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Thermally Assisted Vapour Introduction Atmospheric Pressure Photoionization MS/MS (TAVI APPI MS/MS)

Winner

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Outline

Context of research

Atmospheric Pressure Photo Ionization (APPI)

Apparatus

Results

Future work

Big Picture

Rapid analysis, no clean up, no separation

Specific Analytical Challenge

Synthetic, specifically inorganic, chemists needed quick confirmation of synthesis

Some compounds insoluble usual solvents

Noticed target compounds had aromaticity

MS been widely used

EI GC volatile high energy electrons result in fragmentation

ESI only for ions in solution

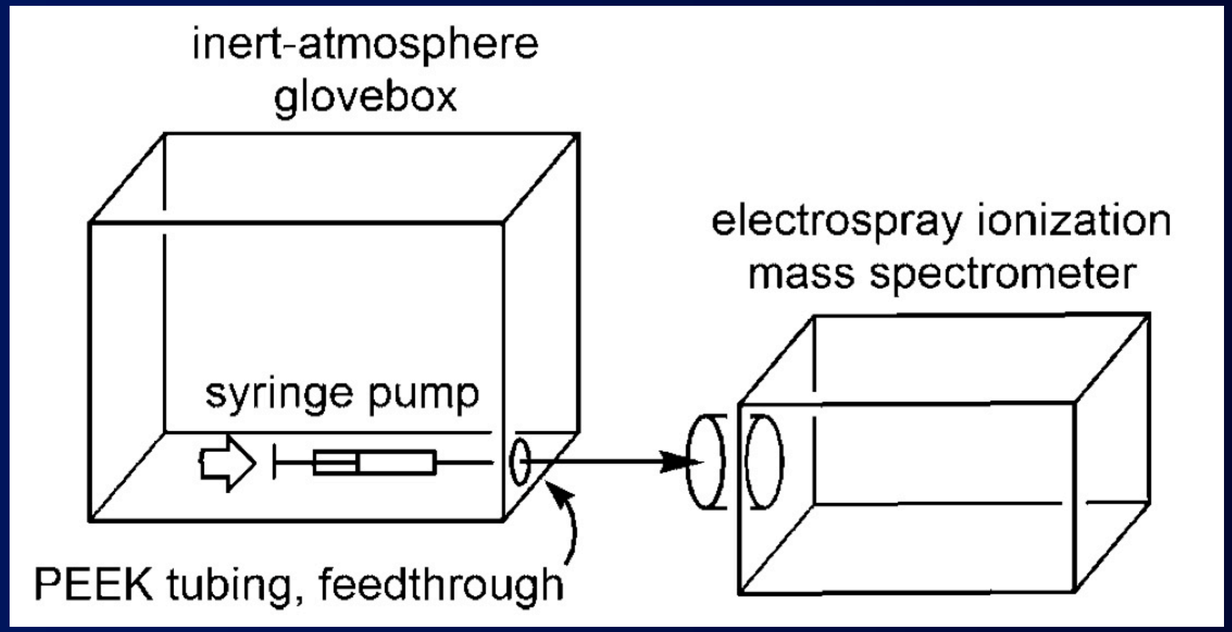
APCI competitive gas phase reactions with matrix effects, requiring separation

MALDI low sensitivity, high background

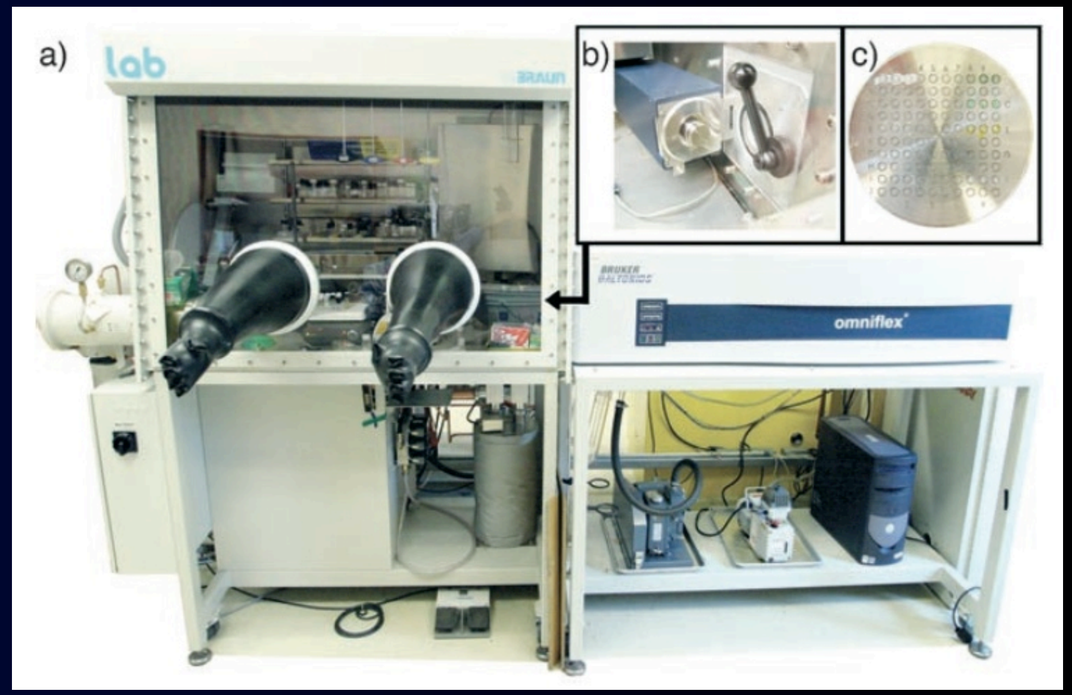
LDI competitive gas phase reactions

Inorganic uses of MS

Some recently reported apparatus



Samples Dissolved in DCM
ESI MS McIndoe (U. Vic)



MALDI- TOF
Fogg (U of O.)

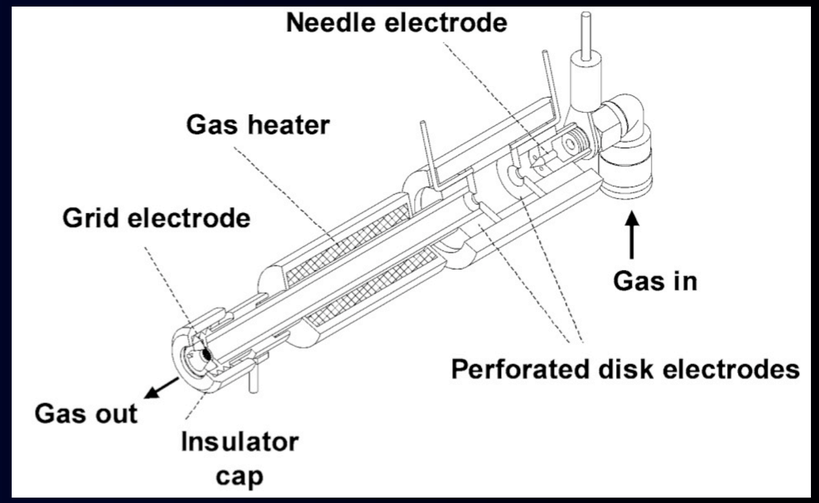
Direct Introduction Methods

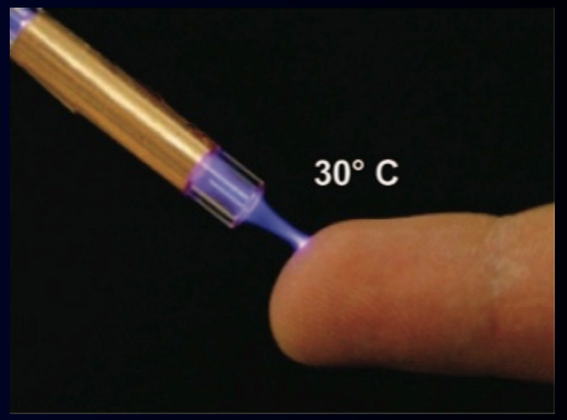
DART - Direct Analysis in Real Time
Electrical discharge in He

