

Welcome to our E-Seminar:

Ion Suppression Minimized in LC/MSD

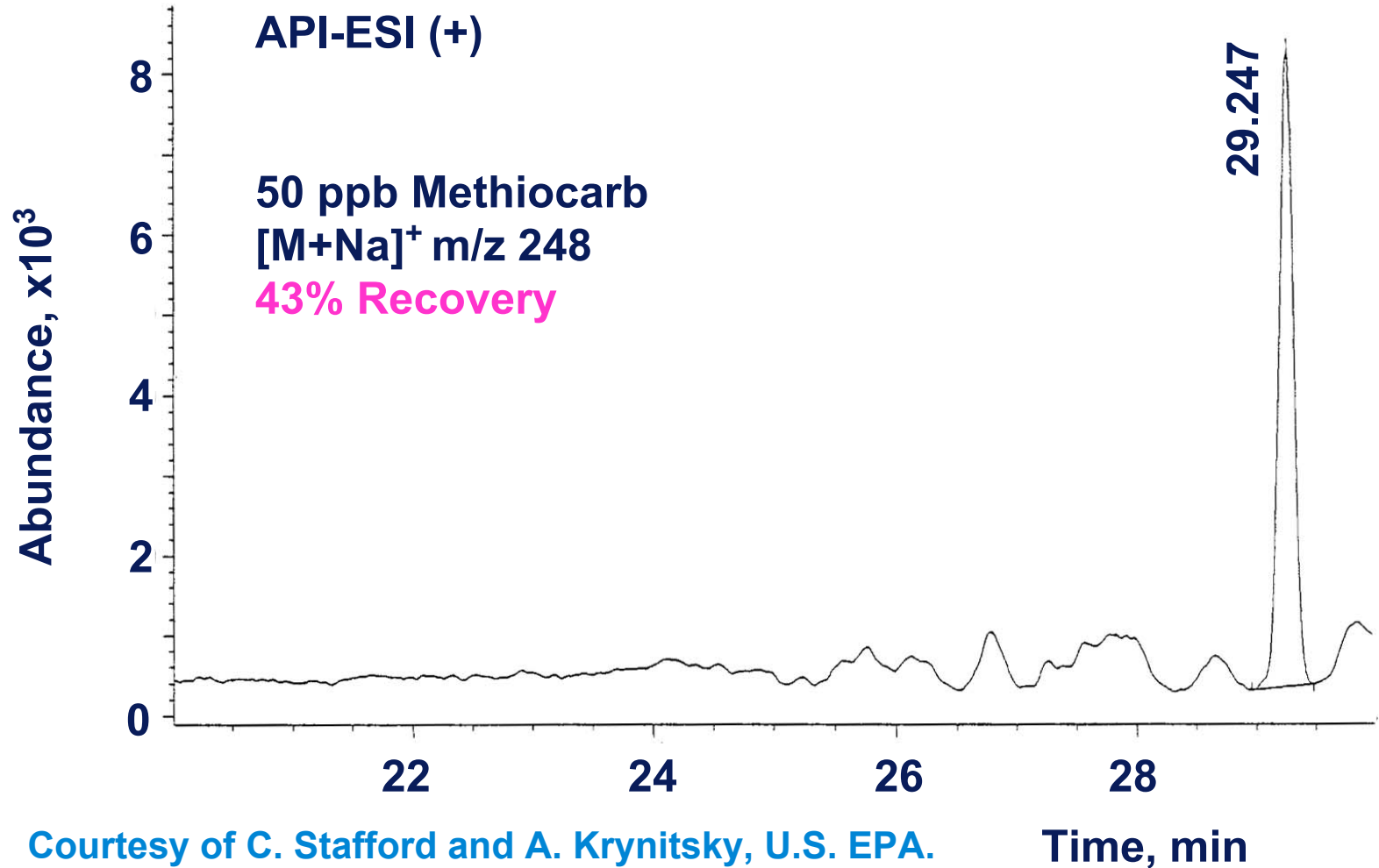
Outline

- What is ion/signal suppression and why
- Approaches to minimize suppression
 - Different ionization process
 - ESI source design
- Fruit and vegetable extract ESI results

What is Ion/Signal Suppression?

- LC/MS response obtained from a clean standard can differ significantly from matrix samples, usually lower in matrices
- Different analytes in a run show large variations in response, in other words, suppression is not a fixed function in a run
- Ion suppression presents a challenge in doing quantitative LC/MS applications

