

# DEVELOPMENT OF A SUPERCRITICAL CARBON DIOXIDE REACTOR WITH ONLINE SAMPLING BY MASS SPECTROMETRY FOR OBSERVATION OF PREBIOTIC CHEMICAL REACTION PRODUCTS

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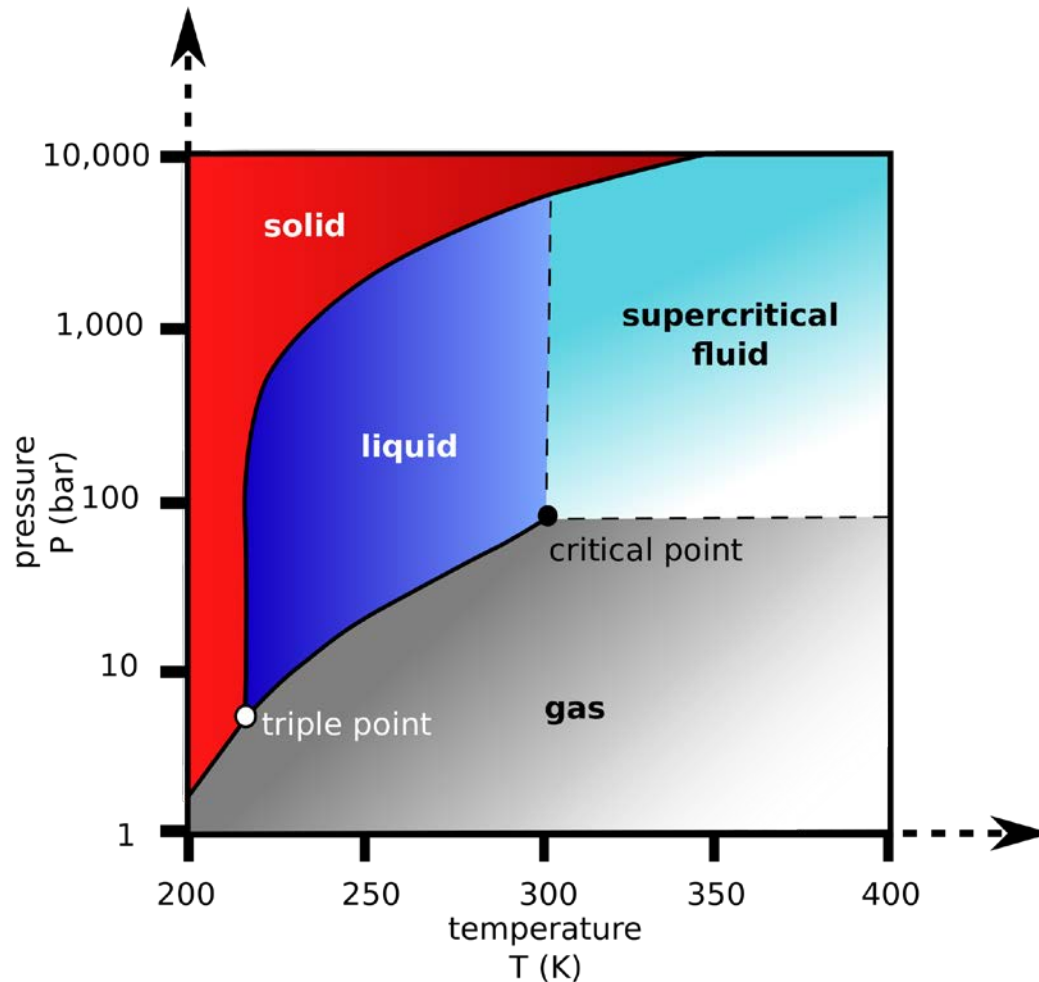
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# Overview

- Supercritical carbon dioxide – what do we know? Why is it interesting
- Experimental apparatus for studying reactions in  $\text{scCO}_2$
- Diagnostic testing of experimental apparatus
- Synthesis of biomolecules in  $\text{scCO}_2$
- Discussion of future work

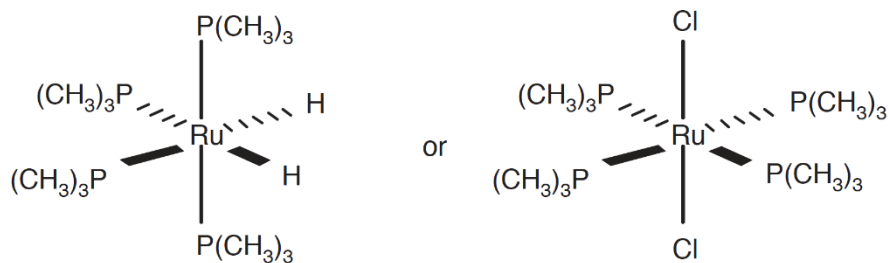
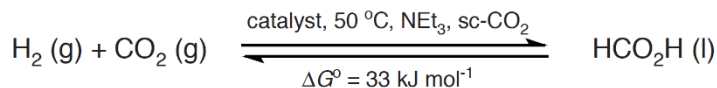
# Supercritical carbon dioxide (scCO<sub>2</sub>)



- $\geq 73.8$  atm
- $\geq 31.3^{\circ}$  C
- Evaporates upon removal of pressure – hence its potential as a green solvent

# Known processes in scCO<sub>2</sub>

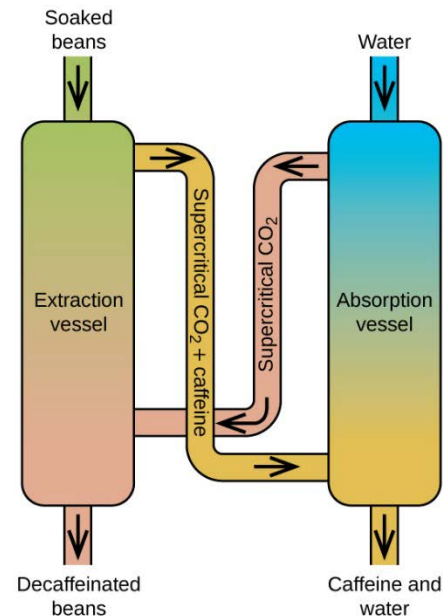
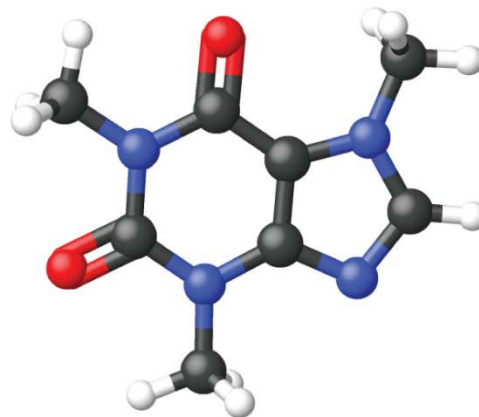
## Hydrogenation



Scheme I. Ruthenium(II)-catalyzed hydrogenation of CO<sub>2</sub> in the supercritical fluid phase

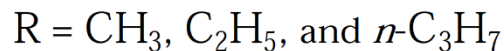
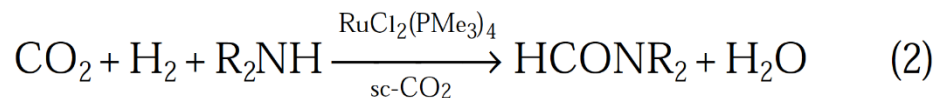
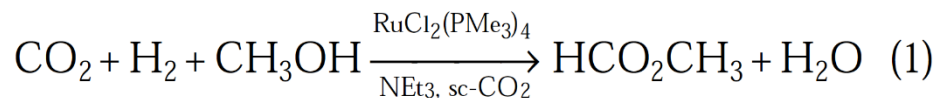
Wai, C. M. *et al. Journal of Chem Ed*, 75, 1641 (1998)

## Decaffeination



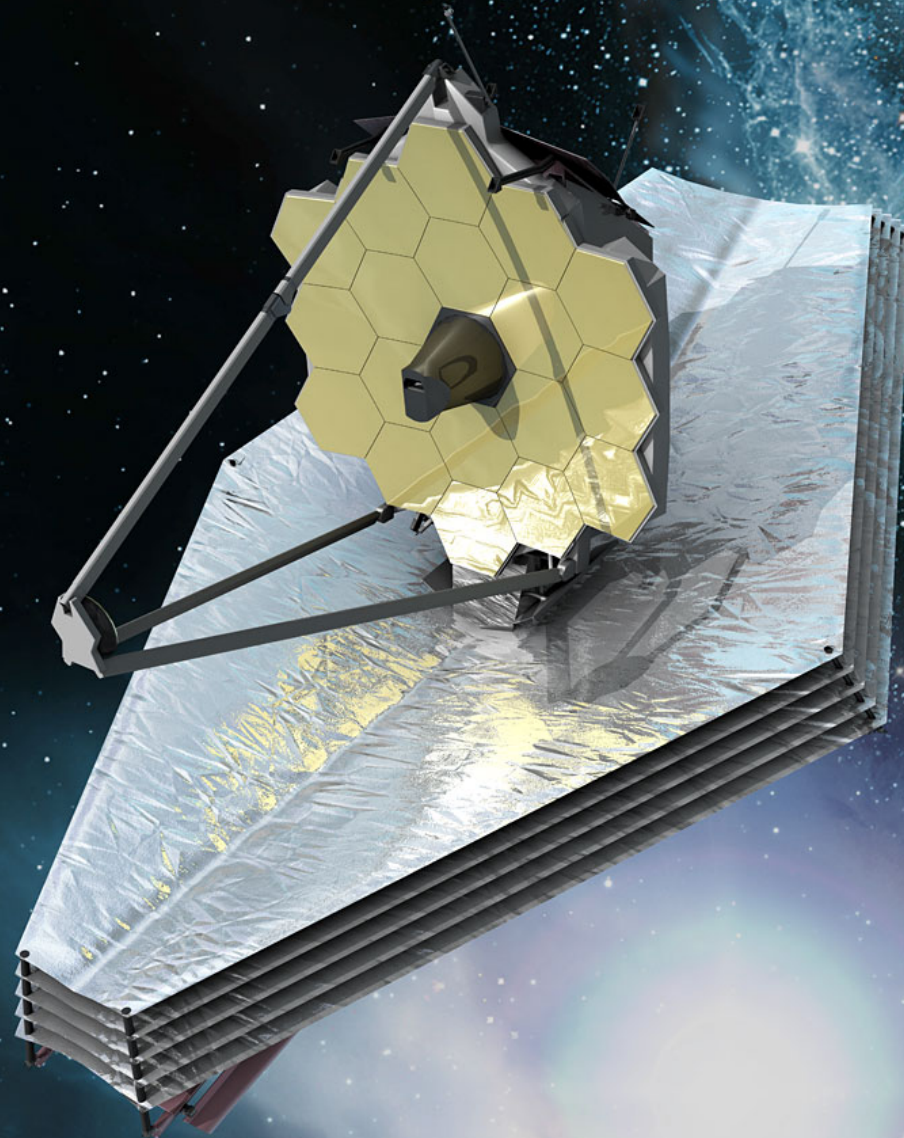
<http://philschatz.com/chemistry-book/contents/m51080.html>

