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Automated Deconvolution of Composite Mass Spectra Obtained with an Open-Air Ionization Source Based on Exact Masses and Relative Isotopic Abundances

Andrew H. Grange and G. Wayne Sovocool

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Office of Research and Development
National Exposure Research Laboratory, Environmental Sciences Division

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DART

JEOL
TOFMS

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Chemical Dispersion Event

- Non-Detect
- Low Amount
- Needs Remediation
- Moderate Amount
- Large Amount

Direction, Distance, Identification

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Single Analyte

Low, Moderate, and High CID Voltages

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Composite Mass Spectra

Low, Moderate, and High CID Voltages

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Three Programs

Most Abundant Ions		
[M+H] ⁺	% IBA	%2 IBA
214.09082	13.19	6.02
77.03004	908.37	0.00
141.00004	8.60	4.90
158.02631	8.31	3.76
94.04125	0.00	7.59
95.05042	0.00	0.00
109.06526	0.00	0.00
72.09030	0.00	0.00
81.06887	0.00	0.00
182.00898	0.00	0.00
79.05280	0.00	0.00
149.02881	0.00	0.00

Program	Ion Type	Mass
Ion Extraction	Precursor Ion	214.09082
Ion Extraction	Product Ion	182.00899
Ion Extraction	Neutral Loss	32.08184
Ion Correlation	Precursor Ion	214.09082
Ion Correlation	Product Ion	182.00899
Ion Correlation	Neutral Loss	32.08184

Input & Output

Input masses and RIAs of the precursor ion and each product ion into the ICP

Store ion correlations, if found

Change upper elemental limits or error limits and recycle

Output a final list of correlated ions

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Ion Extraction Program

Abundance and Exact Mass Difference Tests

Precursor Ions

- Mass peak area exceeds 5000 and 2% of base peak area in both the low and moderate CID voltage spectra
- Exact Mass is not that of a +1 or +2 profile
 - M mass + 0.992 to 1.0084 Da, then M+1
 - M mass + 1.9908 to 2.0117 Da, then M+2
- Exact Mass is not that of an [M]⁺ or [M-H]⁺ ion
 - M mass + (1 or 2 x 1.0078 Da) ± 3 mDa
- Exact Mass is not that of a dimeric or adduct ion
 - M mass + 15.9949 Da ± 5 mDa (oxygenated precursor ion)
 - M mass + 17.0260 Da ± 5 mDa (ammoniated precursor ion)
 - 2 x M mass - 1.0073 Da ± 15 mDa (protonated dimer ion)
 - 2 x M mass - 1.0073 + 17.0260 Da ± 15 mDa (ammoniated dimer ion)
- Exact Mass is not that of a halogen isotopic profile (+2, +4, +6, or +8 Da)

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Ion Extraction Program

Exact Mass Difference Tests

Higher-Mass, Precursor-Related Ions

- Exact mass of M + 15.9949 Da ± 5 mDa is an oxidized precursor ion
- Exact mass of M + 17.0260 Da ± 5 mDa is an ammoniated precursor ion
- Exact mass of 2 x M - 1.0073 Da ± 5 mDa is a protonated dimer ion
- Exact mass of 2 x M - 1.0073 + 17.0260 Da ± 5 mDa is an ammoniated dimer ion

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Exact Mass Difference Tests

Product Ions

- Exact mass difference tests used to select monoisotopic product ions from the high CID voltage spectrum
- Threshold adjusted to provide up to 25 product ions for a single precursor ion or up to 50 for multiple precursor ions

Most Abundant Ions		
[M+H] ⁺	% I RIA	% RIA
214.09082	13.19	6.02
77.03804	908.37	0.00
141.00004	8.60	4.90
158.02631	8.31	3.78
94.04125	0.00	7.89
95.05042	0.00	0.00
109.06526	0.00	0.00
72.08030	0.00	0.00
81.06887	0.00	0.00
182.00898	0.00	0.00
79.05280	0.00	0.00
149.02281	0.00	0.00

RIA Calculations

- M threshold 10,000 or 100,000
- M+1 and M+2 thresholds 500

Precursor Ions		
[M+H] ⁺	% I RIA	% RIA
214.09082		

Adducted Precursor Ions		
[M+H] ⁺	% I RIA	% RIA
444.20377	0.00	0.00
427.17410	25.85	30.78
231.11800	14.48	5.33

