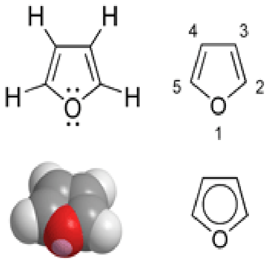
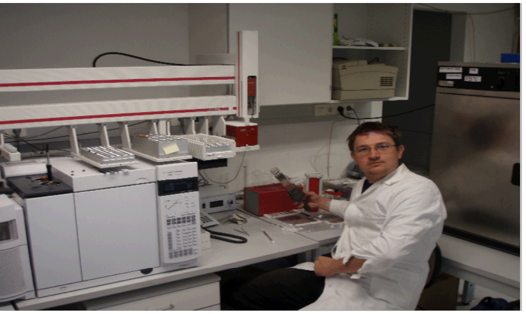
SAND2014-4364C

Analysis of GC-MS Nylon 6.6 Data Using Multivariate Curve Resolution – Alternating Least Squares

Joshua Coon[a], Mark Van Benthem[a], James Hochrein[b], Robert Bernstein[c]





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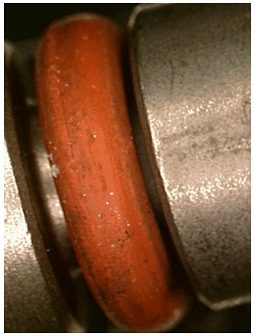
Polymeric Materials Employed in Service for Decades in Critical High Reliability and Performance Applications



O-rings

Nuclear Power Plant Cable Insulation

Aircraft Wire Insulation

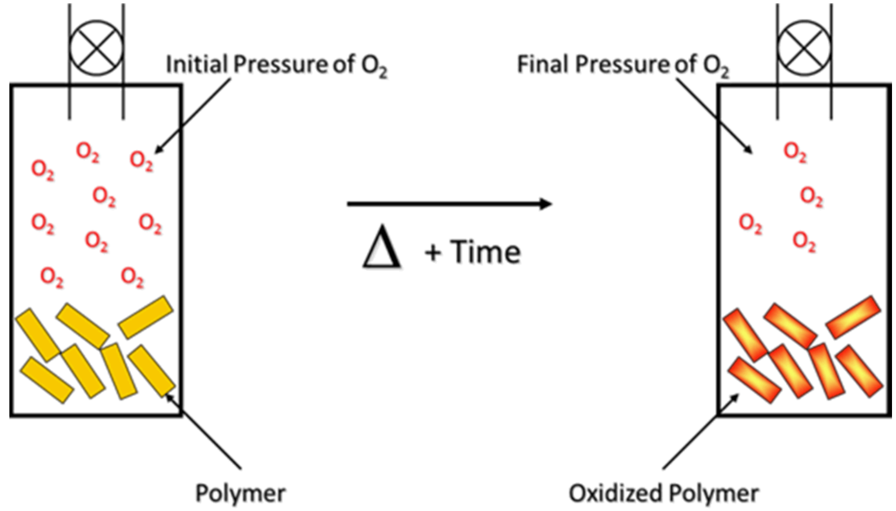
Textiles/Fibers

Study Motivation

- Nylon 6.6 and related materials degrade as a function of age
- Want to know what trace organics are produced during aging
- Chemists can relate information to probable chemical degradation pathways

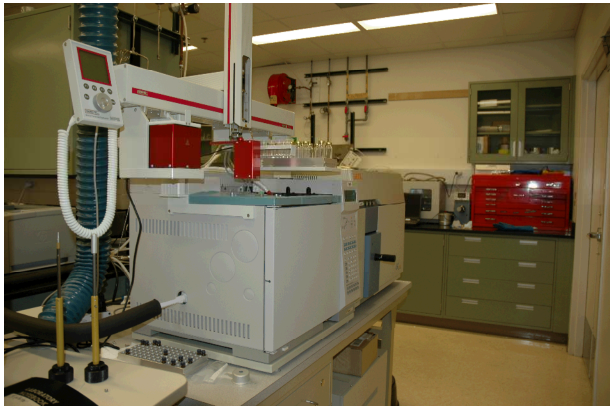
- **Goal: Ensure systems still function after 1, 5, 20, 50 years**

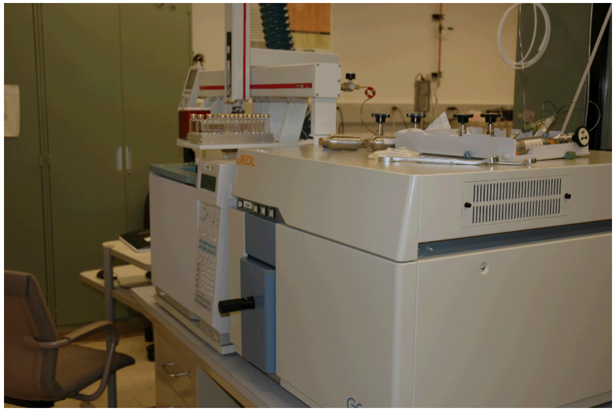
Methodologies



Experimental Methods

- Nylon samples aged in sealed containers and accelerated aging
- Head gas sampled (without replacement) from containers after 1, 34, 63, 143, and 243 days of aging
- Cryofocused Gas Chromatography – Mass Spectroscopy (GC-MS) performed on collected gas samples for each age
- Data analysis performed to extract chemical species present in data



