Examining the Role of Discharge Gas and Vapour Introduction for Atmospheric Pressure Photoionization

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Chemistry

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a place of mind

M. Sc. Thesis Defence

May 14, 2012

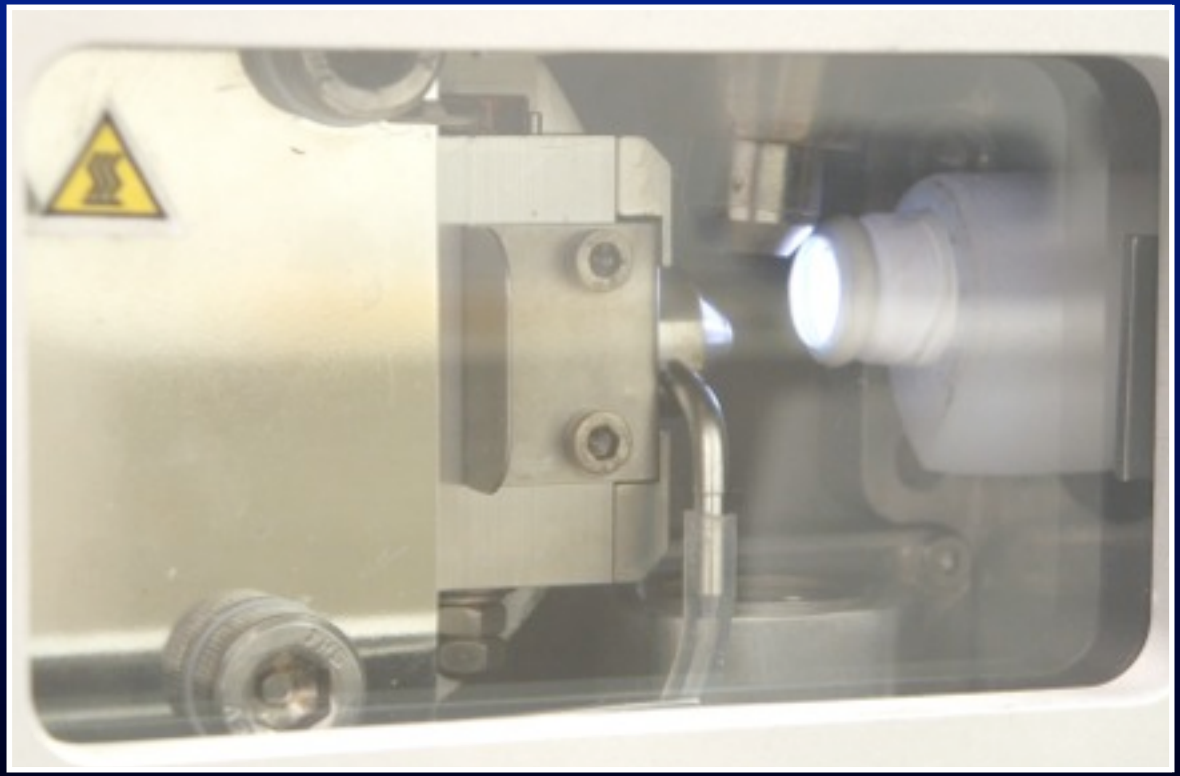
Presentation Outline

Introduction

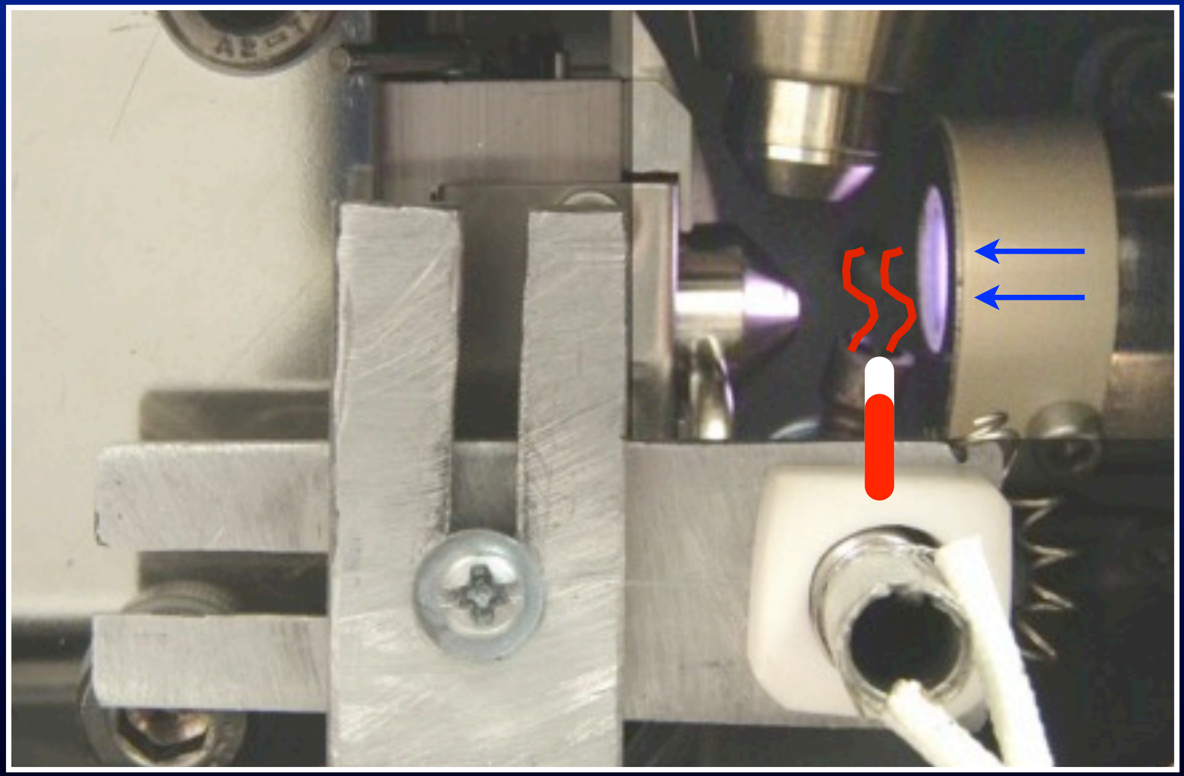
Lightning Ion Source

Thermally Assisted Vapour Introduction

Conclusions



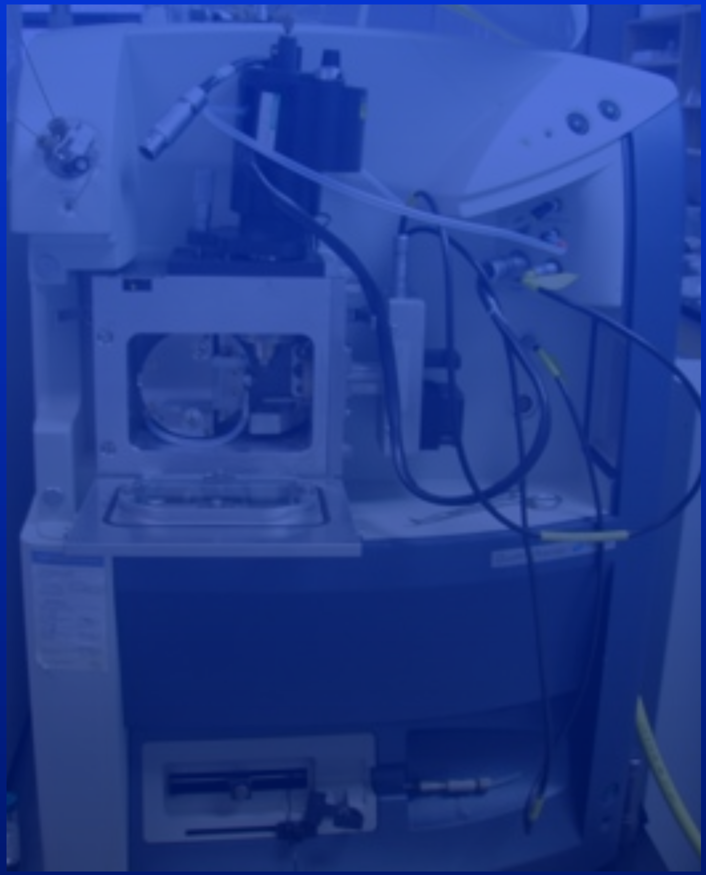
Lightning Ion Source



Vapour Introduction

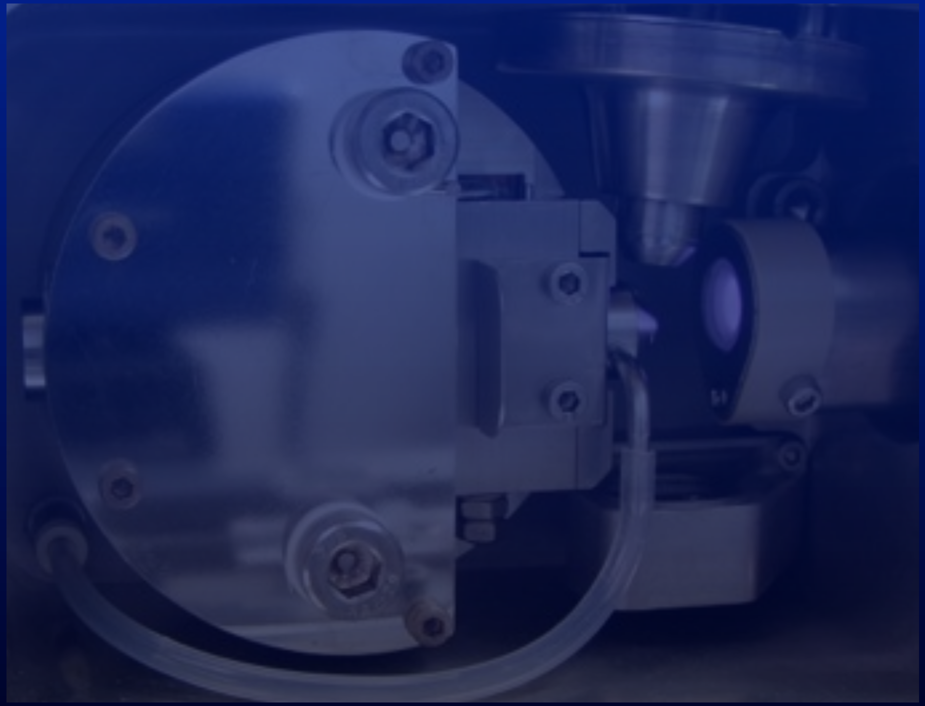
Triple Quadrupole Mass Spectrometer

Waters MS/MS



Waters MS/MS
naked

ionization chamber



Triple Quadrupole Mass Spectrometer

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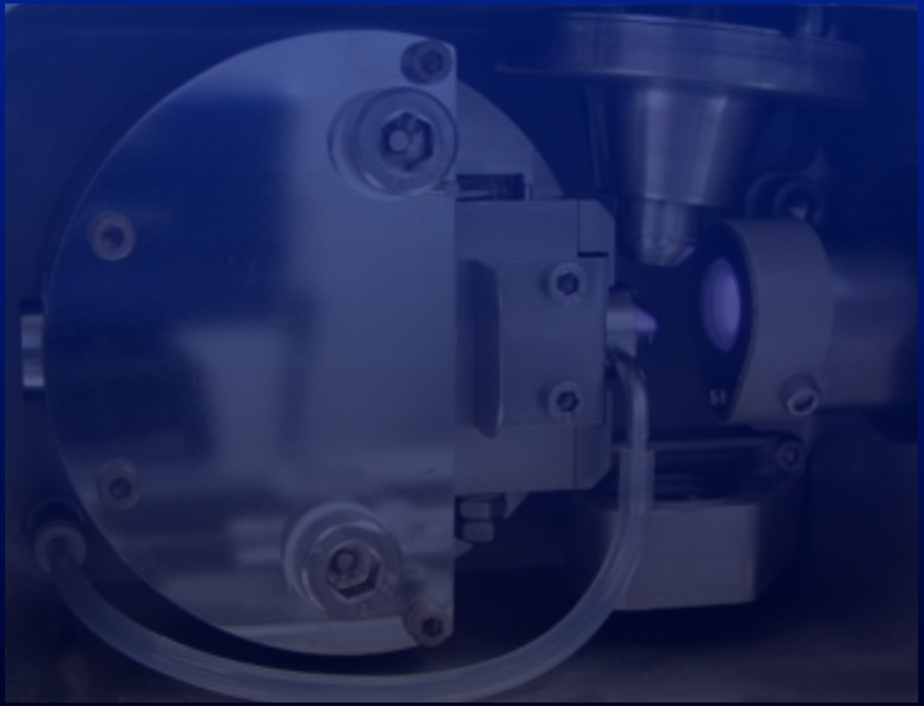

Triple Quadrupole Mass Spectrometer

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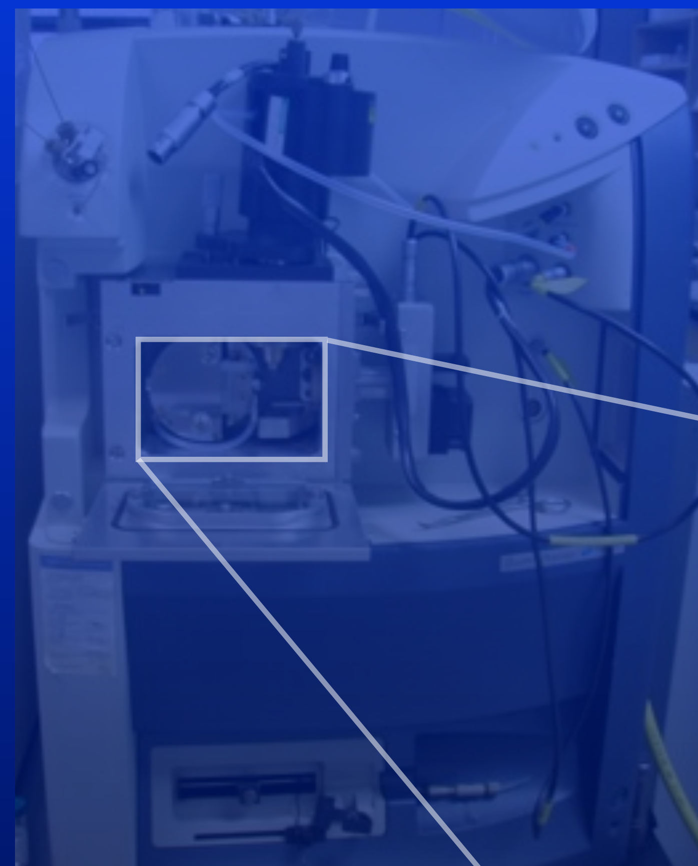

Waters MS/MS
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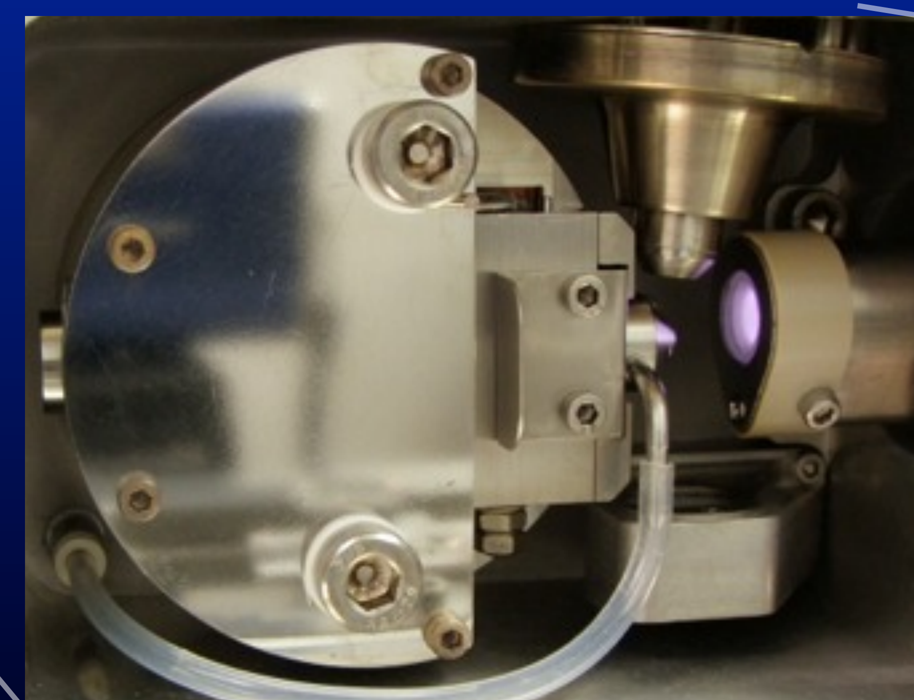
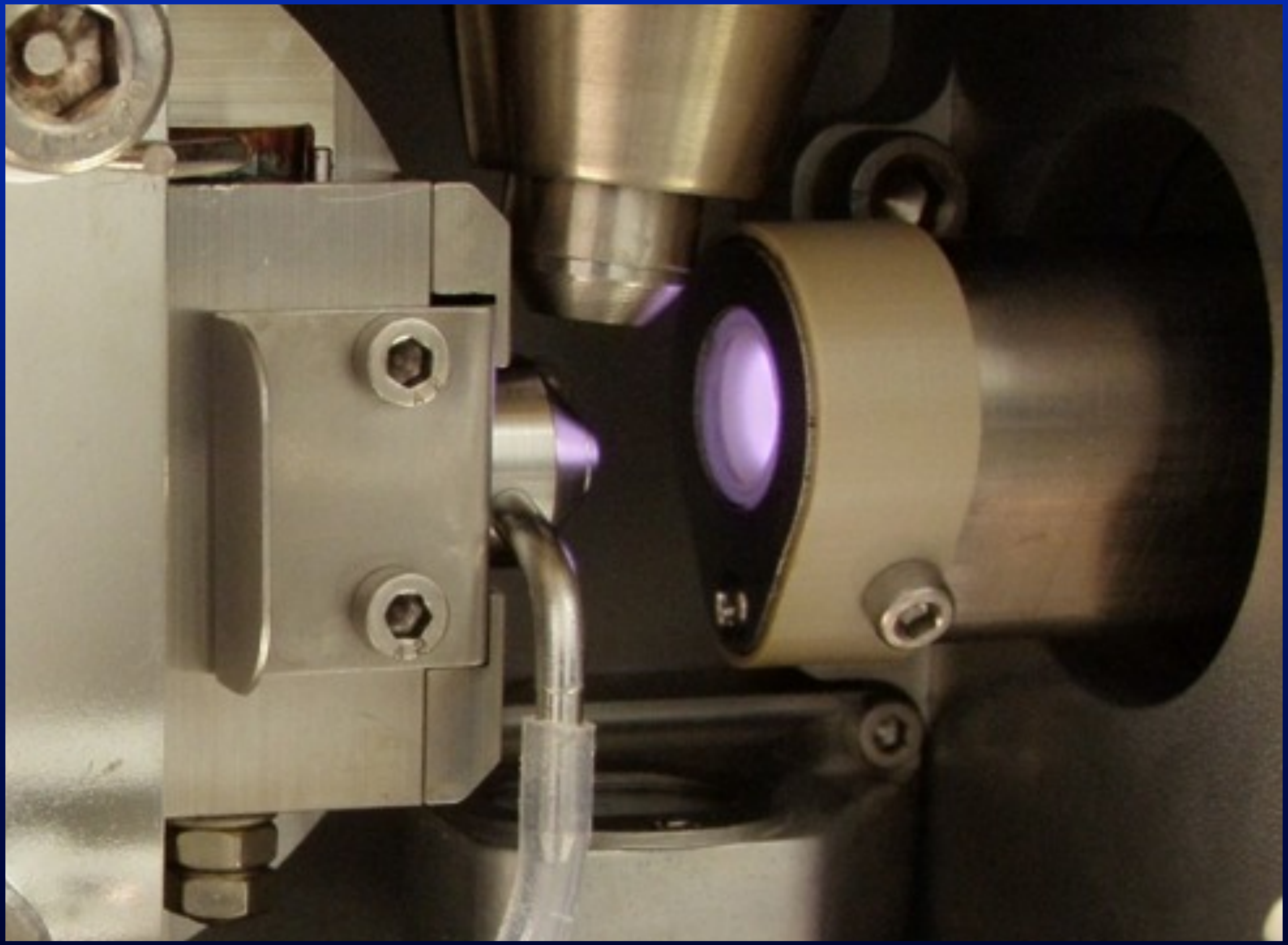
ionization chamber