LTP - Low Temperature Discharge
Dielectric barrier discharge in air

GD - Glow discharge
Electrical discharge in He

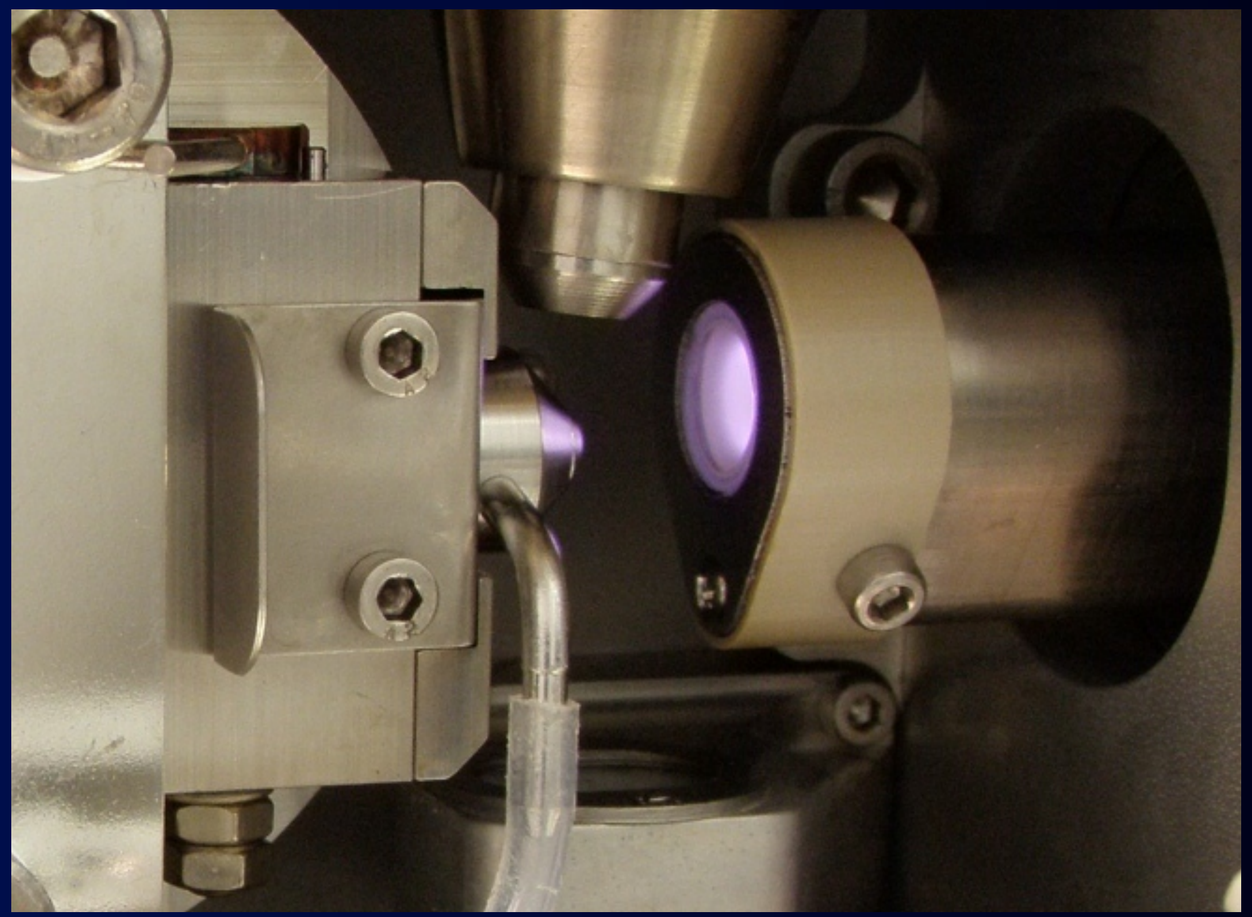
all have poorly defined mechanisms





Atmospheric Pressure Photo ionization

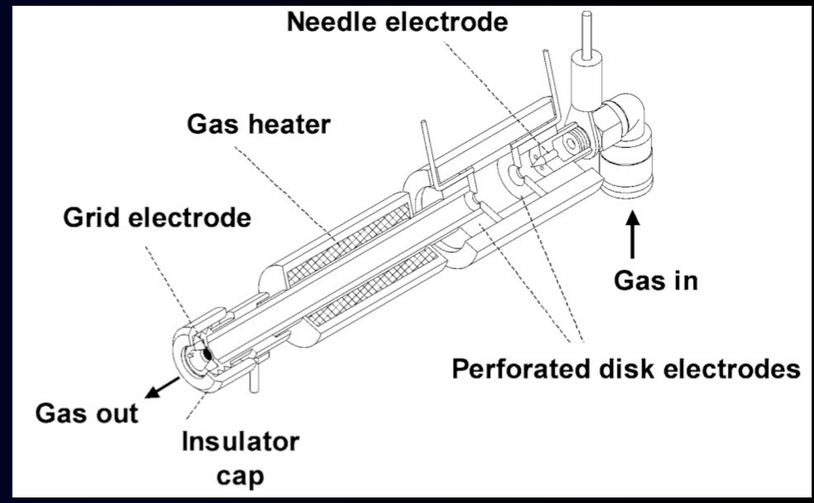
APPI - electrical discharge in Krypton



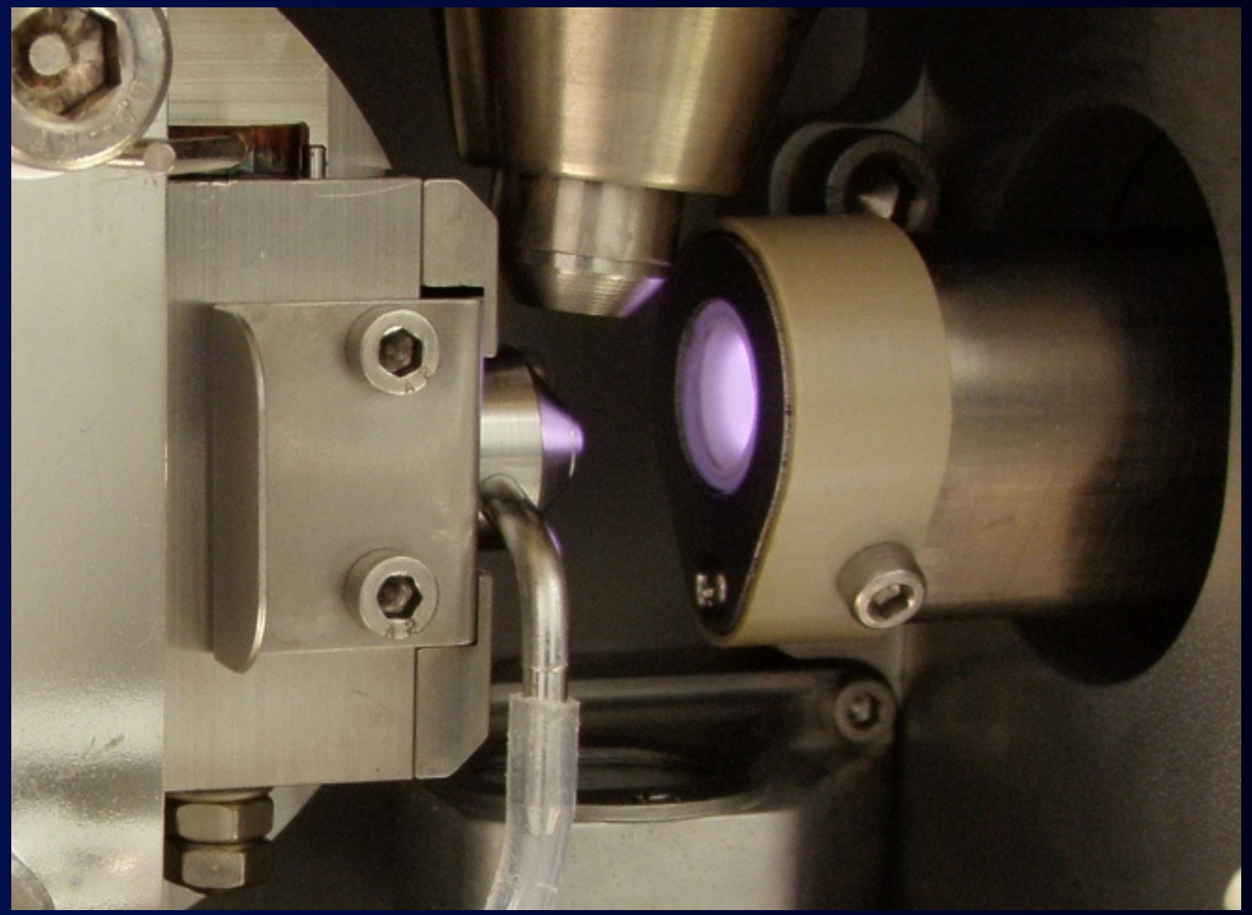
Atmospheric Pressure Photo ionization

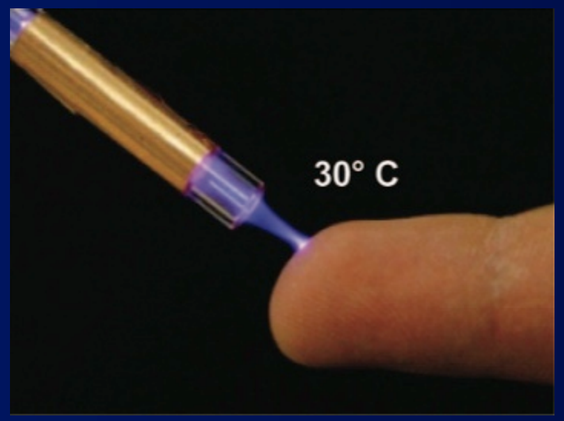
APPI - electrical discharge in Krypton

APPI has a LiF window, DART, LTD, GD's don't



DART





LTD

GD

APPI mechanisms

Primary APPI

$h\nu + A \rightarrow \mathbf{A^+} + e^-$ photoionization (+) tive

Secondary APPI (PICI)