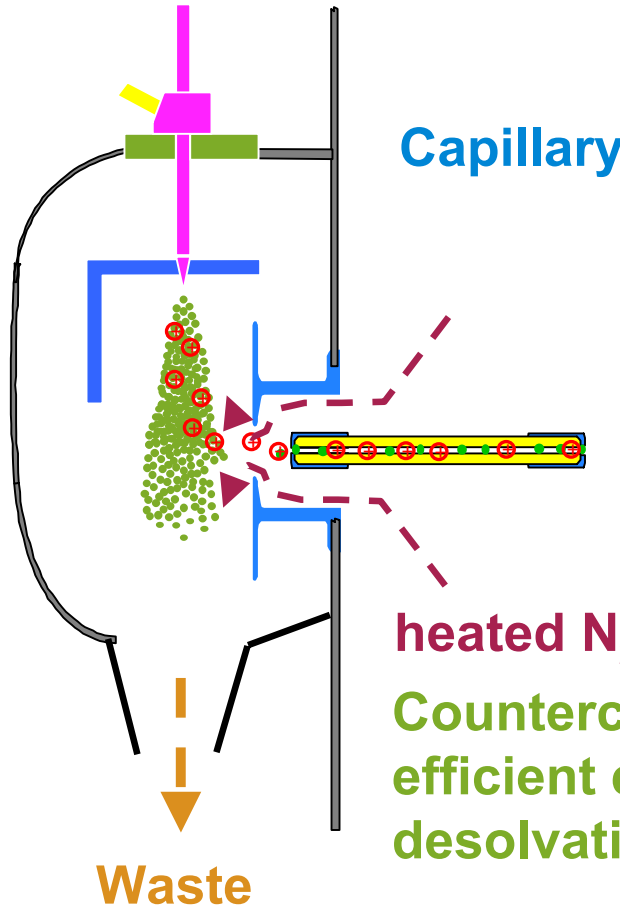
Example of Signal Suppression



ESI Source

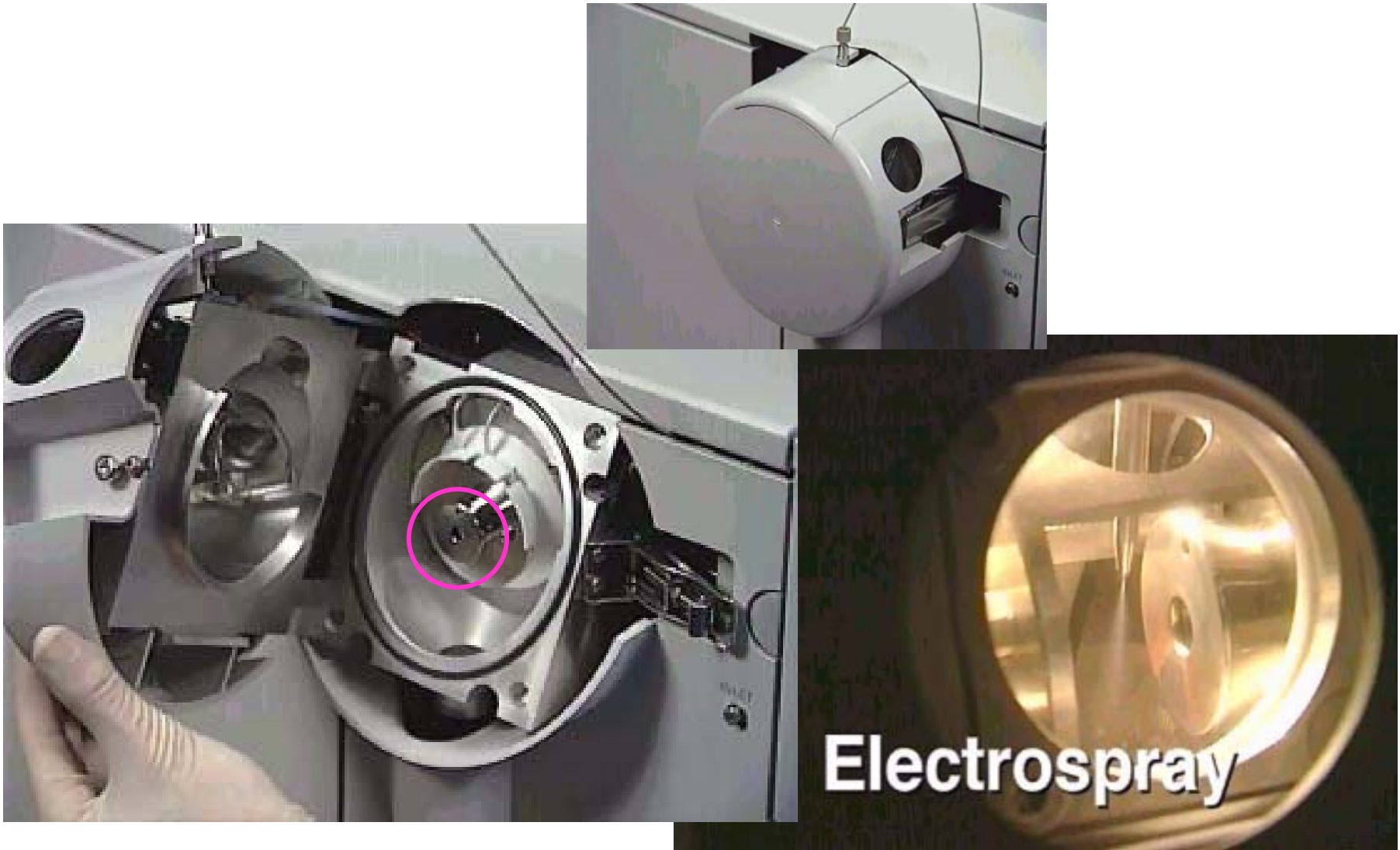
HPLC inlet
Nebulizer gas inlet
Nebulizer

