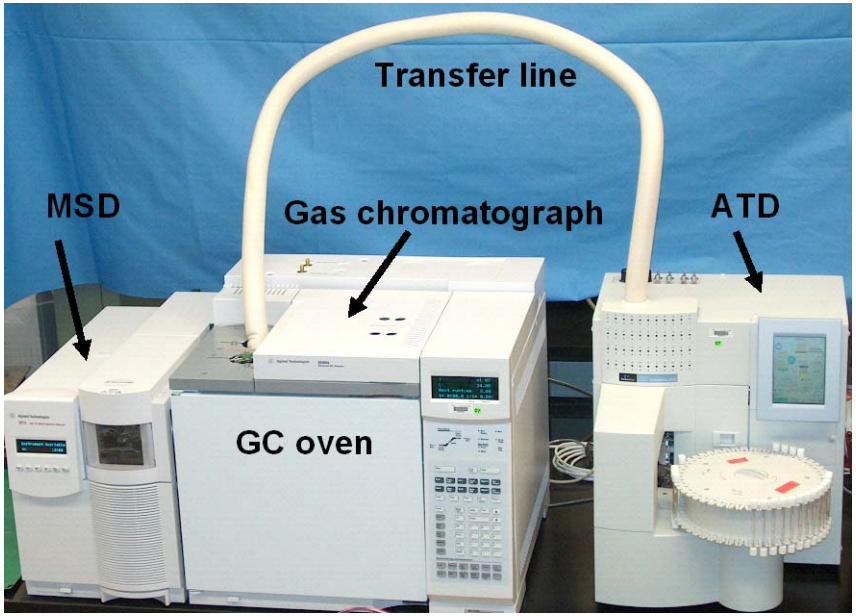
2-Chloroethyl phenyl sulfide (CEPS)

TD-GC/MS

- **Thermal Desorption**
  - Flexible experimental technique
  - Permits the direct analysis of volatile organic species
    - Liquid or solid substrates
  - Typical: Perform TD using single, predetermined desorption temperature
  - Alternative : Step TD temperatures & generate series of desorptions
- **Gas Chromatography coupled Mass Spectrometry**
  - Instrumentation used: widely available, unspecialized, & relative low cost
  - Methods developed can easily be replicated by the widest possible audience responsible for analysis or performing forensic investigations
  - Performed full scan MS: Want to find the needle in the haystack

Apparatus

Instrumentation



Description

- Perkin Elmer model TurboMatrix ATD thermal desorption unit
- Agilent 6890N gas chromatograph
- Agilent model 5975 inert XL MSD mass spectrometer
- No “specialized” equipment
- Affordable and user friendly
- Similar instrumentation available from other instrument vendors

Multivariate Data Analysis

- **Data Scaling**
  - Approximates the assumptions of the factor analysis technique
- **Principal component analysis (PCA)**
  - Decomposes a matrix into two sets of orthogonal of basis vectors
- **Orthogonal Factor Rotation**
  - Maximize some criterion that is consistent with the nature of the data
- **Multivariate Curve Resolution (MCR)**
  - Least squares method to provide physically meaningful representation of data
- **Trilinear Data Analysis**
  - Used to render a three-way model of data that has a trilinear structure
  - PARAFAC-ALS is the most common application