$h\nu + D \rightarrow D^+ + e^- \rightarrow D^+ + A \rightarrow A^+ + D$ dopant assisted (+) tive

$e^- + D \rightarrow D^- \rightarrow D^- + A \rightarrow A^- + D$ dopant assisted (-) tive

$e^- + A \rightarrow A^-$ photo induced e^- capture (-) tive

$h\nu + C_7H_8 \rightarrow C_7H_8^{\bullet+} + e^- \rightarrow C_7H_8^{\bullet+} + (CH_3OH)_3 \rightarrow C_7H_7^{\bullet} + (CH_3OH)_3H^+$

$(CH_3OH)_3H^+ + A \rightarrow \mathbf{AH^+} + 3CH_3OH$

Atmospheric Pressure Photo Ionization

Ions formed cold (excess energy in the departing electron)
stable molecular ion

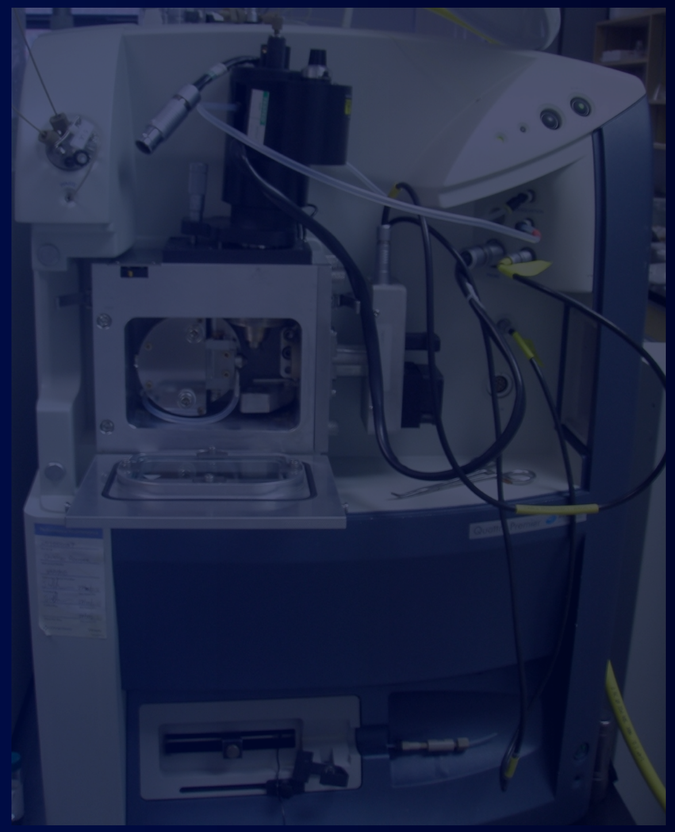
True ionization technique (ESI ion atomization)

Not as matrix dependent (APCI)

Photo Induced Chemical Ionization (PICI) radicals underestimated

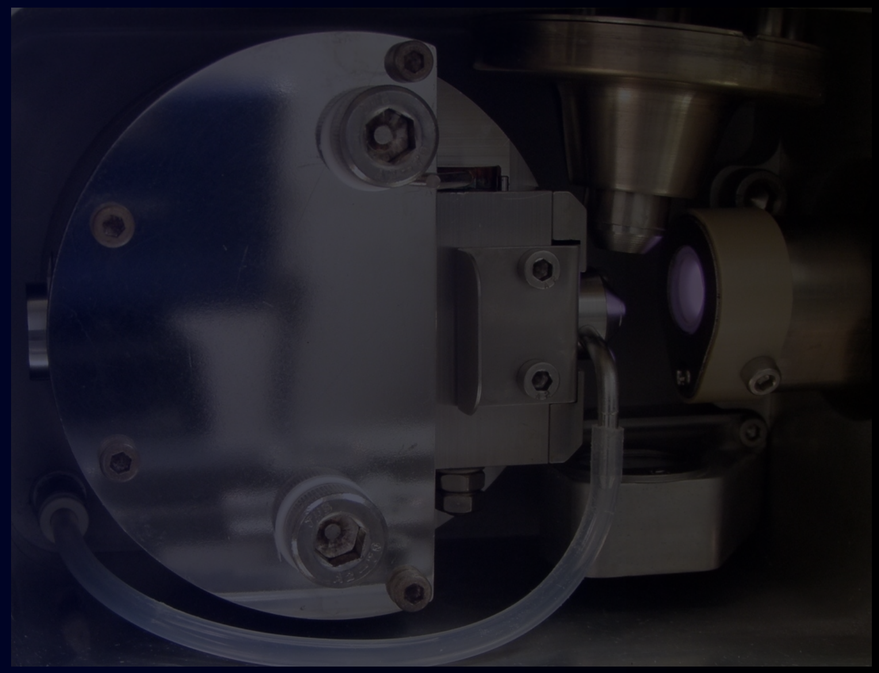
With solvent: $M+H^+$
without Solvents mostly M^+

Waters MS/MS



Waters MS/MS
naked

ionization chamber



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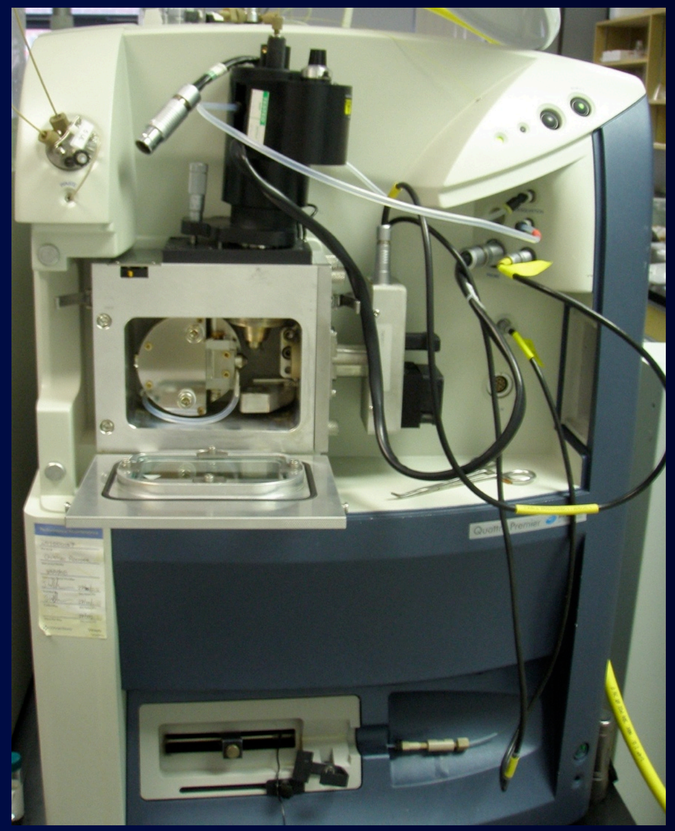

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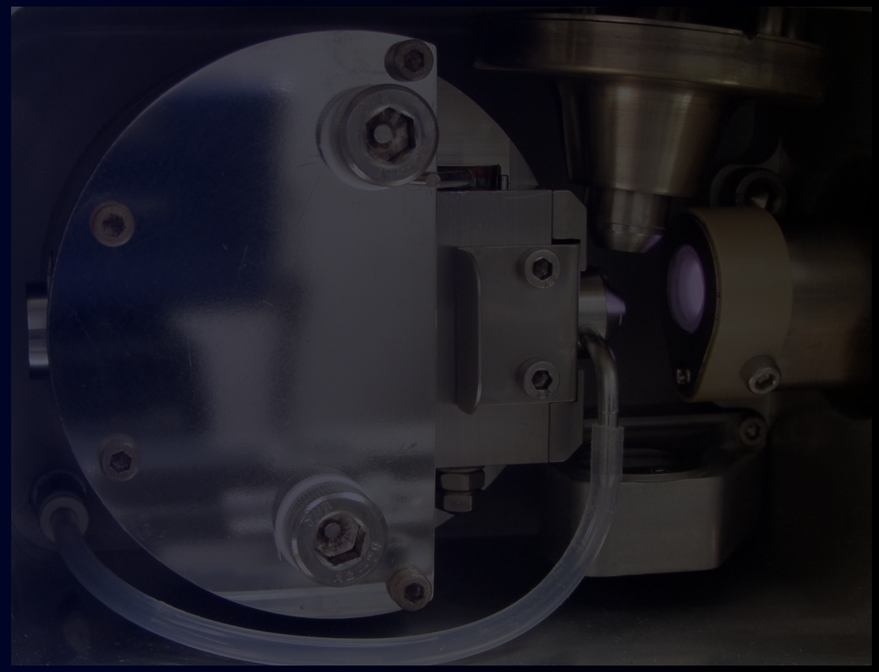