Nebulizer tip
aimed at 90° to
inlet of MS



heated N₂
Countercurrent gas for
efficient evaporation and
desolvation

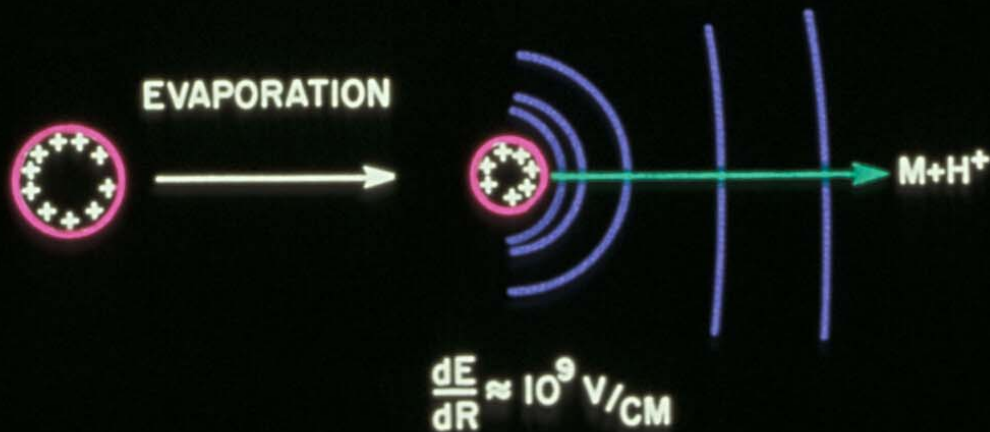
Orthogonal Spraying



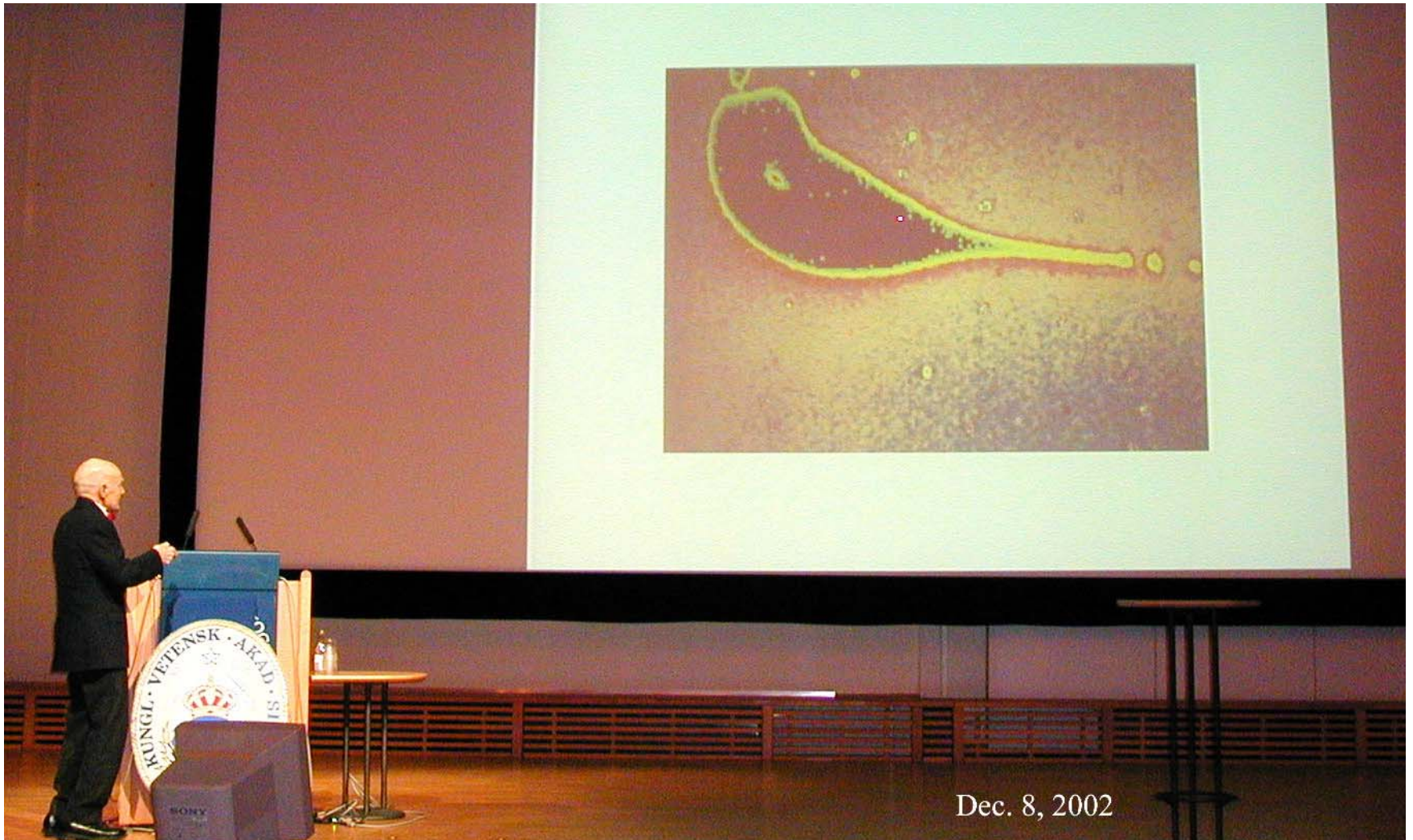
ELECTROSPRAY ION EVAPORATION MECHANISM



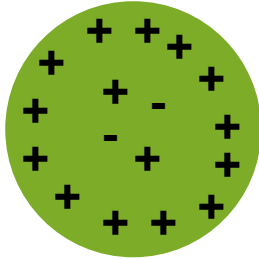
Rayleigh
Limit
Reached
Coulomb Explosions



Dr. John Fenn Nobel Lecture



What Caused Ion Suppression?

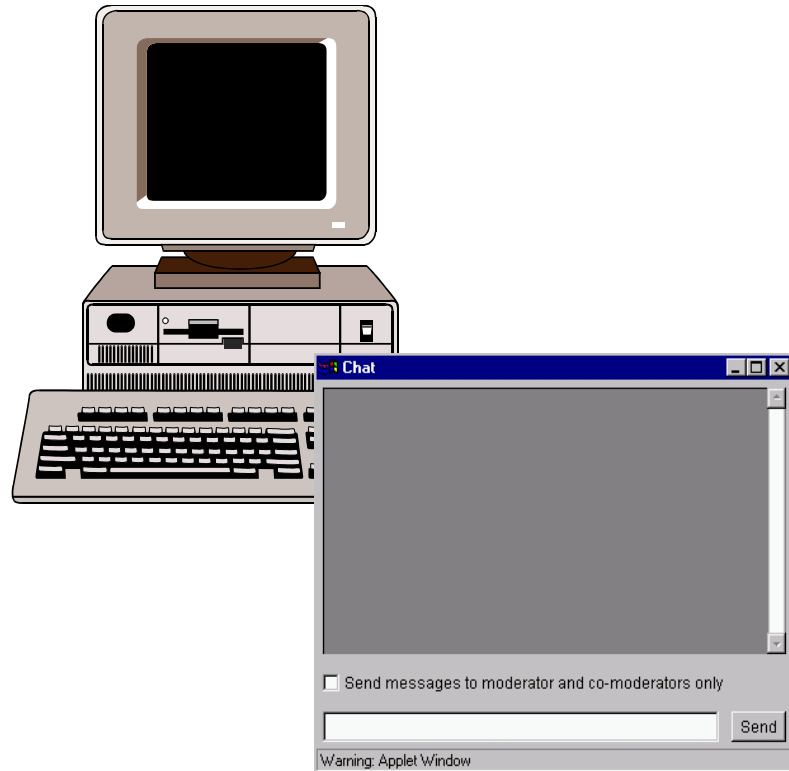


- Charges are on the surface
- Salts, matrix, and many ions are inside

- Competition between matrix components and analytes to get charges in the droplet
- Competition between matrix components and analytes to gain access to the droplet surface
- Surface tension
- Compound polarity (solvation)
-

Break Number 1

Please type your question into the Chat Box at any time during the presentation.



