

Water as a Stationary Phase in Supercritical Fluid Chromatography

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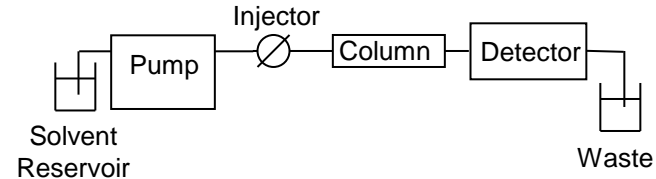
Calgary, Alberta.

Canada



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Conventional HPLC



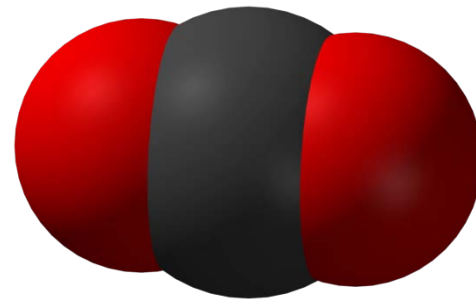
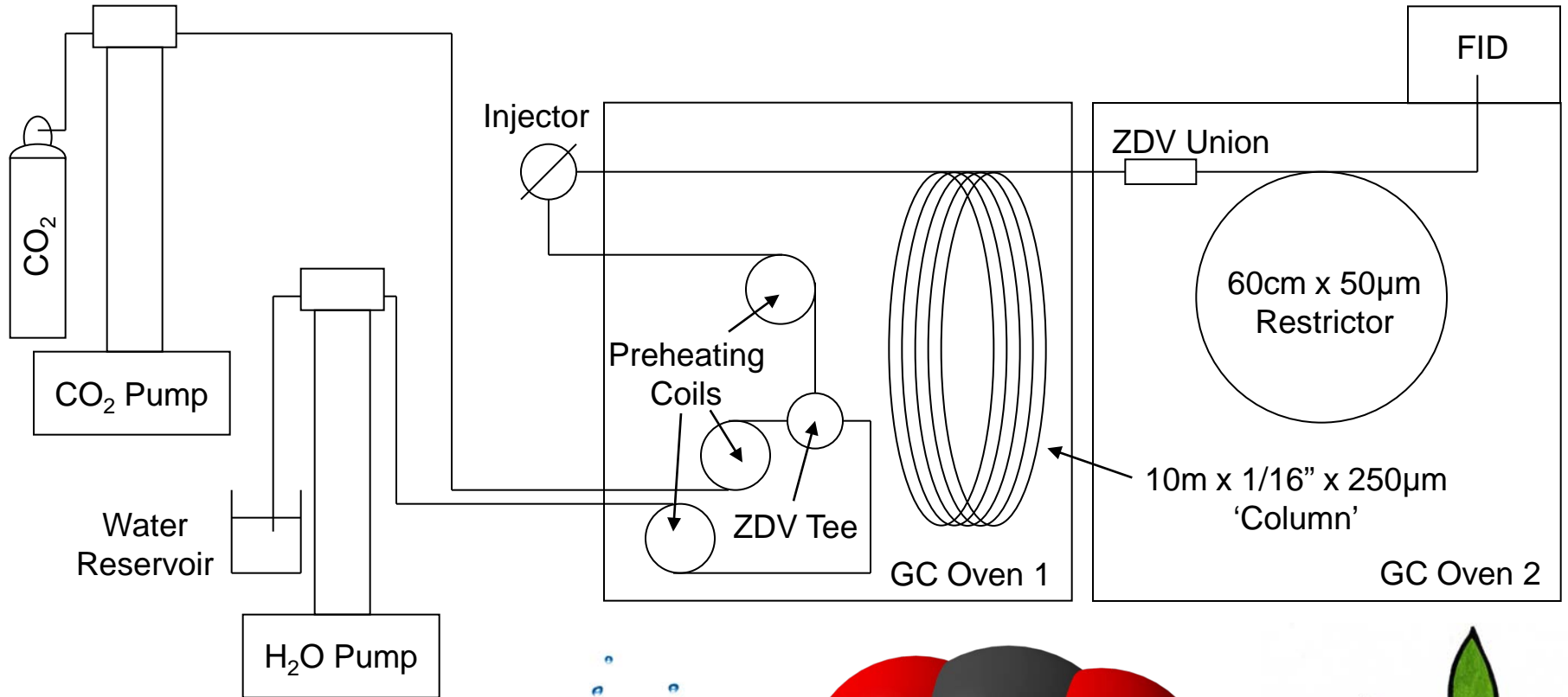
- Common Solvents
 - Methanol, Acetonitrile; expensive, disposal/supply issues
- Detection
 - UV-VIS, ELSD; lack simple/sensitive universal detection
- We've been exploring subcritical water / CO₂ mobile phases
 - Tunable polarity, Inexpensive, Non-toxic, Environmentally 'Green'
 - Flame Ionization Detection (FID) compatible; sensitive/universal