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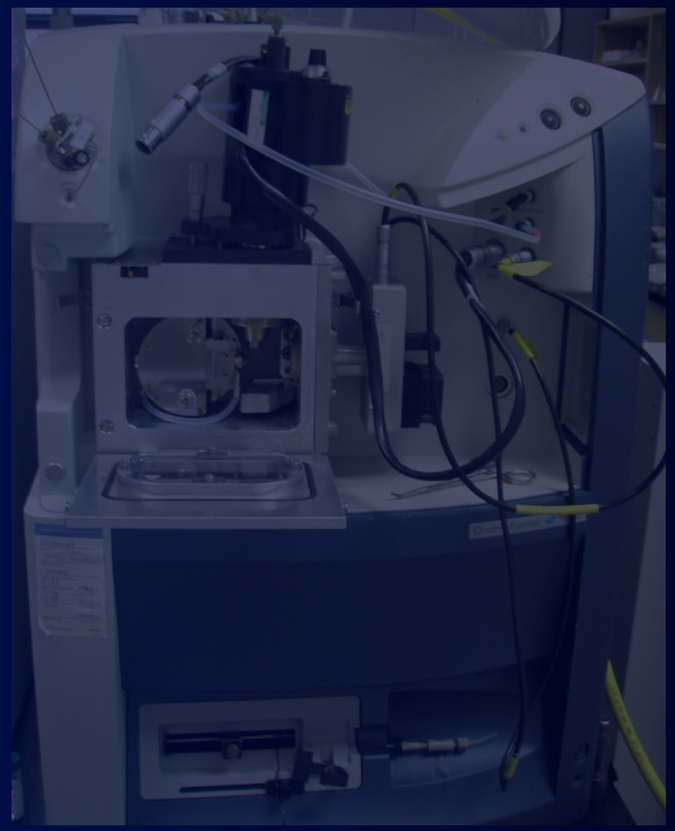

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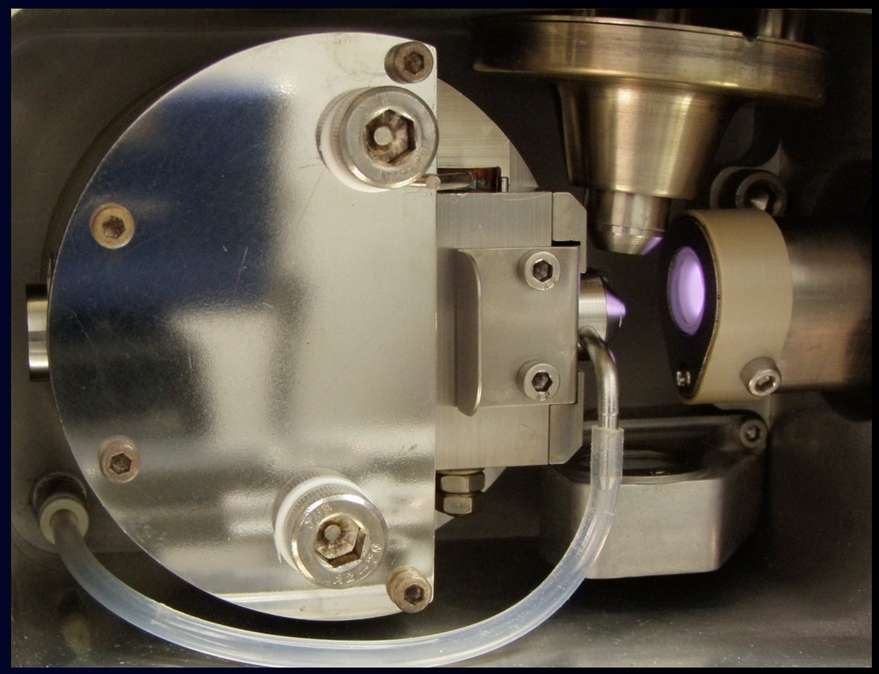
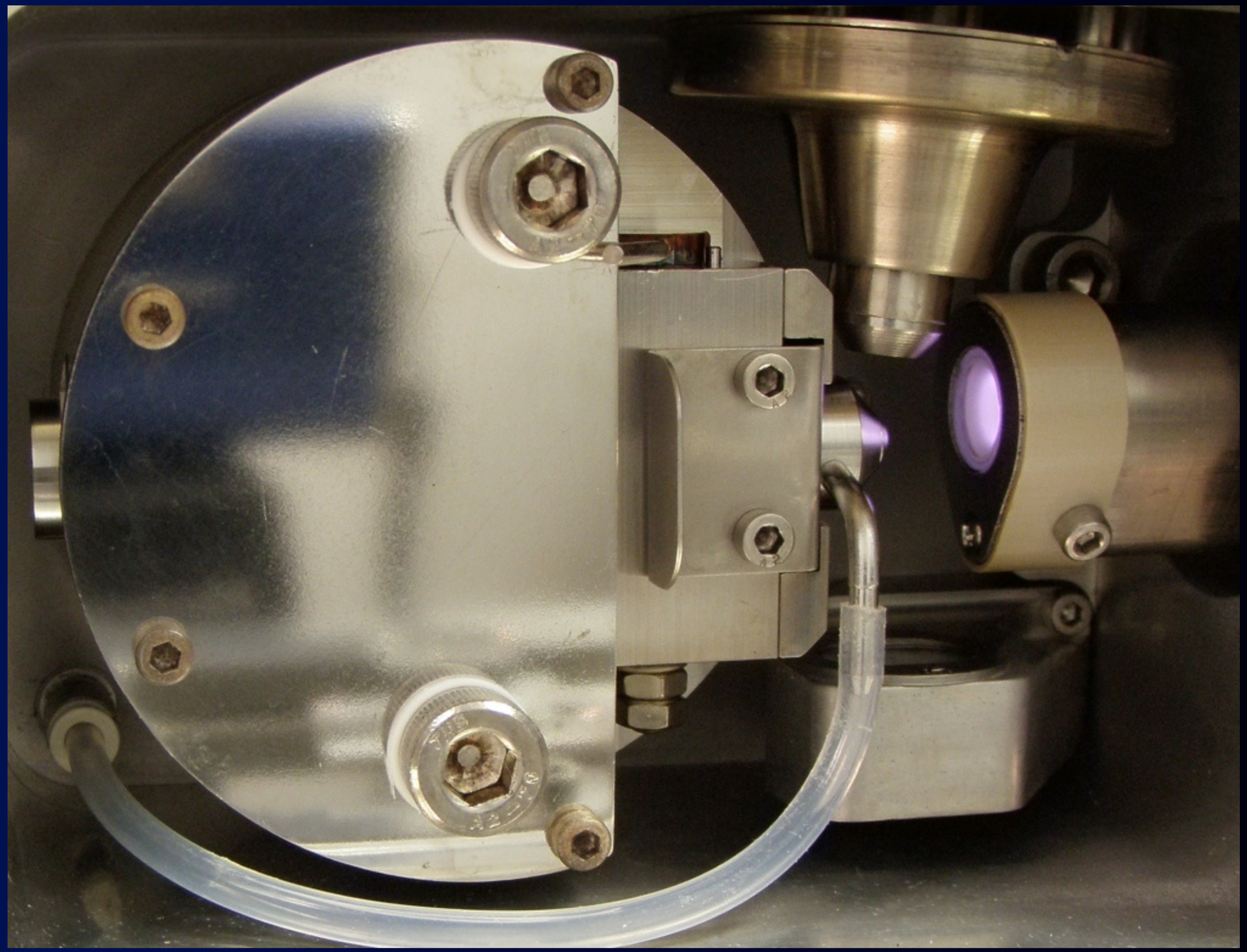
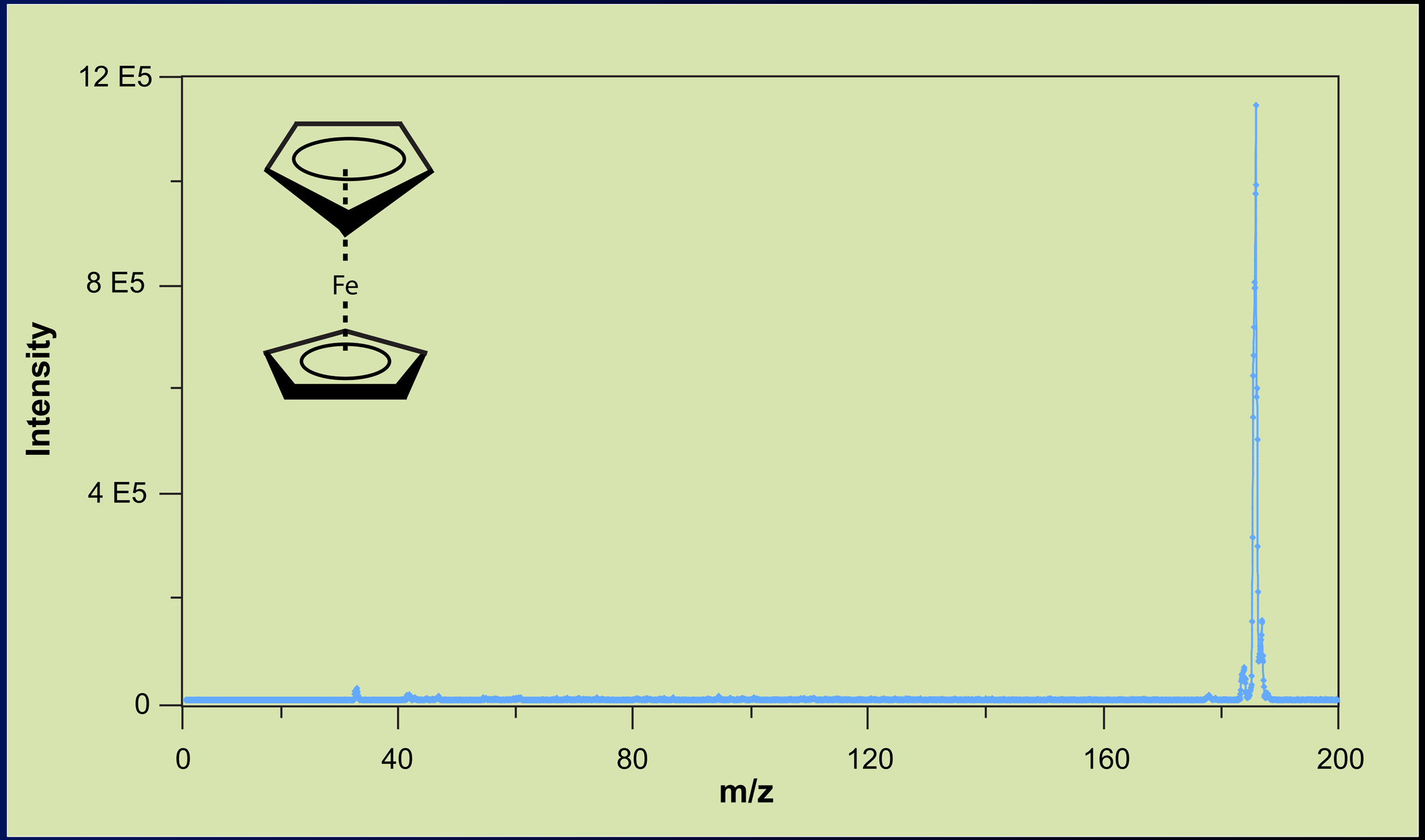