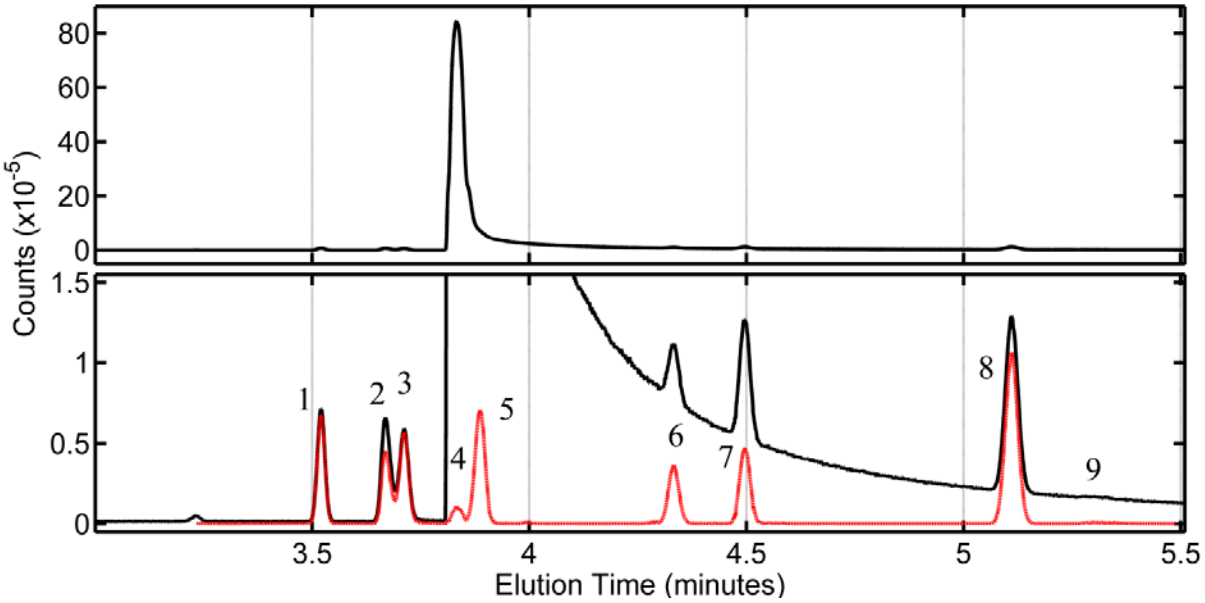
Fabric Spiking and Aging

- **Commercial CEPS used as received**
- **Undyed swatches from a local fabric store**
  - Cotton
  - Ripstop nylon
  - Polyester
  - Silk
- **Humidity**
  - Potassium acetate (23% RH)
  - Magnesium nitrate (56% RH)
  - Potassium chloride (85% RH)
- **Aging: 0, 2, 7, 14, 21, and 28 days**

Chemometric Methods

- **Data Scaling and pretreatment**
  - MS data is count data, so we use Poisson optimal scaling
  - For data in matrix D , compute mean: $\bar{\mathbf{d}}_m = \frac{1}{n}\mathbf{D}\mathbf{1}_n$
  - Scale by $\left(\bar{\mathbf{d}}_m\right)^{-1/2}$ in the MS domain: $\tilde{\mathbf{D}} = \mathbf{H}\mathbf{D}$
  - Selected ion depletion
    - Remove mass channels that contain saturated peaks (e.g., solvent peaks)
- **PCA**
  - Find the solution to: $\tilde{\mathbf{D}} = \tilde{\mathbf{T}}\mathbf{P}^{\mathrm{T}} + \tilde{\mathbf{E}}$
  - Unfortunately, not easily interpretable.
- **Varimax rotation**
  - Find the “most simple” representation of the data in the time mode
  - Rotate the factors $\tilde{\mathbf{D}} = \tilde{\mathbf{T}}\mathbf{P}^{\mathrm{T}} = \tilde{\mathbf{T}}\mathbf{R}\mathbf{R}^{\mathrm{T}}\mathbf{P}^{\mathrm{T}} = \underline{\tilde{\mathbf{T}}}\,\underline{\mathbf{P}}^{\mathrm{T}}$
- **MCR**
  - Use constraints to limit the space of the solution
  - Find the least squares solution to $\tilde{\mathbf{D}} = \tilde{\mathbf{M}}\mathbf{C}^{\mathrm{T}} + \tilde{\mathbf{E}}$