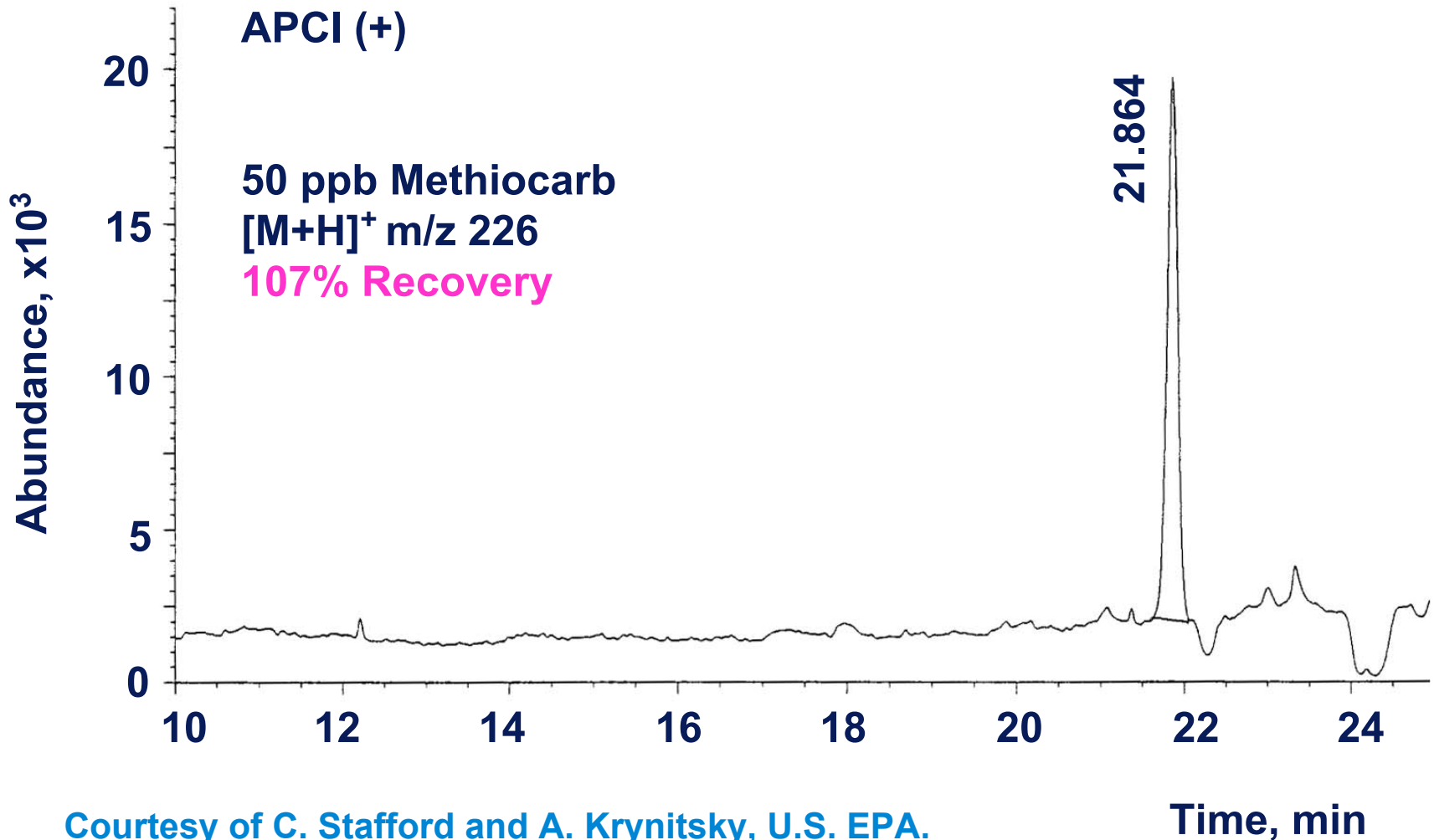
Outline

- What is ion/signal suppression and why
- **Approaches to minimize suppression**
 - Different ionization process
 - ESI source design
- Fruit and vegetable extract ESI results

Approaches to Minimize Suppression

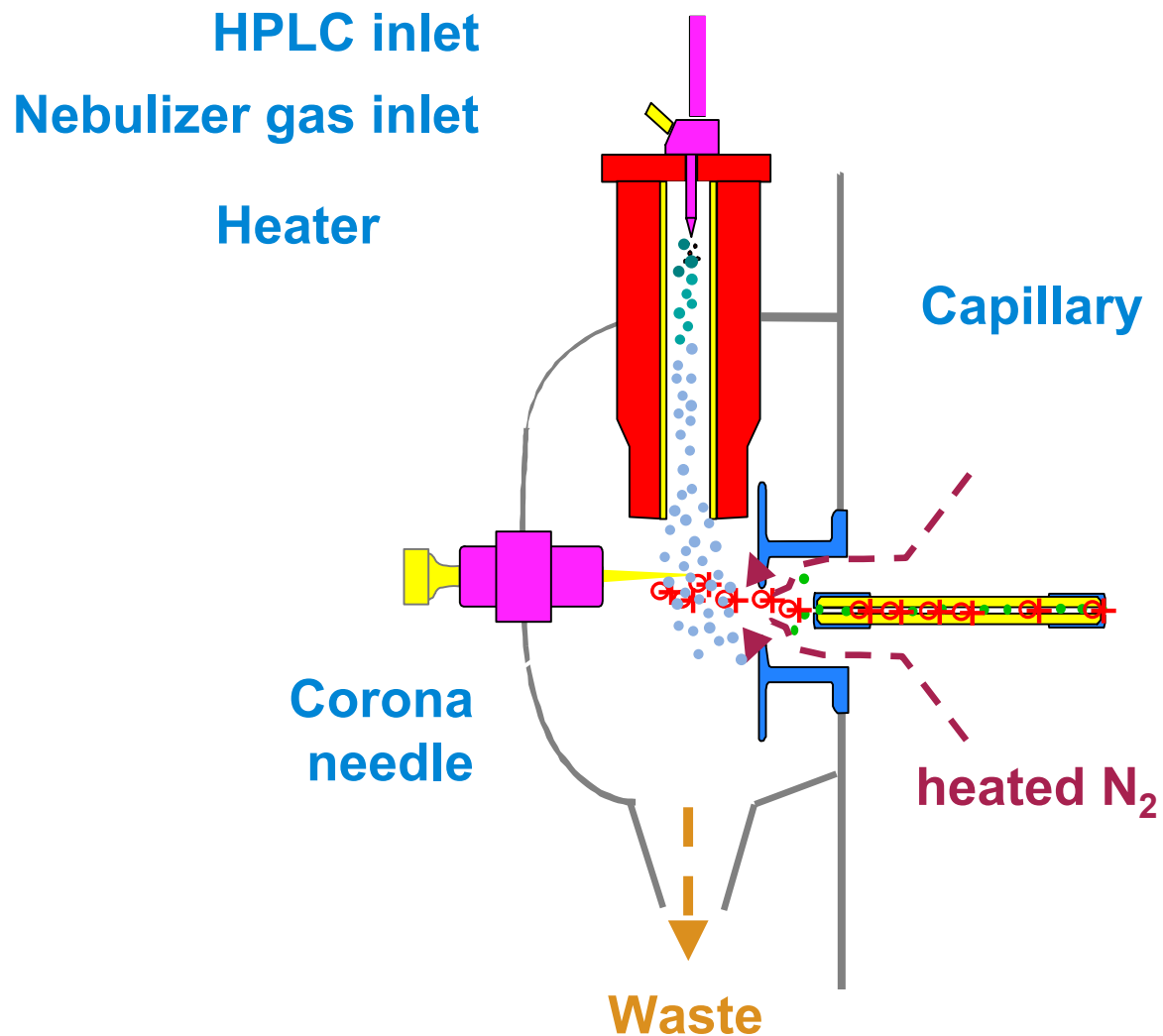
- More selective extraction procedure for matrix cleanup
- More chromatographic retention of analytes
- Changing buffer and its concentration
- Flow-splitting or nano-spray
- Different ionization process
- Post-column addition
- ESI source design
-