Atmospheric Pressure Photoionization

electrical discharge in Krypton producing photons

$e^- + Kr \rightarrow Kr^+ + 2e^-$
$Kr^+ + e^- \rightarrow Kr^*$
$Kr^* \rightarrow Kr + h\upsilon$



Commercial Photoionization Ion Source

Atmospheric Pressure Photoionization
Mechanisms

Primary APPI (M^+)

$h\nu$ + Analyte → Analyte$^+$ + e^-

Secondary APPI ($M+H^+$)

$h\nu$ + Analyte → Analyte$^+$ + e^-

Analyte$^+$ + Solvent → AnalyteH$^+$ + Solvent(-H)

$h\nu$ + Solvent → Solvent$^+$ + e^-

Solvent$^+$ + Analyte → AnalyteH$^+$ + Solvent(-H)

Atmospheric Pressure Photoionization
Overview

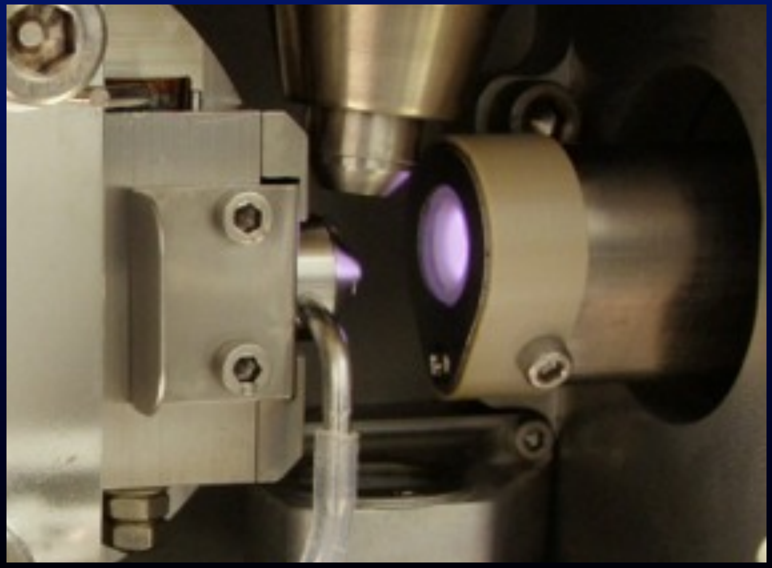
Ions formed cold (excess energy in the departing electron)
stable molecular ion

True ionization technique (ESI is merely “ion atomization”)

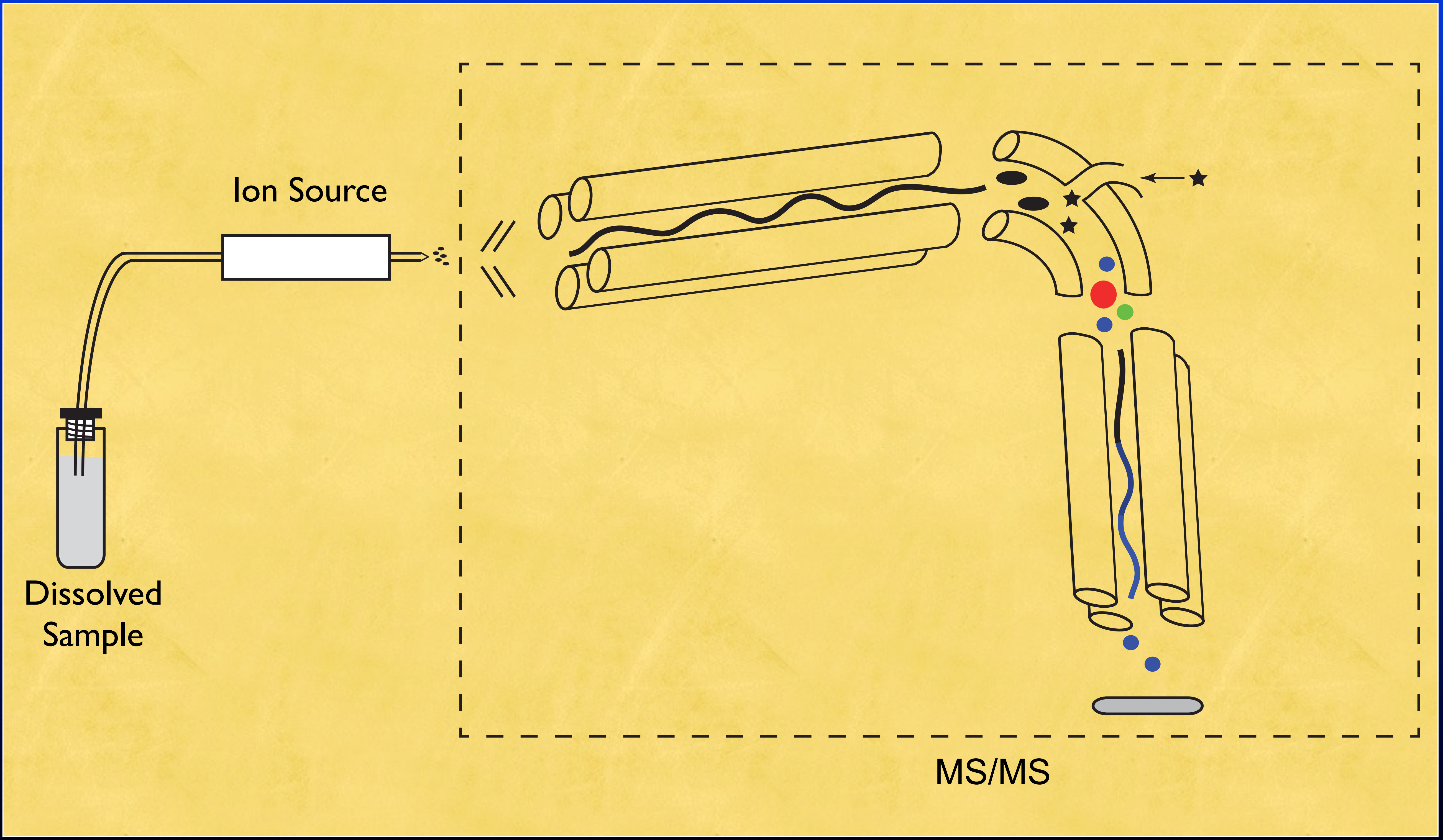
Not as matrix dependent as other techniques like APCI

With solvent: $[M+H]^+$
without solvents mostly M^+

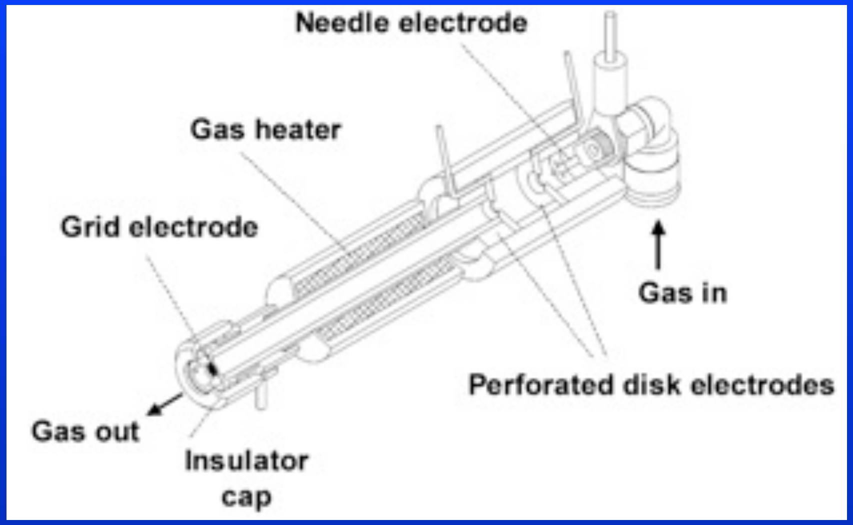
Mechanisms are debated
Photo Induced Chemical Ionization (PICI)



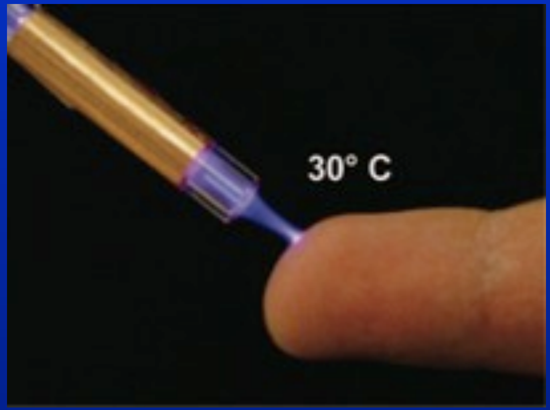
Atmospheric Pressure Photoionization
General workflow



Other Ionization Techniques
Direct Introduction Methods



DART - Direct Analysis in Real Time
Electrical discharge in He



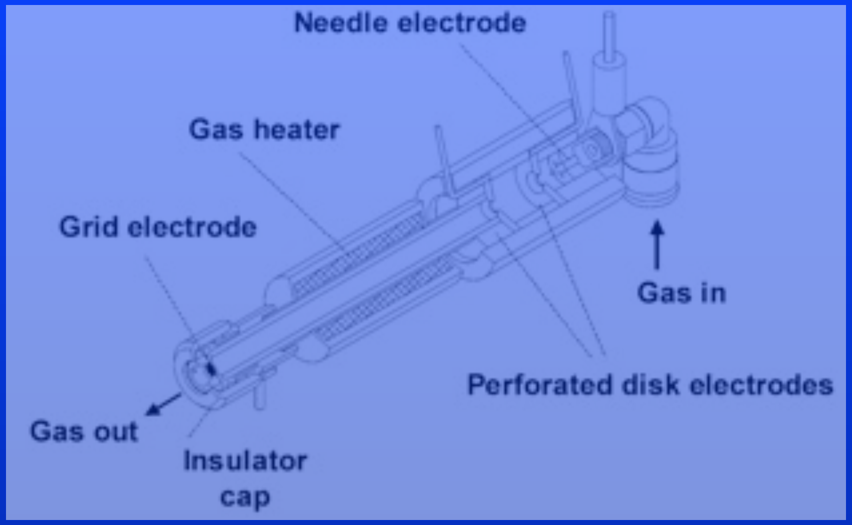
LTP - Low Temperature Discharge
Dielectric barrier discharge in air

GD - Glow discharge
Electrical discharge in He

all have poorly defined mechanisms

APPI - Atmospheric Pressure Photoionization
Electrical discharge in Kr

Other Techniques
Direct Introduction Methods



DART - Direct Analysis in Real Time
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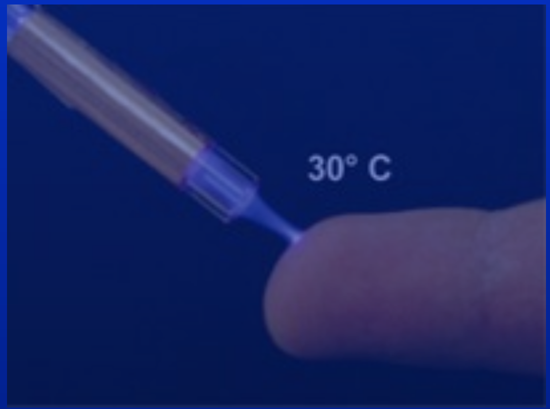

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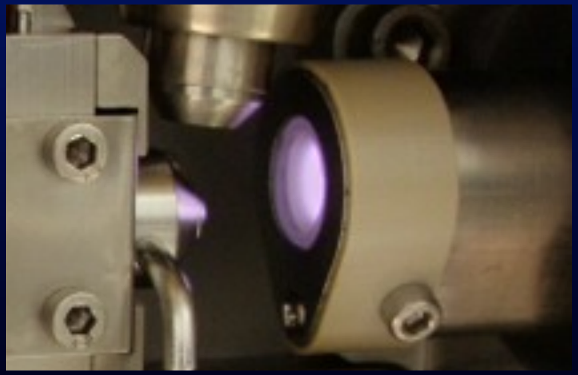
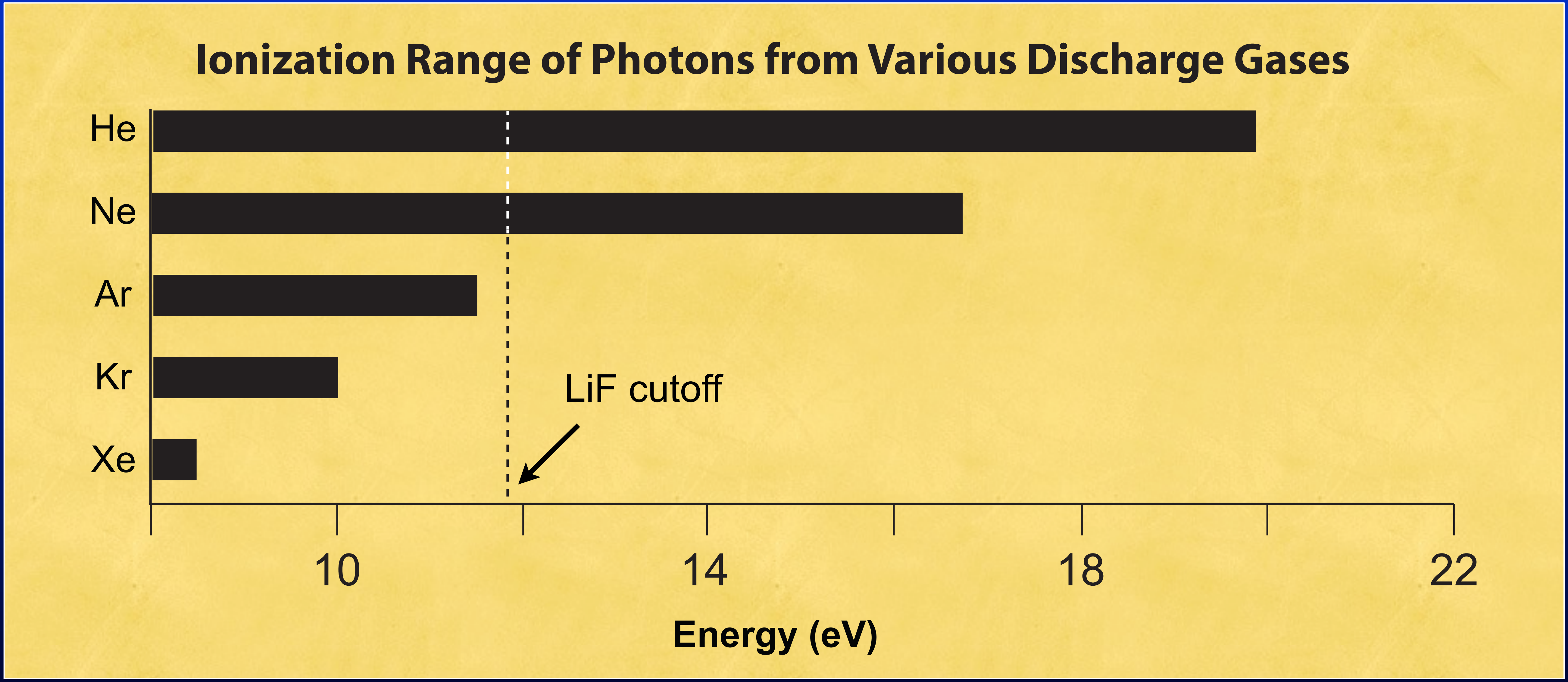
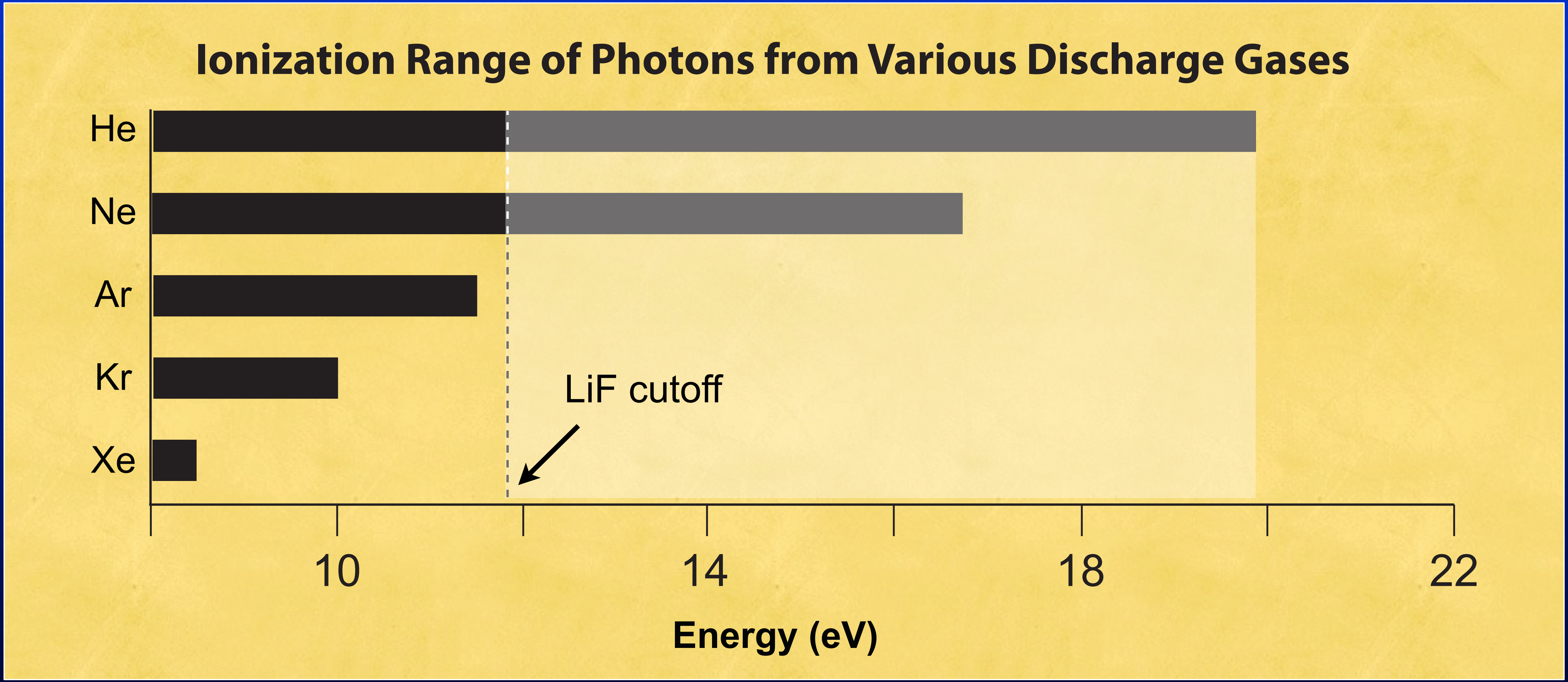