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Ion Correlation Program

Correlation

214.09082	Precursor Ion
C10 H16 N O2 S <3.5 5.5>	
141.00005	Product Ion
C6 H5 O2 S <4.5 6.5>	
73.09078	Neutral Loss
C4 H11 N <0.0>	

Non-Correlation

214.09082	Precursor Ion
182.00899	Product Ion
C8 H8 N S2	
32.08184	Neutral Loss

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Ion Correlation Program

Cycle 1

Upper Elemental Limits: C22 H266 N19 O16 S8 F14 P8

268.18933	Precursor Ion
C11 H22 N7 O <4.5>	
C15 H26 N O3 <3.5 4.5>	
267.18149	Product Ion
C11 H21 N7 O <5.0>	
C15 H25 N O3 <4.0 5.0>	
1.00783	Neutral Loss
H <0.5>	

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Ion Correlation Program

Cycle 1

Upper Elemental Limits: C22 H266 N19 O16 S8 F14 P8

268.18933	Precursor Ion
C11 H22 N7 O <4.5>	
C13 H25 N O F3 <0.5>	
C15 H26 N O3 <3.5 4.5>	
116.10705	Product Ion
C4 H12 N4 <1.0>	
C6 H14 N O <0.5>	
152.08228	Neutral Loss
C5 H8 N6 <5.0>	
C9 H12 O2 <4.0>	
C7 H11 F3 <1.0>	
C7 H10 N3 O <4.5>	

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Ion Correlation Program

Cycle 1 Upper Elemental Limits: C15 H26 N7 O3

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268.18933 Precursor Ion
C11 H22 N7 O <4.5>    C15 H26 N O3 <3.5 4.5>    C15 H26 N O3 <3.5 4.5>
191.10638 Product Ion
C10 H13 N3 O <6.0>    C12 H15 O2 <5.5>
77.08293 Neutral Loss
C H9 N4 <-0.5>        C3 H11 N O <-1.0>        C7 H10 N3 O <4.5>
  
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Ion Correlation Program

Cycle 1 Upper Elemental Limits: C15 H26 N O3

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268.18933 Precursor Ion
C15 H26 N O3 <3.5 4.5>
226.14404 Product Ion
C12 H20 N O3 <3.5 4.5>
42.04528 Neutral Loss
C3 H6 <1.0>
  
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Ion Correlation Program

Cycle 2 Upper Elemental Limits: C15 H26 N O3

```

268.18933 Precursor Ion
C15 H26 N O3 <3.5 4.5>
98.09577 Product Ion
C6 H12 N <1.5>
170.09355 Neutral Loss
C9 H14 O3 <3.0>
  
```

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Input and Output Program

Input masses and RIAs of the precursor ion and each product ion into the ICP	Most Abundant Ions		
	RM+10	%1 RIA	%2 RIA
	214.09082	13.19	6.02
	77.03804	906.37	0.00
	141.00004	8.80	4.50
	158.02631	8.31	3.76
	94.04126	0.00	7.88
	95.05042	0.00	0.00
	109.06526	0.00	0.00
	72.08030	0.00	0.00
	81.06887	0.00	0.00
	182.00698	0.00	0.00
	79.05290	0.00	0.00
	149.02281	0.00	0.00
	Precursor Ions		
	214.09082		
	Adducted Precursor Ions		
	444.20377	0.00	0.00 AmD
	427.17410	25.85	30.78 D
	231.11800	14.48	5.33 Am

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Input and Output Program

Input masses and RIAs of the precursor ion and each product ion into the ICP

Store ion correlations, if found

Change upper elemental limits or error limits and recycle

Precursor Ion

- 2 mDa and 20% for RA1 and RA2 (15% when the RIA > 900)
- 2 mDa and 30% for RA1 and RA2
- 2 mDa and 50% for RA1 and RA2

4 mDa and 20% for RA1 and RA2 (15% when the RIA > 900)

4 mDa and 30% for RA1 and RA2

4 mDa and 50% for RA1 and RA2

5 mDa without consideration of RA1 or RA2.