## Hydroformylation



Wai, C. M. *et al. Journal of Chem Ed*, 75, 1641 (1998)

M  
T  
U  
A

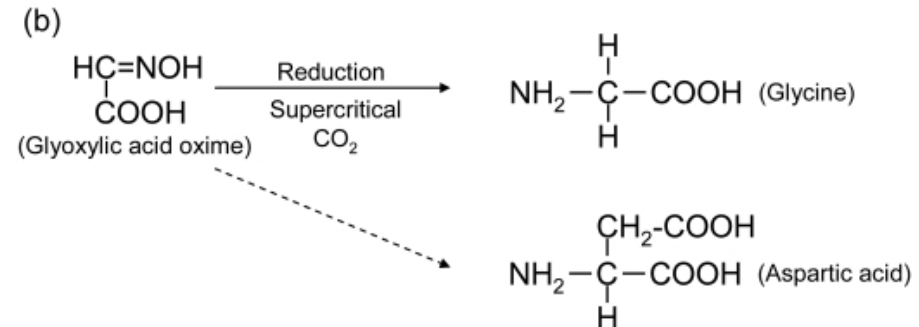
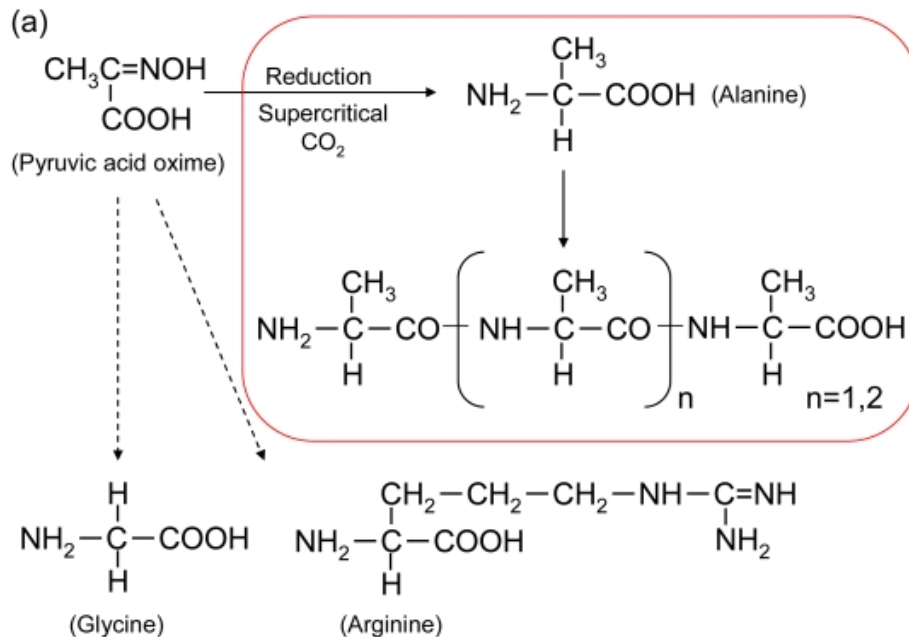
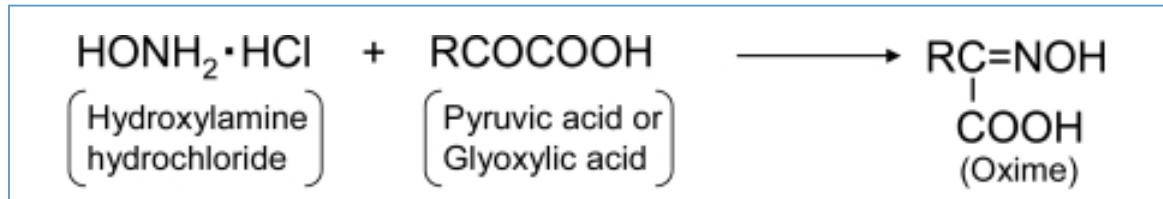


res

0°C

# scCO<sub>2</sub> a possible pre-biotic solvent? (cont.)

- Fujioka and colleagues demonstrated synthesis of some amino acids in an scCO<sub>2</sub>-H<sub>2</sub>O system





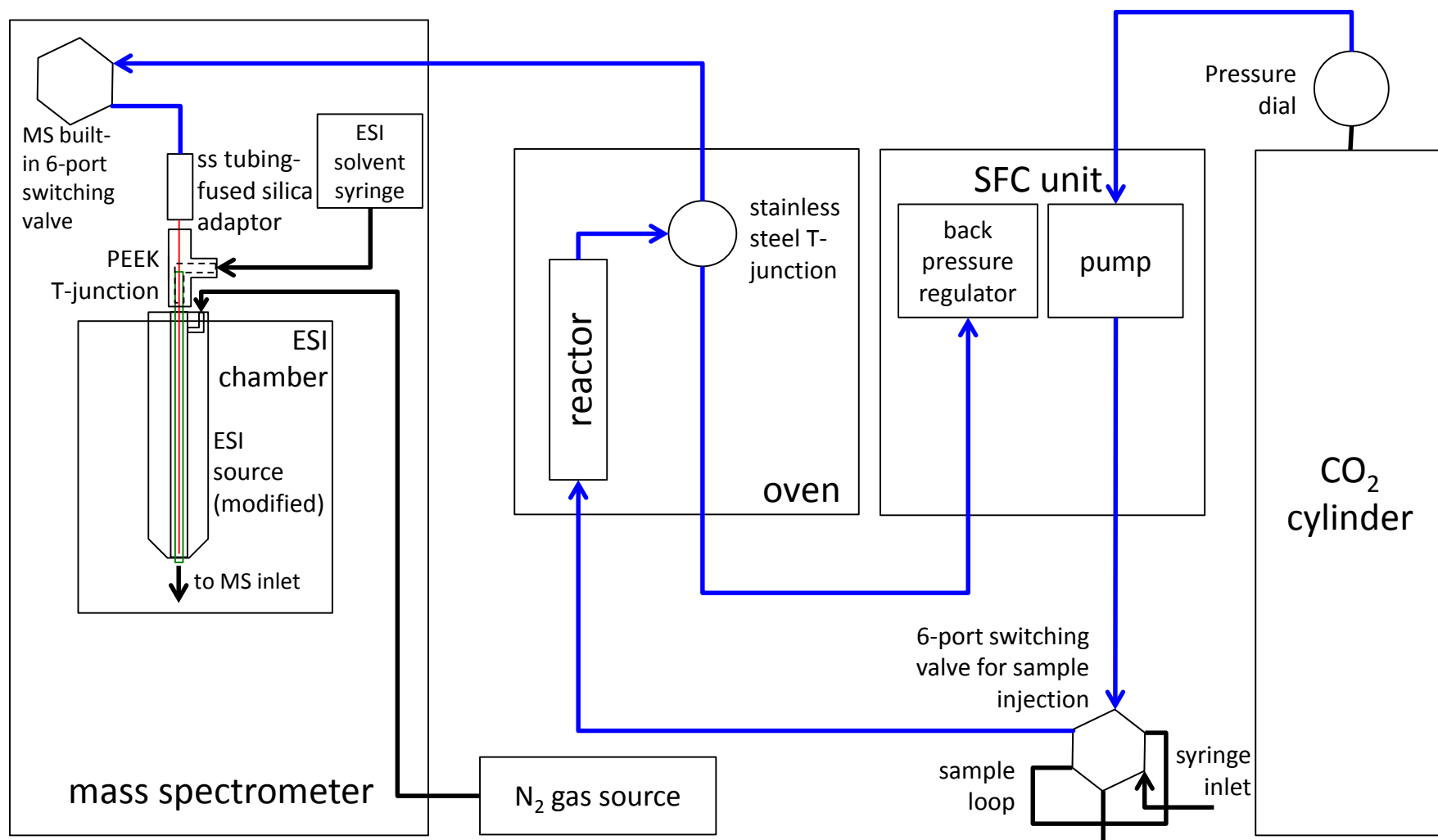
# An scCO<sub>2</sub> – MS coupled reactor

Key:

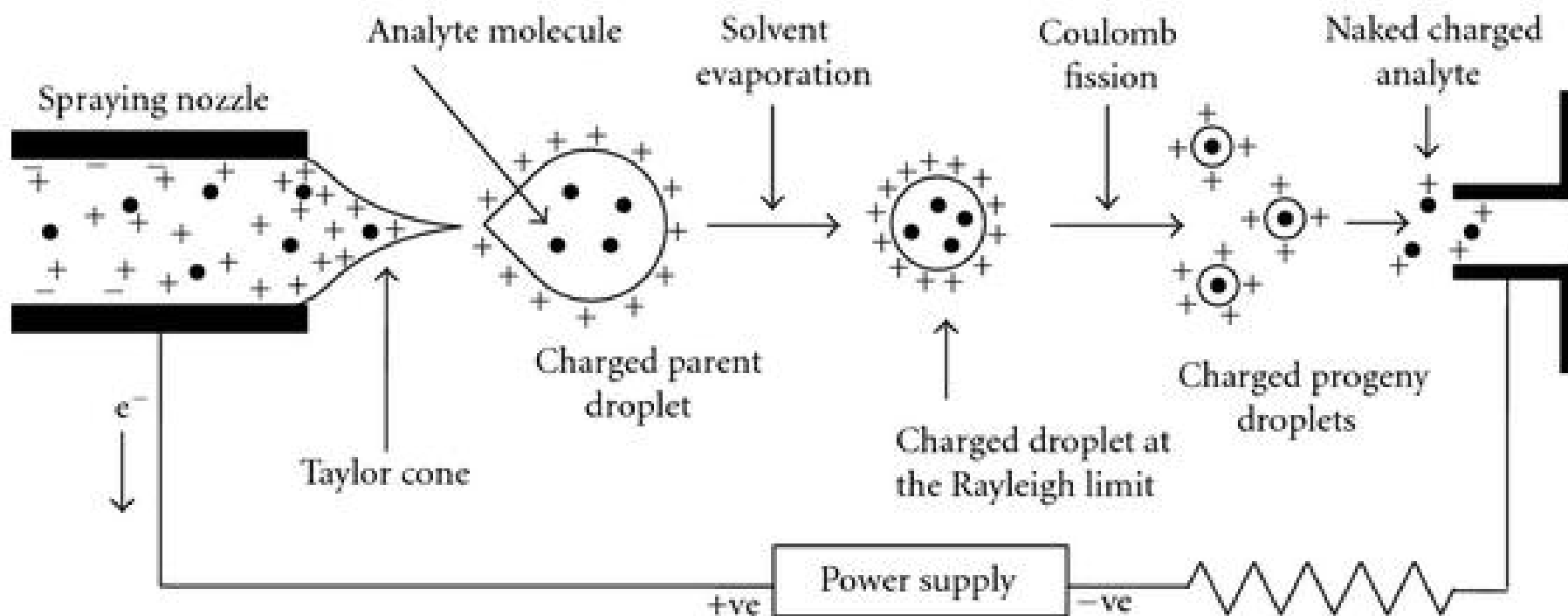
— fused silica capillary

— 26 gauge ss tubing

— 0.005" i.d. ss tubing



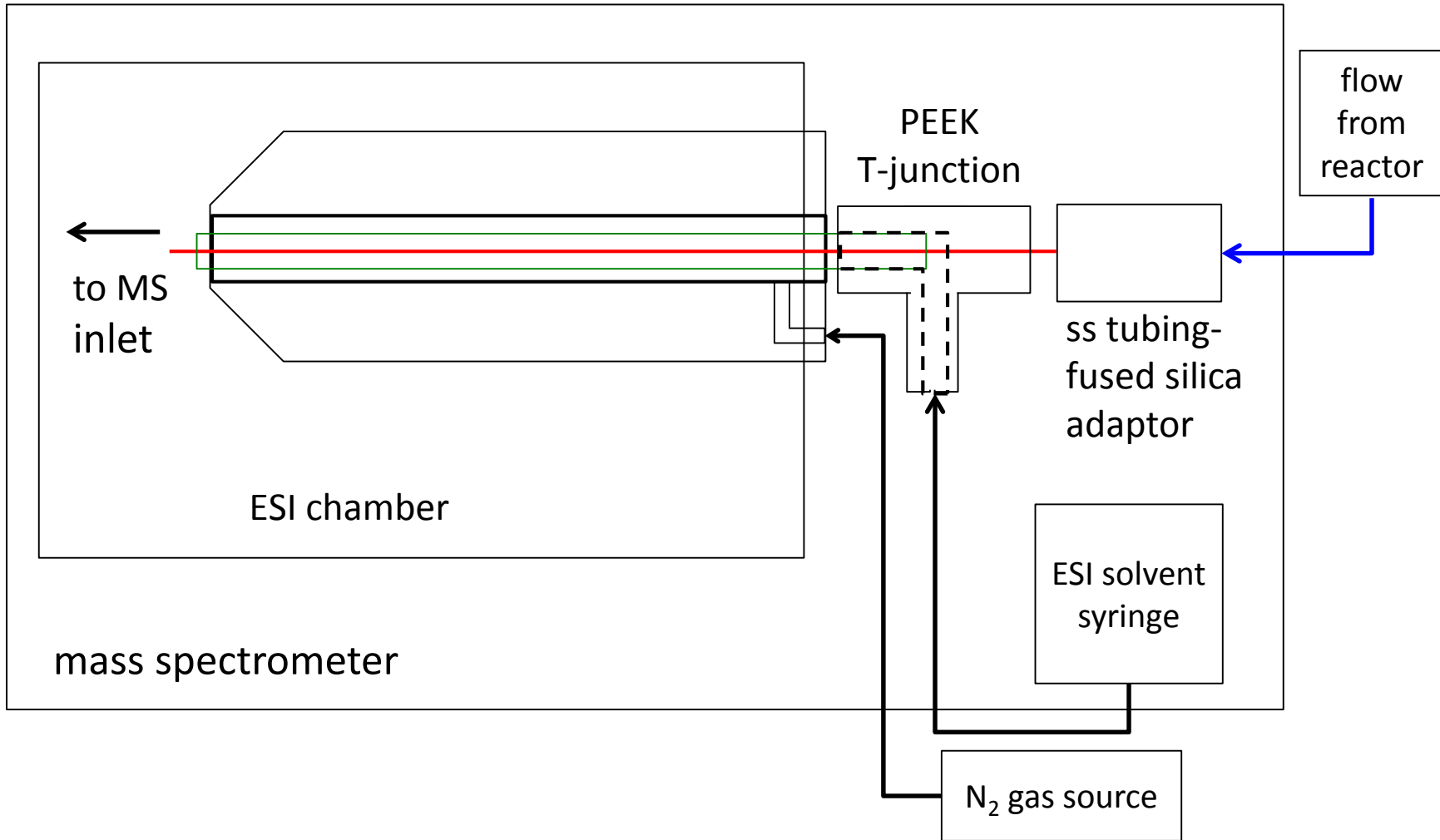
# Electrospray ionization mass spectrometry (ESI-MS)



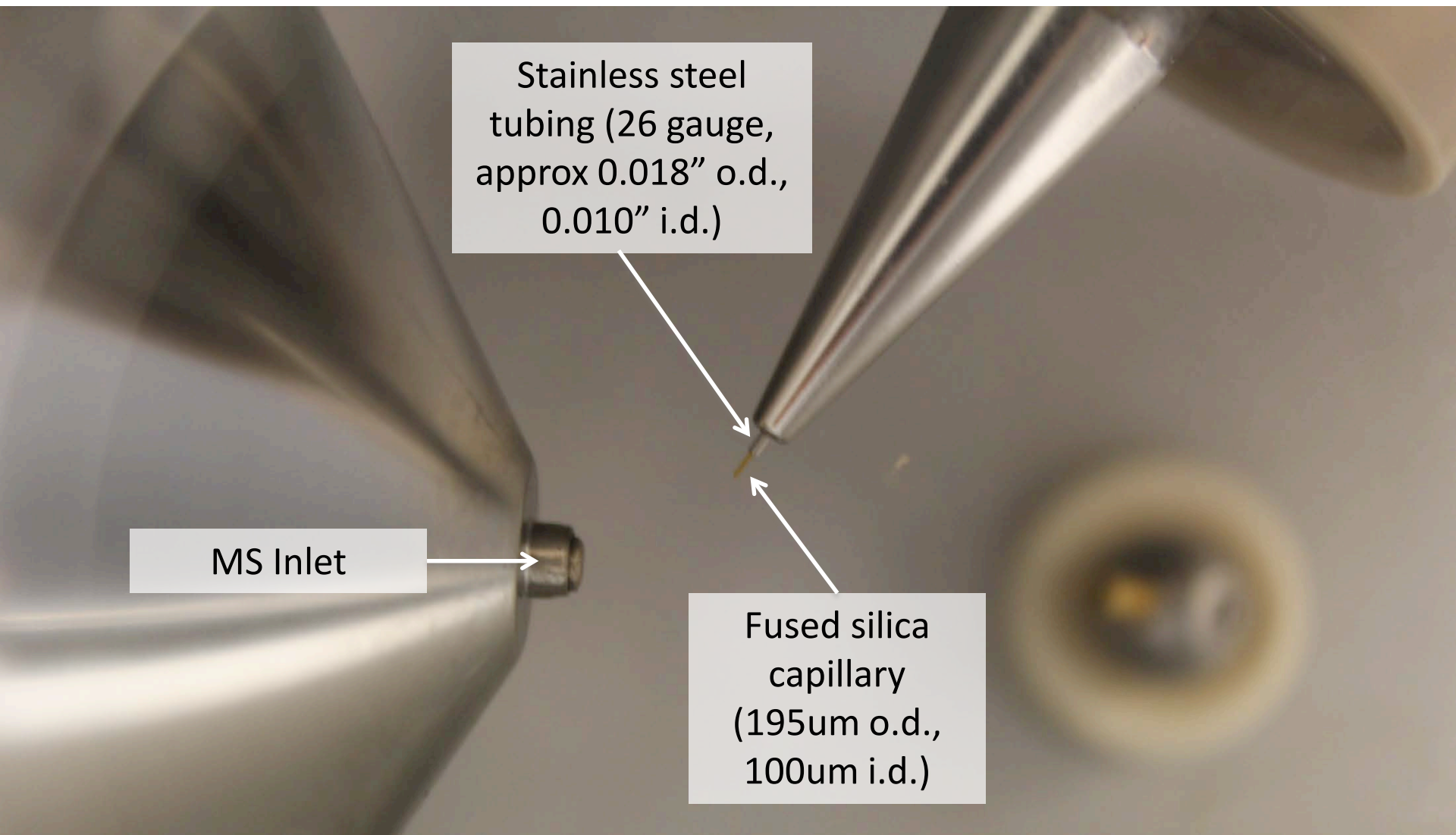


# Modified ESI source

Key: \_\_\_\_\_ fused silica capillary \_\_\_\_\_ 26 gauge ss tubing \_\_\_\_\_ 0.005" i.d. ss tubing



# Modified ESI tip (fused silica protruding)

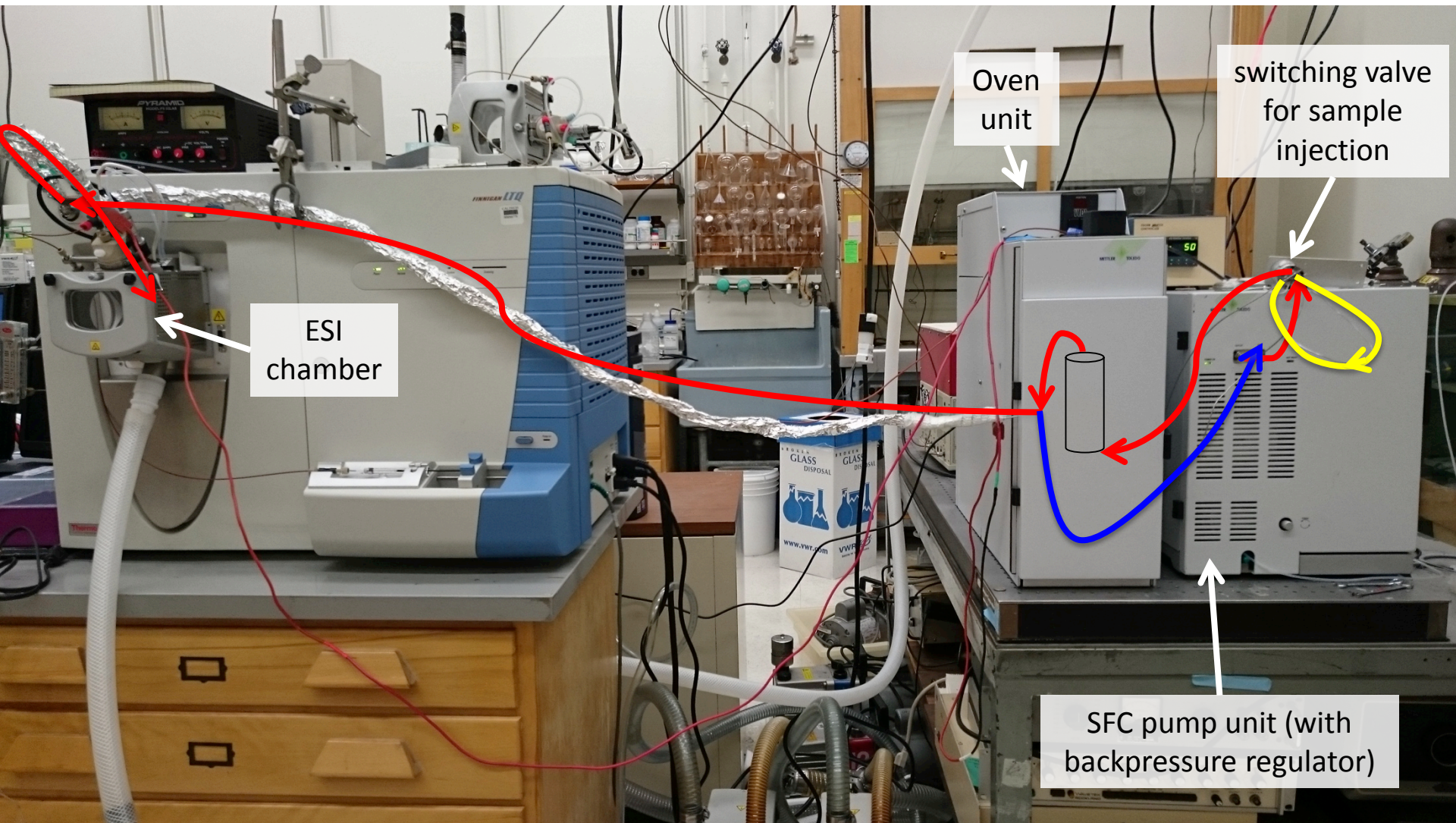


Stainless steel  
tubing (26 gauge,  
approx 0.018" o.d.,  
0.010" i.d.)