APPI - Atmospheric Pressure Photoionization
Electrical discharge in Kr

Photon Energy
Various Gases



Photon Energy
Various Gases



Atmospheric Pressure Photoionization
Thesis investigation

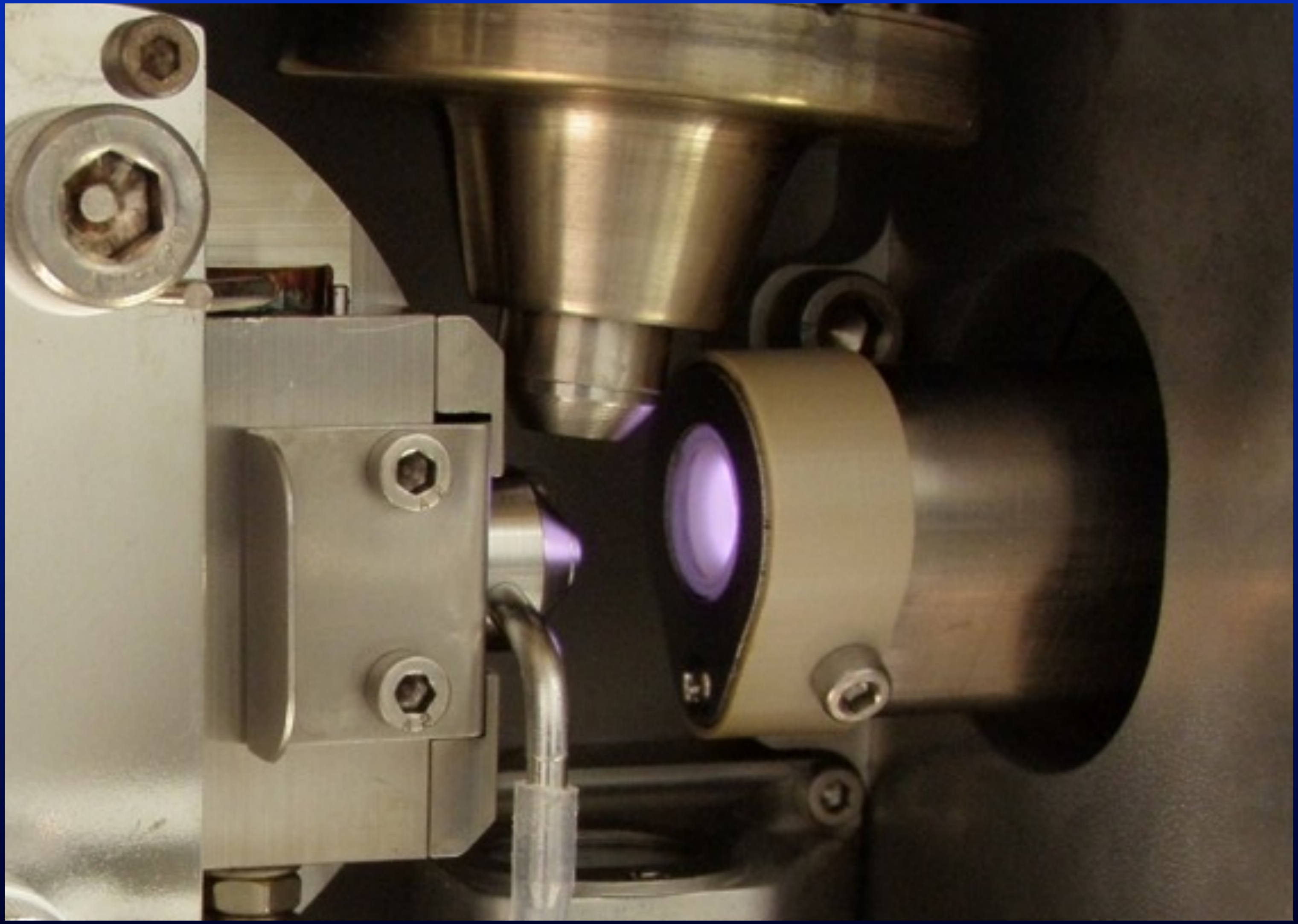
Is photoionization unique to krypton discharge?

Can vapours of various compounds be photoionized and reveal molecular weight and structure?

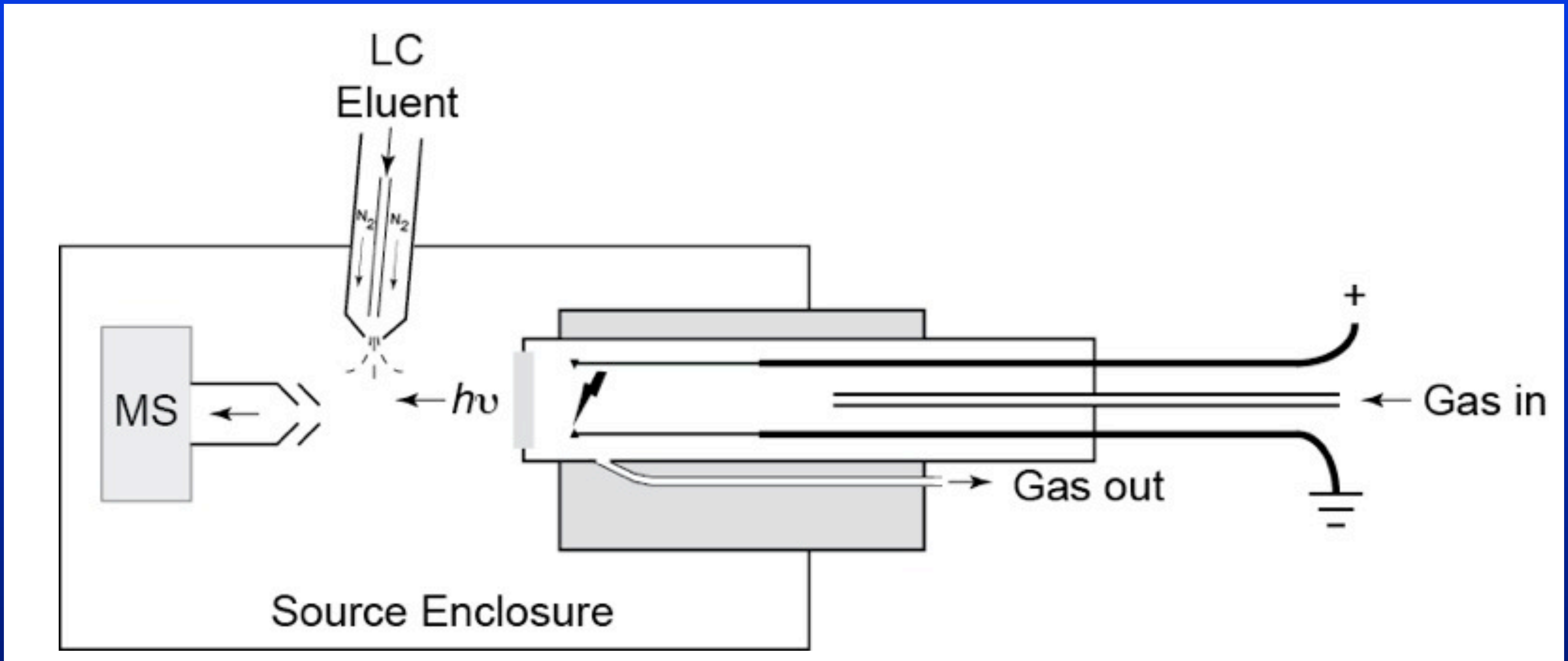
Lightning Ion Source

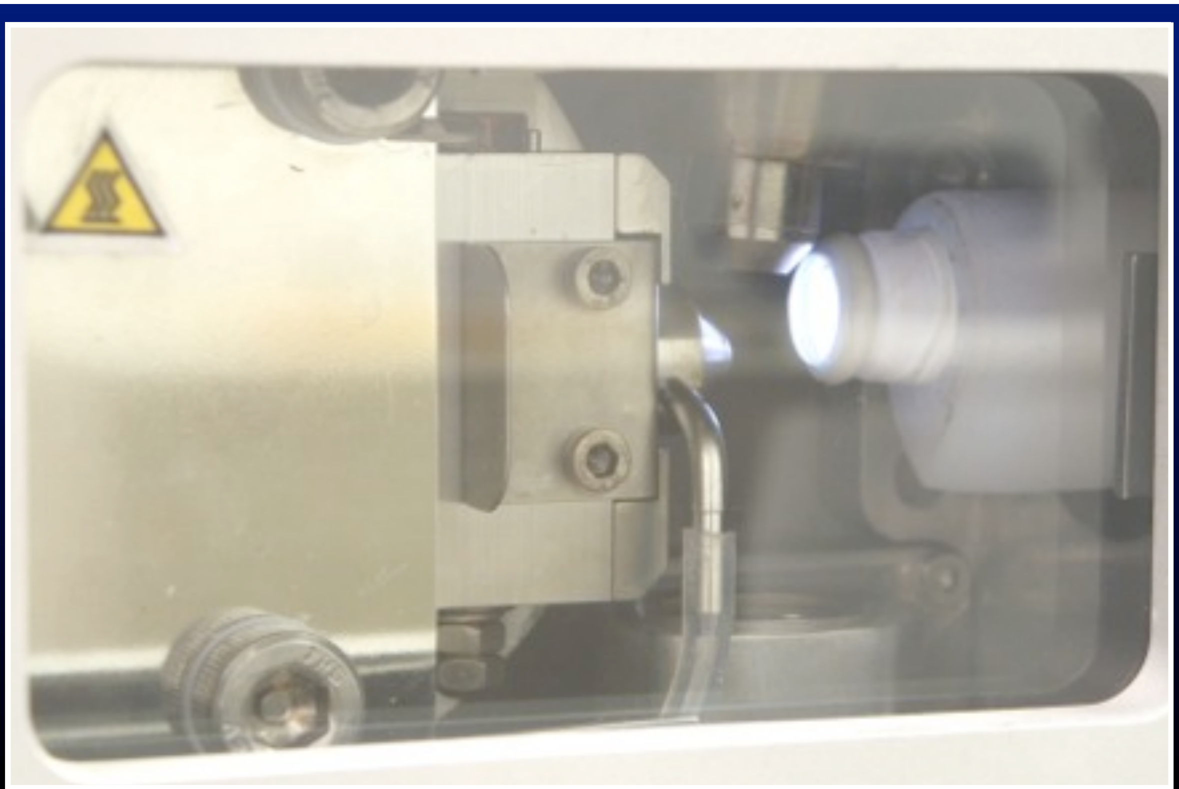
Lightning Ion Source
Question

Is photoionization unique to krypton discharge?