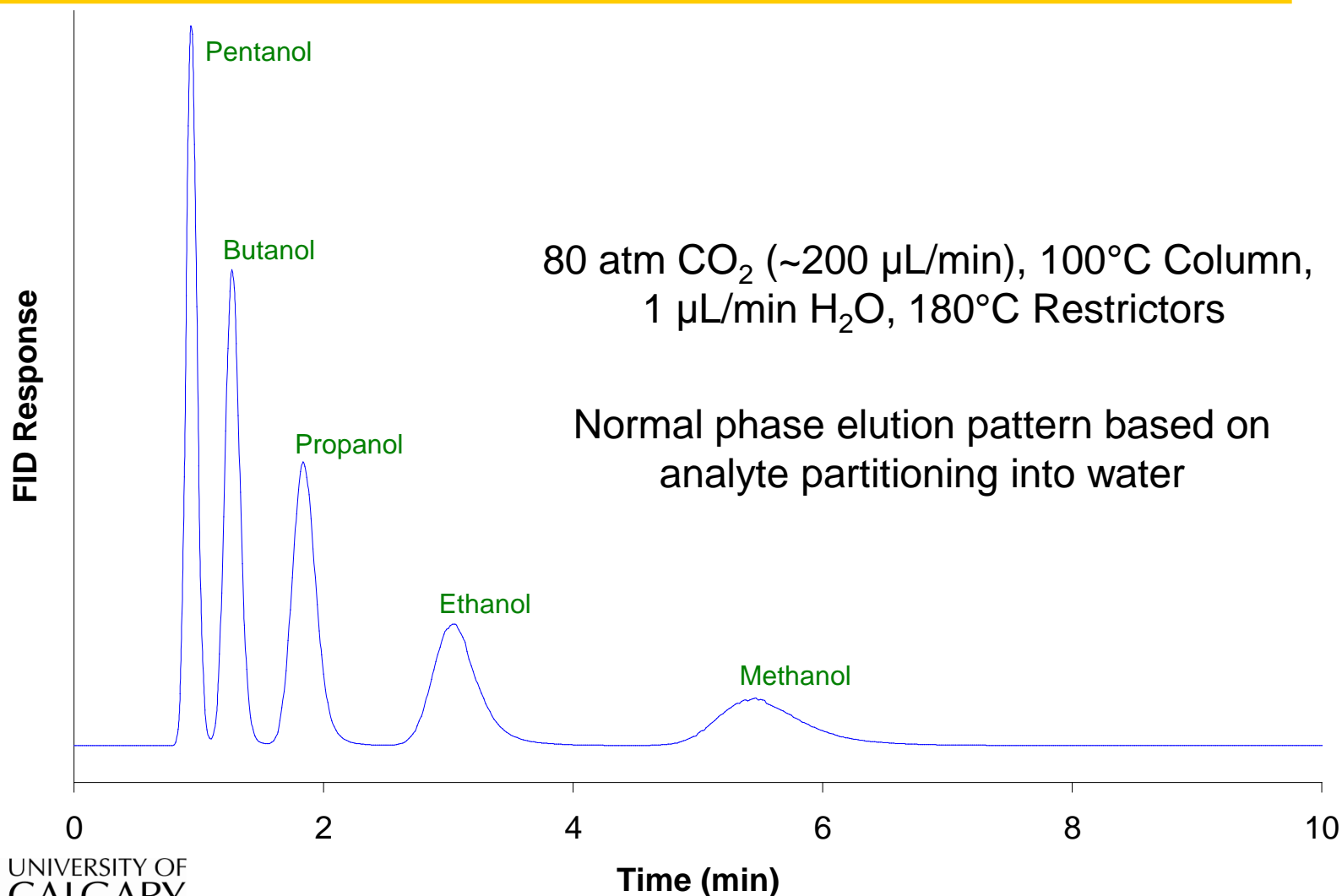
An Unconventional Separation

- In working with CO₂/H₂O system, we observed efficient separations in empty tubing **without a column** in place.
- Separations Based on Two Immiscible Liquids:
 - Counter Current/Centrifugal Partition Chromatography
 - Bubble Column Chromatography
 - Co-Current Chromatography
 - Parcher group forced immiscibility with CO₂:
 - He/CO₂ or Methanol/CO₂: 2 mobile phases at different velocities
 - Observed separation window in an uncoated capillary
- Explore the properties of CO₂/H₂O separations within an empty tube