Factor Analysis with SID

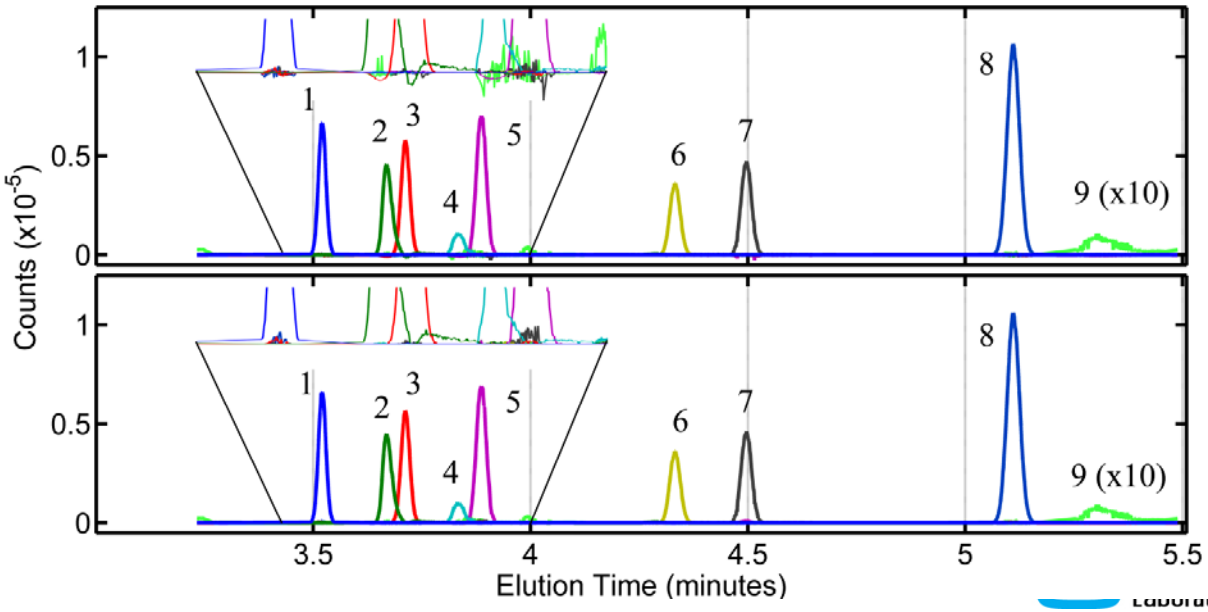


Data

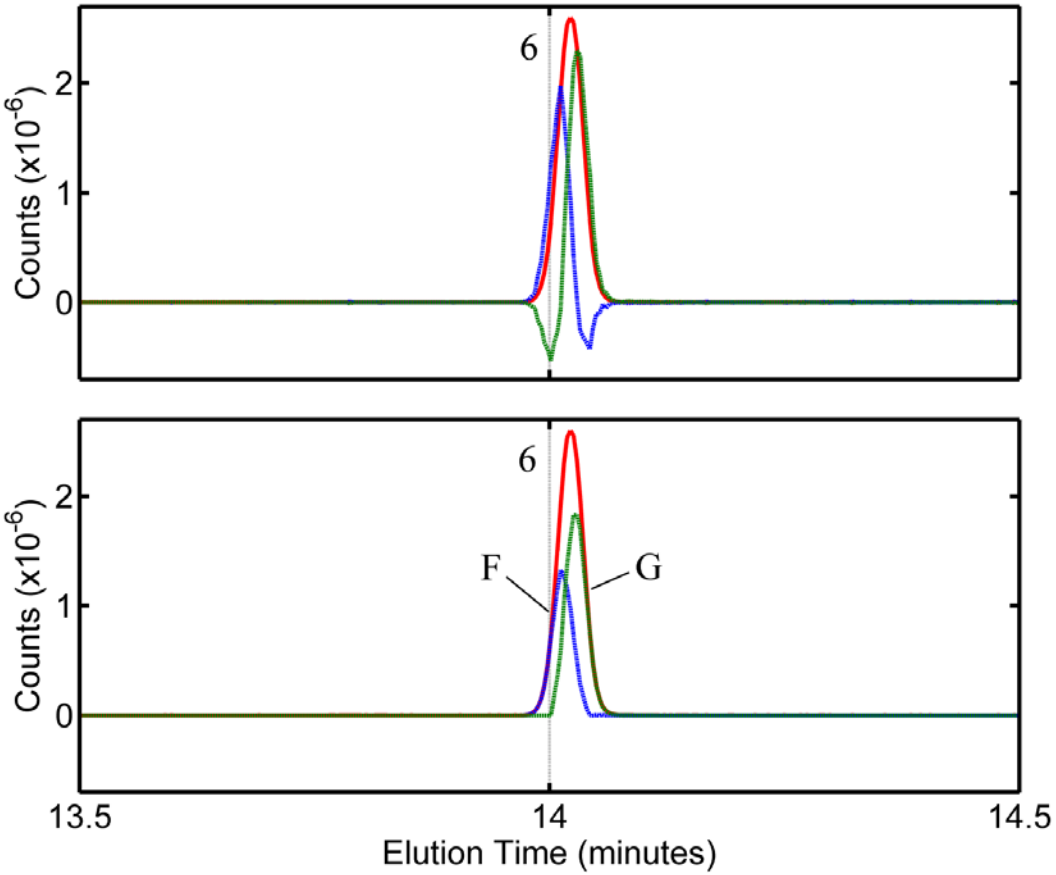
Data after SID

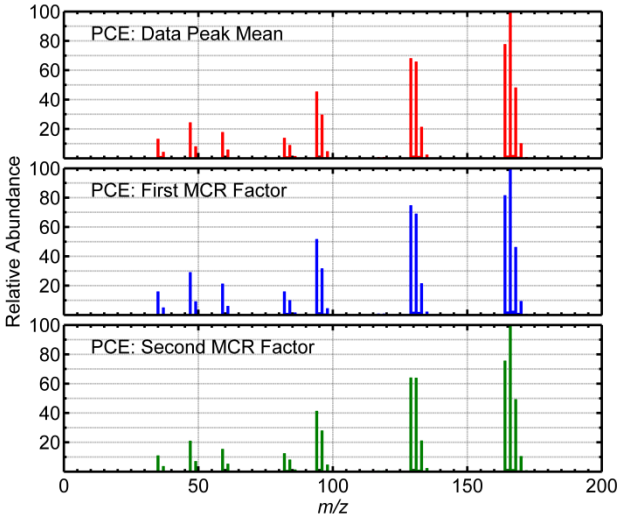
PCA/Varimax Factors

MCR Factors



One Peak or Two?