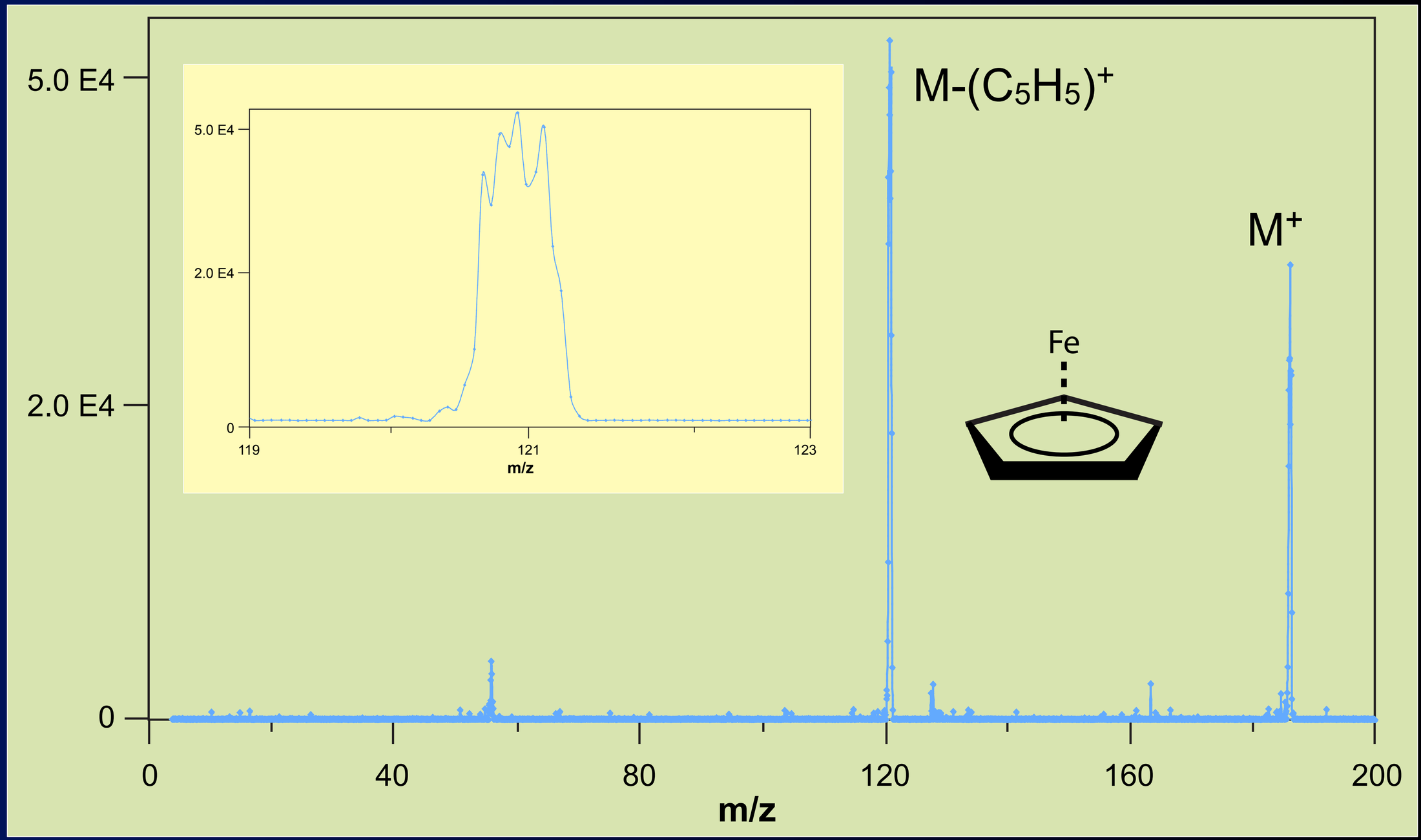



MUX

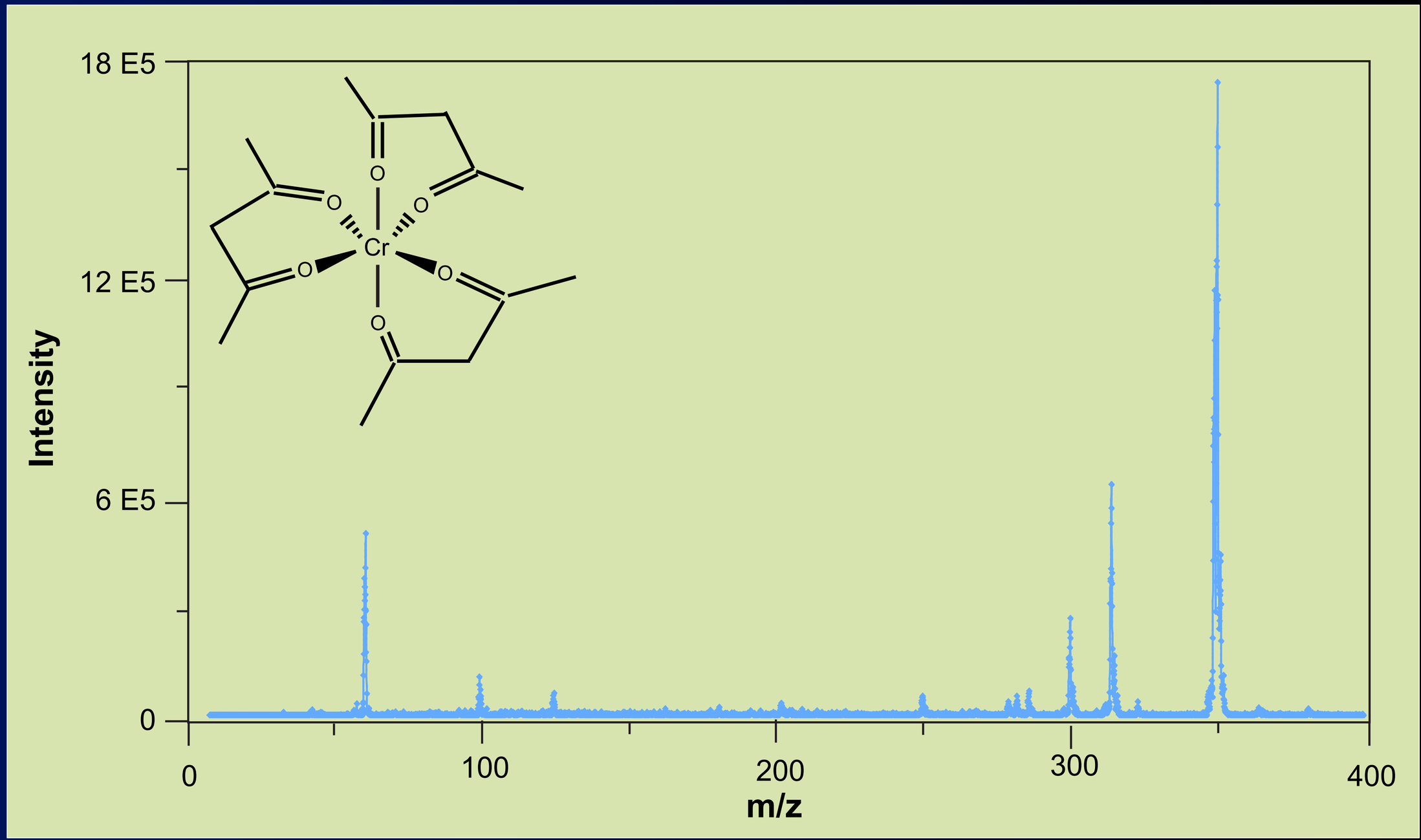
Ferrocene $Fe(C_5H_5)_2$ 186.04 g/mol



MS/MS of Ferrocene $Fe(C_5H_5)_2$ 186.04 g/mol