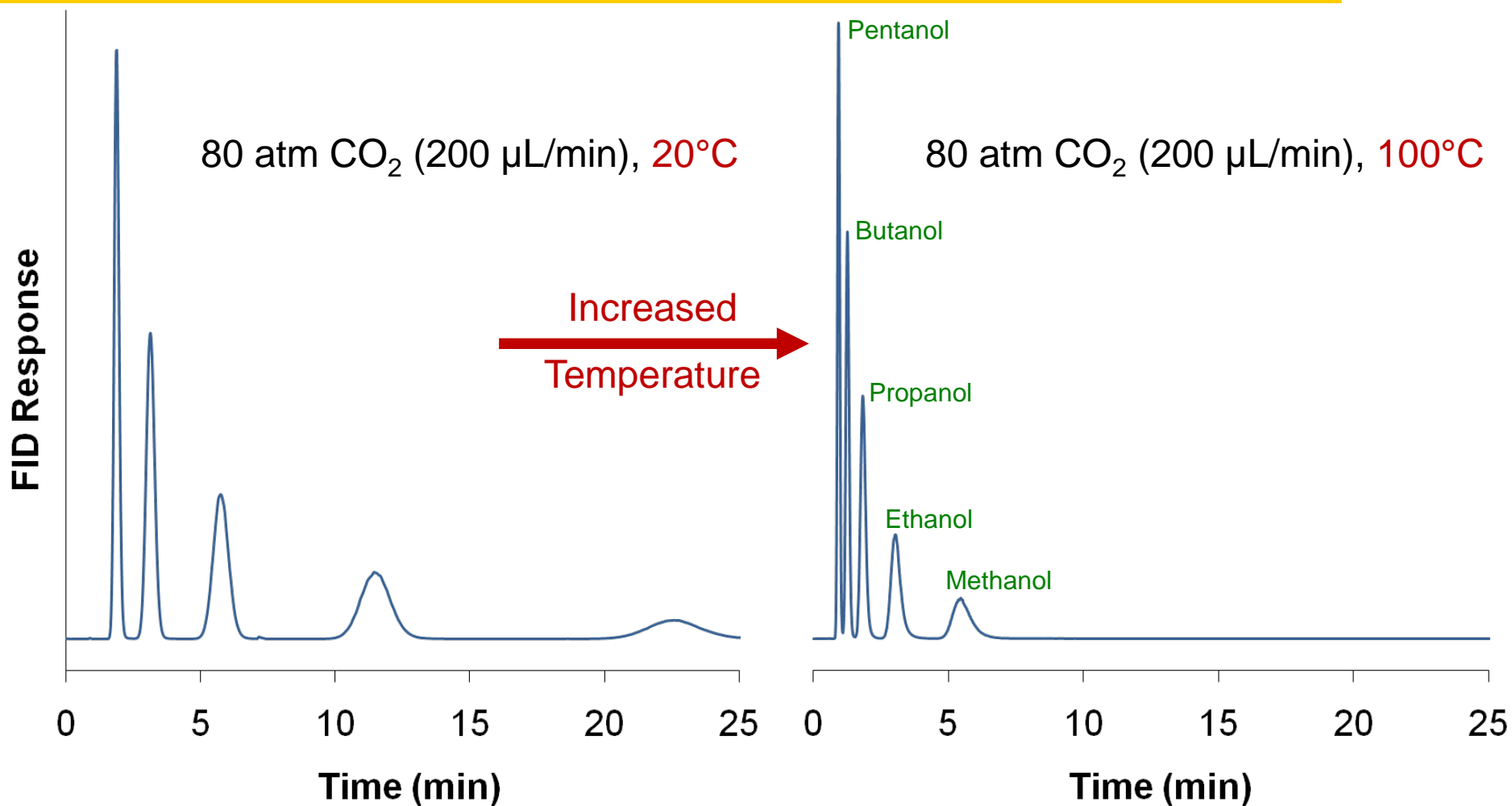
CO₂/H₂O Separation System