Signal Suppression Minimized in APCI Mode

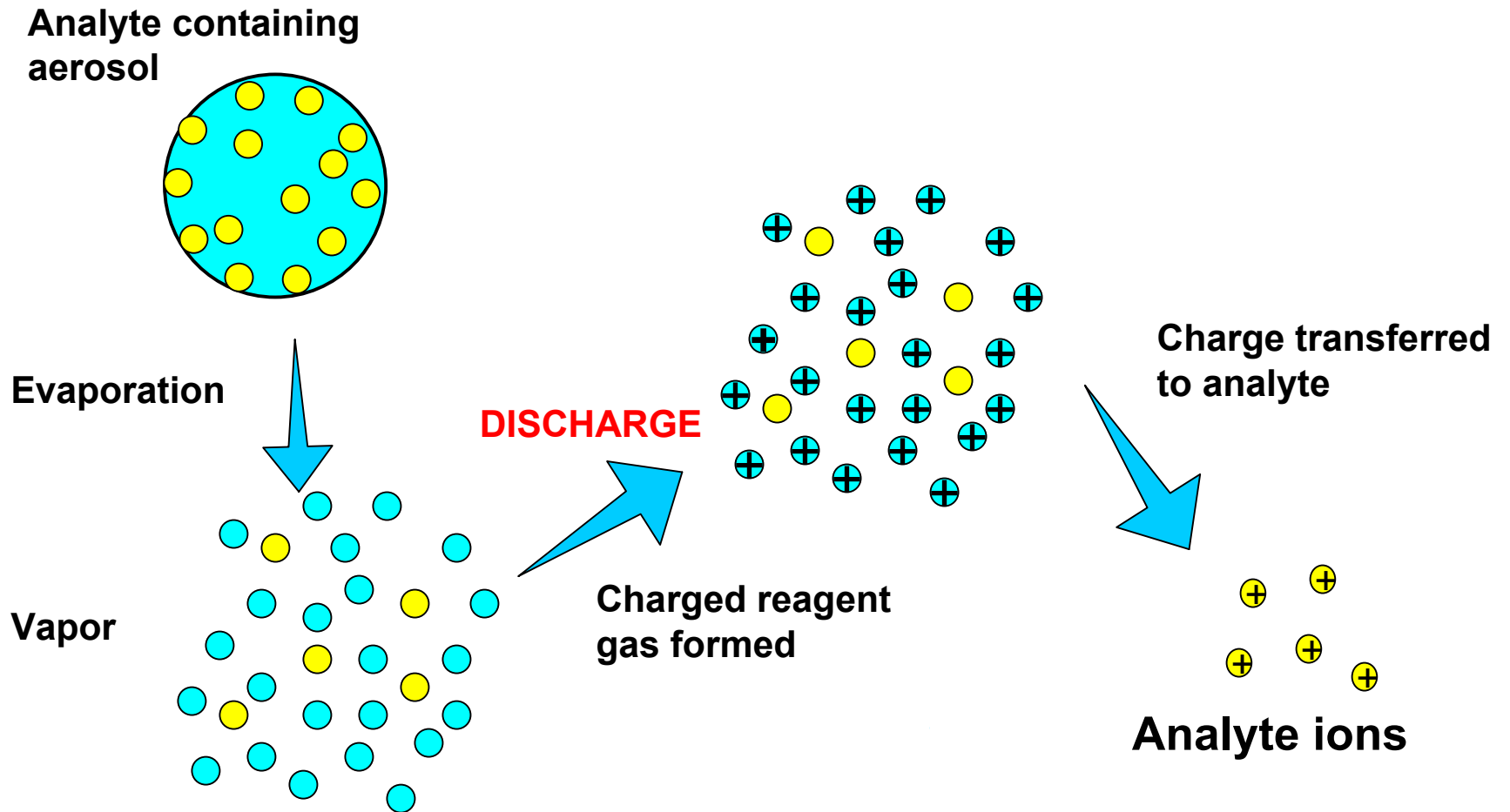


Courtesy of C. Stafford and A. Krynitsky, U.S. EPA.

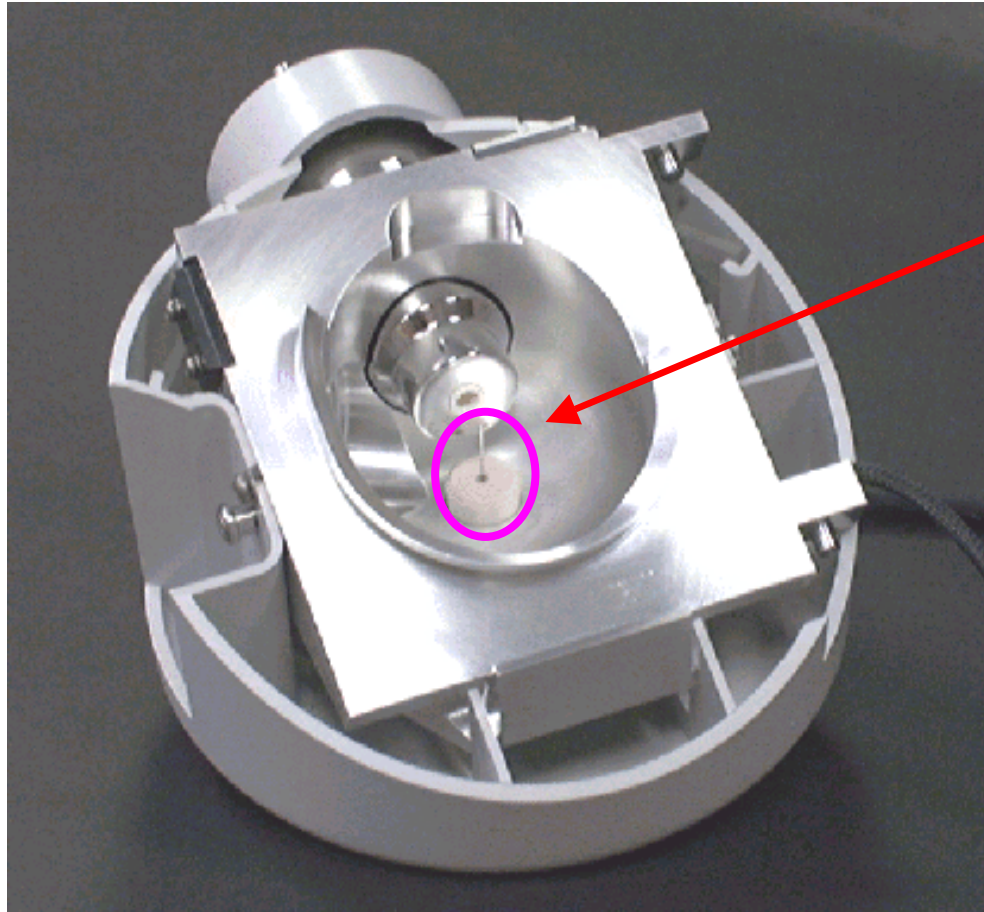
APCI Source



APCI Process



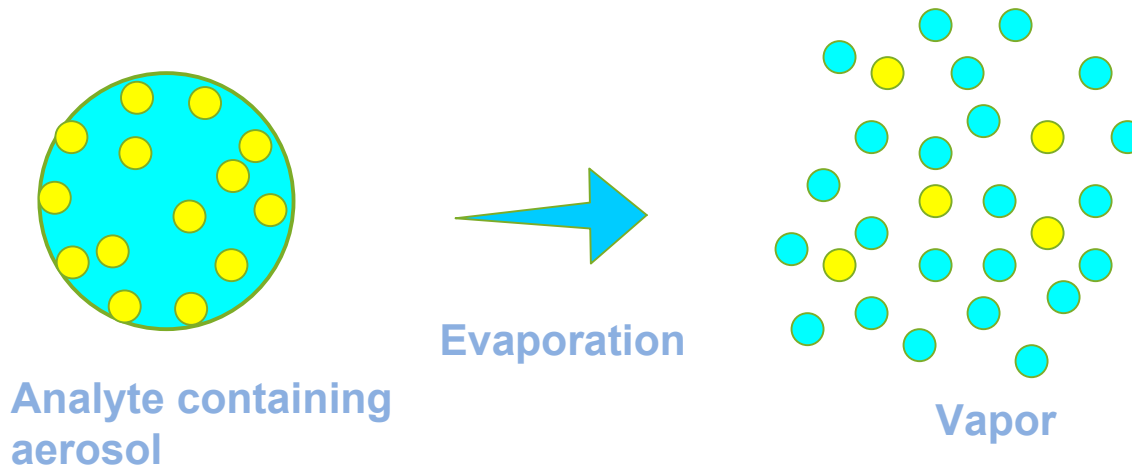
Agilent 1100 LC/MSD APCI Source



Corona Needle

Ionize the gas with a discharge

Ion Suppression in APCI



- Competition between matrix components and analytes to get charges in the droplet -- **ELIMINATED**
- Competition between matrix components and analytes to gain access to the droplet surface -- **REDUCED**
- Surface tension -- **REDUCED**
- Compound polarity (solvation) -- **REDUCED**