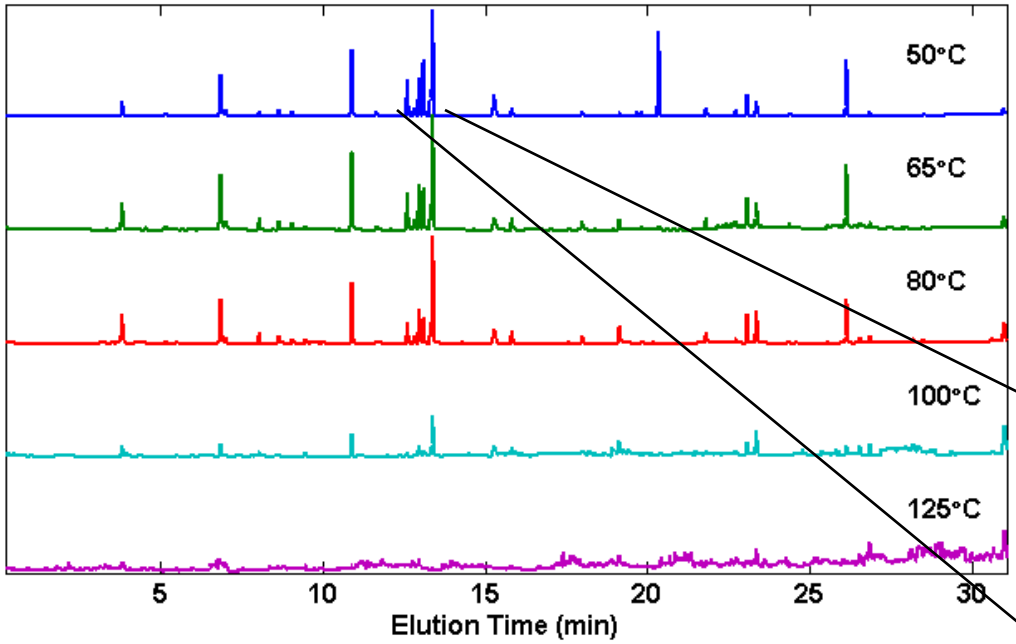


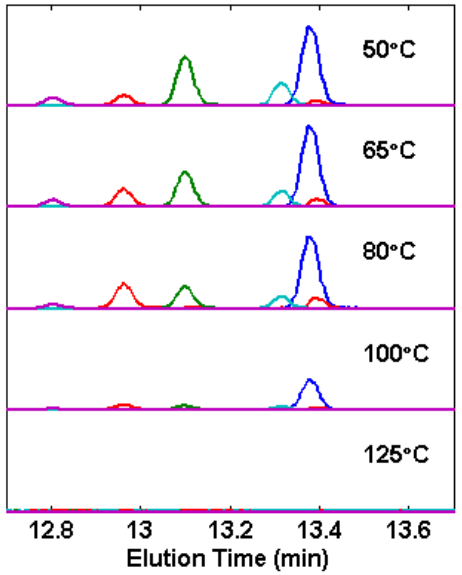


$^{37}Cl/^{35}Cl$ ratio:	0/2	1/1	2/0
Mass C_2Cl_2	94	96	98
Theoretical Prob. (%):	57.4	36.7	5.9
Raw Data Dist. (%):	56.9	37.1	6.0
Peak One Dist. (%):	58.8	36.1	5.1
Peak Two Dist. (%):	55.8	37.8	6.4
NIST data Dist. (%):	56.7	37.2	6.1

Algorithms pulled out subtle isotope effect!