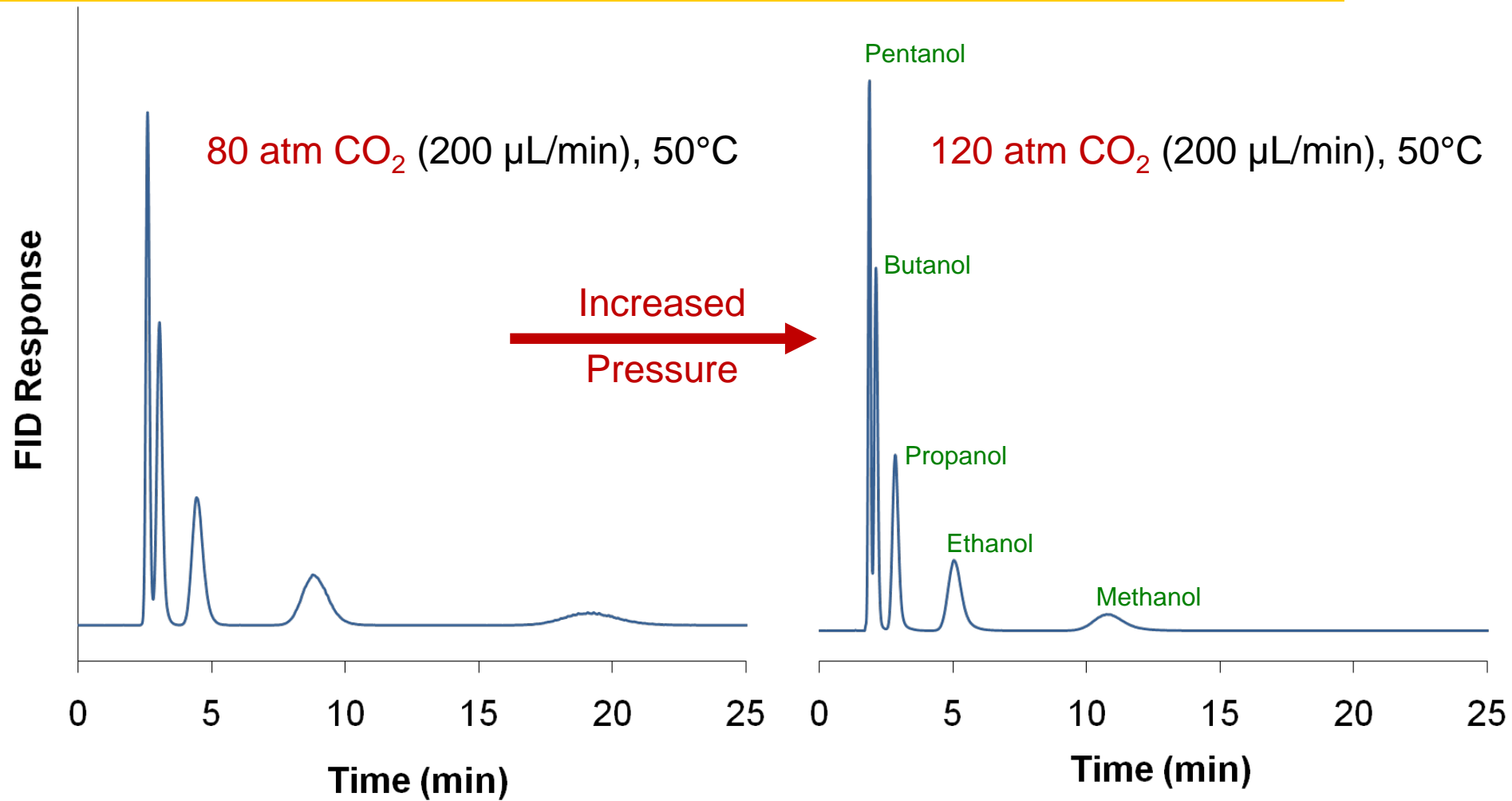
Typical Separation



Column Temperature