APCI-LC/MS

Advantages

- Complementary to API-Electrospray for less polar analytes
- Good sensitivity for compounds of intermediate MW and polarity
- Less sensitive to solution chemistry effects than API-ES

Disadvantages

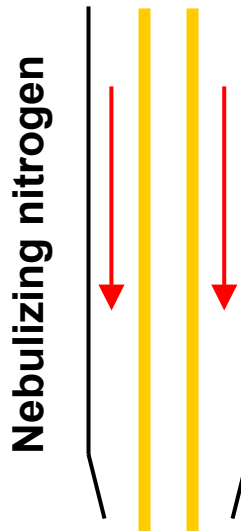
- Less useful for thermally labile compounds
- Requires some compound volatility



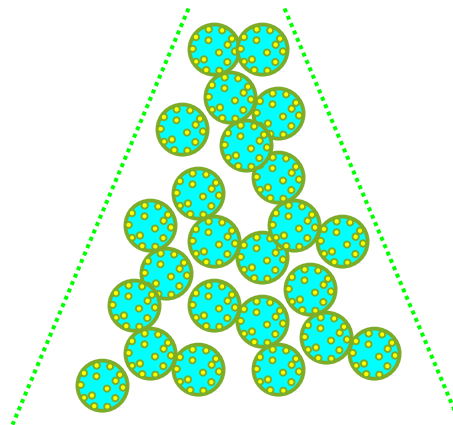
Nebulizing the Sample

Polymeric Damping Mechanism

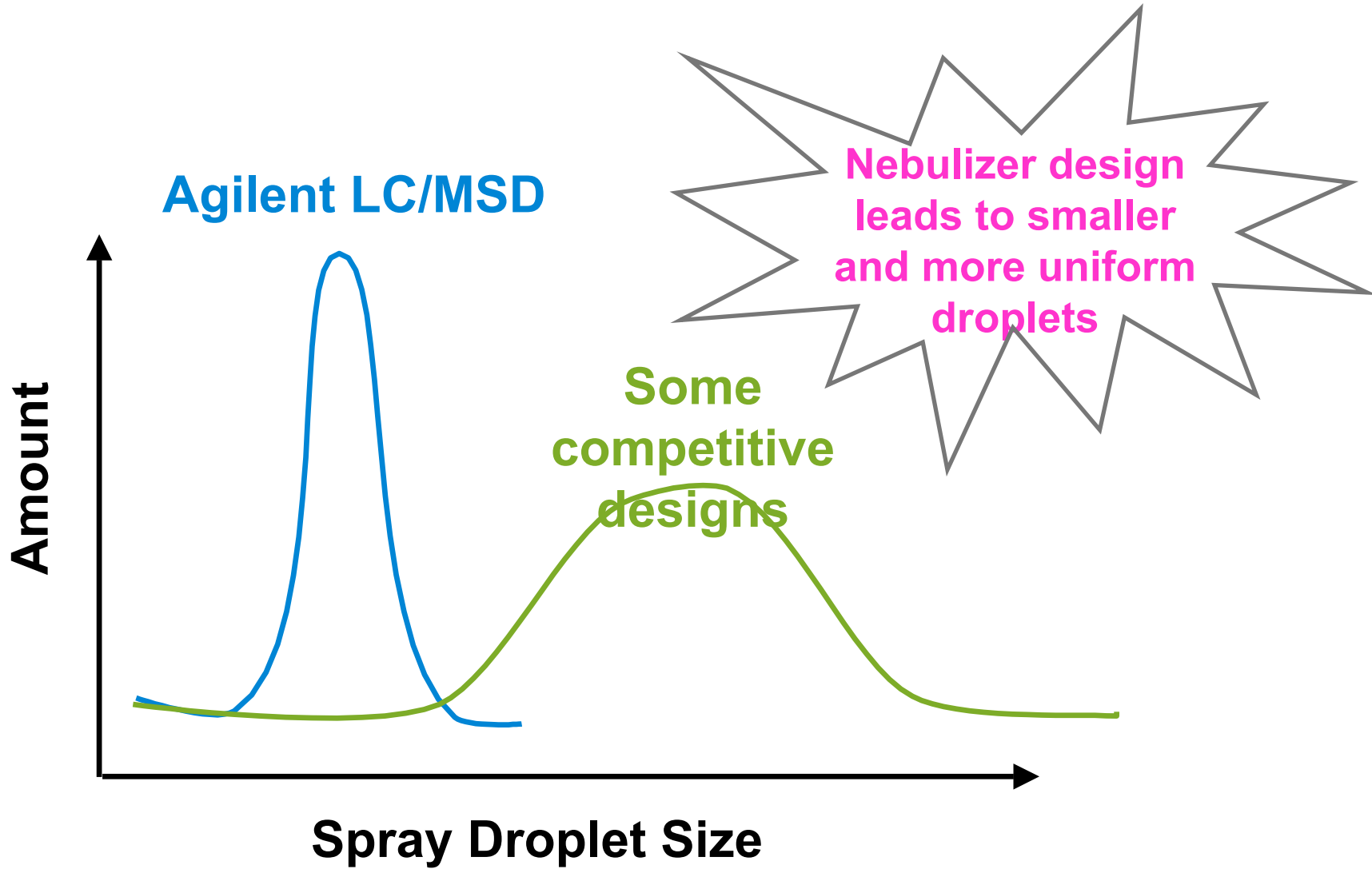
Rigid stainless steel
eluent delivery capillary



Micromachined tip

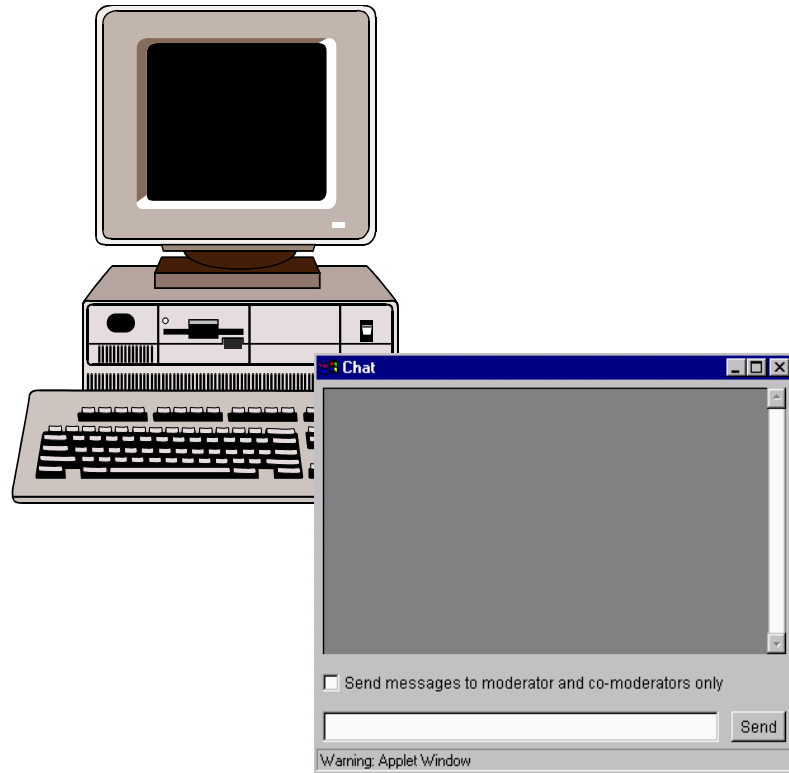


ESI Droplets Distribution



Break Number 2

Please type your question into the Chat Box at any time during the presentation.