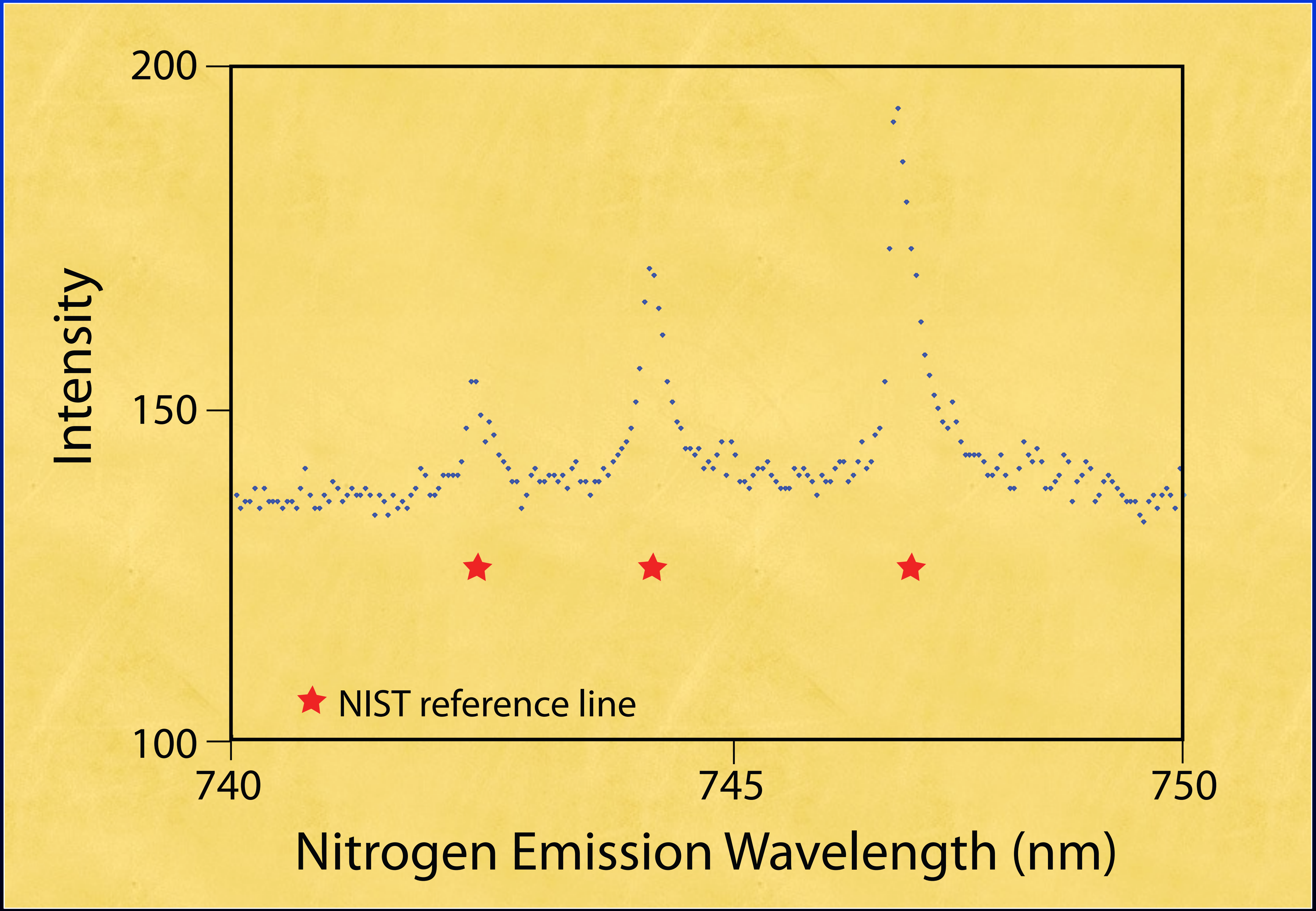
Lightning Ion Source
Design





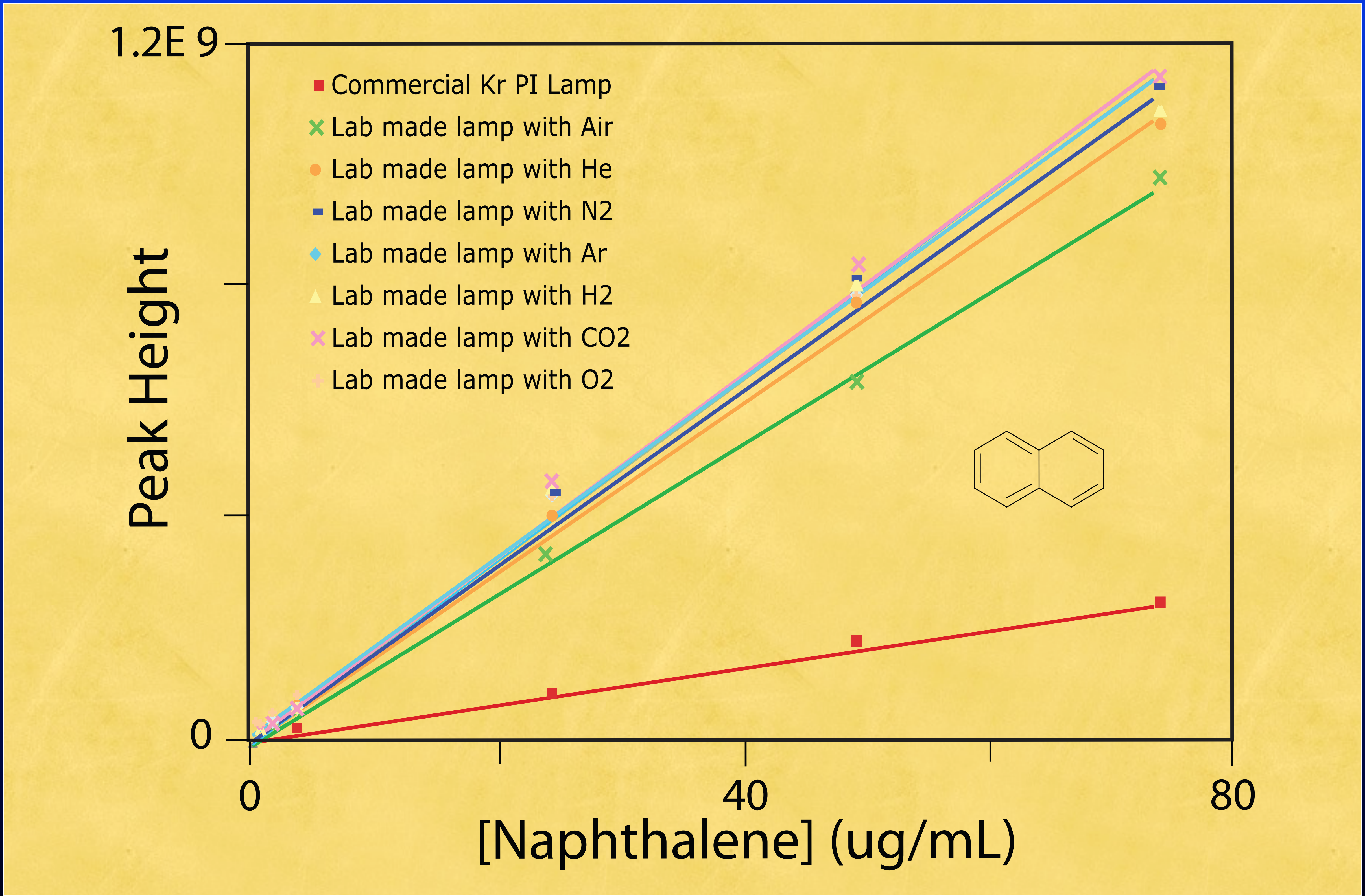
Lightning Ion Source

Results - emission lines

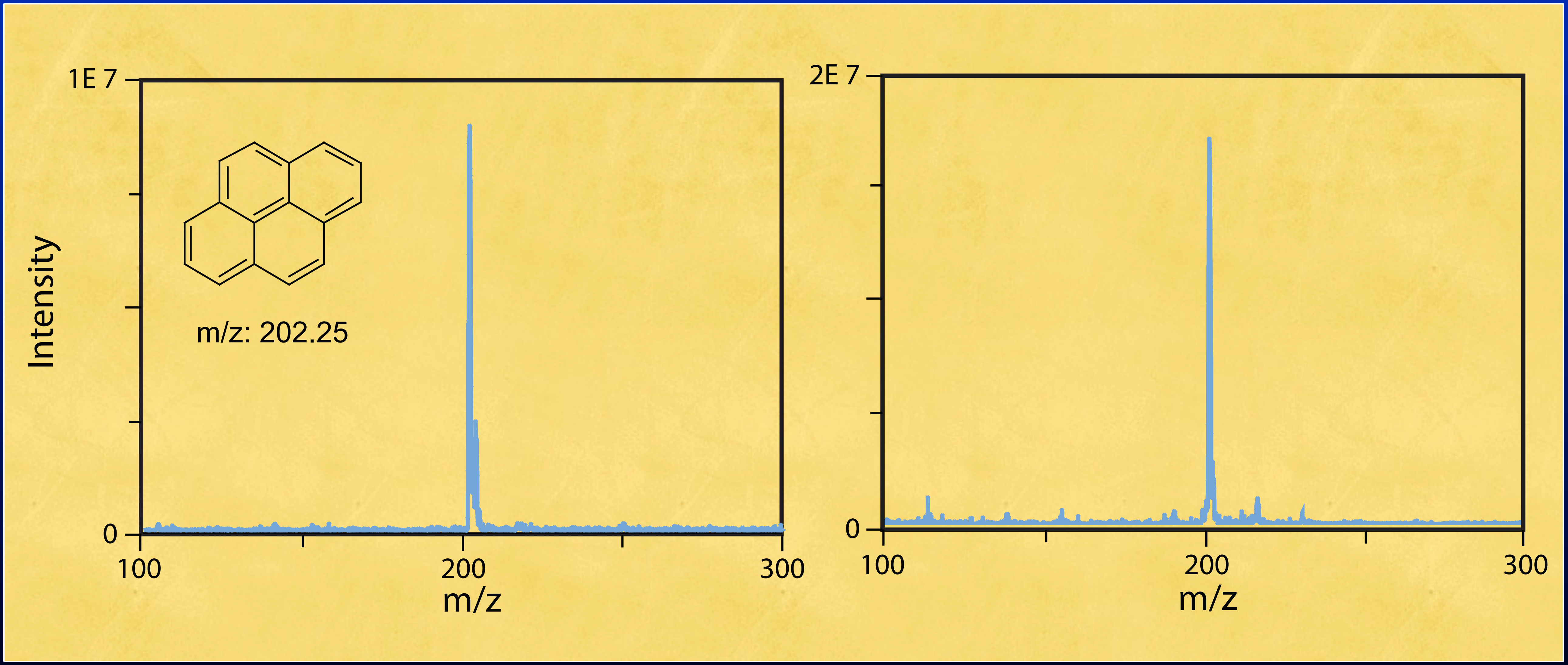


Lightning Ion Source

Results - calibration curve



Lightning Ion Source
Results - Pyrene



Krypton Lamp **Lightning Ion Source**

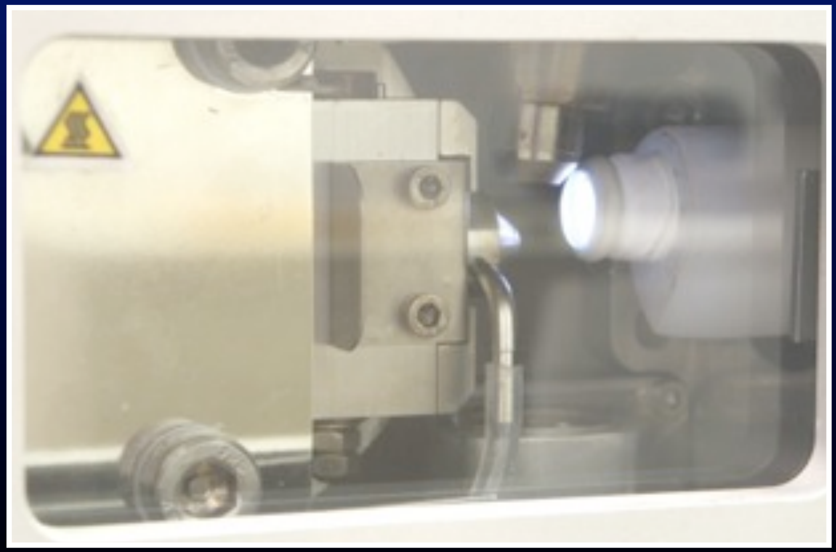
Lightning Ion Source
Conclusions

inexpensive ion source

variety of gases can photoionize

Future Study

refine LIS design (electrode orientation)



Vapour Introduction

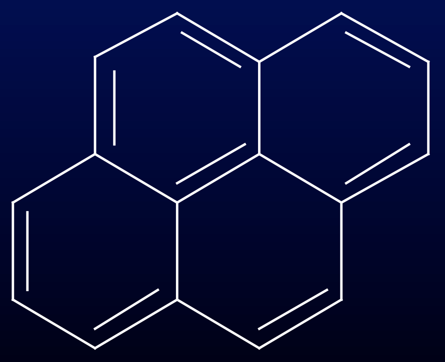
Thermally Assisted Vapour Introduction

Challenge

Synthetic, specifically inorganic, chemists needed quick confirmation of synthesis

Some compounds insoluble usual solvents

Noticed target compounds had aromaticity



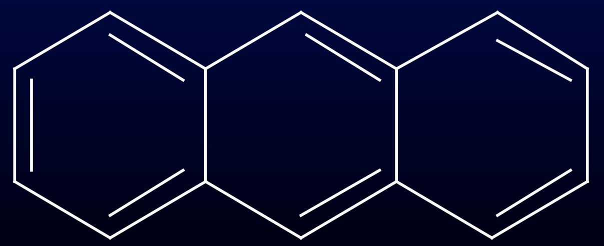
Thermally Assisted Vapour Introduction
Other available techniques

MALDI: Matrix Assisted Laser Desorption Ionization
high background, adducts, not well defined

ESI: Electrospray Ionization
ions in solution

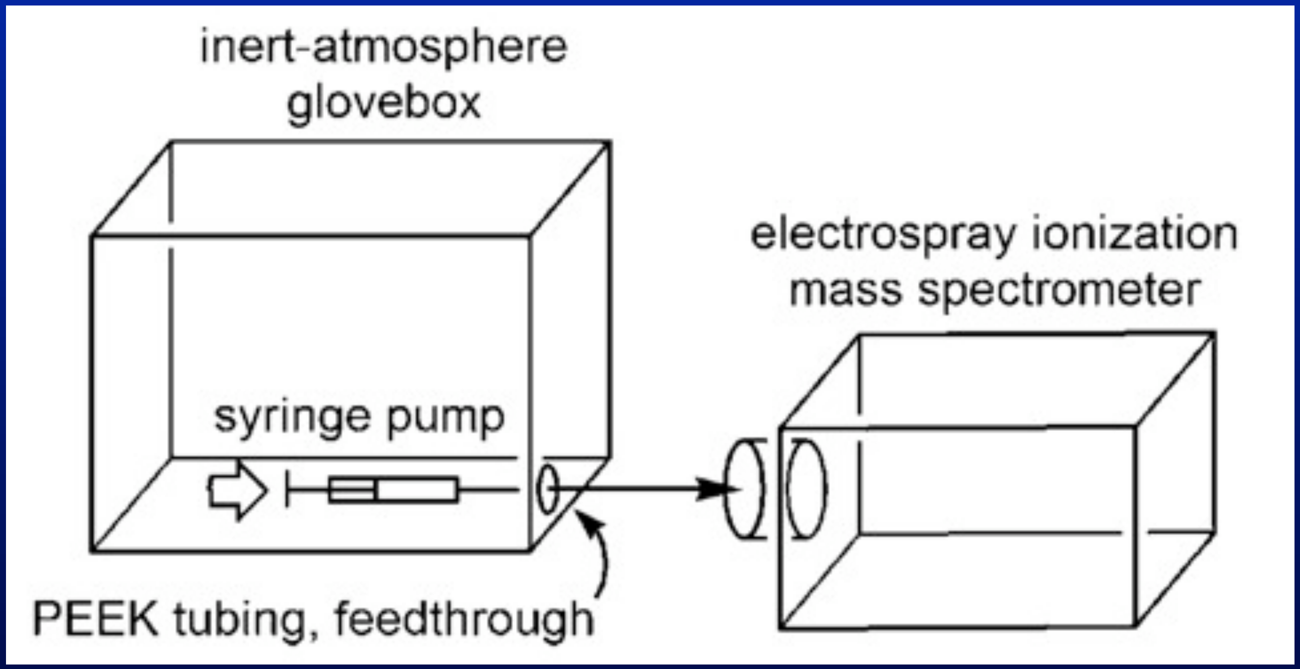
EI: Electron Impact
high energy leads to fragmentation, inefficient source

CI: Chemical Ionization

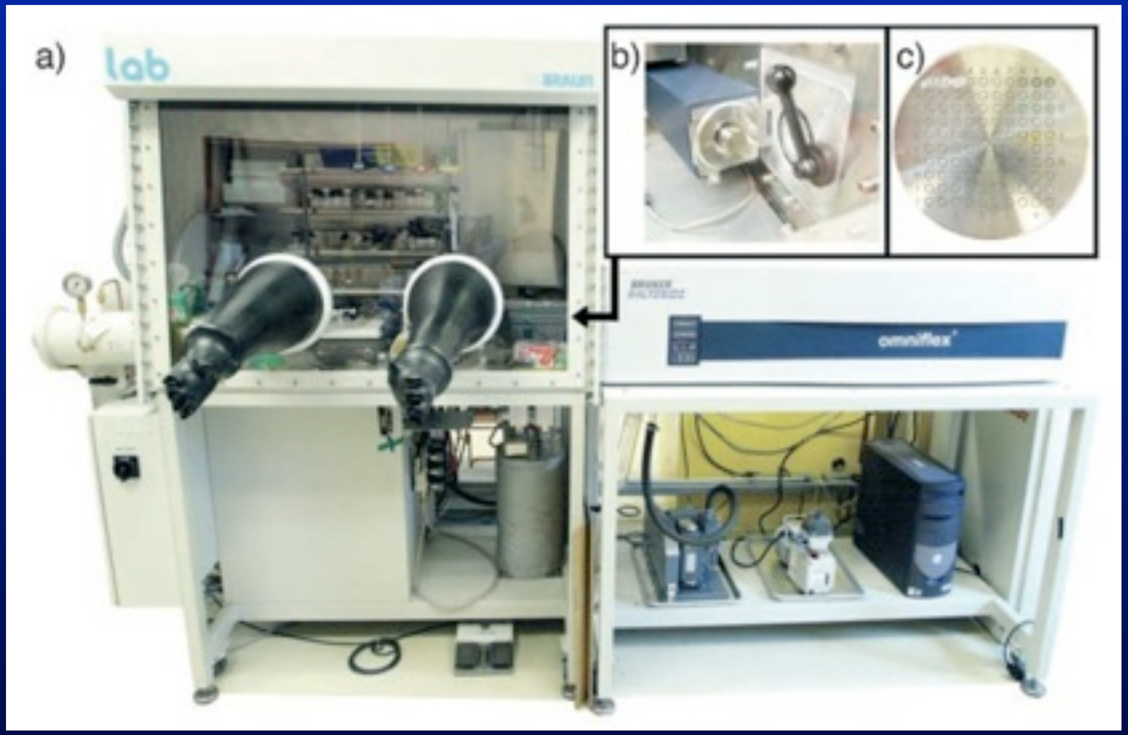


Thermally Assisted Vapour Introduction
Previous uses of Mass Spectra

Some recently reported apparatus



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



MALDI- TOF
Fogg (U of O.)