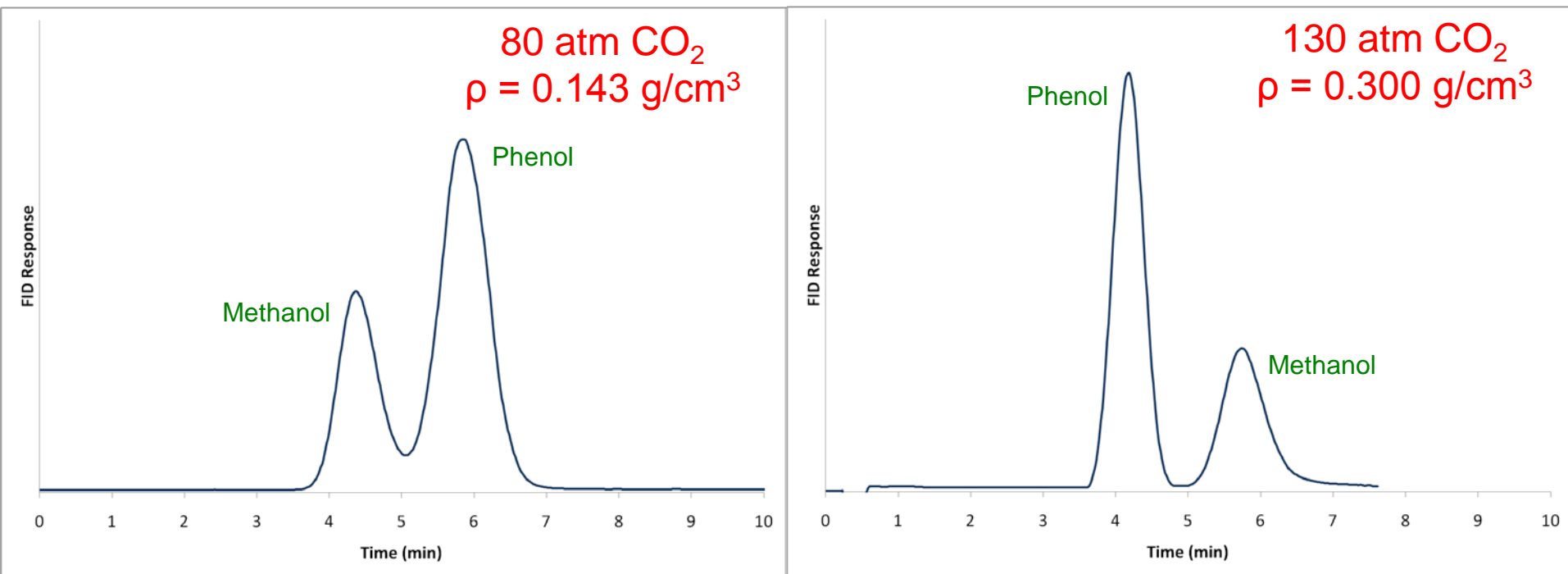
CO₂ Pressure



Variable Selectivity