MS Inlet

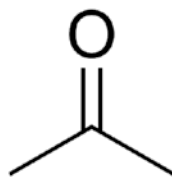
Fused silica  
capillary  
(195um o.d.,  
100um i.d.)

# Laboratory set-up

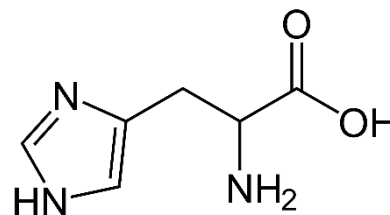


# Diagnostic tests

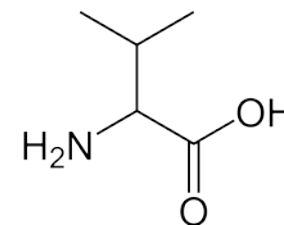
- Solvent injection tests
  - 100  $\mu\text{L}$  injection volume



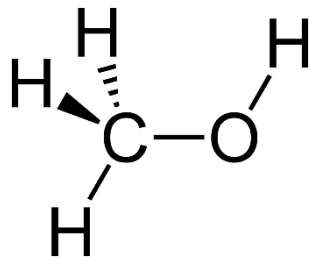
Acetone



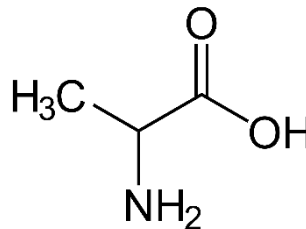
Histidine (1 mM)



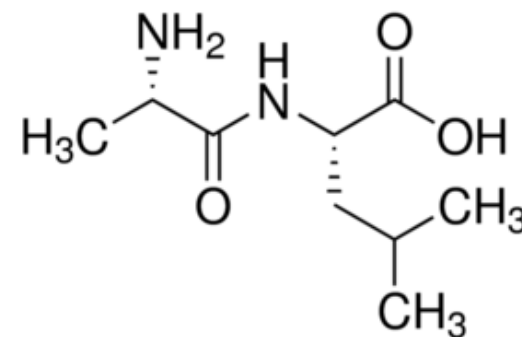
Valine (1 mM, 10  $\mu\text{M}$ )



Methanol



Alanine (1 mM)

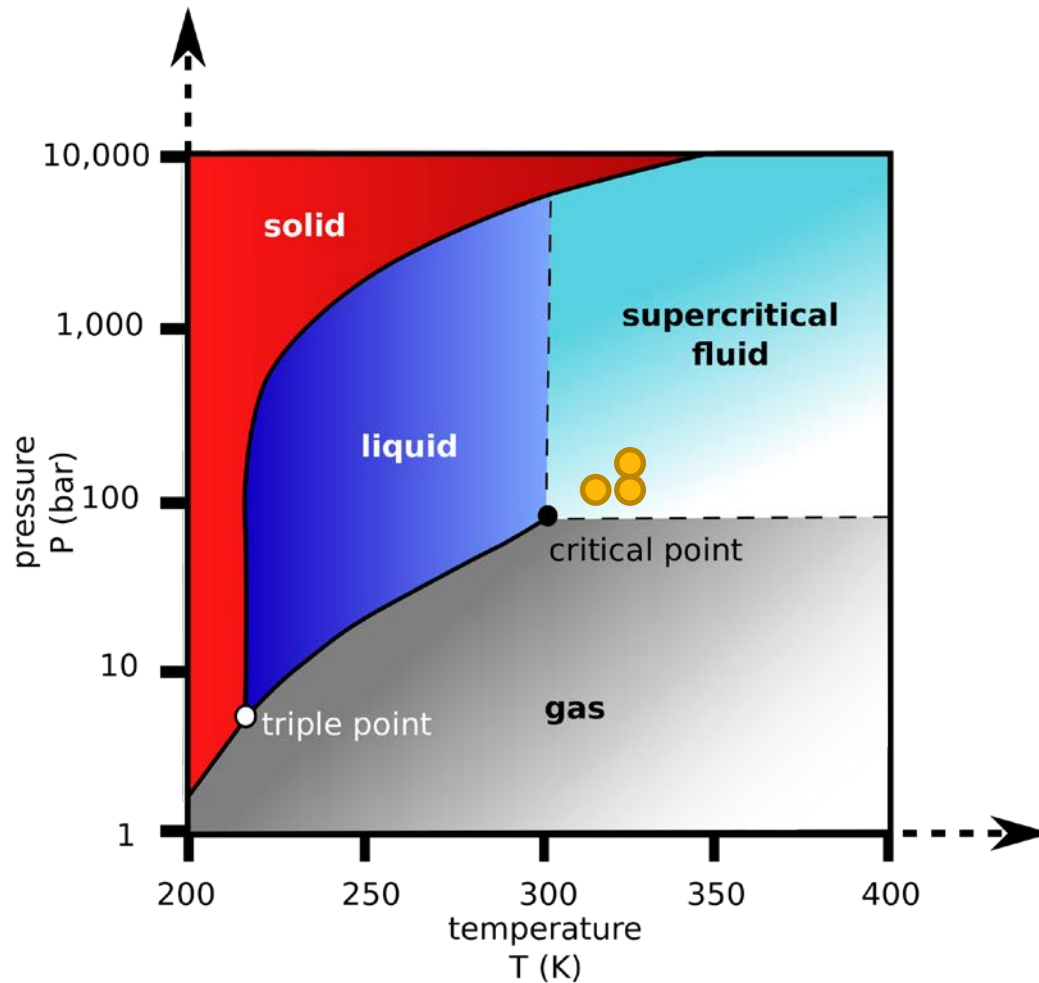


Ala-Leu (1 mM, 10  $\mu\text{M}$ )

- Amino acid & peptide tests
  - Dissolved in methanol, 100  $\mu\text{L}$  injection