Thermally Assisted Vapour Introduction

Solventless Photoionization Mass Spectrometry

Mechanism of $[M + H]^+$ Formation in Photoionization Mass Spectrometry

Jack A. Syage
Syagen Technology, Inc., Tustin, California, USA

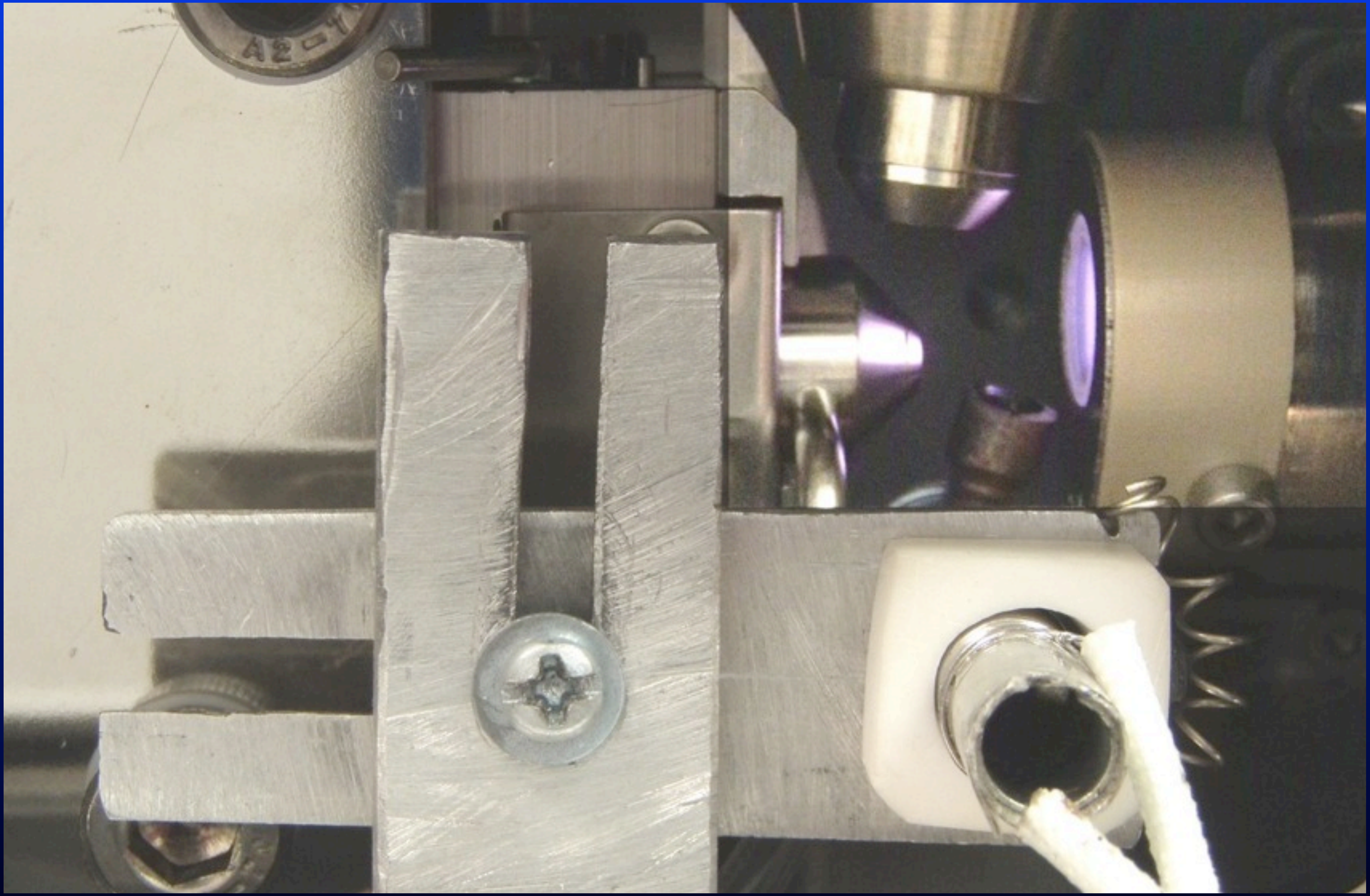
In this paper we examine the mechanism of $[M + H]^+$ (henceforth MH^+) formation by direct photoionization. Based on comparisons of the relative abundance of M^+ and MH^+ ions for photoionization of a variety of compounds M as vapor in air versus in different solvents, we conclude that the mechanism is $M + h\nu \rightarrow M^+ + e^-$ followed by the reaction $M^+ + S \rightarrow MH^+ + S(-H)$. The principal evidence for molecular radical ion formation M^+ followed by hydrogen atom abstraction from protic solvent S are: (1) Nearly exclusive formation of M^+ for headspace ionization of M in air, (2) significant relative abundance of MH^+ in the presence of protic solvents (e.g., CH_3OH, H_2O, c-hexane), but not in aprotic solvents (e.g., CCl_4), (3) observation of induced equilibrium oscillations in the abundance of MH^+ and M^+, and (4) correlation of the ratio of MH^+/M^+ to reaction length in the photoionization source. Thermodynamic models are advanced that explain the qualitative dependence of the MH^+/M^+ equilibrium ratio on the properties of solvent S and analyte M. Though the hydrogen abstraction reaction is endothermic in most cases, it is shown that the equilibrium constant is still expected to be much greater than unity in most of the cases studied due to the very slow reverse reaction involving the very low abundant MH^+ and $S(-H)$ species. (J Am Soc Mass Spectrom 2004, 15, 1521–1533)

The use of photoionization (PI) in analytical mass spectrometry is a relatively new development [1]. The introduction of compact, sensitive PI sources for commercial analytical MS instruments at atmo-

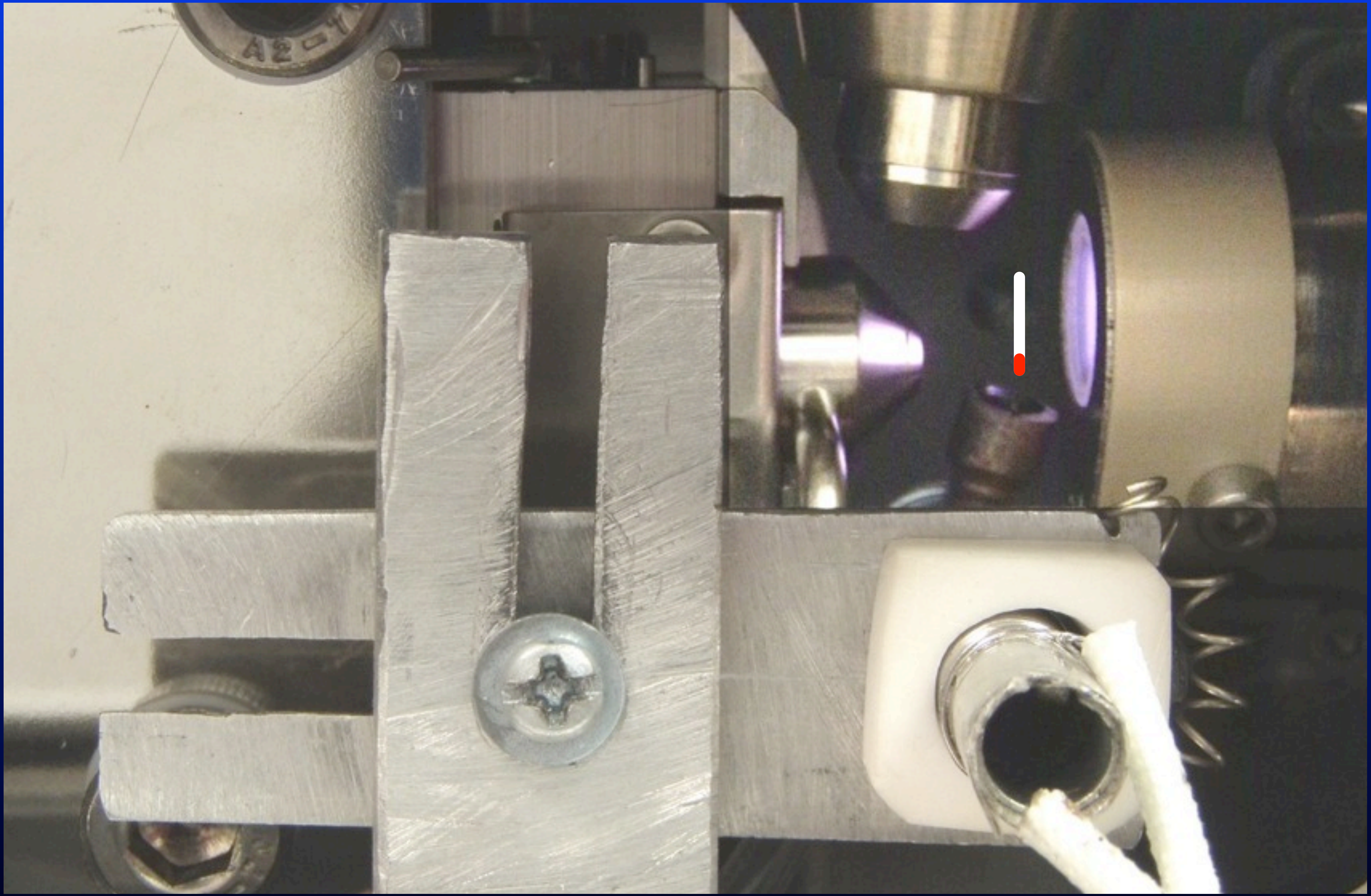
from studies of photoionization under collisionless conditions in vacuum that M^+ is typically formed [13]. However, it is not certain whether this process dominates at atmospheric pressure. There are two general

Thermally Assisted Vapour Introduction
Hardware design Challenges

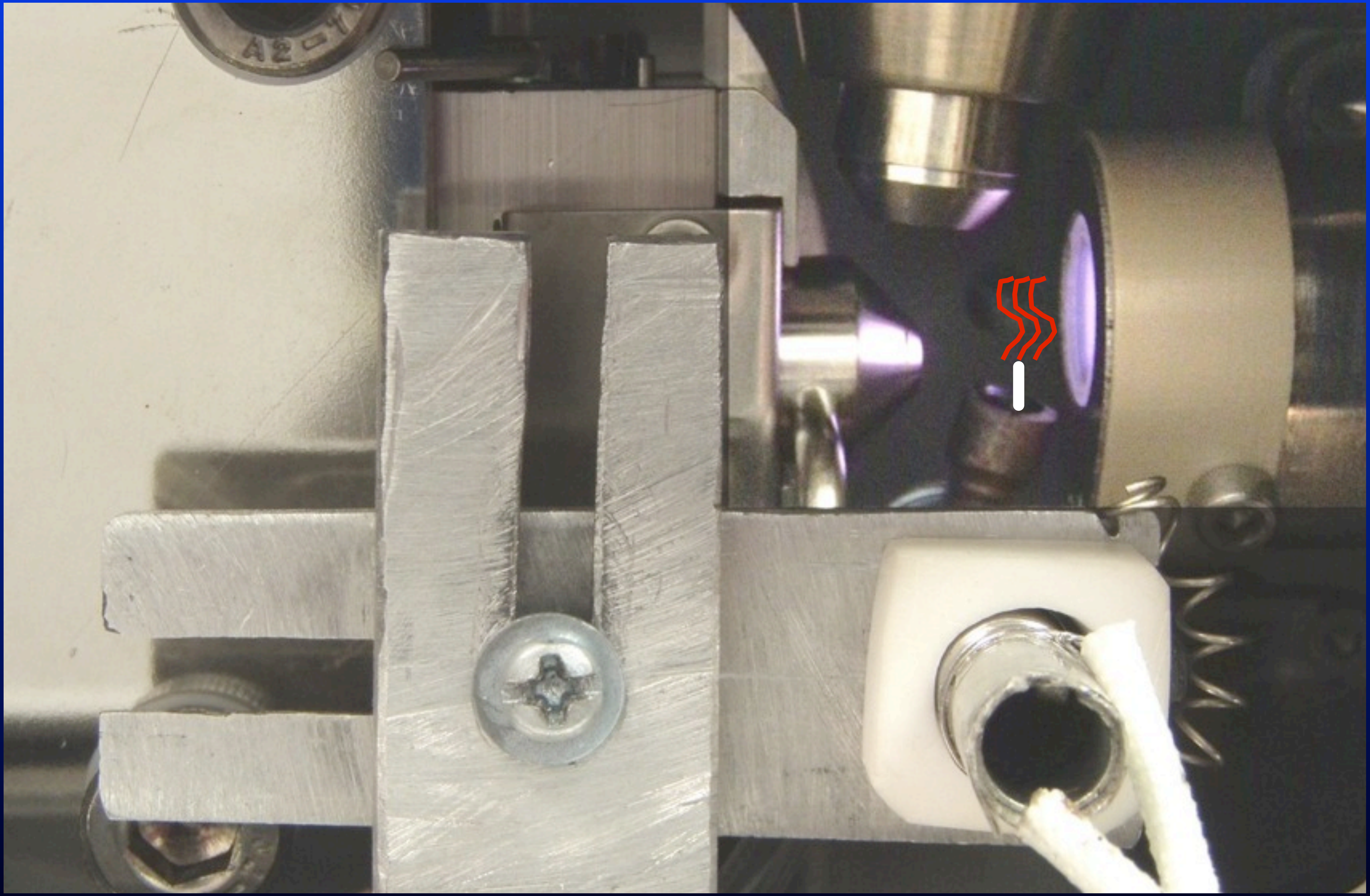
Thermally Assisted Vapour Introduction
Hardware design



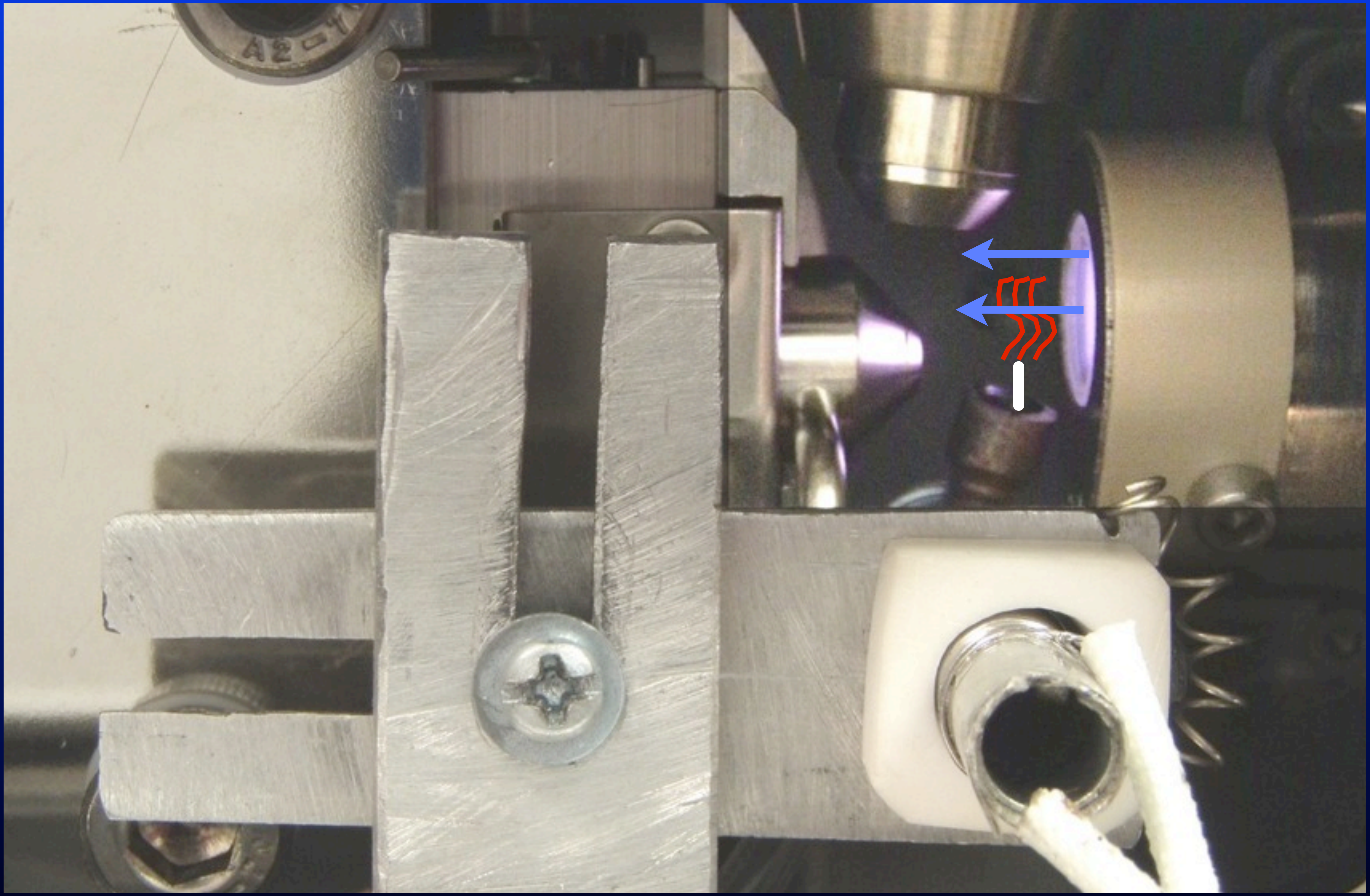
Thermally Assisted Vapour Introduction
Hardware design