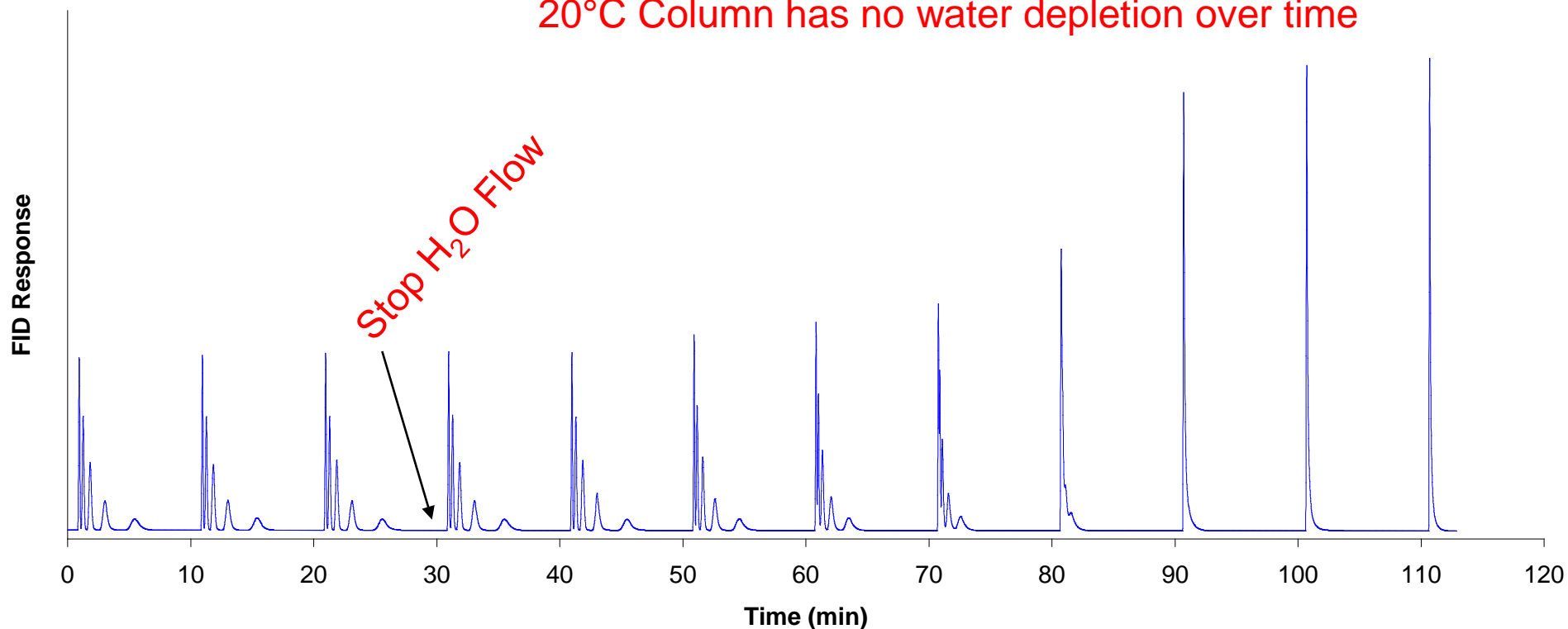
Peak Elution Order Changes with CO₂ Pressure