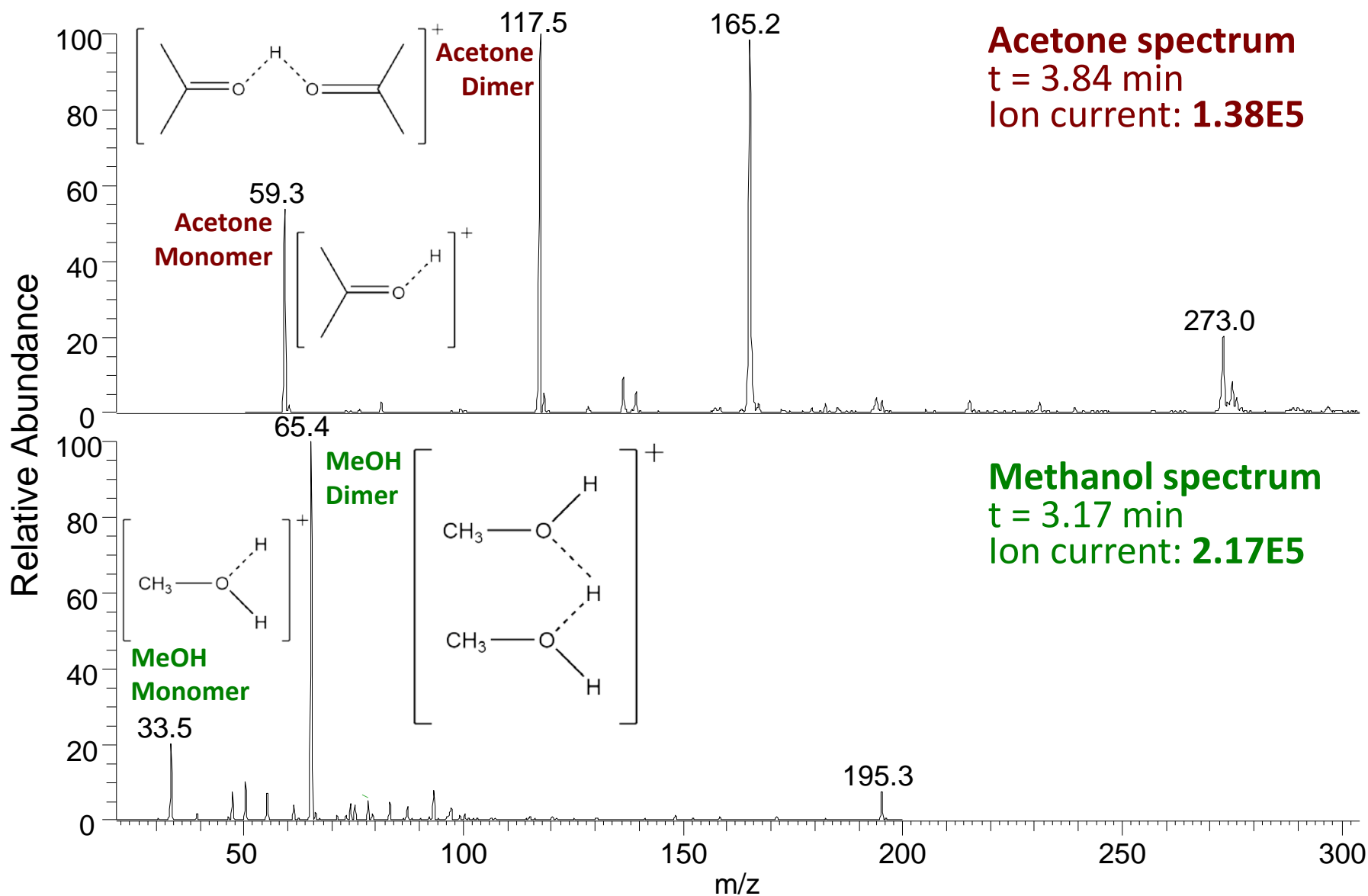


# Conditions for testing



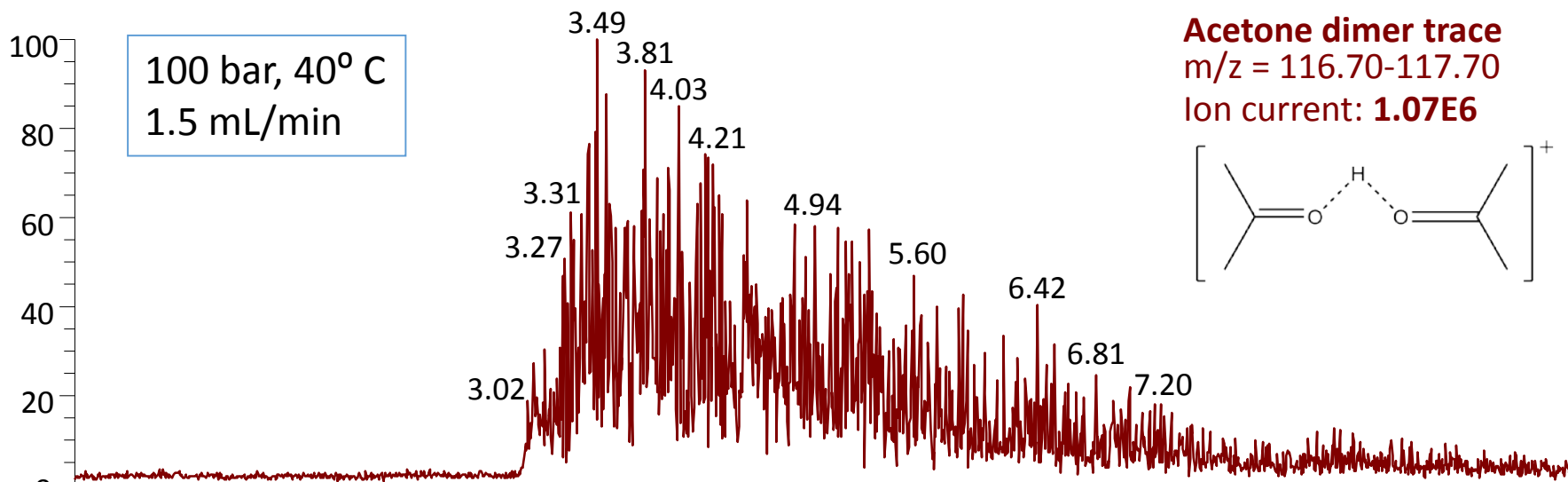
- 100 bar, 40° C
- 150 bar, 60° C
- 100 bar, 60° C

# Solvent tests – acetone & methanol spectra

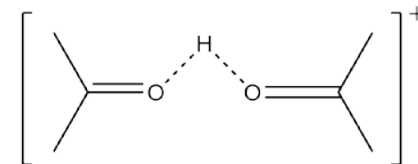


# Solvent tests – acetone & methanol

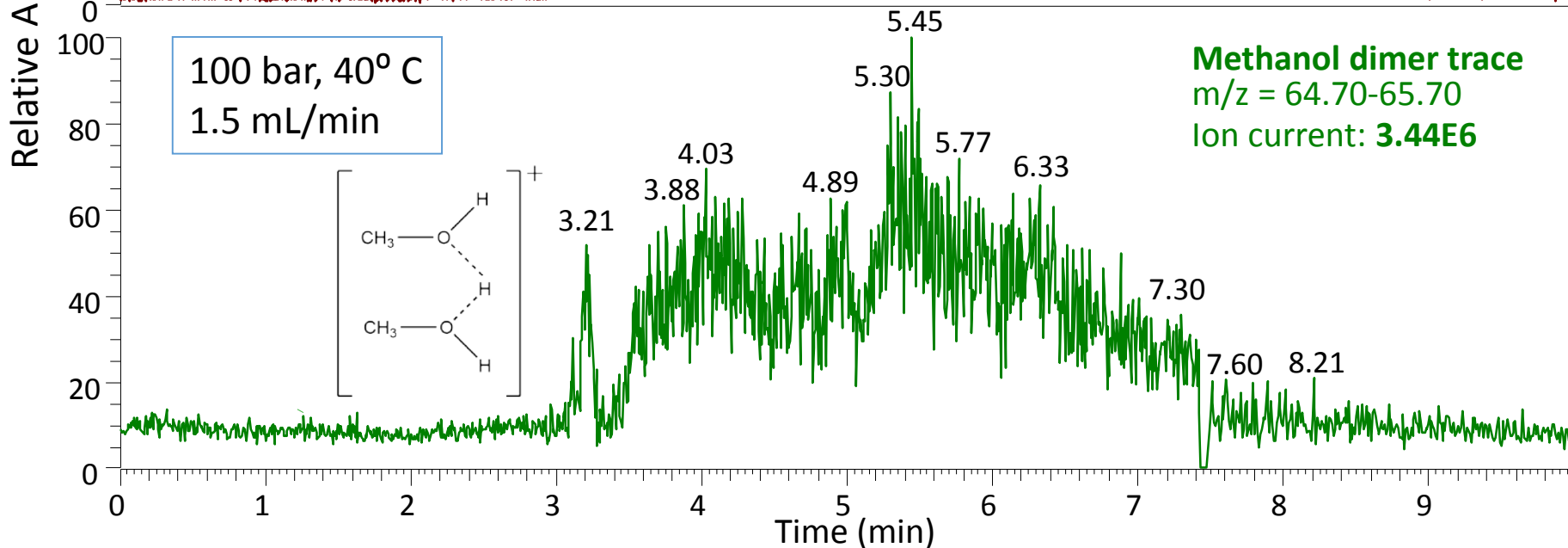
100 bar, 40° C  
1.5 mL/min



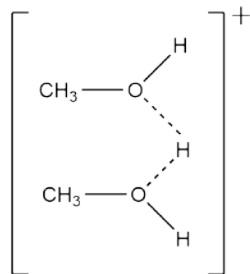
**Acetone dimer trace**  
m/z = 116.70-117.70  
Ion current: **1.07E6**