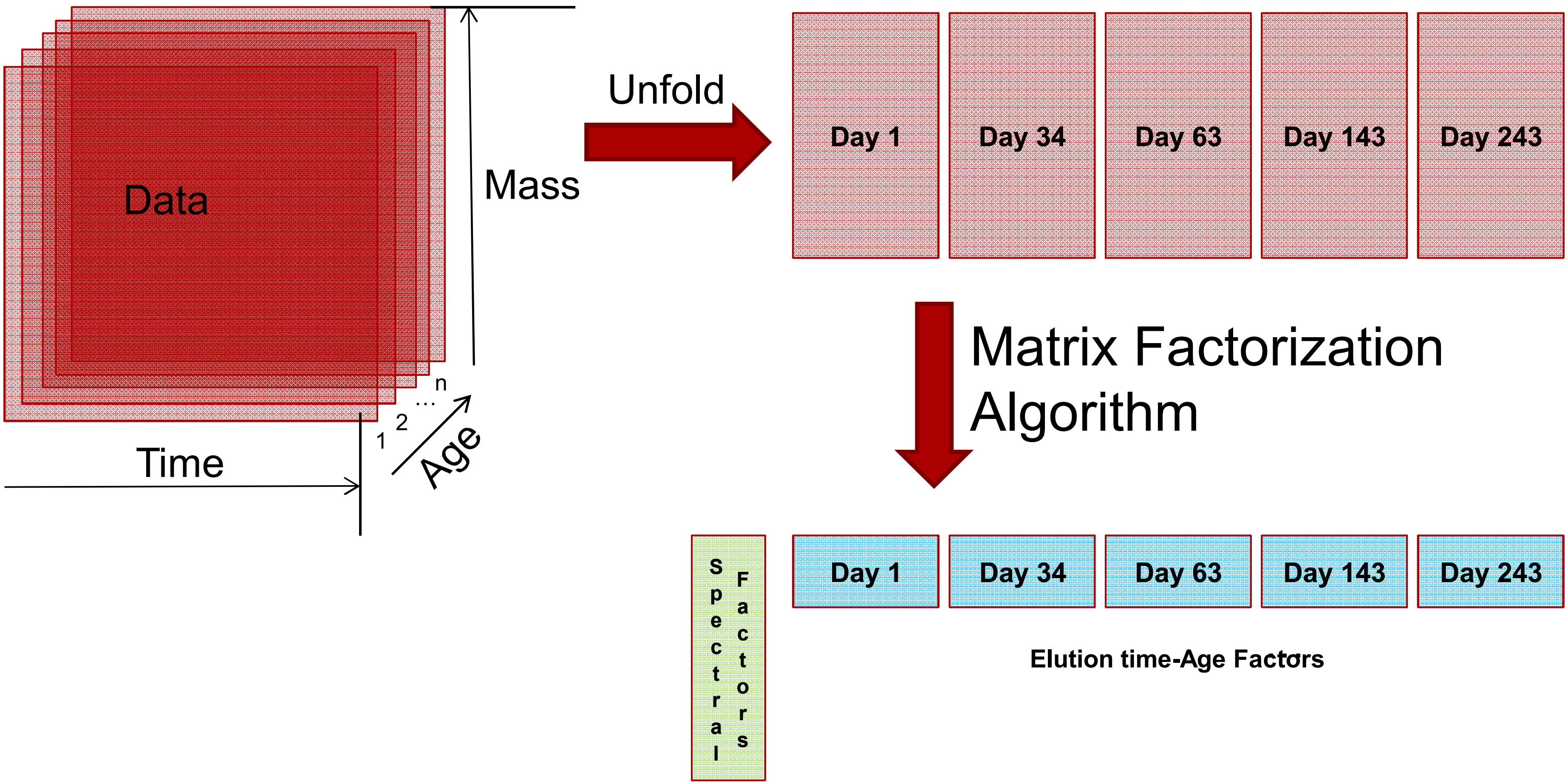


Courtesy of Lance Miller

Data Preparation

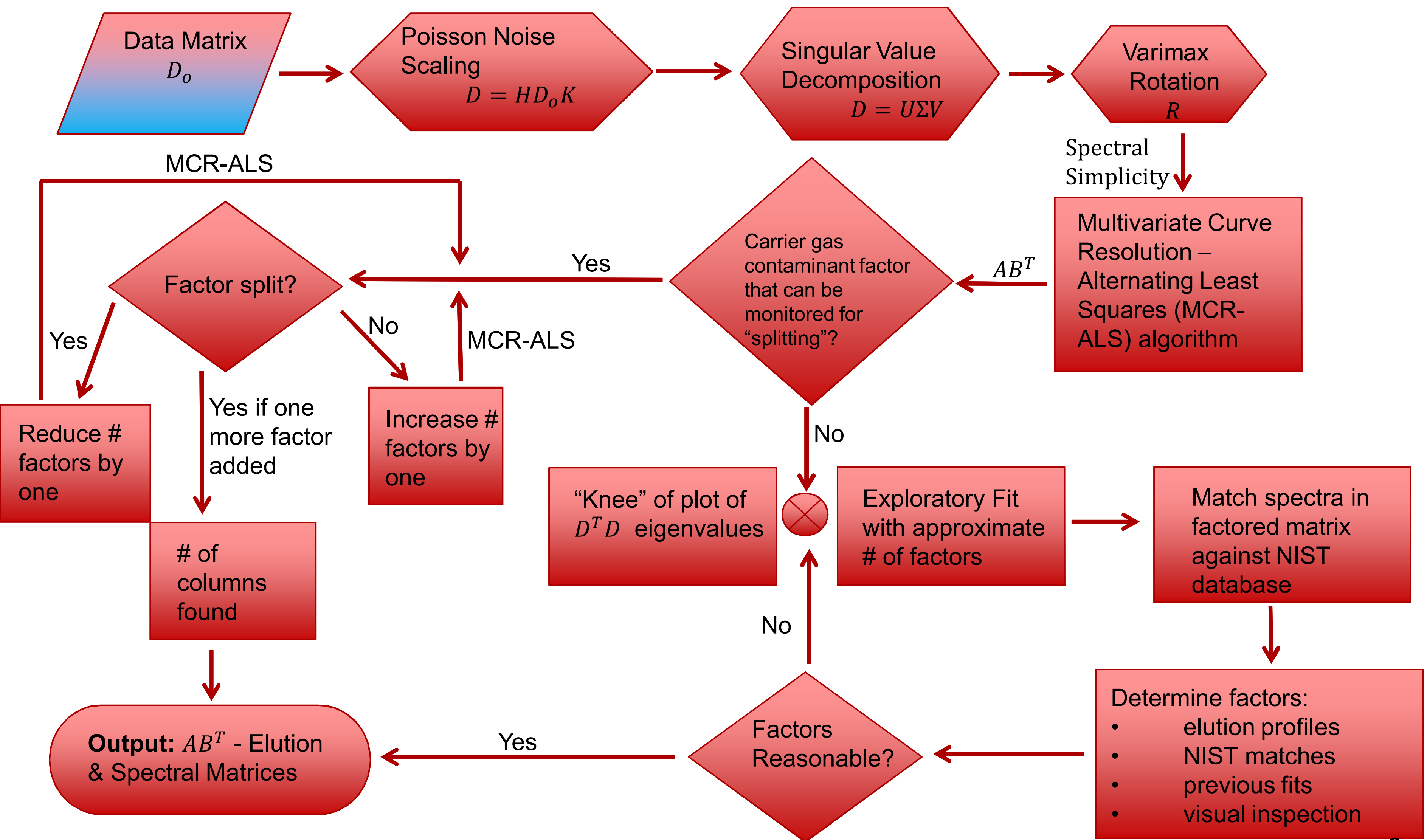
- Reanalysis of previously published data
  - J Am Soc Mass Spectrom. 2012 Sep;23(9):1579-92. doi: 10.1007/s13361-012-0415-x. Epub 2012 Jun 19.
- Data binned along mass/time axis to 2 second and 1 m/z resolution
- Data forms 3-D matrix of $time \times \ mass \times age$
  - Appended to 2-D matrix along age axis
- Appended matrices analyzed in small time axis intervals (3 minutes)
  - Found to improve quality of fits
- 32, 28, and <20 mass peaks suppressed
  - Contaminants in carrier gas
- Poisson noise correction
  - Data matrix multiplied by diagonal matrix of inverse of row & column averages
  - Scales data such that noise is more uniform