100°C, 1 μL/min H₂O, ~200 μL/min CO₂



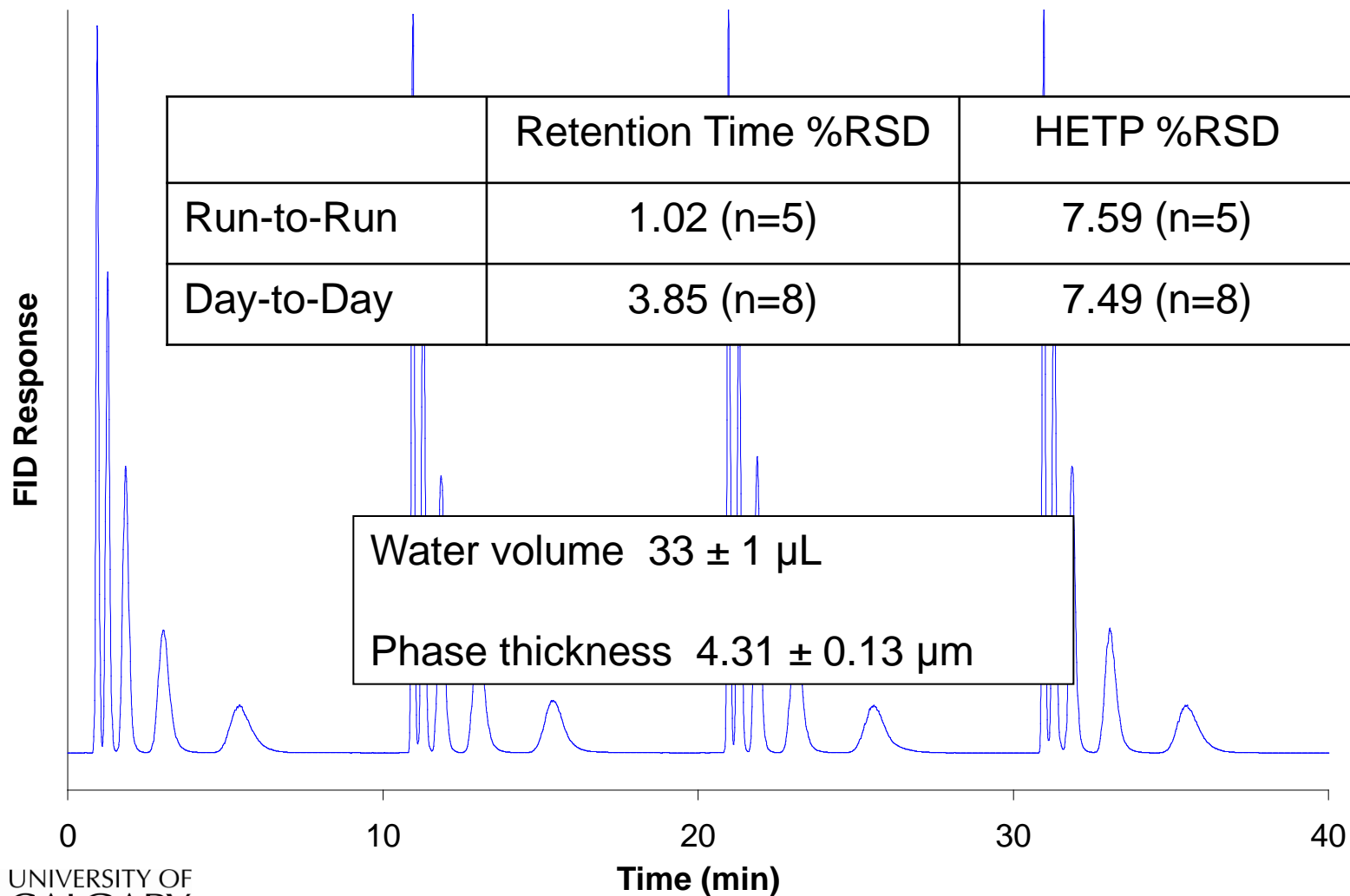
Water Phase Properties

20°C Column has no water depletion over time