100 bar, 40° C  
1.5 mL/min

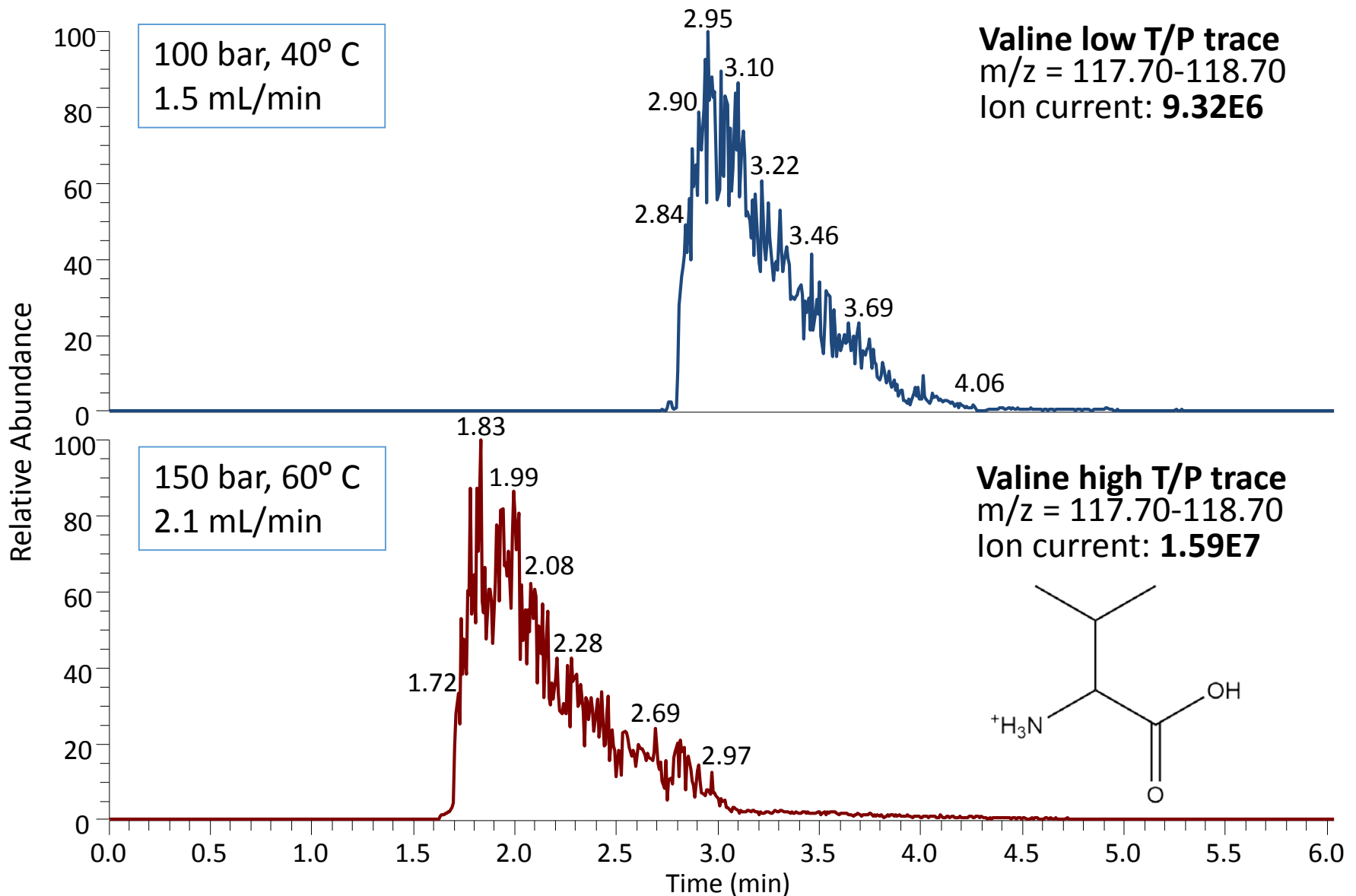


**Methanol dimer trace**  
m/z = 64.70-65.70  
Ion current: **3.44E6**

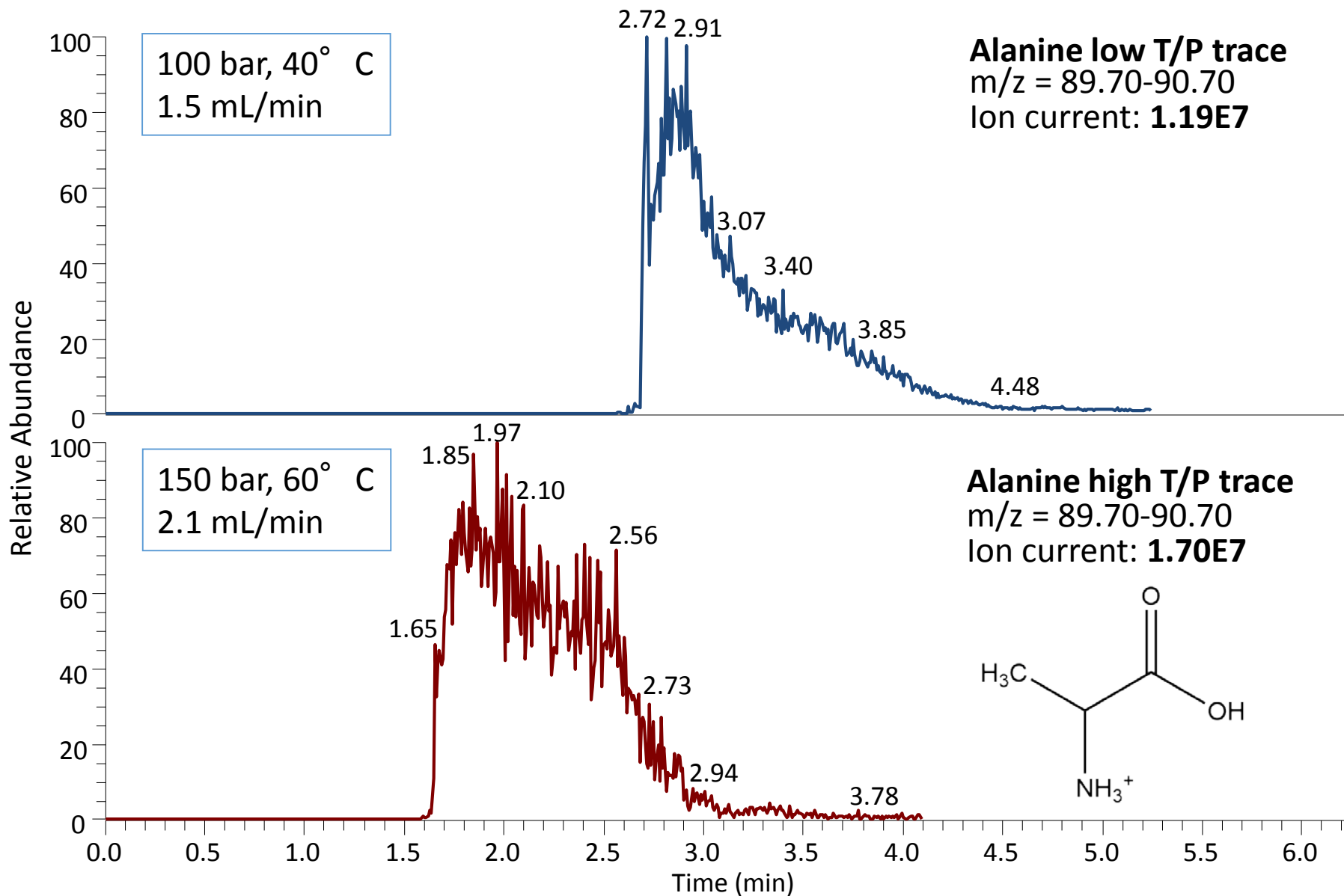




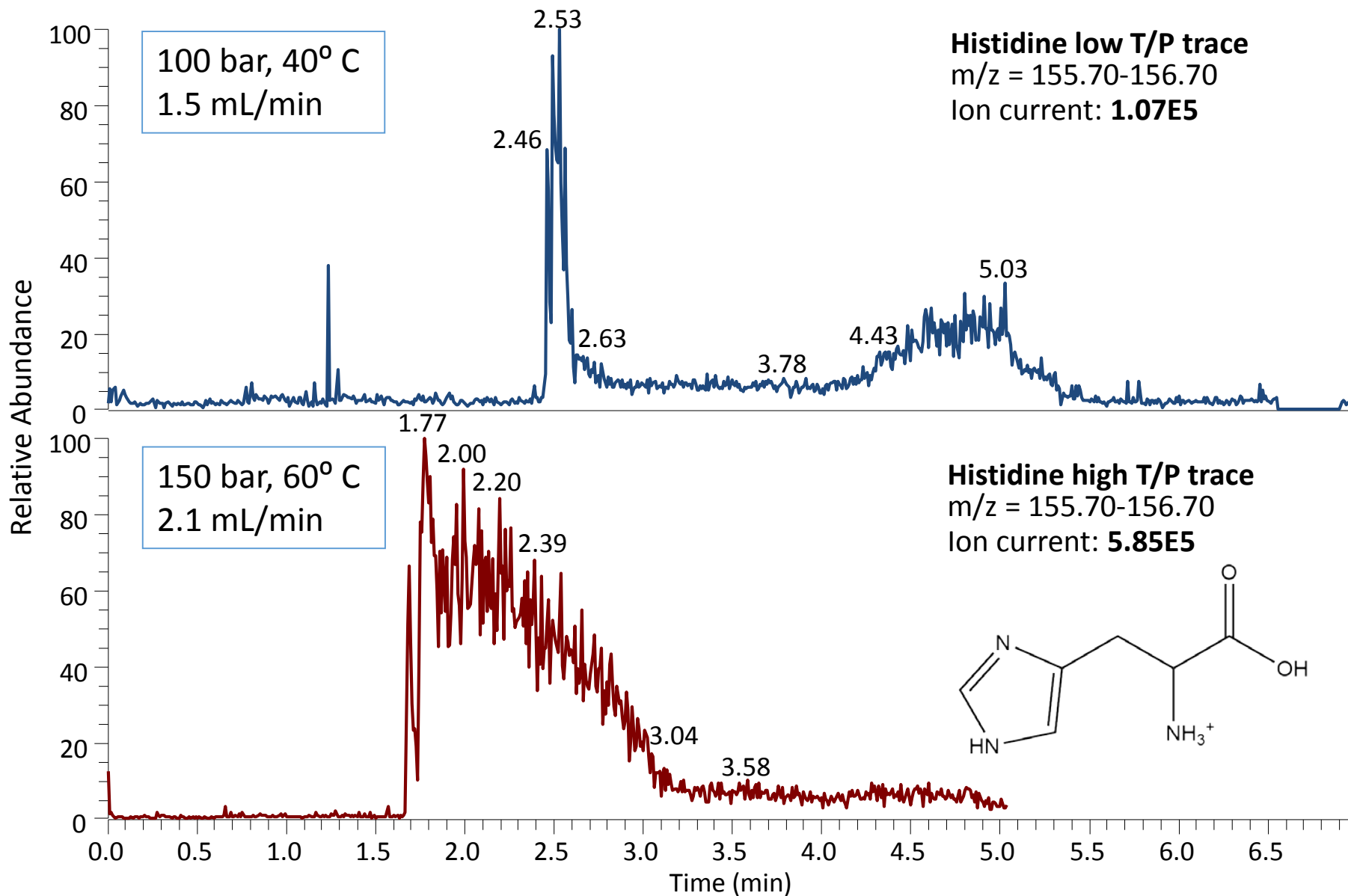
# Valine tests (low T/P & high T/P)



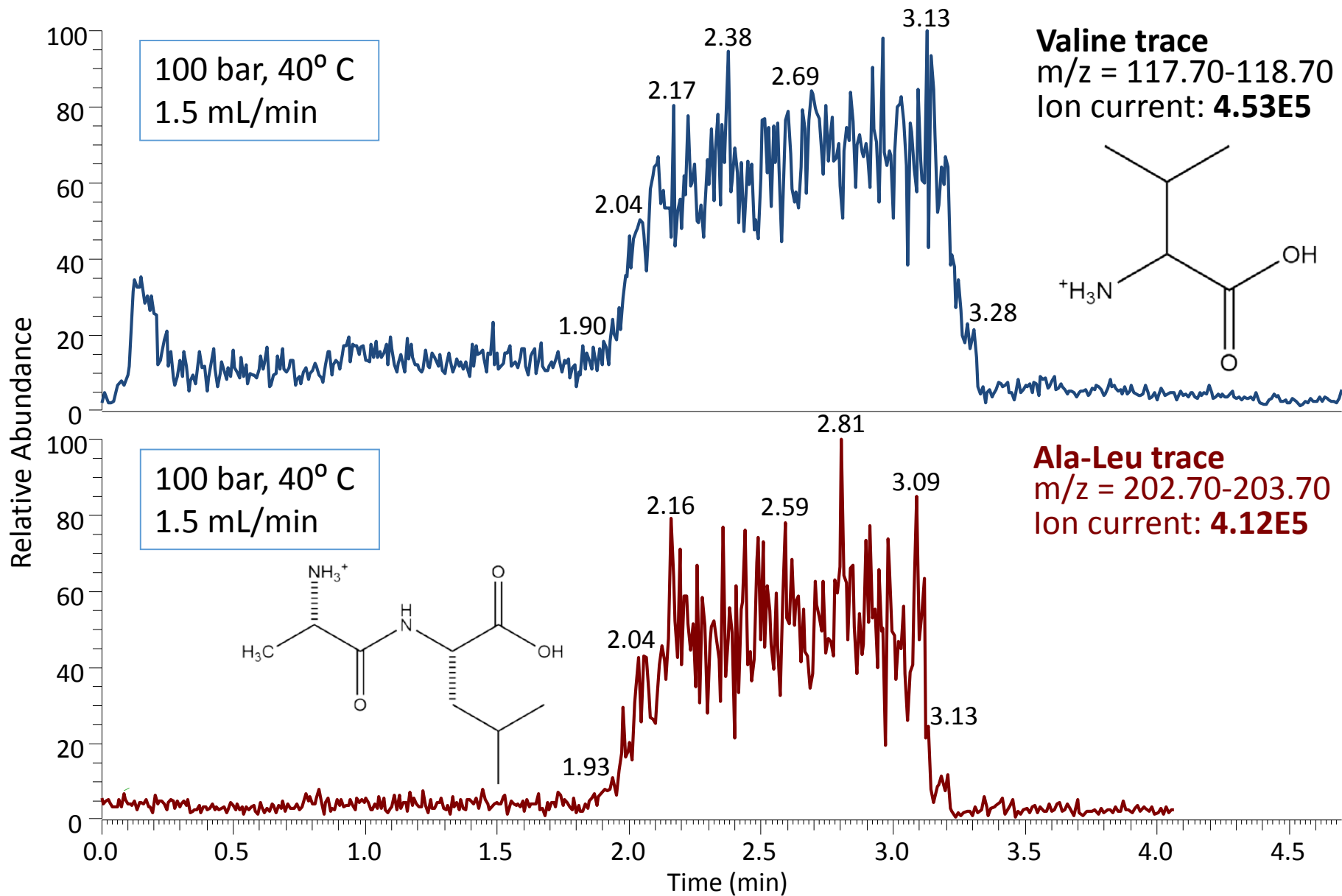
# Alanine tests (low T/P & high T/P)