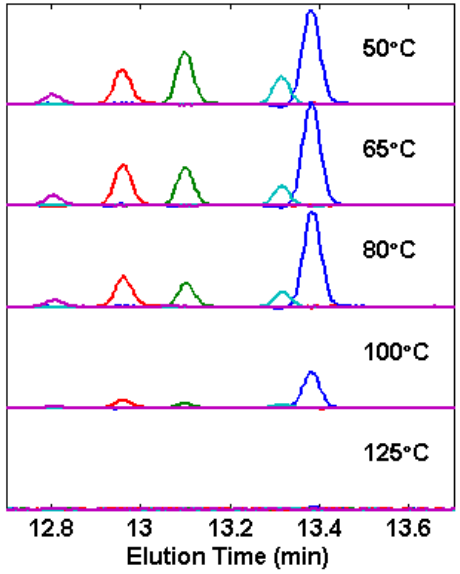
TD-GC/MS CEPS Data





PARAFAC Factors

PCA/Varimax Factors



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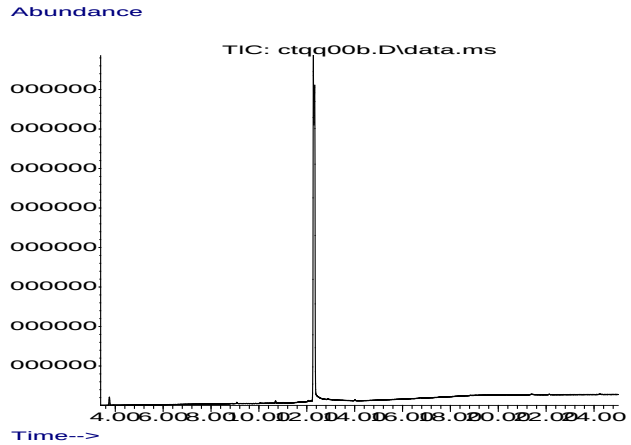
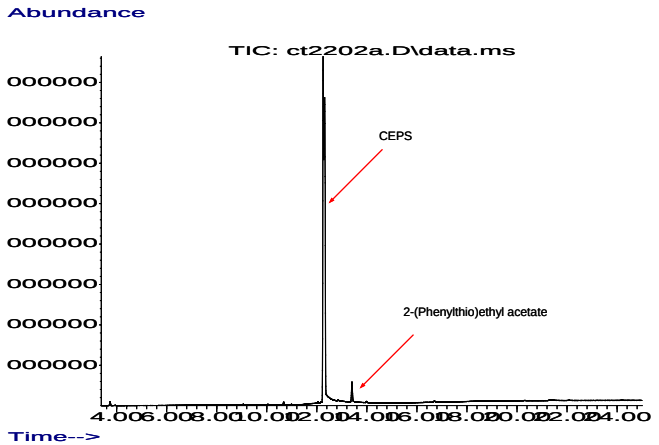
Neat "New" &"Old" CEPS library matches for MCR Model Factors

"New" Time(s) min	"New" match value	NIST Assigned Compound	Formula	CAS #	"Old" match value	"Old" Time(s) min
26.5	933	Benzo[b]thiophene *	C8H6S	95-15-8	939	26.5
31.0	926	Biphenyl	$C_{12}H_{10}$	92-52-4	937	31.0
22.7	912	Benzene, (methylthio)-	C_7H_8S	100-68-5	910	22.7
23.3, 28.3	899	Benzene, (ethenylthio)-	C_8H_8S	1822-73-7	898	23.3, 28.3
30.6	891	Acetaldehyde, (phenylthio)-	C_8H_8OS	66303-55-7	922	30.6
30.9	876	2-Chloroethyl phenyl sulfide	C_8H_9ClS	5535-49-9		
8.6	874	Ethane, 1,2-dichloro-	$C_2H_4Cl_2$	107-06-2	940	8.6
26.1	867	Decane, 1-chloro-	$C_{10}H_{21}Cl$	1002-69-3	937	26.1
20.3	853	Octane, 1-chloro-	$C_8H_{17}Cl$	111-85-3	959	20.3
24.6	805	Benzene, nitro-	$C_6H_5NO_2$	98-95-3	864	24.6†
19.6	764	Octanal	$C_8H_{16}O$	124-13-0	940	19.6
N/A⁺	748	Endrin	$C_{12}H_8C_{l6}O$	72-20-8		
23.0†	720	p-hydroxyphenyl-Phosphonic acid	$C_6H_7O_4P$	33795-18-5		
26.8	678	1,2-Benzenedithiol, 4-methyl-	$C_7H_8S_2$	496-74-2	695	26.8
		Phenol	C_6H_6O	108-95-2	851	23.0†
		Pentane, 3-methyl-	C_6H_{14}	96-14-0	806	5.5†
		Benzenethiol	C_6H_6S	108-98-5	770	19.1
		Olean	$C_{30}H_{50}O_6$	15399-43-6	713	N/A⁺
		Ruthenium organometallic	$C_{14}H_{21}BO_3RuSeSi$	118772-38-6	687	N/A‡
		1-Decanol	$C_{10}H_{22}O$	112-30-1	681	28.2†