$Cr(acac)_3$ 349.3 g/mol



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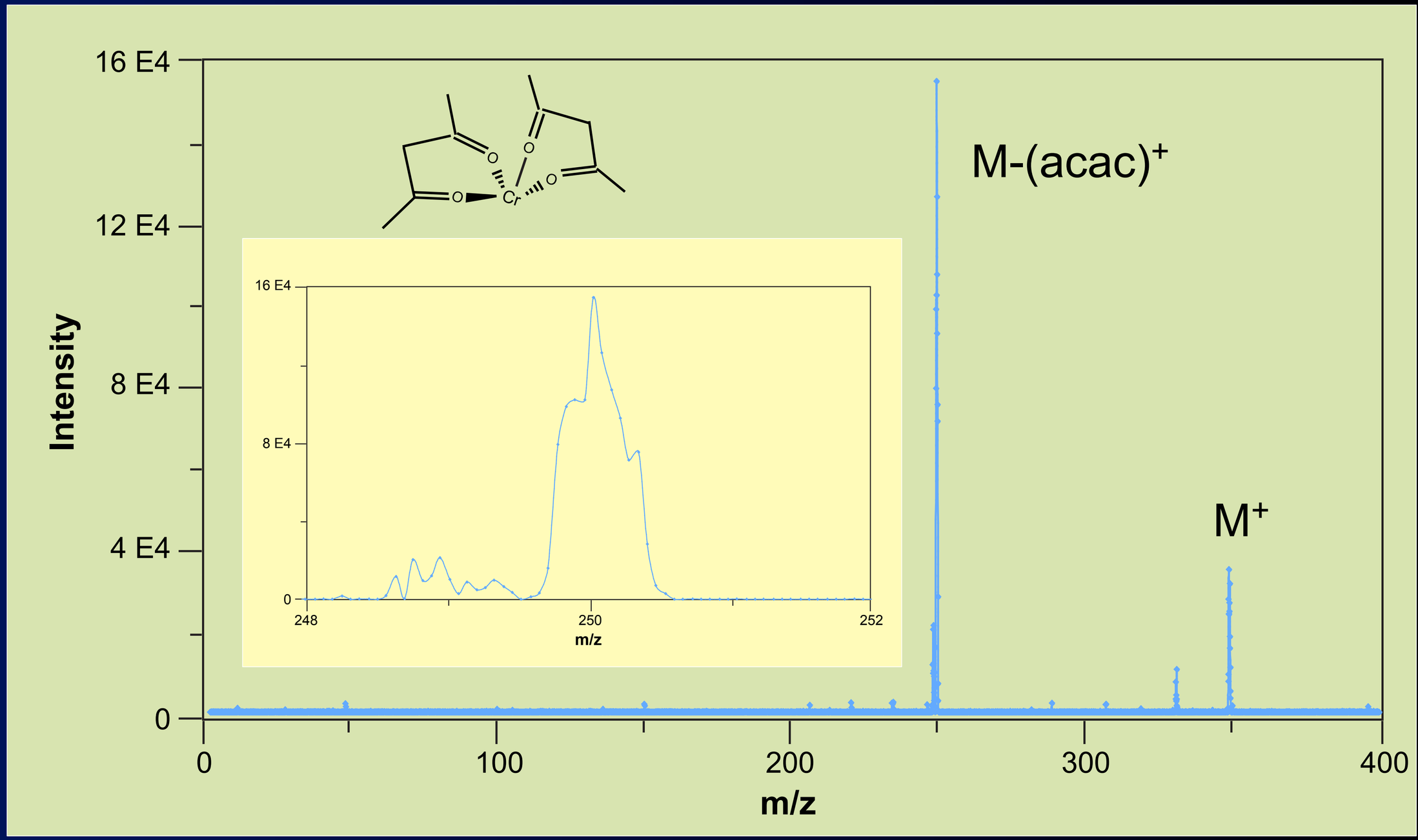
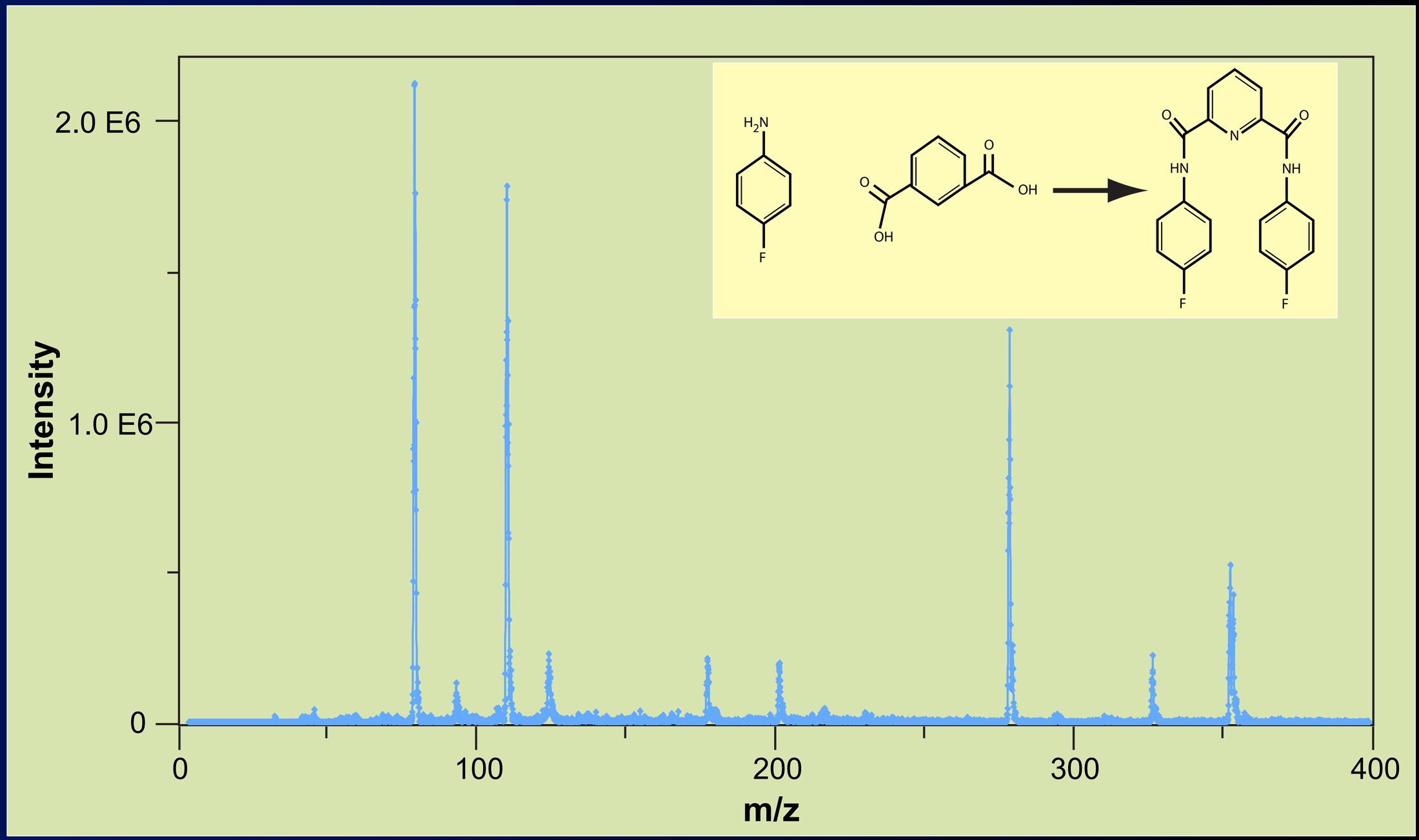