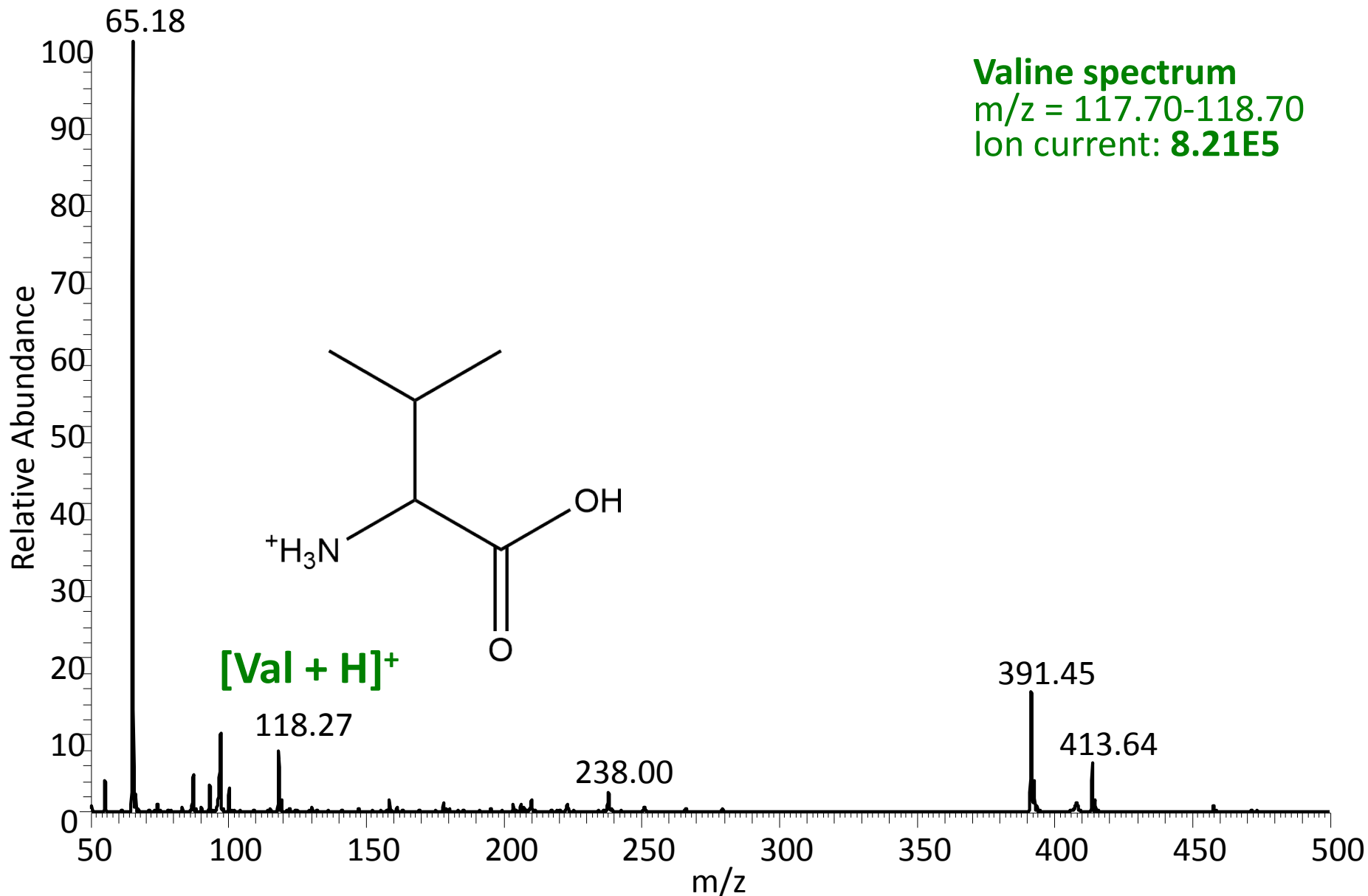
# Histidine tests (low T/P & high T/P)



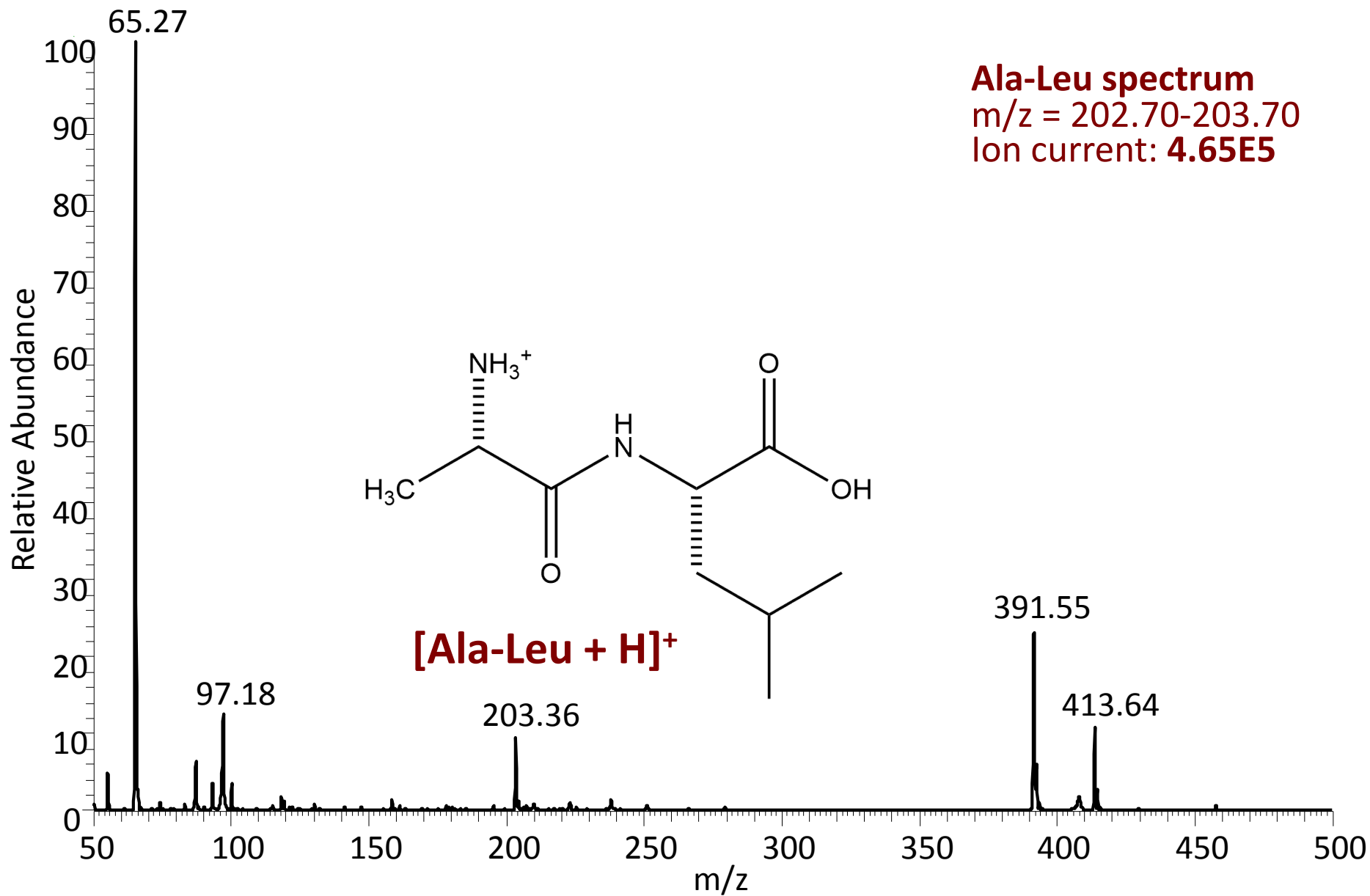
# 10 $\mu\text{M}$ val & ala-leu (low T/P)



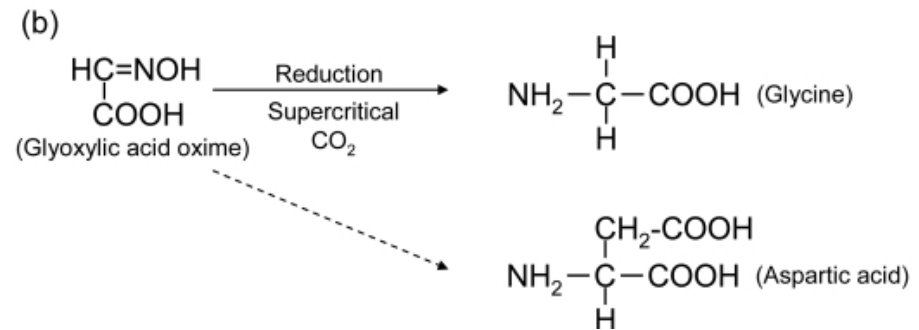
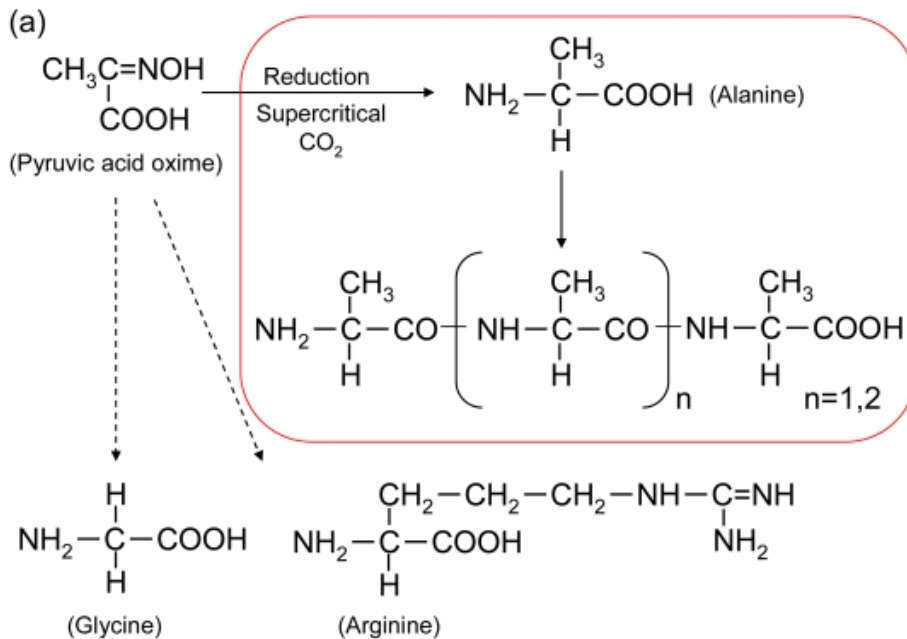
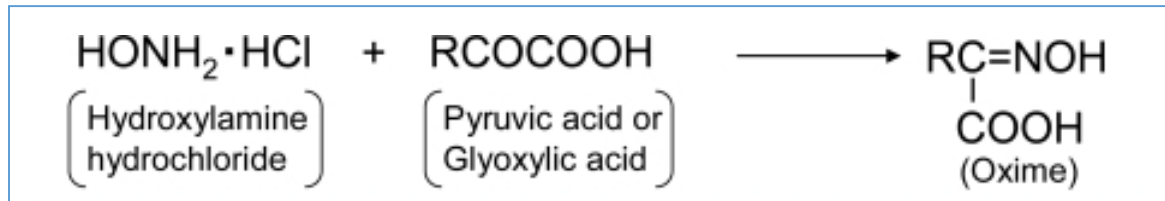
# 10 $\mu\text{M}$ valine – spectrum