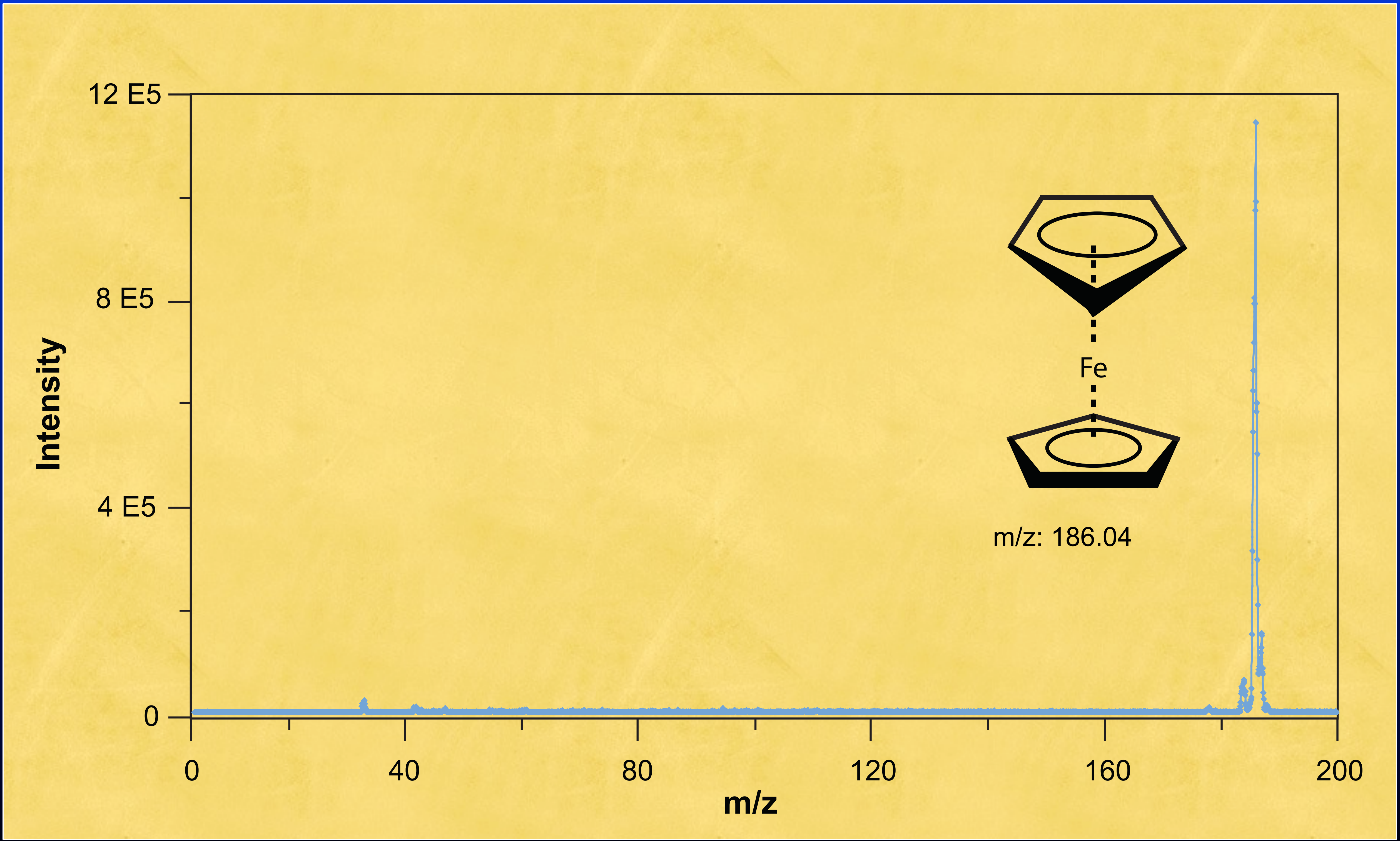
Thermally Assisted Vapour Introduction
Hardware design



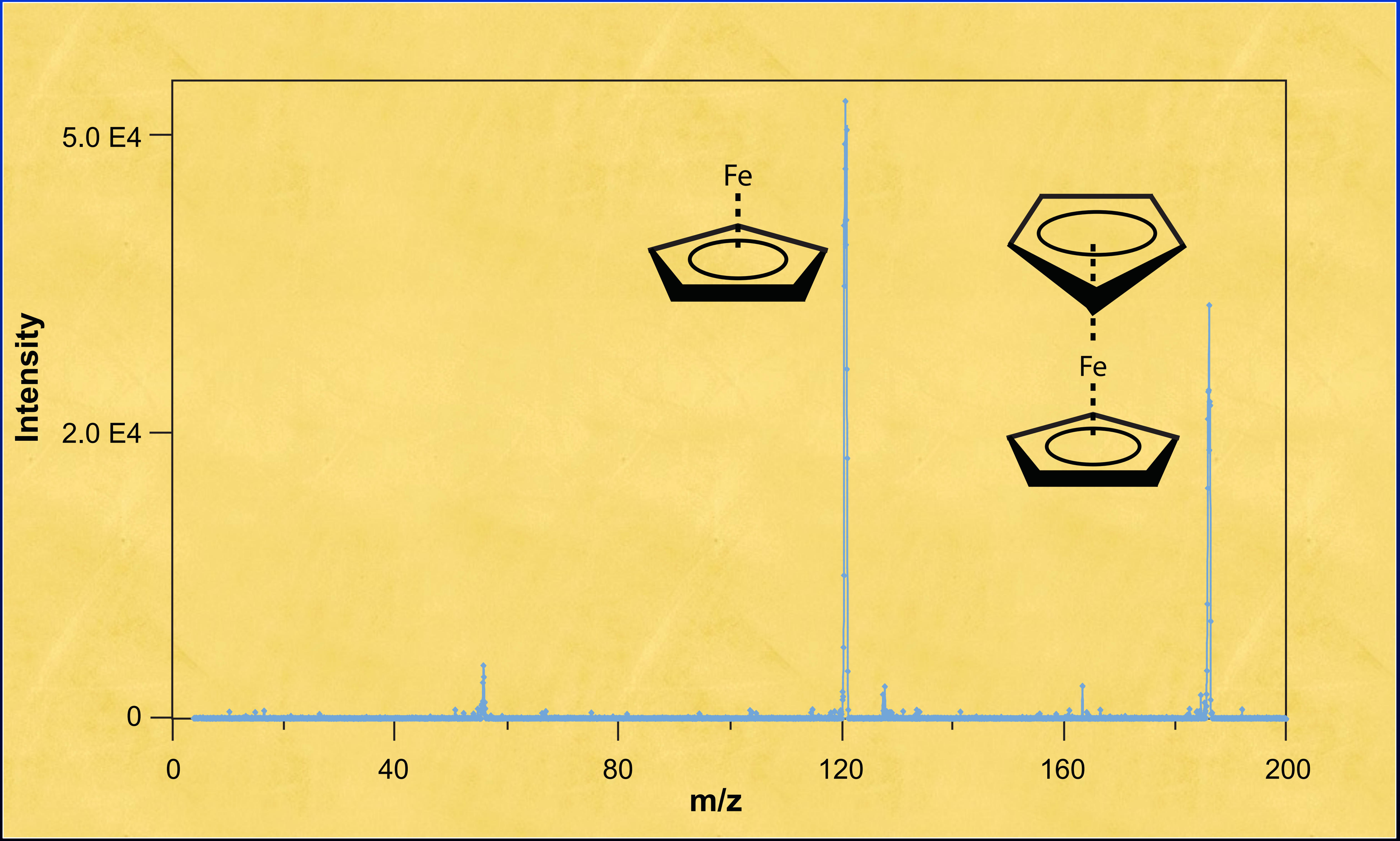
Thermally Assisted Vapour Introduction
Hardware design



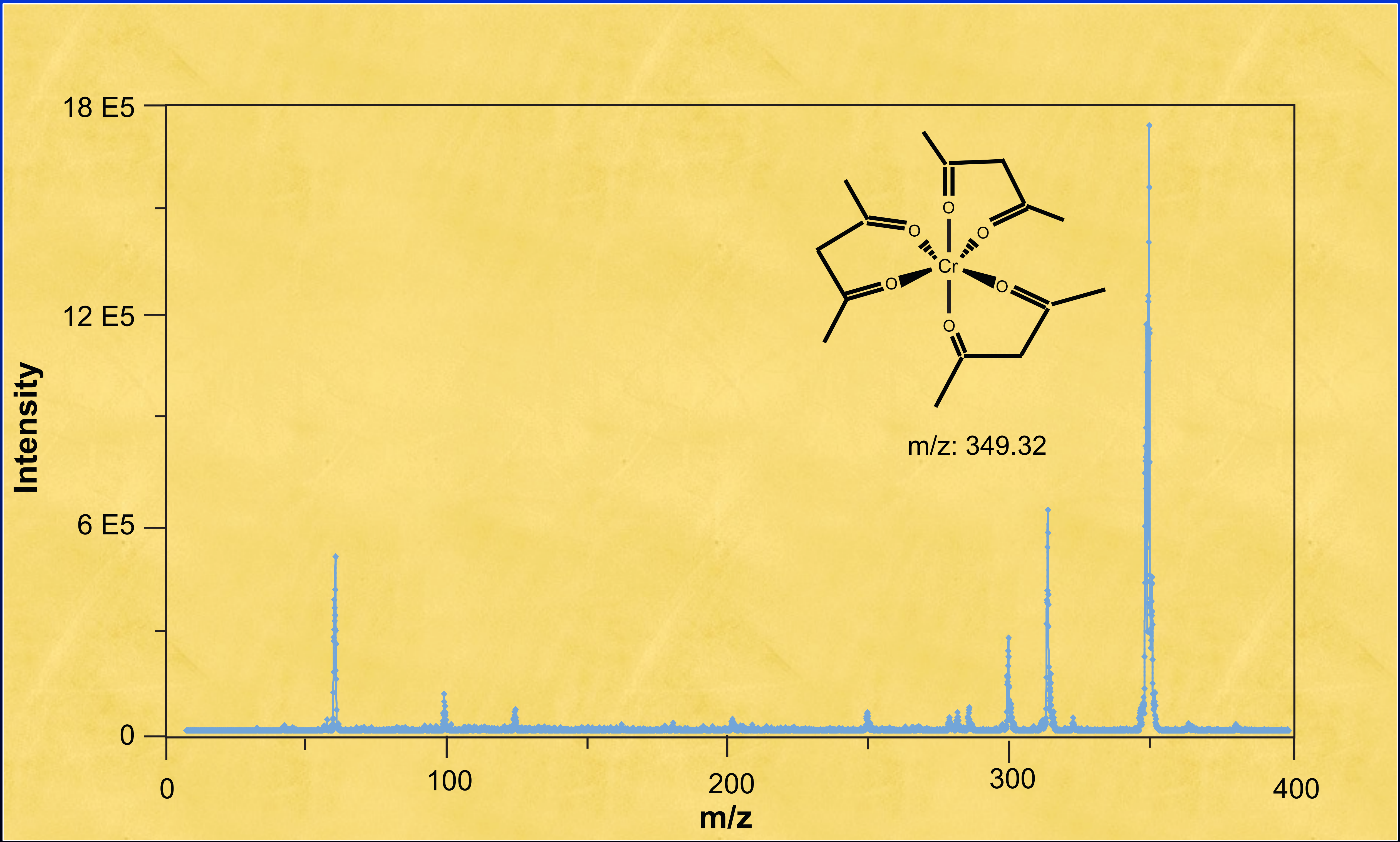
Thermally Assisted Vapour Introduction
Ferrocene $Fe(C_5H_5)_2$



Thermally Assisted Vapour Introduction
MS/MS of Ferrocene $Fe(C_5H_5)_2$ 186.04 g/mol