Data Array Appending



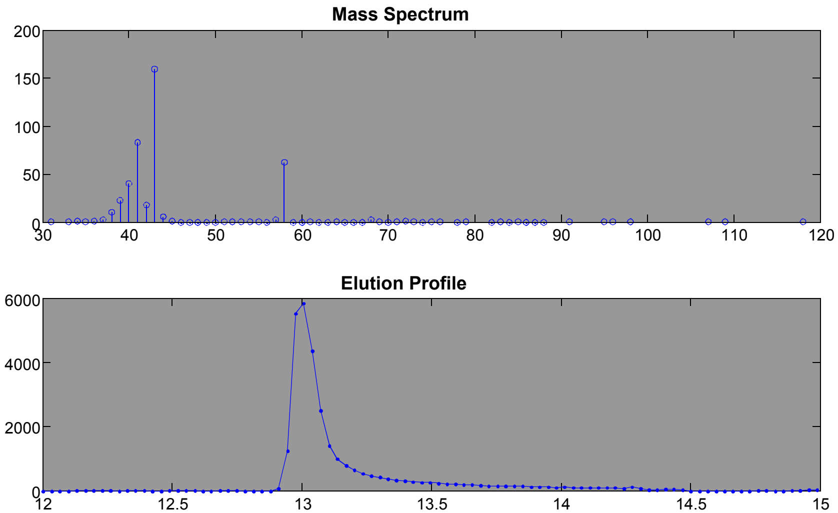
- Many samples analyzed simultaneously

Matrix Factorization Algorithm

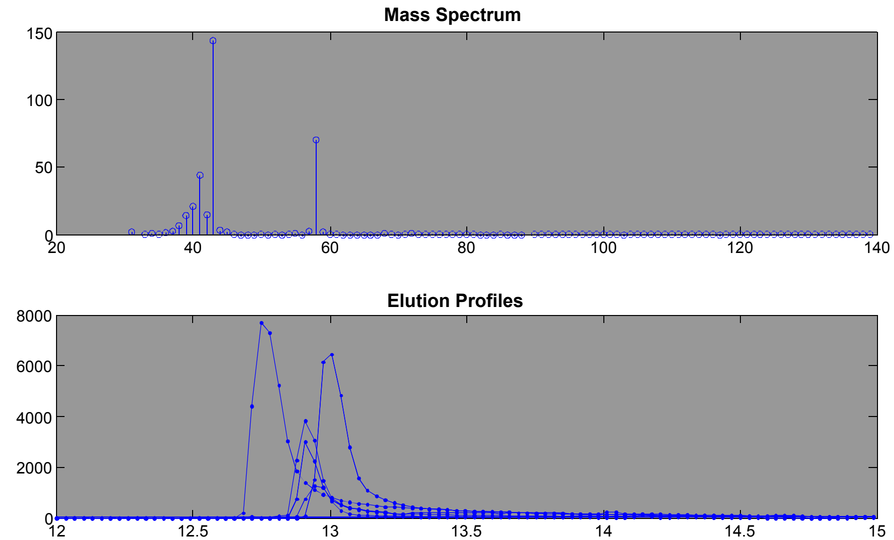


Matrix Factorization Output

One Sample



Unfolded Matrix (5 samples)