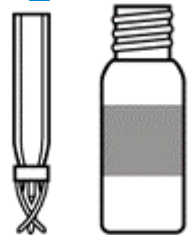
Outline

- What is ion/signal suppression and why
- Approaches to minimize suppression
 - Different ionization process
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- **Fruit and vegetable extract ESI results**

Samples Preparation

MATRIX EXTRACTS: Beans, Carrots, Corn, Endive, Escarole, Grapes, Lettuce, Oranges, Potatoes, Squash, Tomato, Zucchini
(courtesy of Walter Hammack and Donna Kilpatrick at Florida Dept of Agriculture & Consumer Services)

- Pipette 80 μL matrix solution into a 1.5-mL high-recovery vial
- Air dry in hood
- Add 80 μL of the 40 ppb standard solution in MeOH
- Shake and inject 2 μL



Standards: Thiabendazole, Methomyl, Imazalil

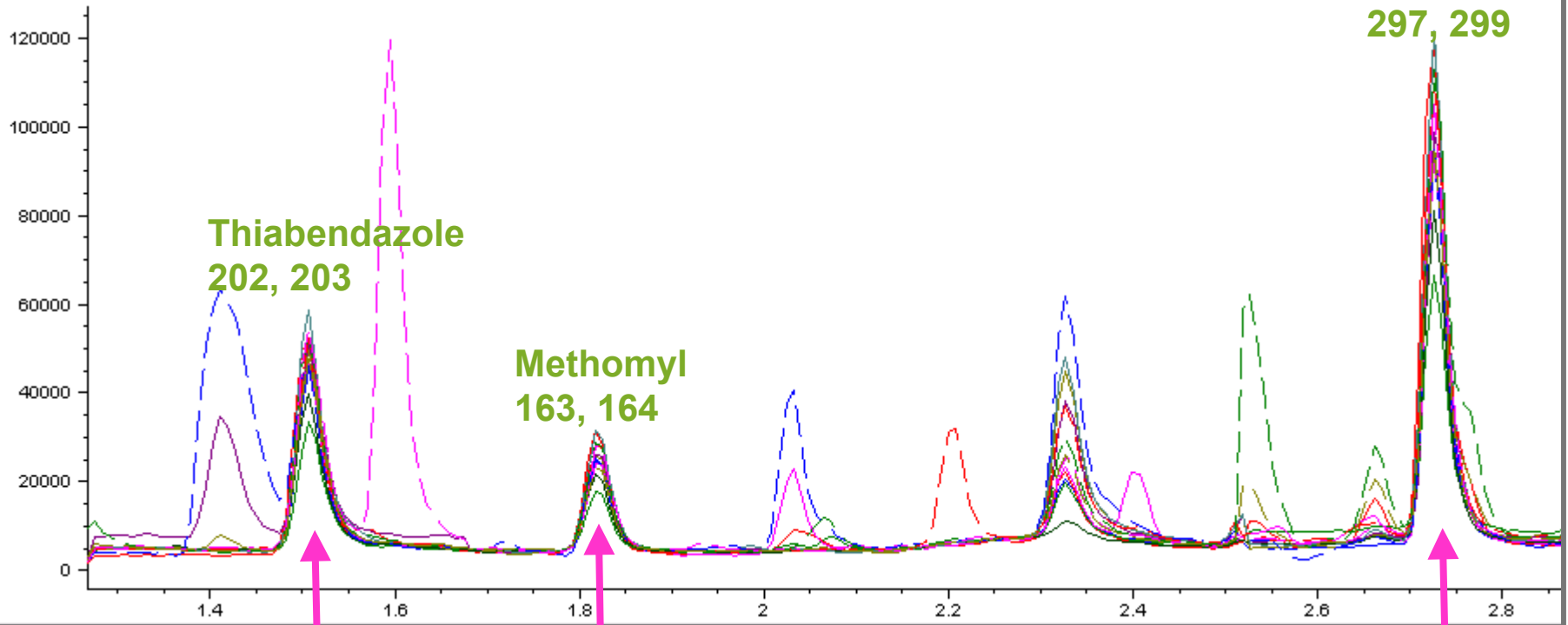
Ion Suppression?

- MSD1 TIC, MS File (FLAG522\0-04PPMB.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\BEANS.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\CARROTX.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\CORNA.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\ENDIVE.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\ESCAROLE.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\GRAPESX.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\LETTUCE.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\ORANGED.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\POTATO.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\SQUASHA.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\TOMATO.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"
- MSD1 TIC, MS File (FLAG522\ZUCCHAX.D) API-ES, Pos, SIM, Frag: 70 (TT), "pos SIM"

(2 µL of 40 ppb injected)

All traces in the SAME Scale

(SIM)