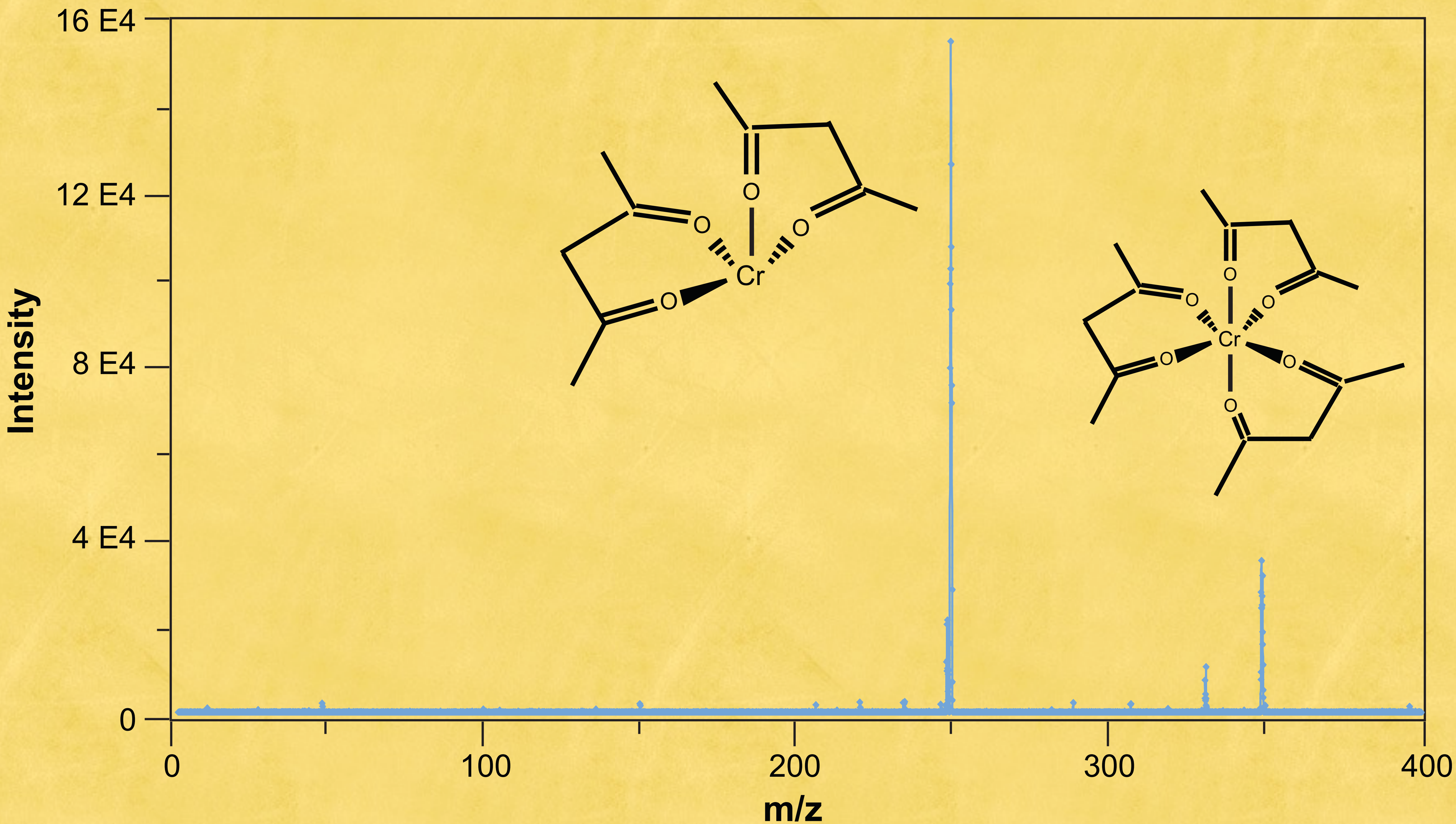


Thermally Assisted Vapour Introduction
Cr(acac)$_3$



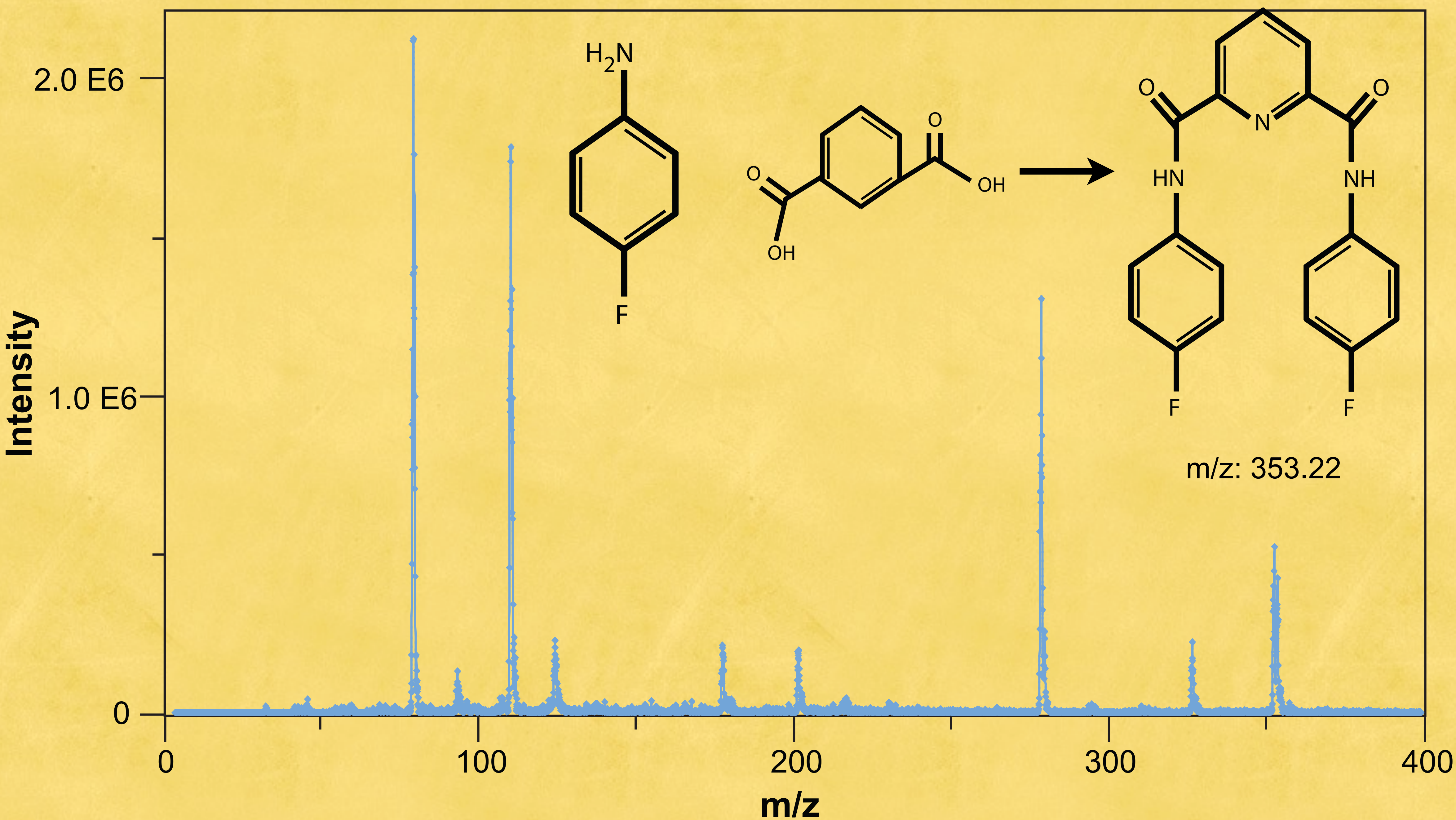
Thermally Assisted Vapour Introduction

MS/MS of Cr(acac)$_3$



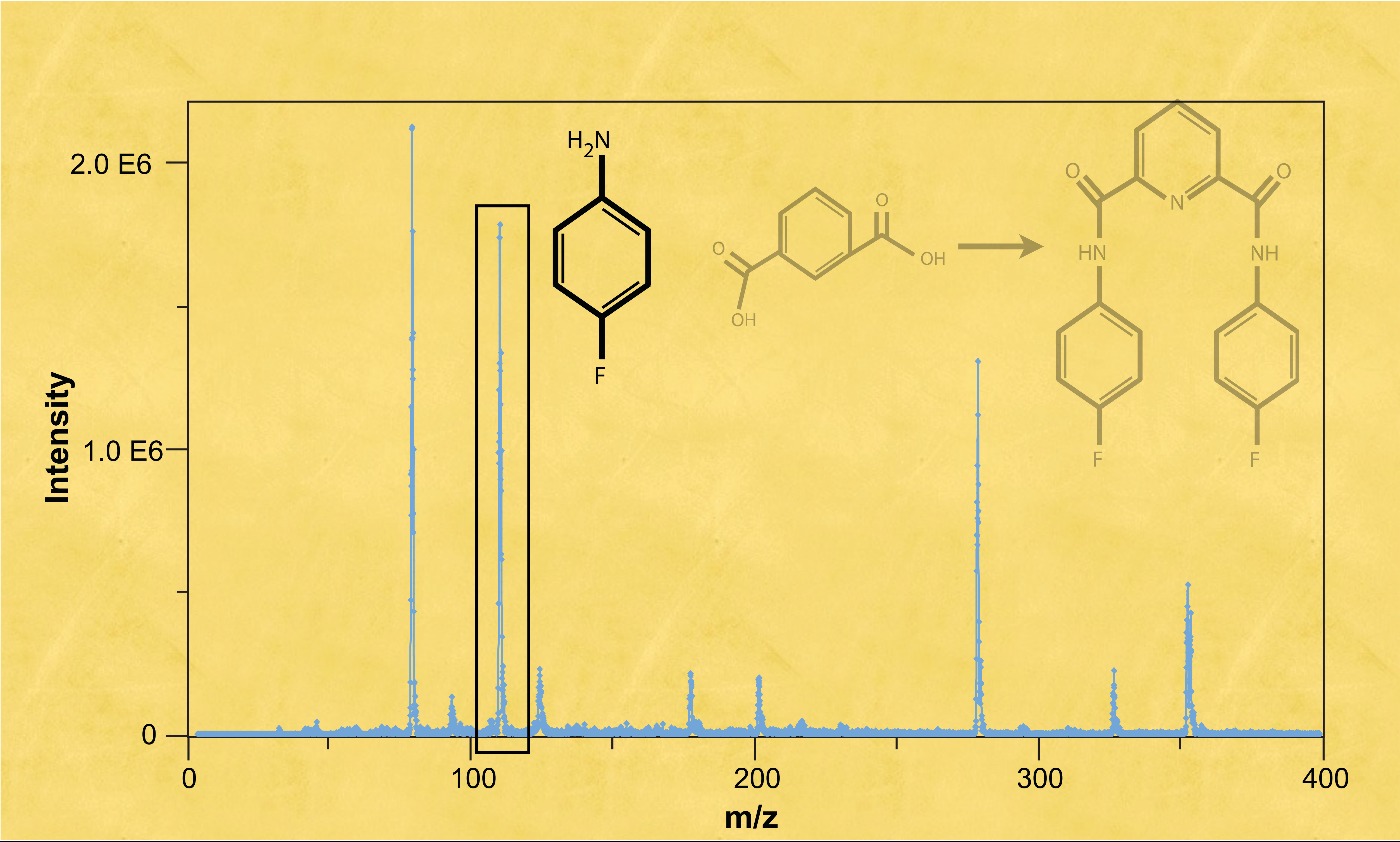
Thermally Assisted Vapour Introduction

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



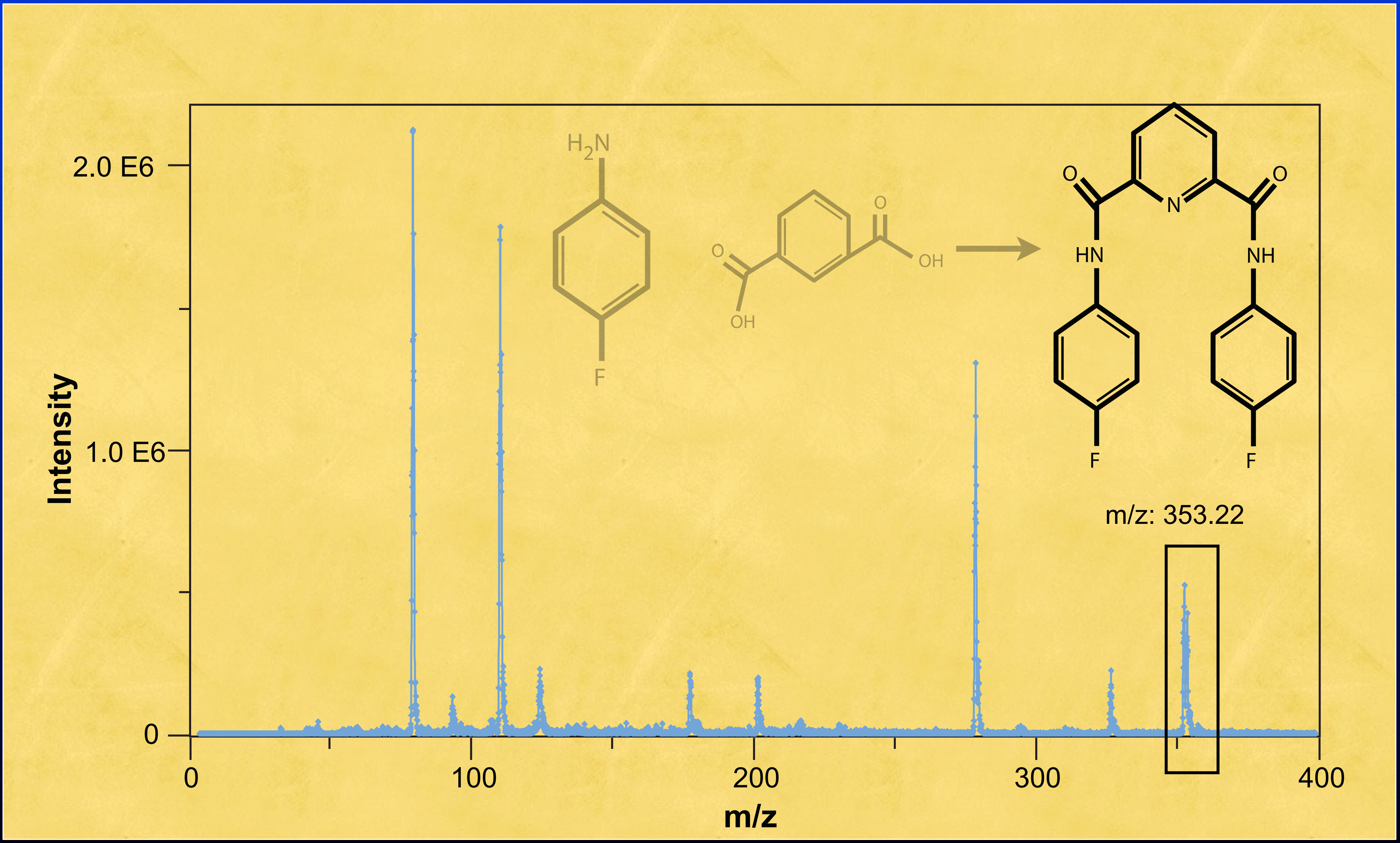
Thermally Assisted Vapour Introduction

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



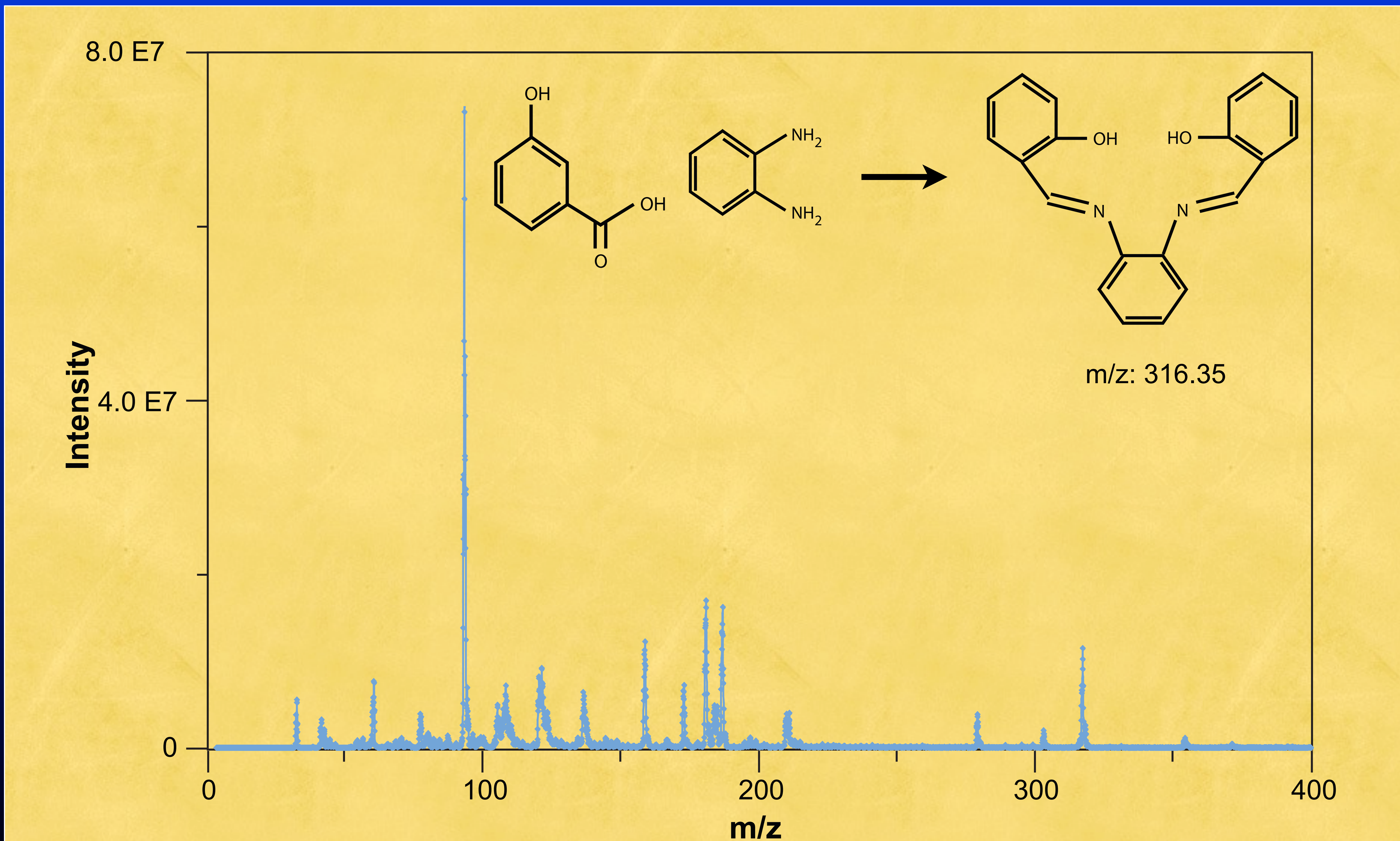
Thermally Assisted Vapour Introduction

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



Thermally Assisted Vapour Introduction

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



Thermally Assisted Vapour Introduction

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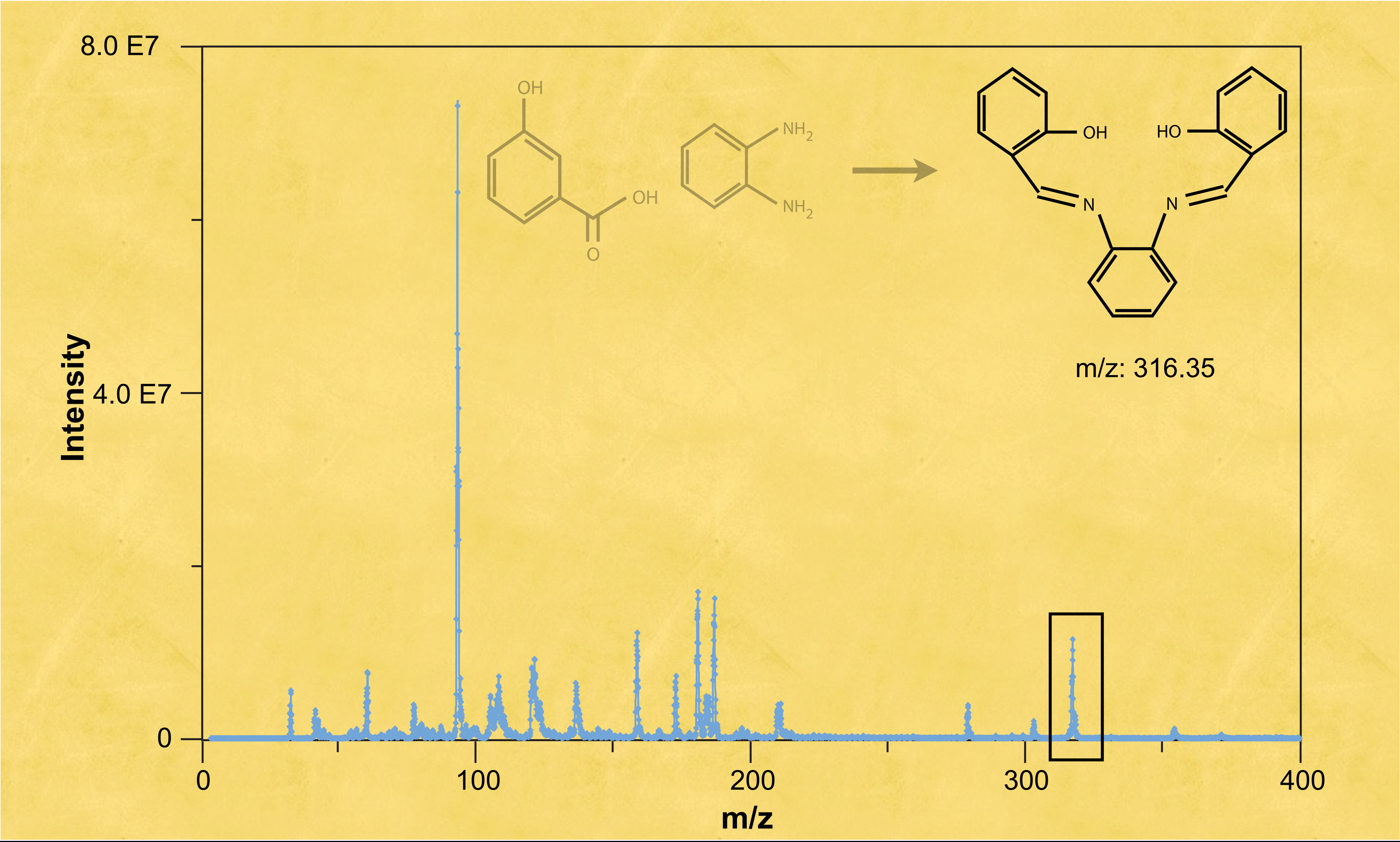


Thermally Assisted Vapour Introduction
Conclusions

Rapid, analysis able to characterize synthetic compounds

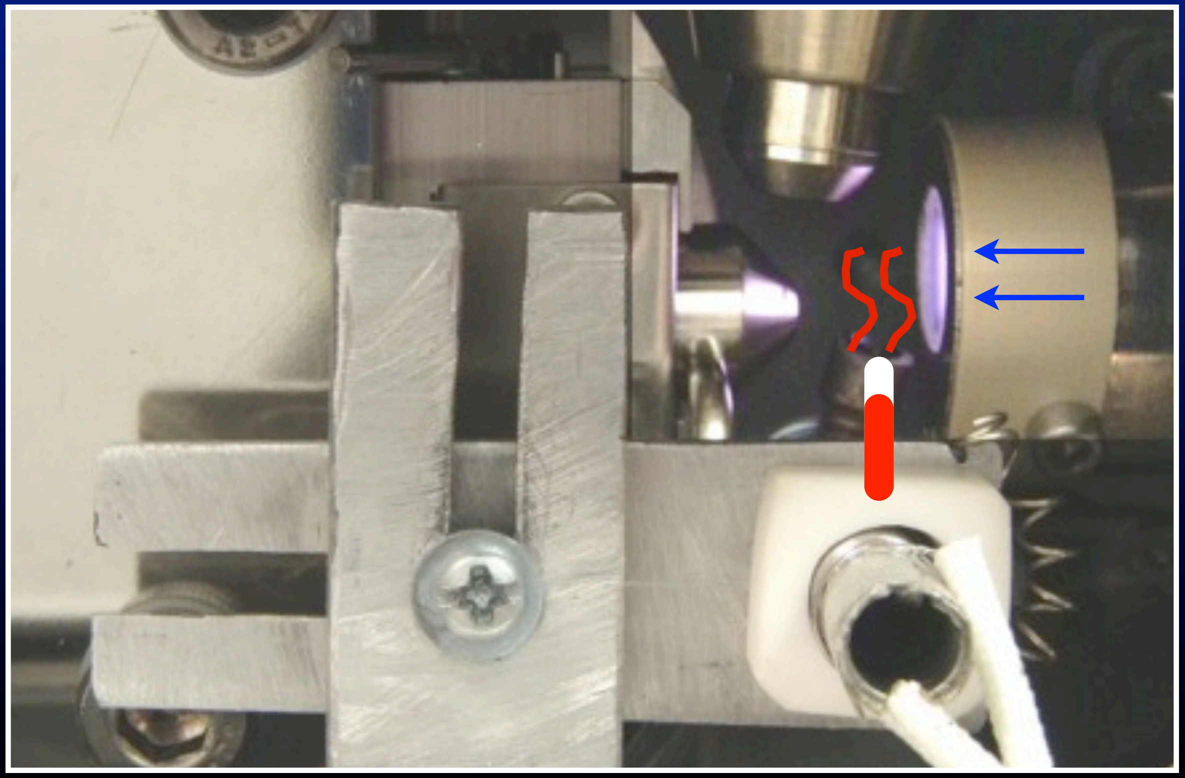
Easy to use on existing APPI instruments