Spectral Factors

Day 1

Spectral Factors

Day 1 | Day 34 | Day 63 | Day 143 | Day 243

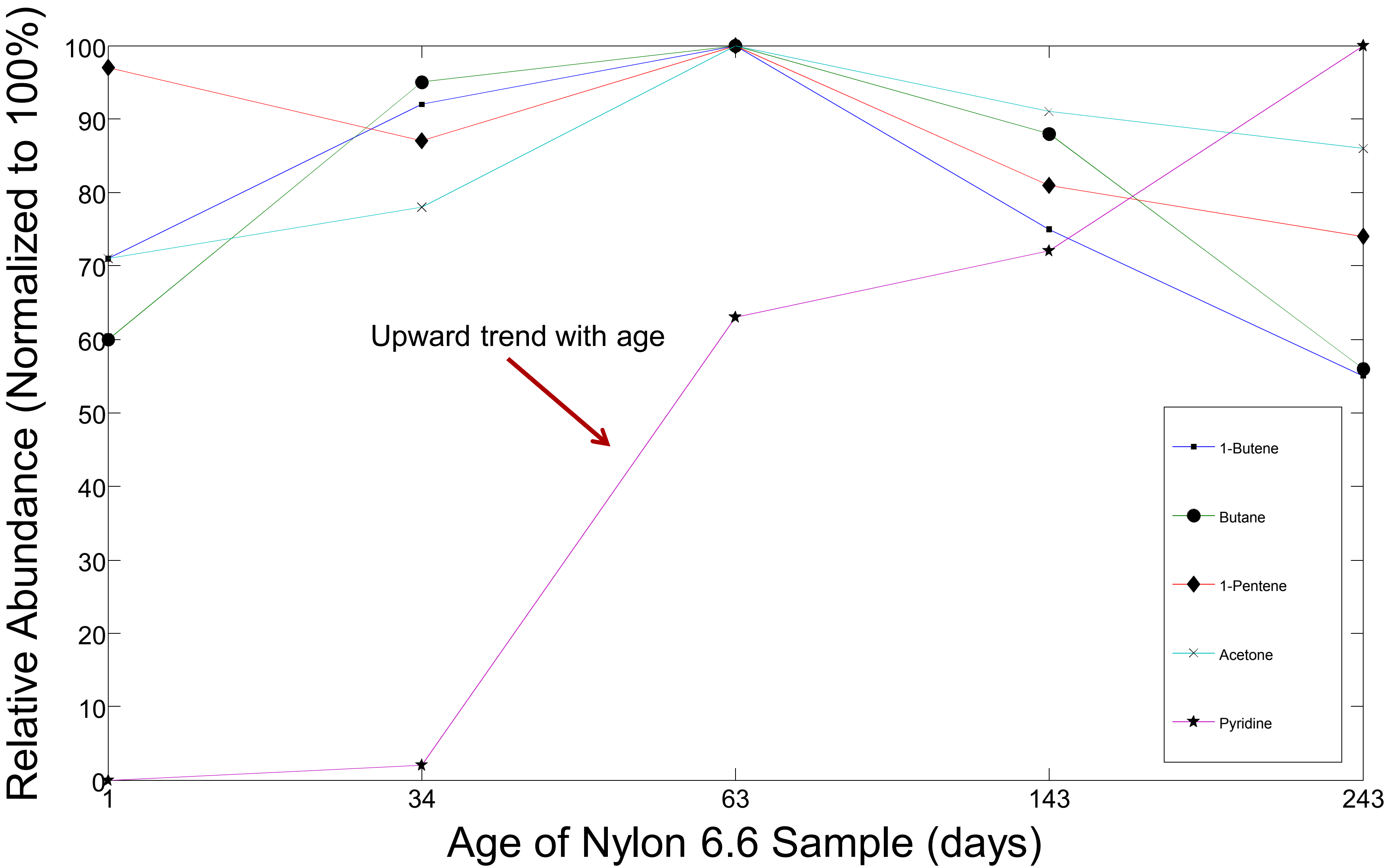
Elution time-Age Factors

RESULTS – UNFOLDED DATA & ISOTOPIC LABELING STUDY

Chemicals in Unfolded Nylon 6.6

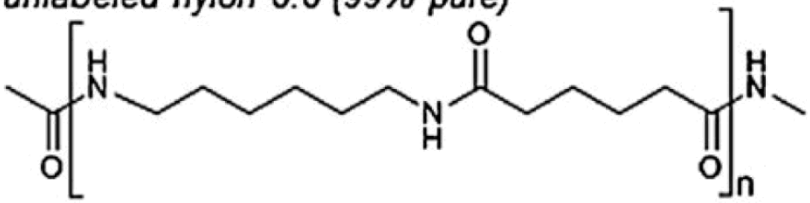
	Approximate Retention Peak(s) (min)	Total Counts	Angle Cosine (x 1000)	Correlation Coefficient (x 1000)	Notes
Butane	9.9-10.3	$4.2x10^7$	904	906	
1-Propene, 2-methyl- / 2-Butene / 1-Butene	9.8-10.2	$2.2x10^7$	897	948	
Carbon Dioxide	10.0-13.0	**Saturated**	904	934	**Saturated**
Acetone	12.8-13.0	$5.1x10^7$	829	851	**Saturated**
Acetic acid, methyl ester	13.0-14.1	$1.8x10^6$	703	791	
Ethanol	12.4-12.8	$6.5x10^6$	700	722	
Cyclopentene	12.8-14.9	$1.5x10^6$	779	881	
1-Pentene	12.5-13.0	$3.1x10^6$	709	741	
Methylene chloride	14.3	$2.0x10^6$	753	849	
1,3-Cyclopentadiene	14.1-14.3	$1.4x10^6$	656	820	
Trichloromethane	17.7	$1.0x10^7$	846	855	