Product Ions

- 2 mDa and 20% for RA1 and RA2 (15% when the RIA > 900)
- 4 mDa and 40% for RA1 and RA2

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Input and Output Program

Input masses and RIAs of the precursor ion and each product ion into the ICP

Store ion correlations, if found

Change upper elemental limits or error limits and recycle

Output a final list of correlated ions

Precursor Ion

- 2 mDa and 20% for RA1 and RA2 (15% when the RIA > 900)
- 2 mDa and 30% for RA1 and RA2
- 2 mDa and 50% for RA1 and RA2

4 mDa and 20% for RA1 and RA2 (15% when the RIA > 900)

4 mDa and 30% for RA1 and RA2

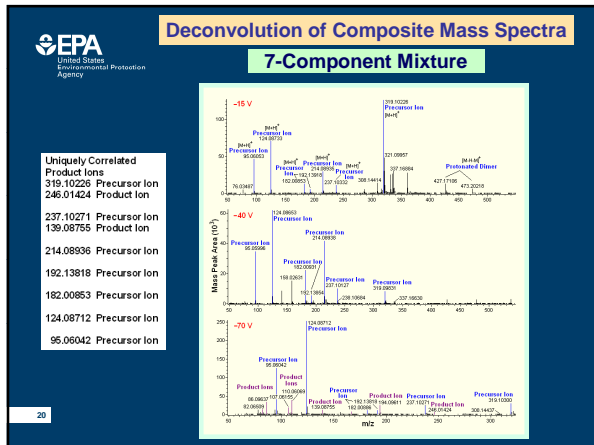
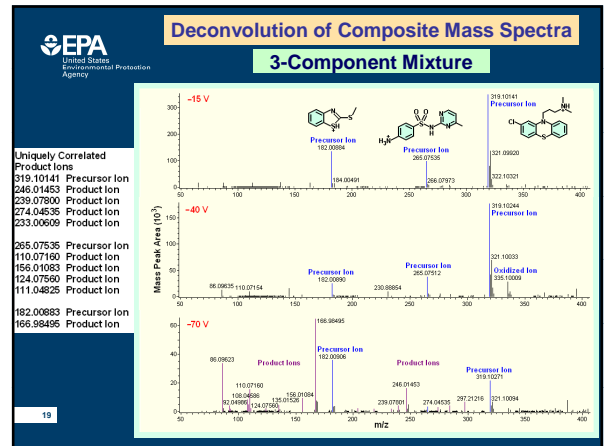
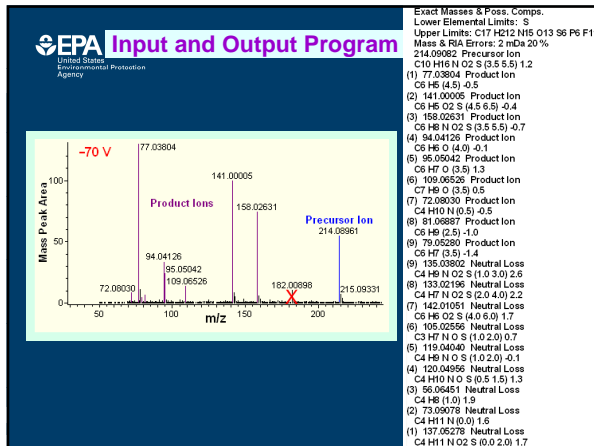
4 mDa and 50% for RA1 and RA2

5 mDa without consideration of RA1 or RA2.

Product Ions

- 2 mDa and 20% for RA1 and RA2 (15% when the RIA > 900)
- 4 mDa and 40% for RA1 and RA2

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EPA Summary
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Rapid characterization of sites and compound identification

Done

- Autosampler/DART/TOFMS and field sample carrier provide rapid analyses and high throughput
- Ion Extraction – Ion Correlation – Input and Output Software provides rapid determination of ion compositions and partial mass spectral interpretation

To Do

- Acquire cotton swab, wipe samples to assess semi-quantitative capabilities for mapping dispersants
- Simulate arrival of 1000 wipe samples, acquire mass spectra, and prepare a dispersant map in one 8-hour shift