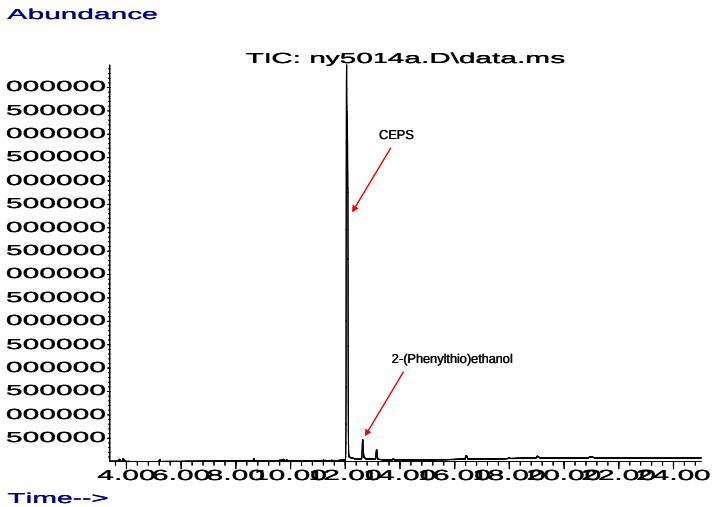
Aging of CEPS on Cotton, Nylon



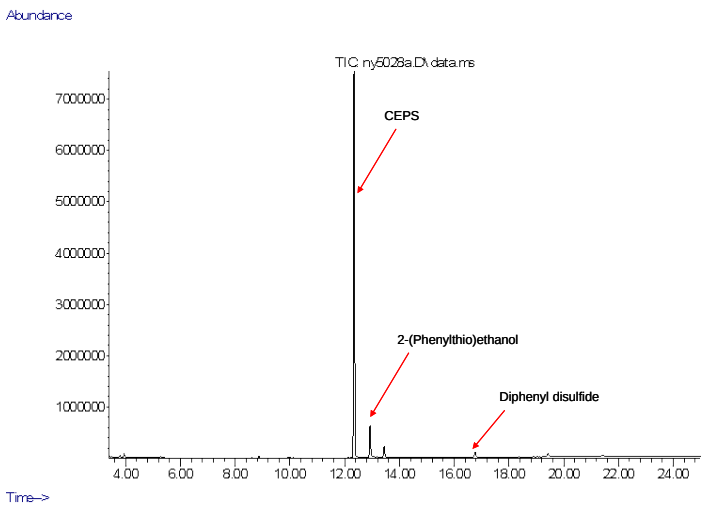
Day 0, CEPS on Cotton



Day 2, CEPS on Cotton, 23% RH



Day 14, CEPS on Nylon, 56% RH



Day 28, CEPS on Nylon, 56% RH

Principal CEPS aging product observed was 2-(phenylthio) ethyl acetate, a reaction product of CEPS and acetic acid.

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Major Accomplishments

- **Submitted manuscript to *Analytical Chemistry***
  - Van Benthem, M.H. , Borek III, T.T. Mowry, C.D. and Kotula, P. G.; *"Factor Analysis of GC/MS Data with Selected Ion Depletion"*
- **Filed US Patent Application No. 12/754,041**
  - Van Benthem, M.H., Kotula, P.G., and Keenan, M.R.; *"Method for Factor Analysis of GC/MS Data"*
- **Preparing R&D 100 Award Application**
  - GC Interpreter (Gas Chromatography Interpreter), Van Benthem, Kotula, Borek, Mowry, and Keenan
- **Final report published as SAND2010-0981**
  - Van Benthem, M.H. , Borek III, T.T. Mowry, C.D. and Kotula, P. G.; *"Multicomponent Forensic Signature Development: Interactions with Common Textiles; Mustard Precursors and Simulants"*

Next Steps

- **Pursue internal investigations of progressive TD-GD/MS analysis for materials analysis**
  - Have applied for internal funding to extend this technique to other areas
- **Explore commercial applications for GC-Interpreter software with GC/MS manufacturers**
  - Hope to replicate the commercial success of AXSIA software for GC/MS applications
- **Demonstrate algorithms on LC/MS data**
  - Applicable toward targets that cannot be analyzed by GC, *i.e.,* toxins
- **Continue mustard research using *live agents* in a collaboration with Lovelace Respiratory Research Institute (LRRI)**
  - MOU is already in place and the principals have agreed to pursue this line of research with DHS funding

Conclusions

- Successfully completed our project on mustard simulants
- Plans are in place to extend this research to other areas of national interest
- Working to make this technology available commercially
- We have arranged with a research partner to take the next logical and meaningful step for this study
- Looking forward to continuing our scientific relationship with DHS and conducting more interesting and important research!