Relative Abundance of Chemicals

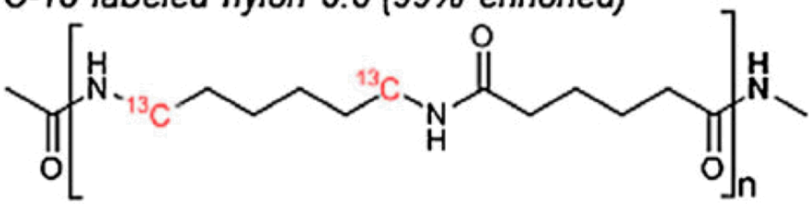


Isotopic Labeling Study

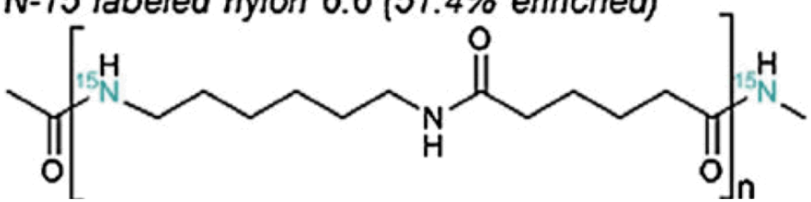
(d) *unlabeled nylon 6.6 (99% pure)*

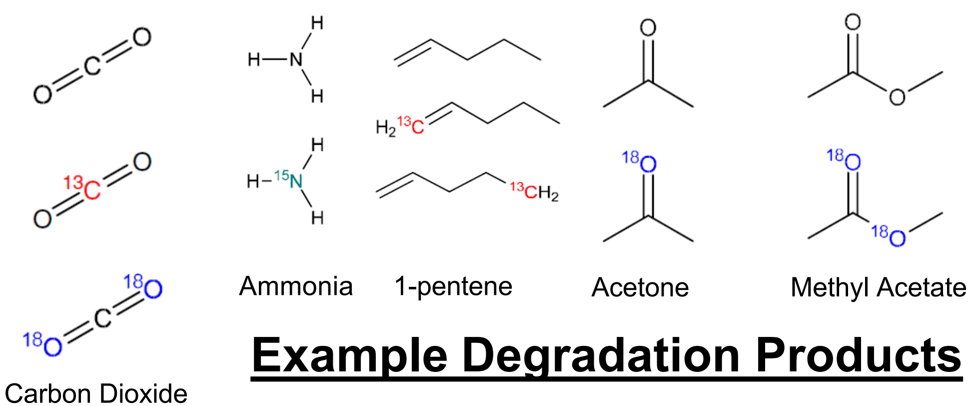


(e) *C-13 labeled nylon 6.6 (99% enriched)*



(f) *N-15 labeled nylon 6.6 (51.4% enriched)*



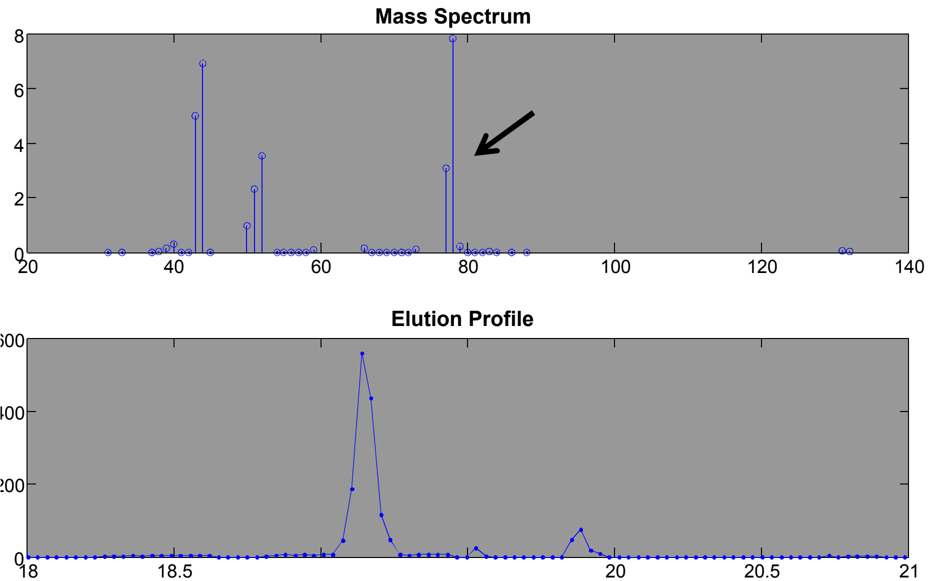


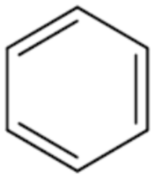
Example Degradation Products

- Four types of Nylon 6.6 aged in sealed containers:
  - Unlabeled Nylon 6.6
  - ^{13}C Labeled
  - ^{15}N Labeled
  - Unlabeled Nylon 6.6 in ^{18}O enriched atmosphere
- Aged 1, 34, 63, 153, 243 days
- Trace organics (degradation products) measured via Cryo-GC-MS
- Purpose: Allows chemists to deduce chemical pathway(s) to degradation