LG 113 353.22 $C_{19}H_{13}F_2N_3O_2$



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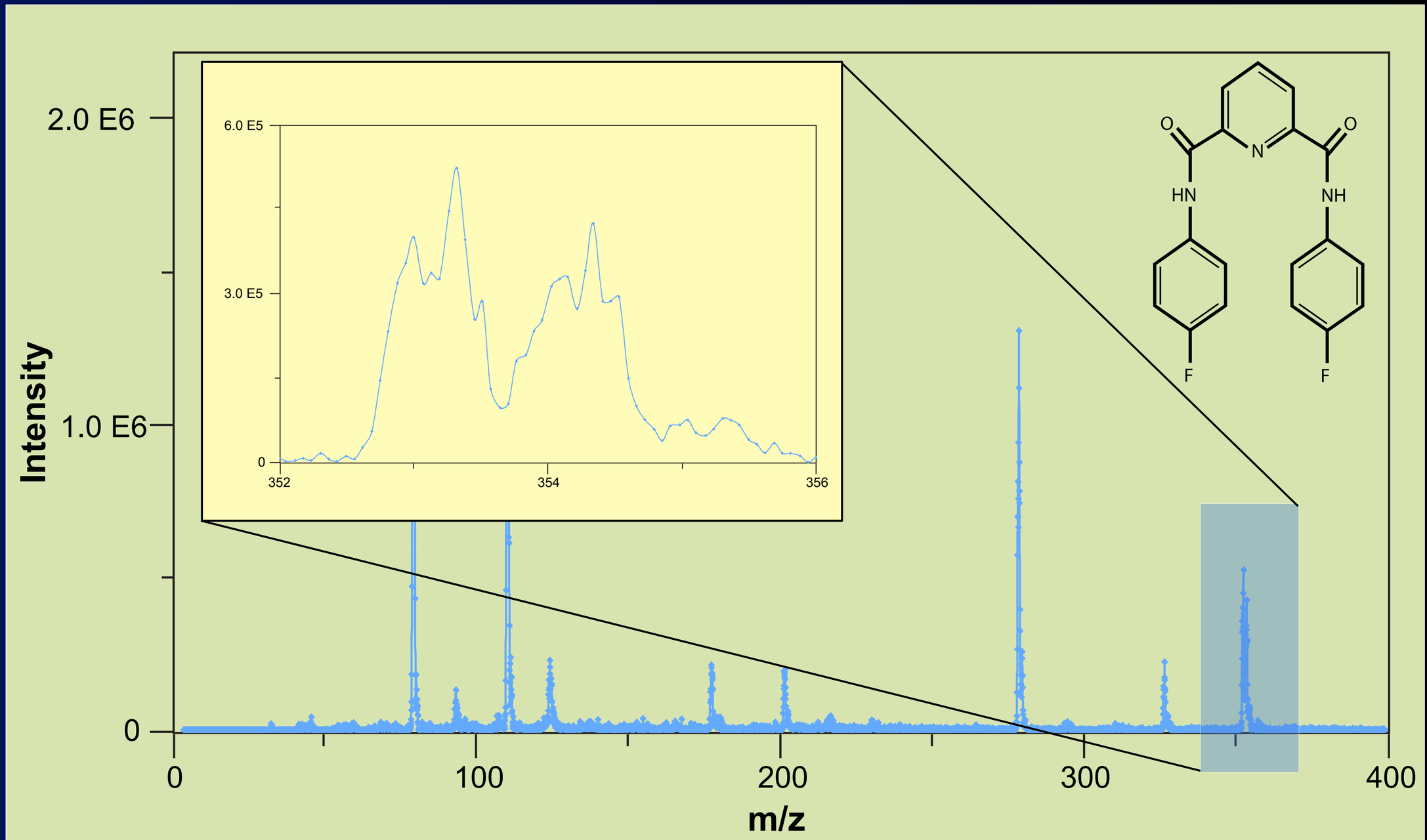