# 10 $\mu\text{M}$ Ala-Leu – spectrum



# Hydroxylamine and Carboxylic Acid Tests

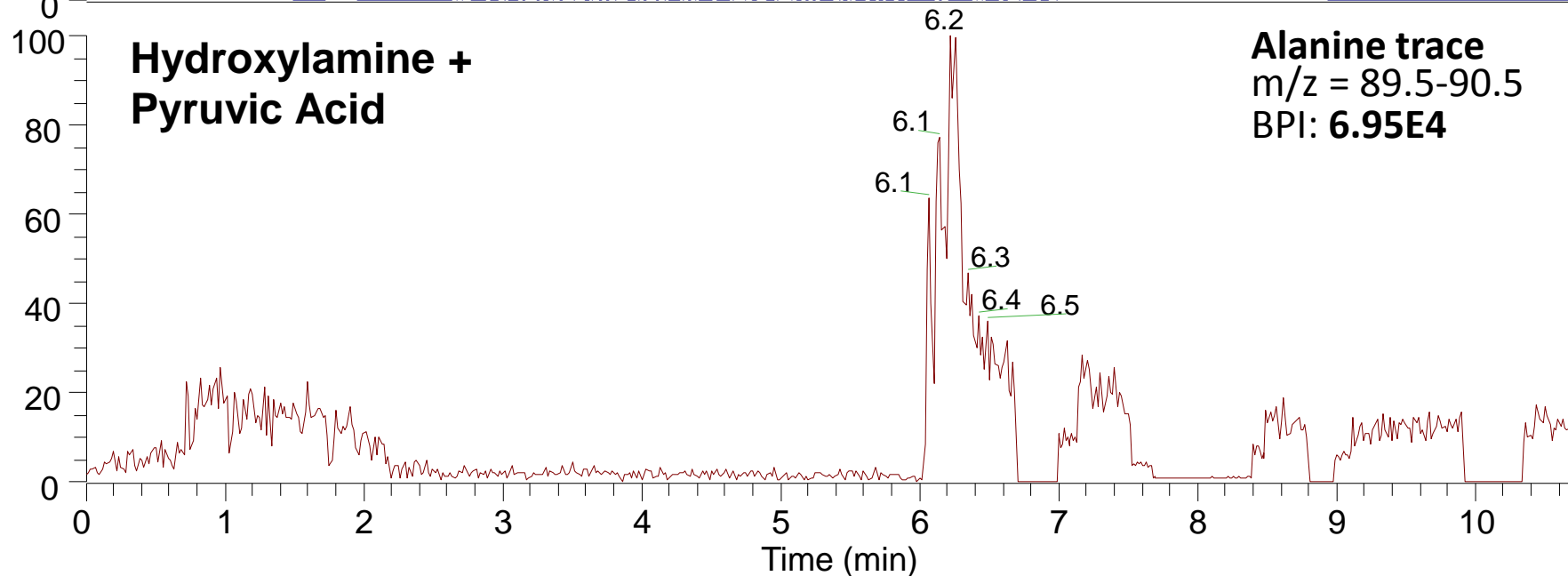


Fujioka, K. *et al. Int J Mol Sci.*, 10, 2730 (2009)

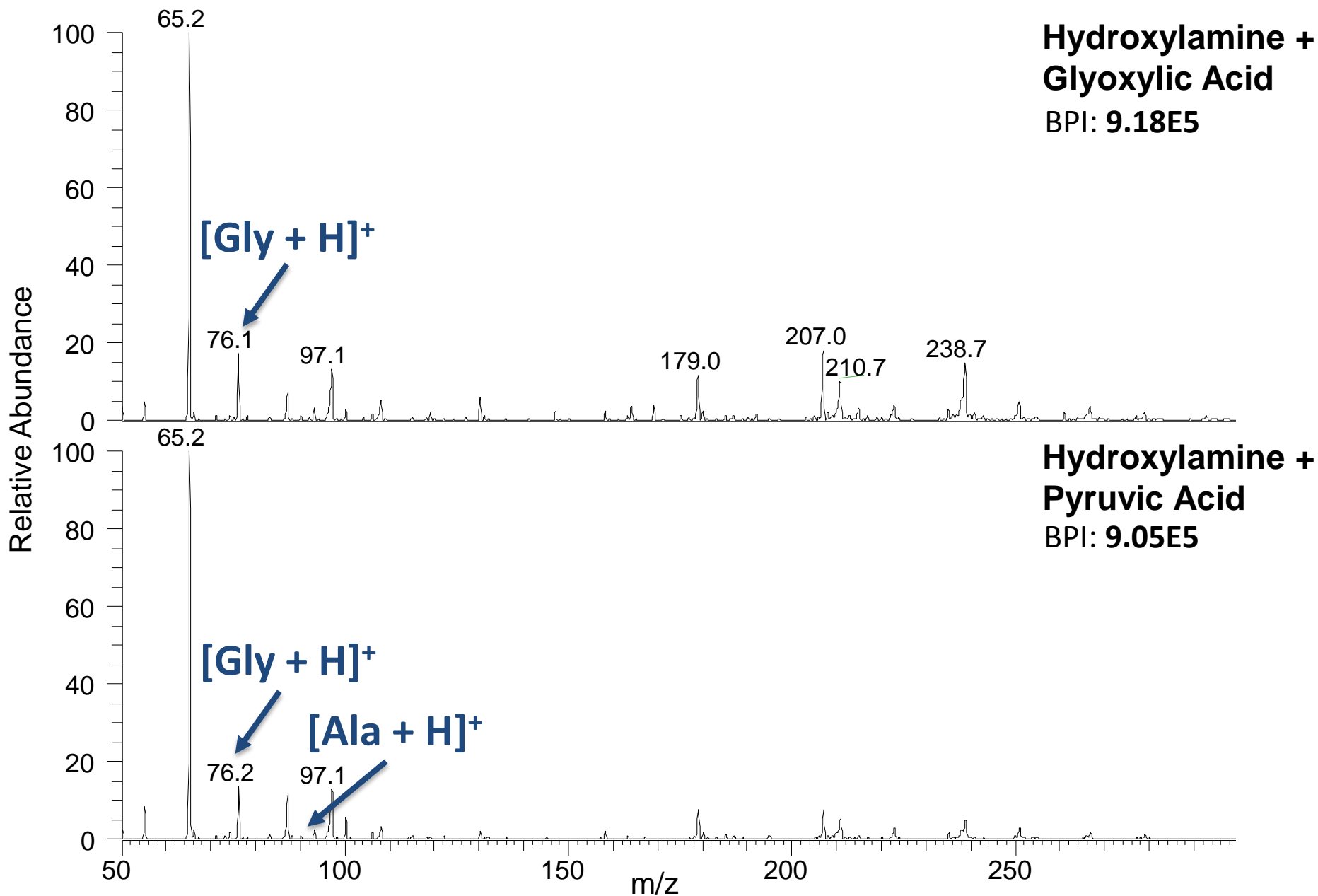
- Injected 50  $\mu\text{L}$  of 1 mM Hydroxylamine + 50  $\mu\text{L}$  of 1 mM Glyoxylic/Pyruvic Acid in 75/25 (v/v) MeOH/H<sub>2</sub>O
- Ran in reactor for 2 h at 60<sup>o</sup> C and 100 bar



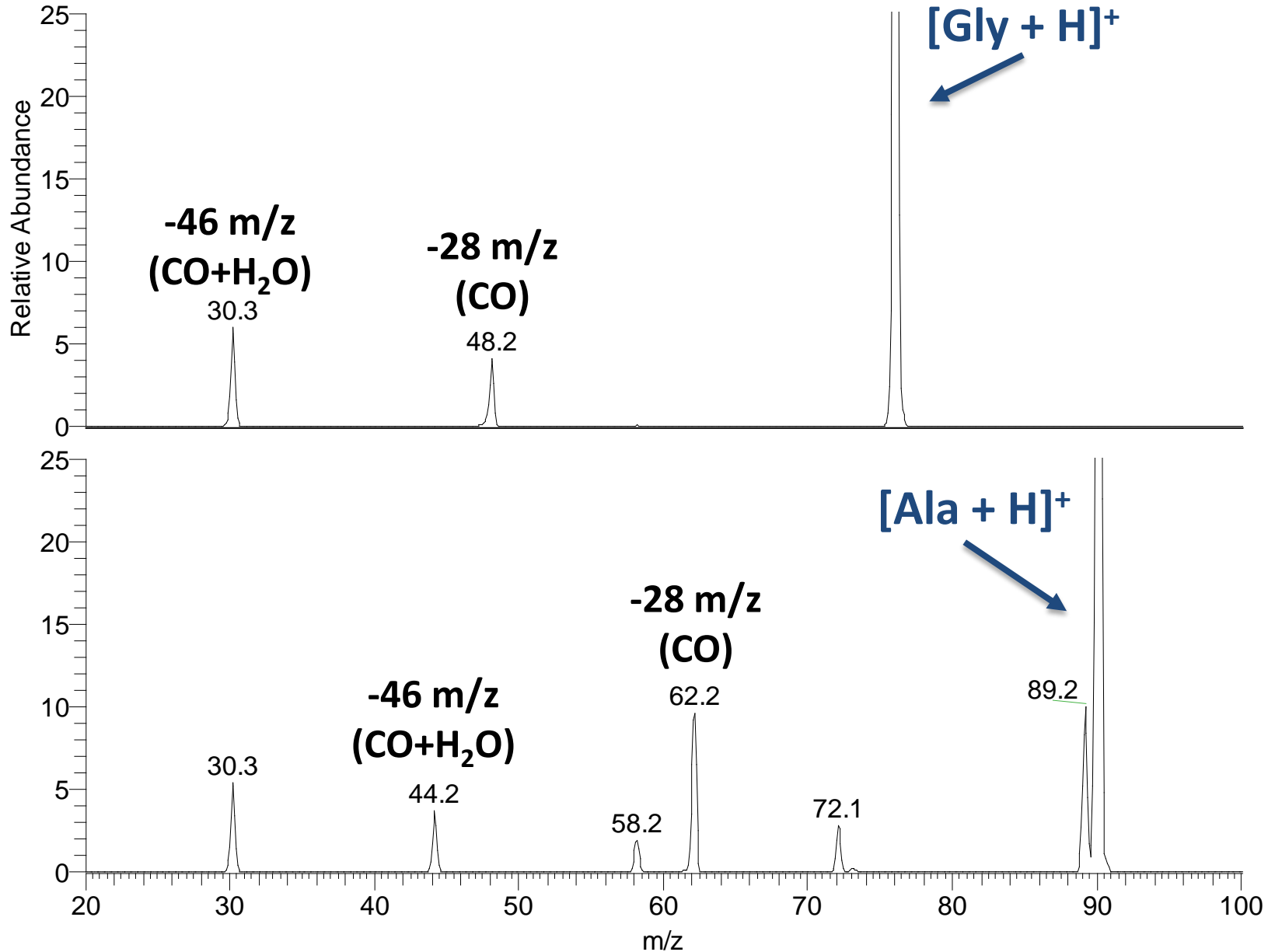
# Hydroxylamine and Carboxylic Acid Tests



# Hydroxylamine and Carboxylic Acid Tests



# MS/MS to Confirm Glycine and Alanine



# Conclusions & future work

- Built system for coupling of supercritical CO<sub>2</sub> reactor to online sampling by mass spectrometry
- Electrospray ionization is capable of ionizing analytes of prebiotic interest dissolved in scCO<sub>2</sub>
- Amino acid solubility impacted by temperature, pressure, cosolvent, so need to make sure have solubility during loading and sampling
- Can detect down to 10 μM concentration of amino acids and peptides
- Observed strong evidence for formation of glycine from hydroxylamine and glyoxylic acid in supercritical carbon dioxide, evidence for alanine formation from pyruvic acid not as definitive
- Future work: understanding the role of supercritical solvents vs water or subcritical solvents in these conditions
- Further reactions of interest?

# Acknowledgements

- Jenny Fan
- Beauchamp group
- Scott Virgil, 3CS Manager
- Nathan Dalleska, EAC Director
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- Caltech SFP Office