Spectral Shifting from Isotopes

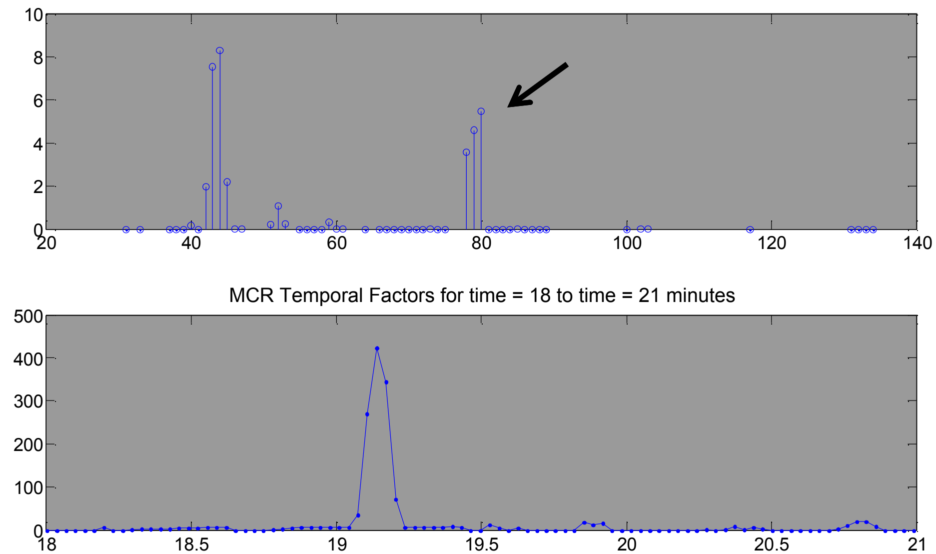
Benzene

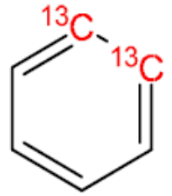




Benzene

Benzene : ^{13}C Labeled





Benzene: ^{13}C

Ratio of Chemical Isotopes

Species	^{13}C	^{15}N	^{18}O
Butene (1- or 2-)	-	-	-
Butane	-	-	-
Carbon Dioxide	100:50 100:45	-	100:95:55 30:100:90
1-Pentene	100:50 25:100	-	
Acetone	-	-	100:40 100:45
Methyl Acetate	-	-	75:100:50
Cyclopentene	100:35 100:35	-	-
2-Butanone	-	-	-
Ethyl Acetate	-	-	Not detected
Tetrahydrofuran	-	-	80:100 75:100
Benzene	45:55:100 40:40:100	-	-

- All species listed present in unlabeled aging study
- Red values from Smith et al., 2012

Conclusions

- Found all chemicals reported in Smith et al., 2012 paper except Tetrahydropyran & Ammonia
  - Ammonia not found because of process data filtering
- Relatively fast analysis (hours not days)
- Resolution of co-eluted chemical species
- Easier quantitative measurements
- Good agreement between Smith et al. 2012 paper and data analysis
  - ^{18}O data noisy and difficult to analyze
- Isotopic spectral shifting identified in factored data
- Some isotopic ratios match Smith paper; some different

Future Work

- Apply method to analyze EVA degradation data
- Explore weighing methods to correct saturated data
- Move towards automated analysis
    - Algorithms to identify number of columns in fit
- Verify quantitative measurements by solutions “spiked” with known chemical ratios

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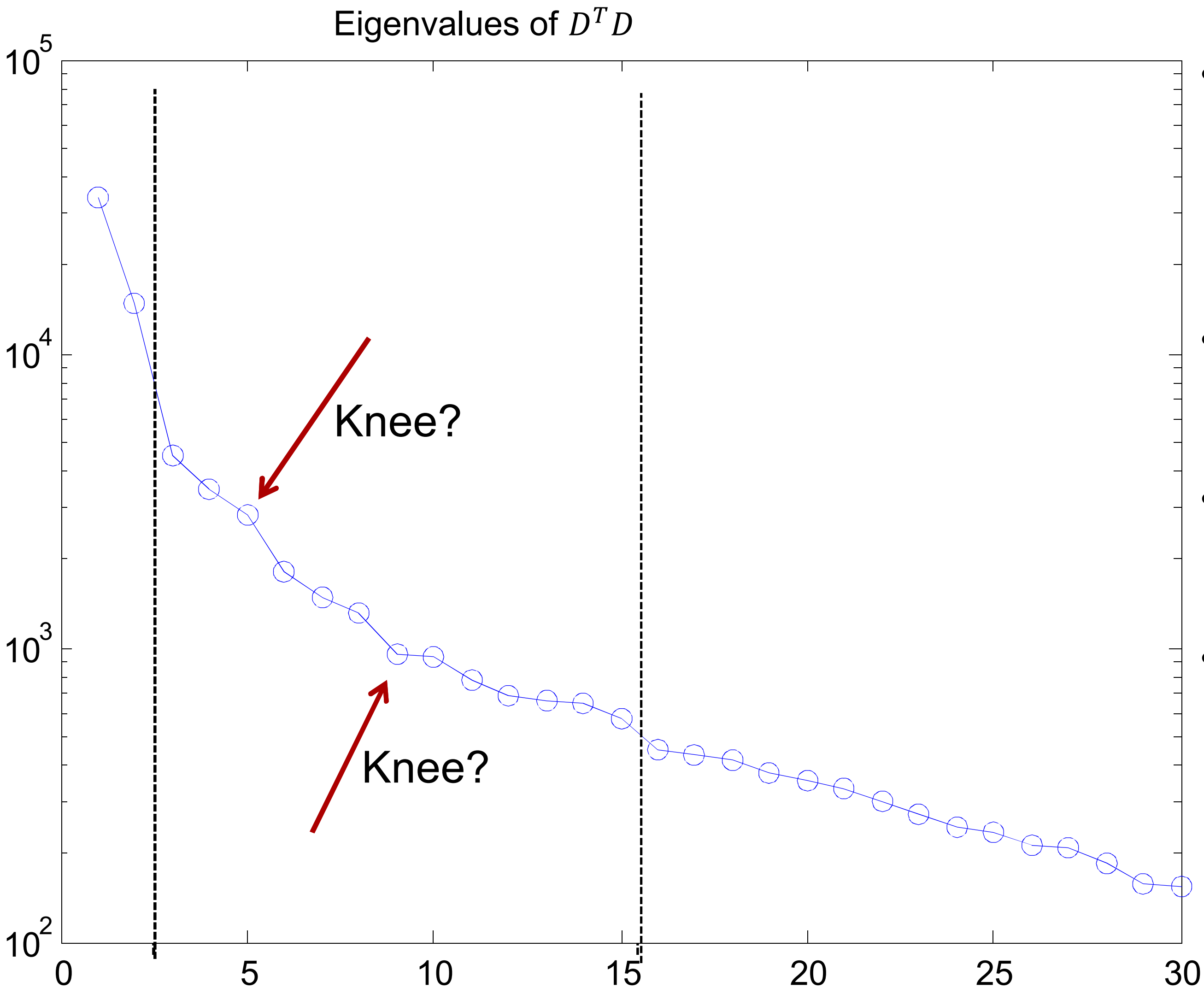
Example of $D^T D$ Eigenvalue Plot