Inexpensive

Future Study

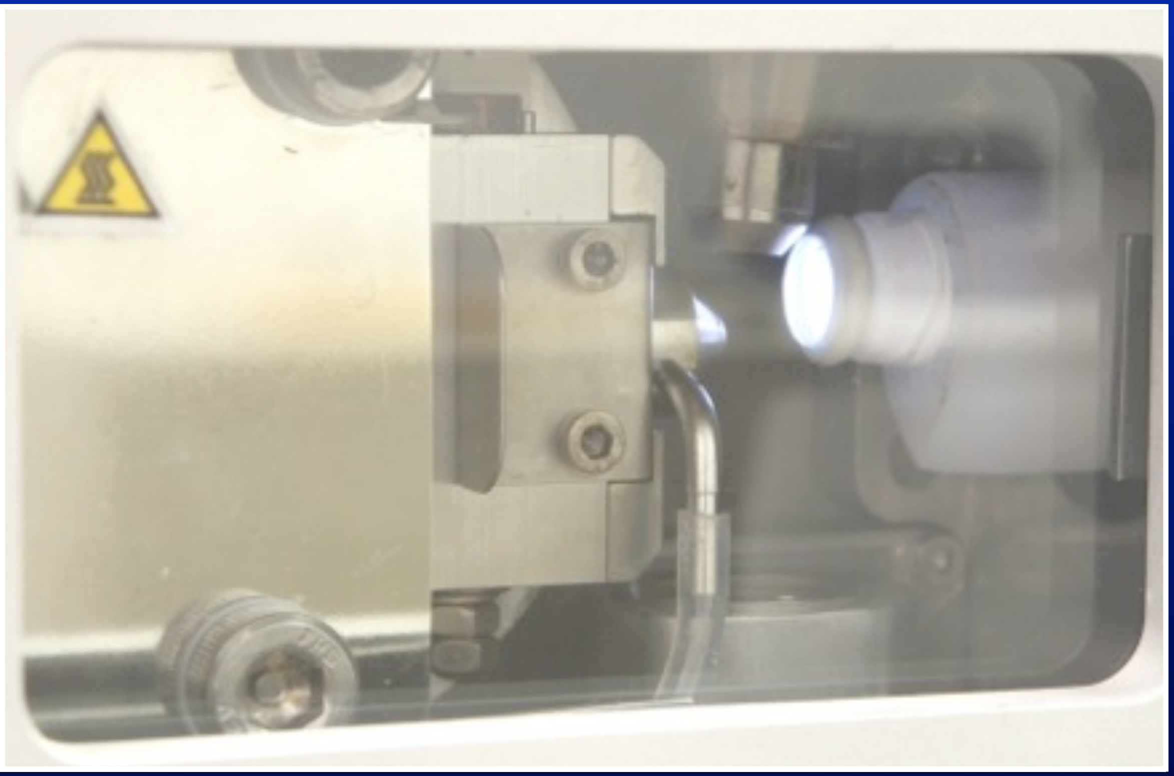
Control chaotic flows in source

Air sensitive compounds

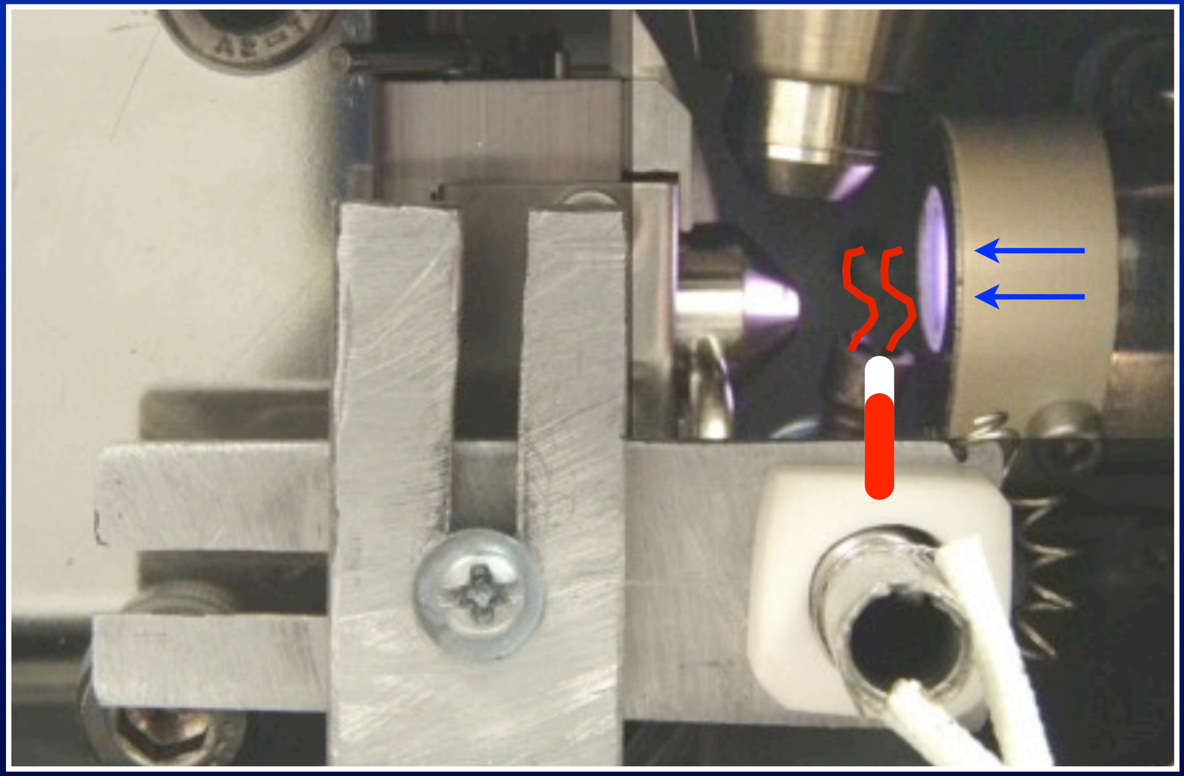


Lightning Ion Source & Vapour Introduction

Summary



Lightning Ion Source



Vapour Introduction

Acknowledgements

Supervisory Committee

Wuppertal collaboration

Dr. Rob O'Brien

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Davin Carter
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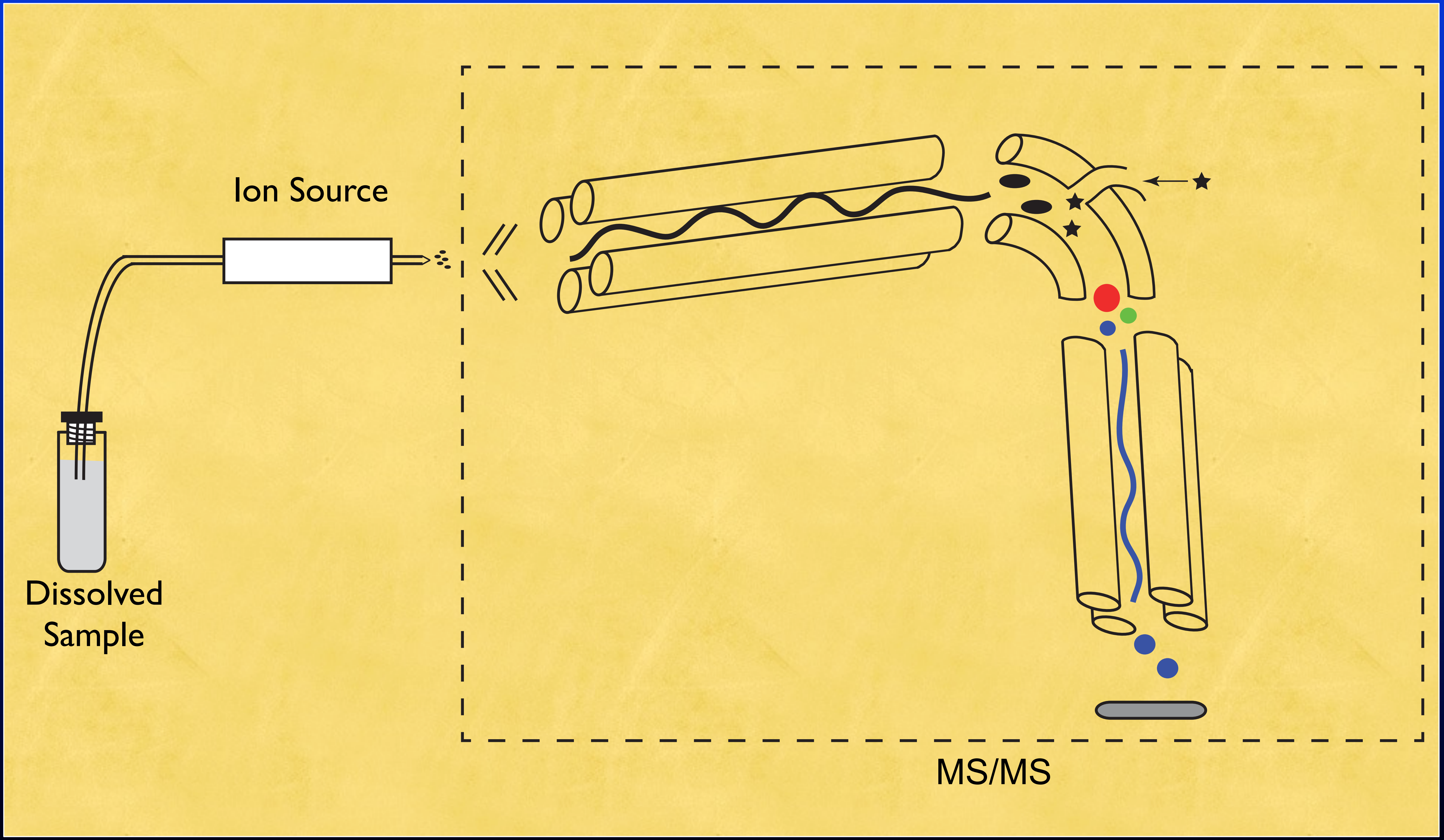
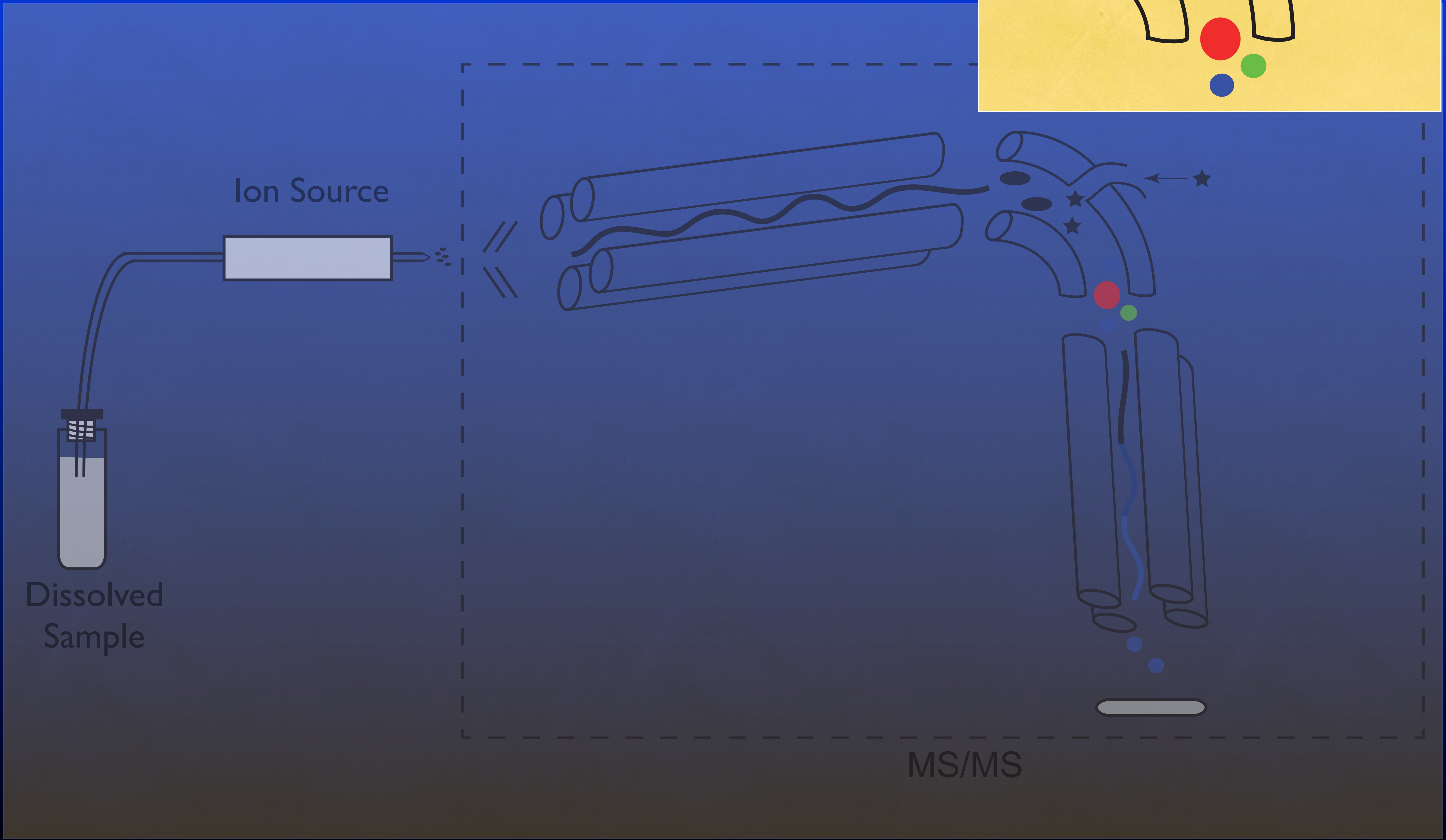
a place of mind

M. Sc. Thesis Defence
May 14, 2012

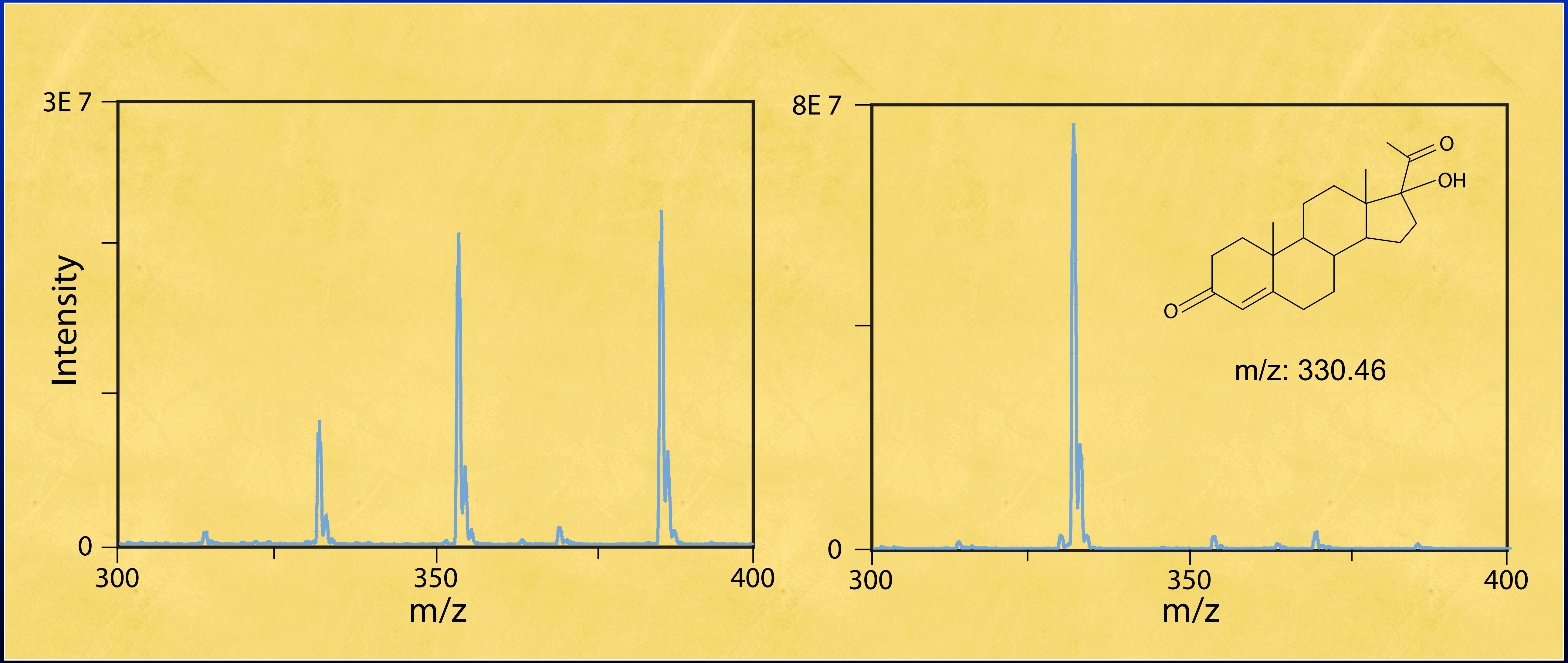
Atmospheric Pressure Photoionization
General workflow



Atmospheric Pressure Photoionization
CID



Lightning Ion Source
Results - Progesterone



Krypton Lamp **Lightning Ion Source**