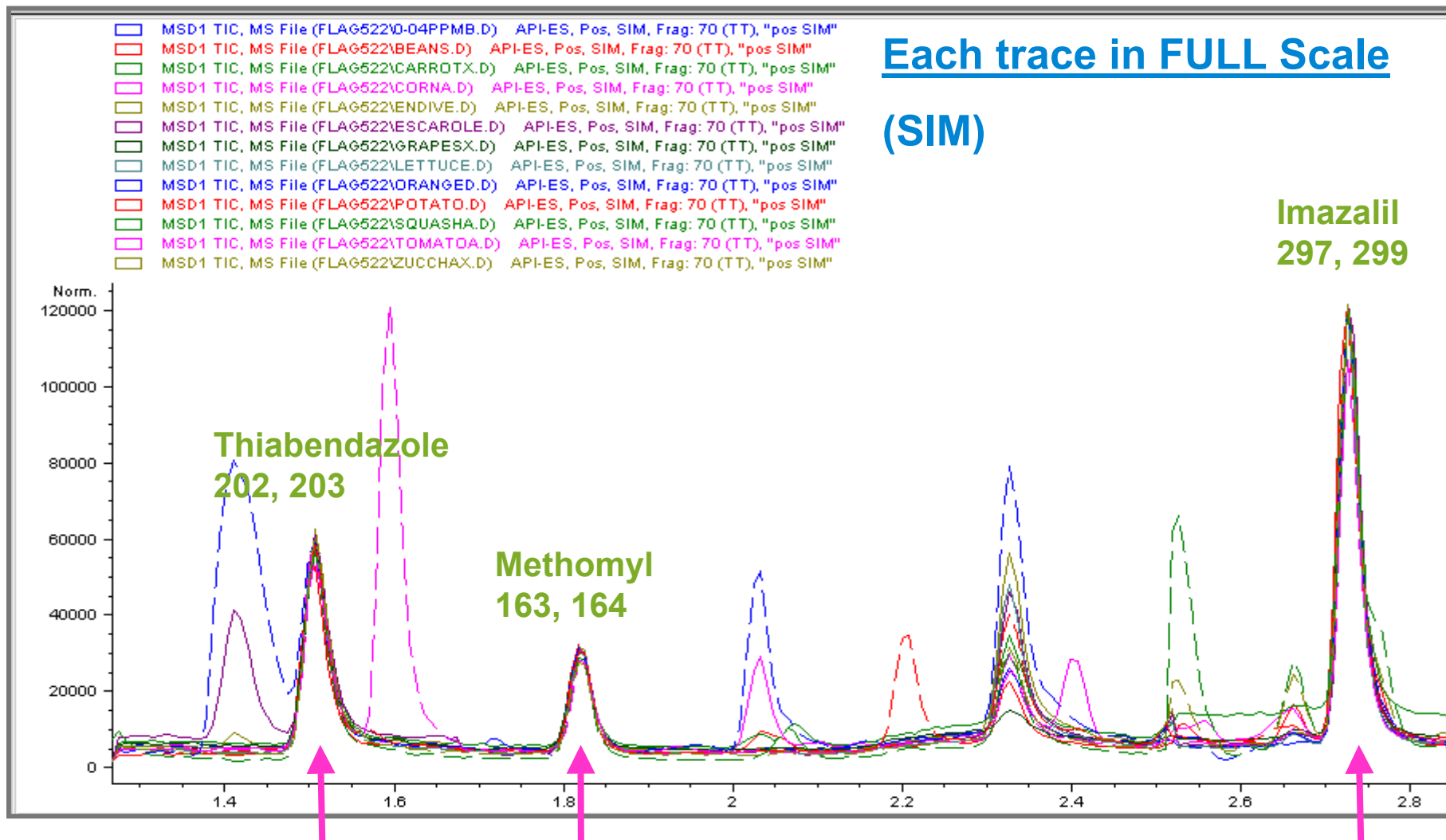


Area %RSD = 20%

Area %RSD = 19%

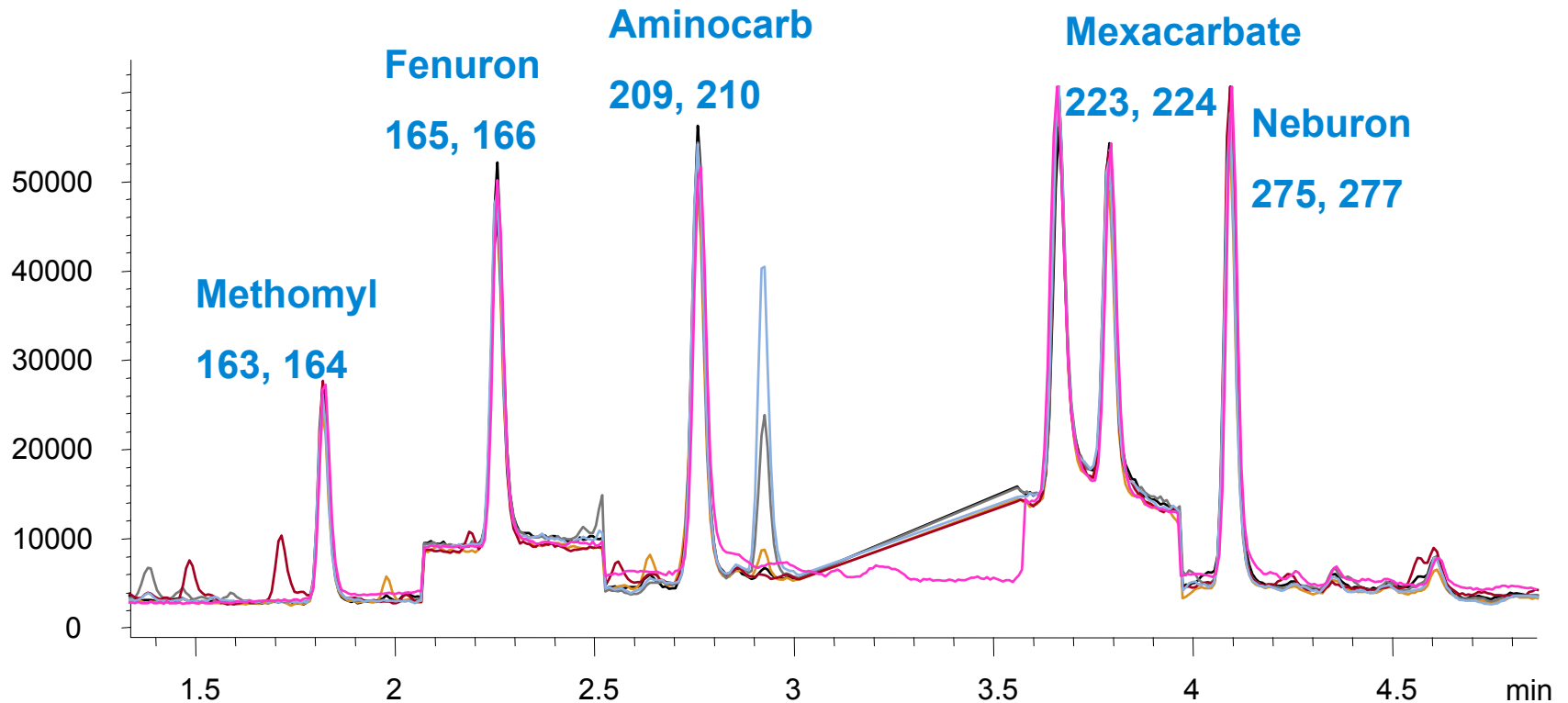
Area %RSD = 20%

Ion Suppression?



BEANS-GR, LETTUCE, SQUASH-Y, TOMATO,
ZUCCHINI, 40PPB(MeOH) (80 pg on column)

Each trace in Full Scale



2 μ L of 1 ppm 5-std mix in MeOH was added to 48 μ L of matrix solution. (1 ppm / 25 = 40 ppb)

Summary

- Signal suppression is sometimes due to the ionization process of Electrospray Ionization
- Different ionization process (e.g., APCI) could minimize the suppression
- The electrospray nebulizer design could play an important role in minimizing the suppression
 - Polymeric damping mechanism
 - Small and uniform droplets

References

- More selective extraction procedure
Matuszewski BK, Constanzer ML, Chavez-Eng CM, ANAL CHEM 70 (5): 882-889 MAR 1 1998
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