Analytical Chemistry: How do you know if you're right?

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Analytical Chemistry

Exams substances by separating them into their chemical components and identifying each one and their abundances.
How to identify Chemical Compositions?

Mass Spectrometry Analysis

Sample of a Substance

H2O
CO
C2H4
C6H6
O2
N2O3
CO2
SO2

78 m/z
64 m/z
44 m/z
76 m/z
32 m/z
30 m/z
18 m/z
28 m/z
28 m/z

Sample of a Substance
Applications

• Climate Change:
  Analyze the effects of Global Warming

• Carbon dioxide and pollution monitoring

• Carbon dating
• Soil contamination assessment
• Food contamination detection
• Pesticides Control
• Drinking water quality

2nd Report on pesticide contamination monitoring on fruits and vegetables 2016

Comparison of fruit and vegetables with residues above maximum limit (MRL)

- Oranges Nam Pueng variety: 8 residues above MRL, 1 no residues found
- Dragon fruit: 7 residues above MRL, 1 no residues found
- Guava: 6 residues above MRL, 1 no residues found
- Papaya: 3 residues above MRL, 3 no residues found
- Watermelon: 3 residues above MRL, 4 no residues found
- Cantaloupe: 1 residue above MRL, 5 no residues found
- Chinese kale: 10 residues above MRL, 1 no residues found
- Red chillies: 9 residues above MRL, 3 no residues found
- Long beans: 8 residues above MRL, 2 no residues found
- Holy basil: 8 residues above MRL, 4 no residues found
- Morning glory: 7 residues above MRL, 1 no residues found
- Thai aubergines: 6 residues above MRL, 2 no residues found
- Cucumber: 5 residues above MRL, 4 no residues found
- Tomatoes: 3 residues above MRL, 6 below MRL, 2 no residues found
- Cabbage: 2 residues above MRL, 1 no residues found
- Chinese cabbage: 2 residues above MRL, 10 no residues found

158 samples were collected on 23-29 August 2016, sent to laboratory certified to ISO/IEC 17025:2005 standard, tested for over 450 different chemicals

https://www.ag.ndsu.edu/williamscountyextension/a-little-bit-country/pesticide-certification-training/pesticide-certification-training-increase-nutrition-requirements-increase/image_mini
Drug testing and discovery
Drug abuse confirmation

Genetics: Protein identification and Mutations
Disease screening
Cancer screening and diagnostics

Forensic analysis:

Trace evidence:
- Fibers in carpet
- Polymers in paint

Explosive residues:
- Bombing investigation
- Fire Accelerants
FTICR-Mass Spectrometry
( Fourier Transform Ion Cyclotron Mass Spectrometry)

Measures the ‘weight’ (in m/z) of ions based on the cyclotron frequency of the ions in a fixed magnetic field.
Mass Spectrometry Analysis

Assigning a molecular formula for each component/peak by their ‘weight’ (m/z)
How do you know if your molecular formula assignments are correct?

There is uncertainty and noise in the process

Wu, Rogers – Soybean Oil
Goal

To measure the uncertainty of substance identification

Statistical Model

$P(\text{CH}_4 \text{ is correct}) = ?$

$P(\text{CH}_4 \text{ is there?}) = ?$

[Diagram of molecules]
Statistical Approach

Capture the uncertainty of molecular formula assignments

<table>
<thead>
<tr>
<th>Theoretical m/z</th>
<th>Identified Component</th>
<th>Observed m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>214.159026066</td>
<td>C_{15}H_{20}N_{1}</td>
<td>214.15902</td>
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<tr>
<td>466.252926451</td>
<td>C_{35}H_{32}N_{1}</td>
<td>466.25292</td>
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<tr>
<td>523.379767240</td>
<td>C_{33}H_{52}N_{1}O_{1}S_{1}^{13}C_{1}</td>
<td>523.37927</td>
</tr>
</tbody>
</table>

**Diagram**

- **Monoisotopic Peak**
- **Isotopomers**

https://www.researchgate.net/figure/A-calculated-isotope-distribution-The-mass-spectrum-of-a-peptide-or-oligonucleotide_fig1_23401650
Uncertainty of assignments
(noise, split peaks = non-unique theoretical candidate)

Published in: Feng Xian; Christopher L. Hendrickson; Greg T. Blakney; Steven C. Beu; Alan G. Marshall; Anal. Chem. 2010, 82, 8807-8812. DOI: 10.1021/ac101091w. Copyright © 2010 American Chemical Society
Direct Contributions of our Model

• Gives the confidence in each chemical component identified

• Improve research in several fields

• How much resolution is enough?
Thank you!

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