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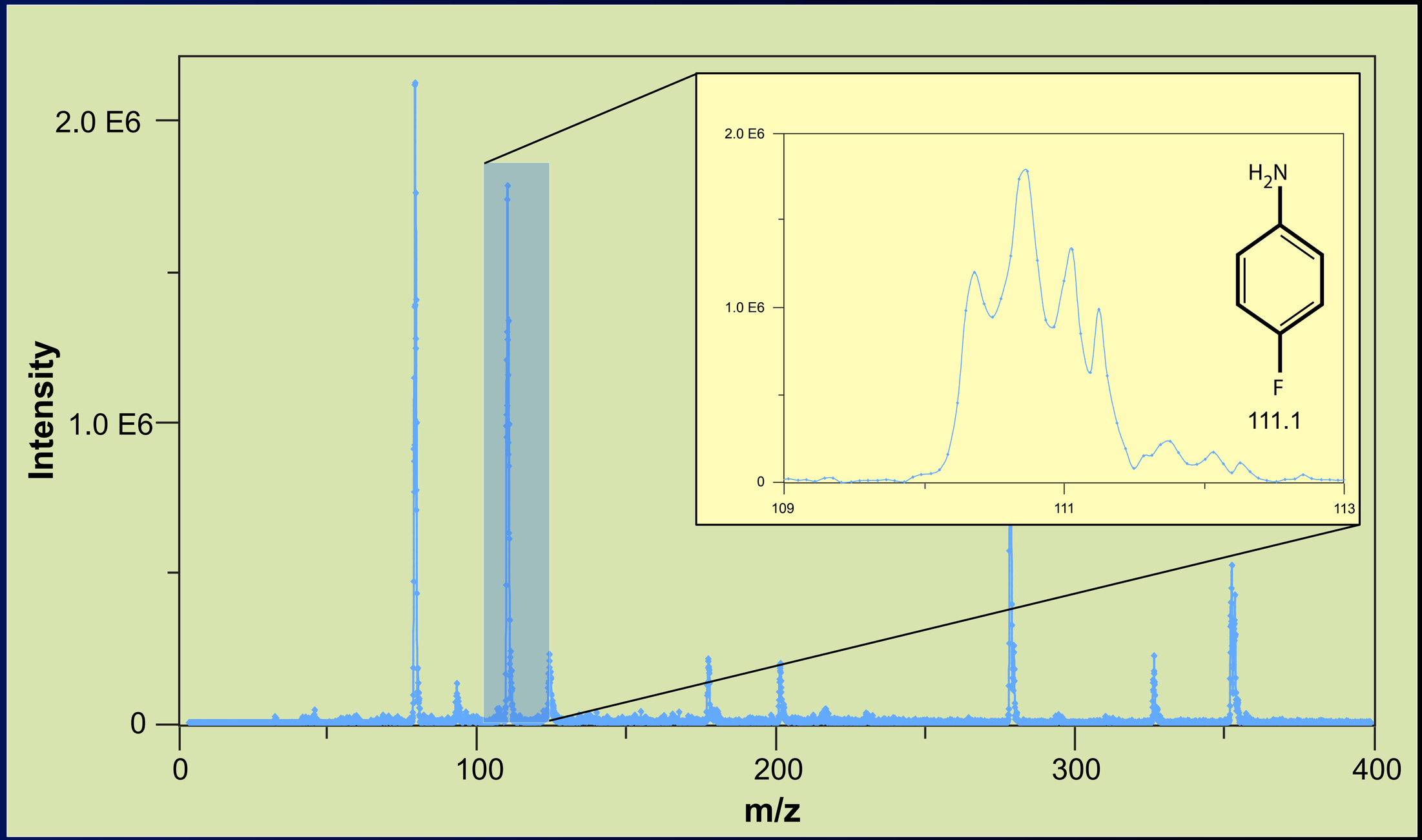
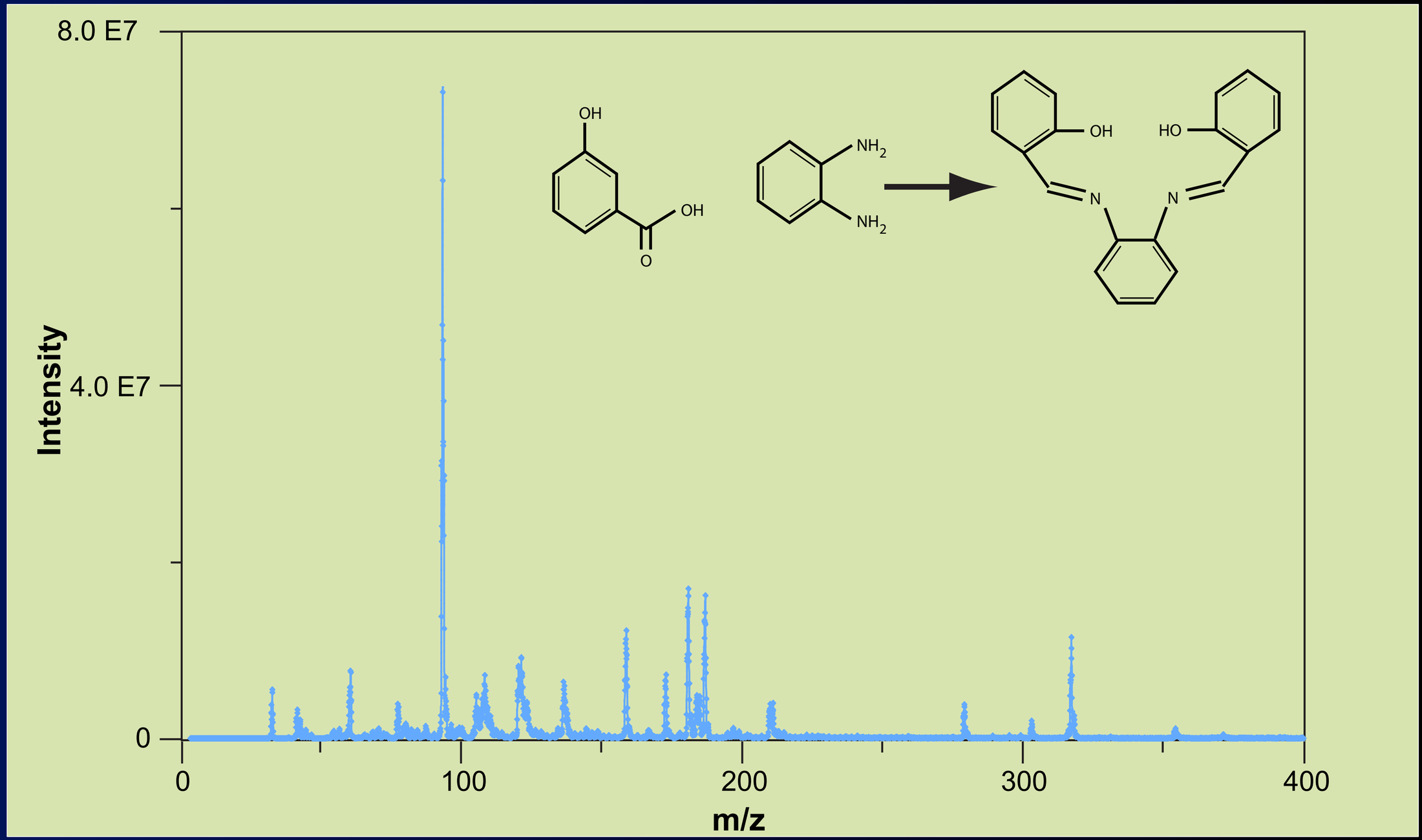


LG 159 316.35 $C_{20}H_{16}N_2O_2$



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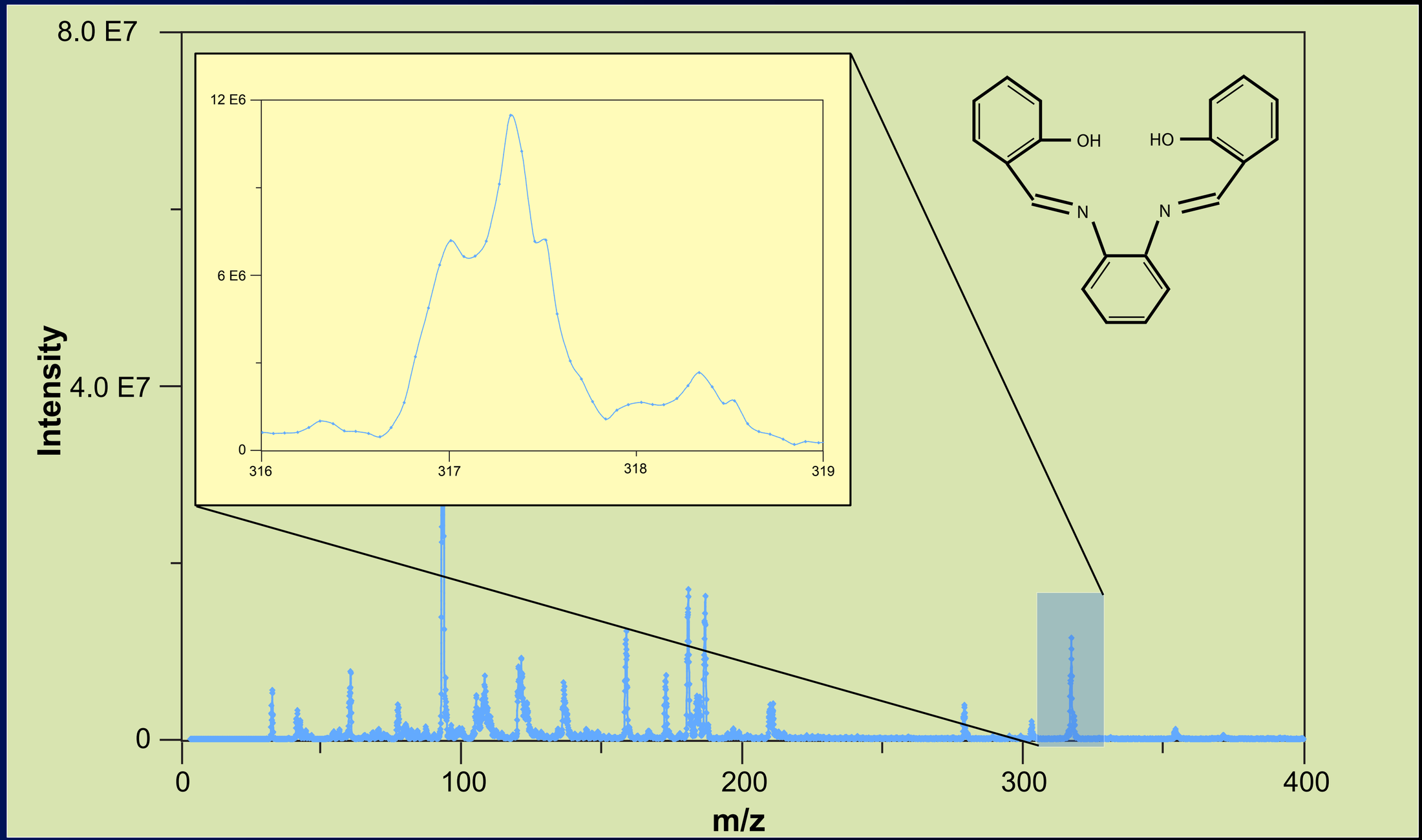

Conclusions

Rapid, analysis able to characterize synthetic compounds

Easy to use on existing APPI instruments

Inexpensive

Future work

Control choatic flows in source
    Quantification

Air sensitive compounds

Acknowledgements

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Questions

Thank you

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