- Number of eigenvalues equals number of significant columns in factored matrices
- Ideally curve comes to pronounced "knee"
- Often knee is difficult to see or missing
- Examine fits with different numbers of columns

Sensitivity to Underfit / Overfit

Underfit

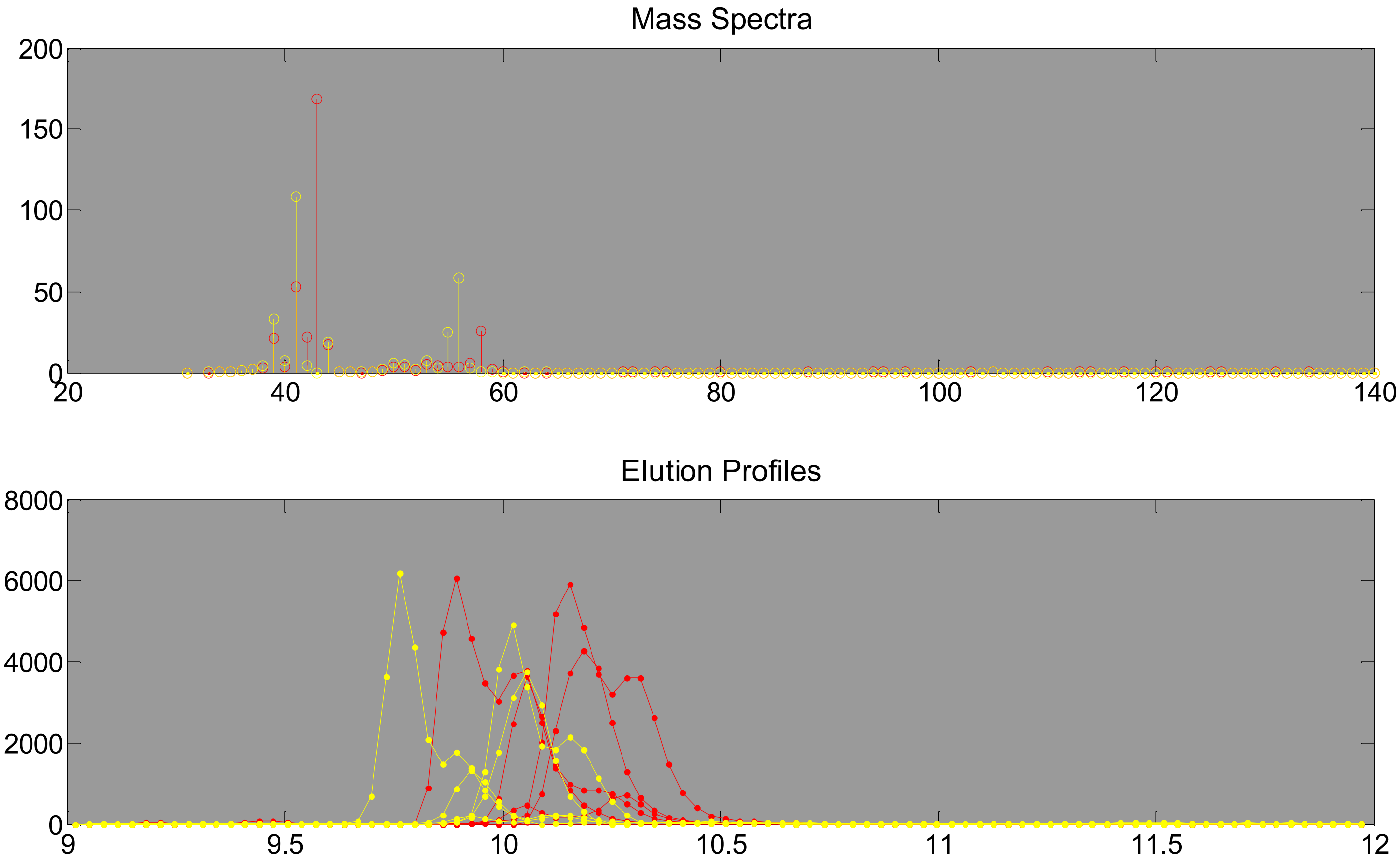
- Miss chemical signals present in data
- Slightly overestimate number of counts

Overfit

- Create false chemical signals not present in data
- Slightly underestimate number of counts

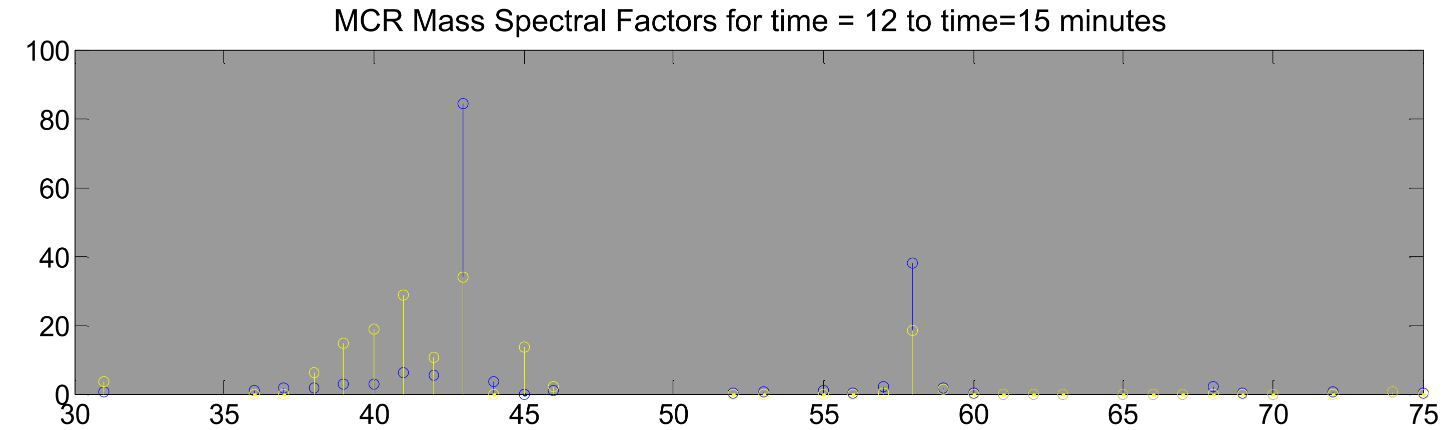
- Counts found empirically to be relatively stable if data overfit or underfit
- When in doubt, it's better to overfit the data and use NIST matches to discard false matches

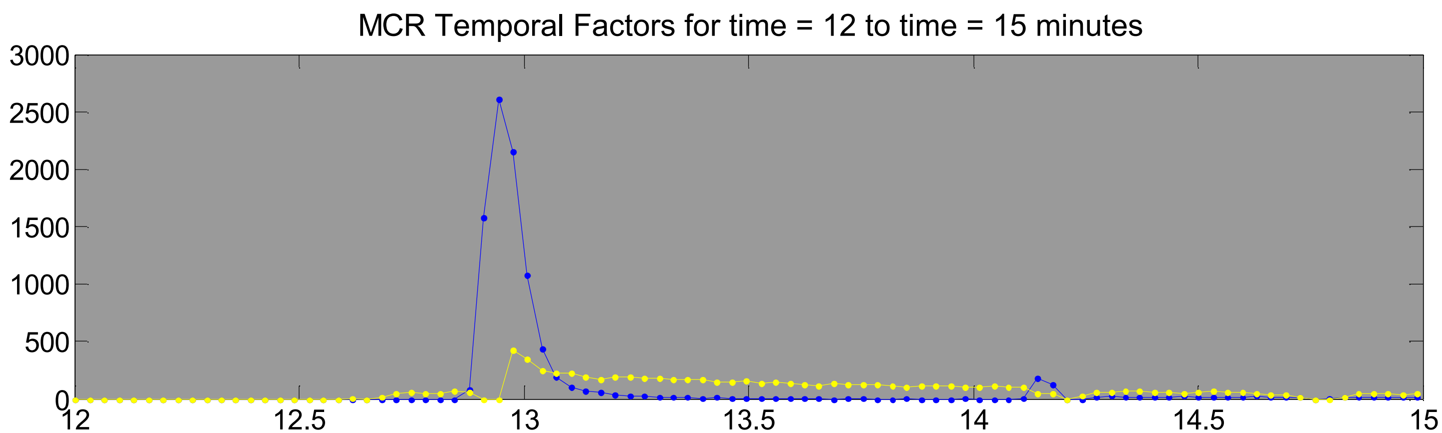
Co-eluted Chemicals



- Able to resolve co-eluted chemical species
- Difficult to do with traditional analysis

Detector Saturation





- High spectral and spatial correlation
- Detector is registering maximum counts at 43 m/z
- Algorithm resolves as separate column

Relative % of Chemicals

	Day 1	Day 34	Day 63	Day 143	Day 243	Notes
1-Butene	71	92	100	75	55	
Butane	60	95	100	88	56	
Carbon Dioxide	100	60	45	35	28	Strong trend
1-Pentene	97	87	100	81	74	
Acetone	71	78	100	91	86	
Methyl Acetate	30	40	100	96	87	
Cyclopentene	80	78	98	77	100	
2-Butanone	29	51	90	100	81	

Relative % of Chemicals

	Day 1	Day 34	Day 63	Day 143	Day 243	Notes
Trichloromethane	100	49	32	33	31	
Tetrahydrofuran	66	80	82	100	93	
Benzene	70	70	100	90	77	
2-Pentanone	47	61	100	86	69	
Tetrahydropyran						
Pyridine	0	2	63	72	100	Strong trend
2-Hexanone	61	72	100	93	72	
Toluene	31	56	100	94	72	
Cyclopentanone	36	64	86	100	86	

Conclusions

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- Relatively fast analysis (hours not days)
- Resolution of co-eluted chemical species
- Easier quantitative measurements

Chemicals in Unfolded Nylon 6.6

	Approximate Retention Peak(s) (min)	Total Counts	Cosine	Correlation	Notes
2-Butanone	16.4-16.6	7.9x10^6	860	914	
Tetrahydrofuran	17.7-17.9	4.4x10^6	867	890	
Silanol, trimethyl-	15.8-16.4	1.1x10^7	830	876	
Silicone Species (Column Bleed)	19.8-20.0	3.3x10^6	546	551	**Low Cos/Corr scores**
Butane, 1-chloro-	18.8-19.8	4.0x10^6	788	834	
2-Pentanone	20.4-20.9	4.2x10^6	711	791	
Benzene	19.0-19.2	1.1x10^6	719	826	
Pyridine	23.6	7.0x10^5	902	909	
Butanoic acid, methyl ester	21.4-22.3	3.7x10^6	677	727	
n-Propyl acetate	21.8-21.9	3.5x10^5	680	793	
Tetrahydropyran					Reported in Smith et al., 2012

	Approximate Retention Peak(s) (min)	Total Counts	Cosine	Correlation	Notes
Toluene	24.6-24.7	4.7x10^6	884	889	
Cyclopentanone	26.1	1.9x10^6	712	747	
2-Hexanone	24.7-26.7	1.1x10^6	613	751	

Ratio of Chemical Isotopes

	^{13}C	^{15}N	^{18}O	Control	Notes
2-Pentanone	85:100	-	-	Present	Noisy ^{18}O
Tetrahydropyran	100:100	-	100:40	Present	
Pyridine	35:100	85:100	-	Present	Noisy ^{18}O
Butyric acid, methyl ester	-	-	Not detected	Present	
n-Propyl acetate	-	-	Not detected	Present	
2-Hexanone	100:60	-	Not detected	Present	Noisy ^{13}C
Toluene	-	-	-	Present	
Cyclopentanone	100:30	-	Not detected	Present	