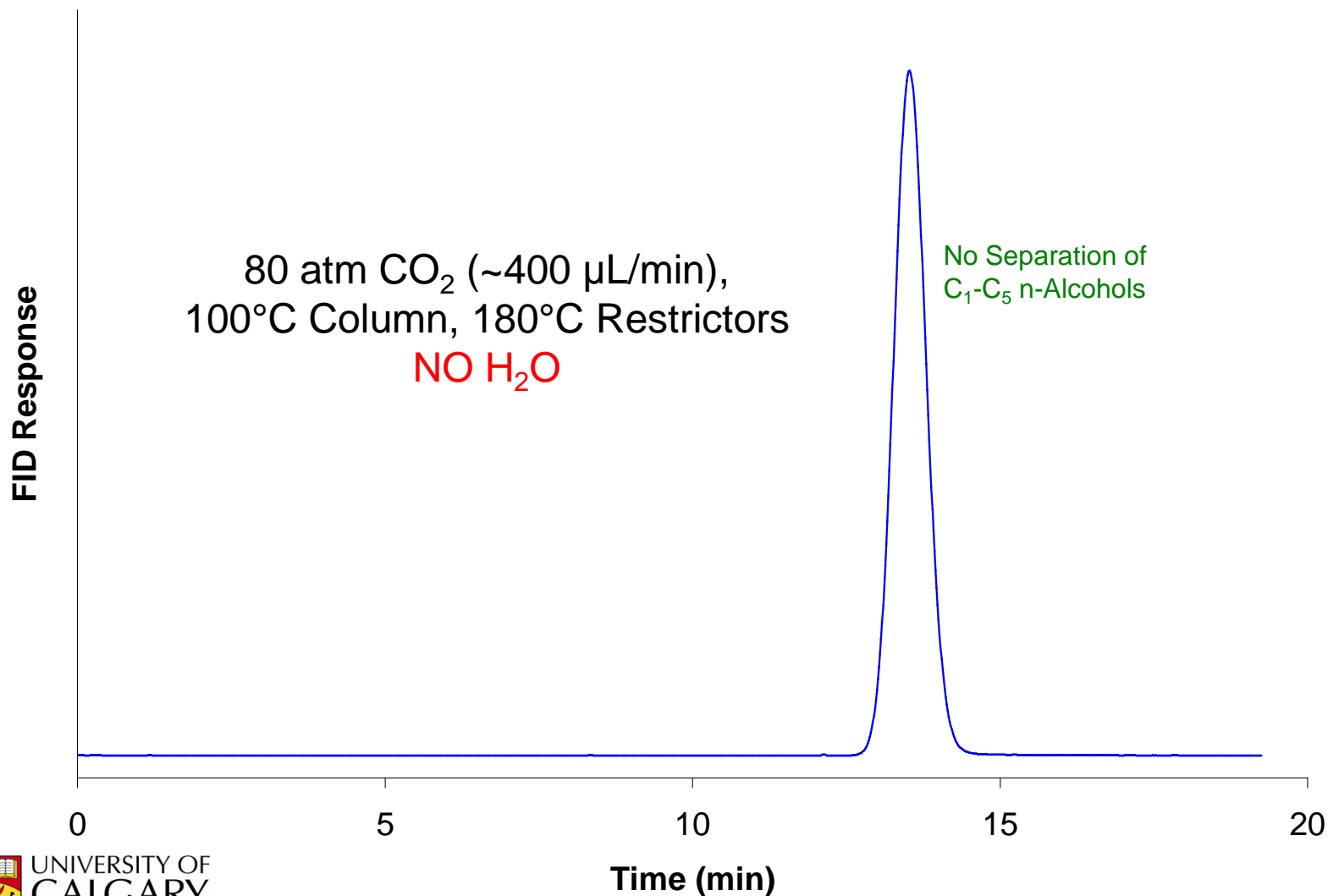


80 atm CO₂ (~200 μ L/min), 100°C Column, 1 μ L/min H₂O, 180°C Restrictors
C₁-C₅ n-Alcohols injected every 10 min

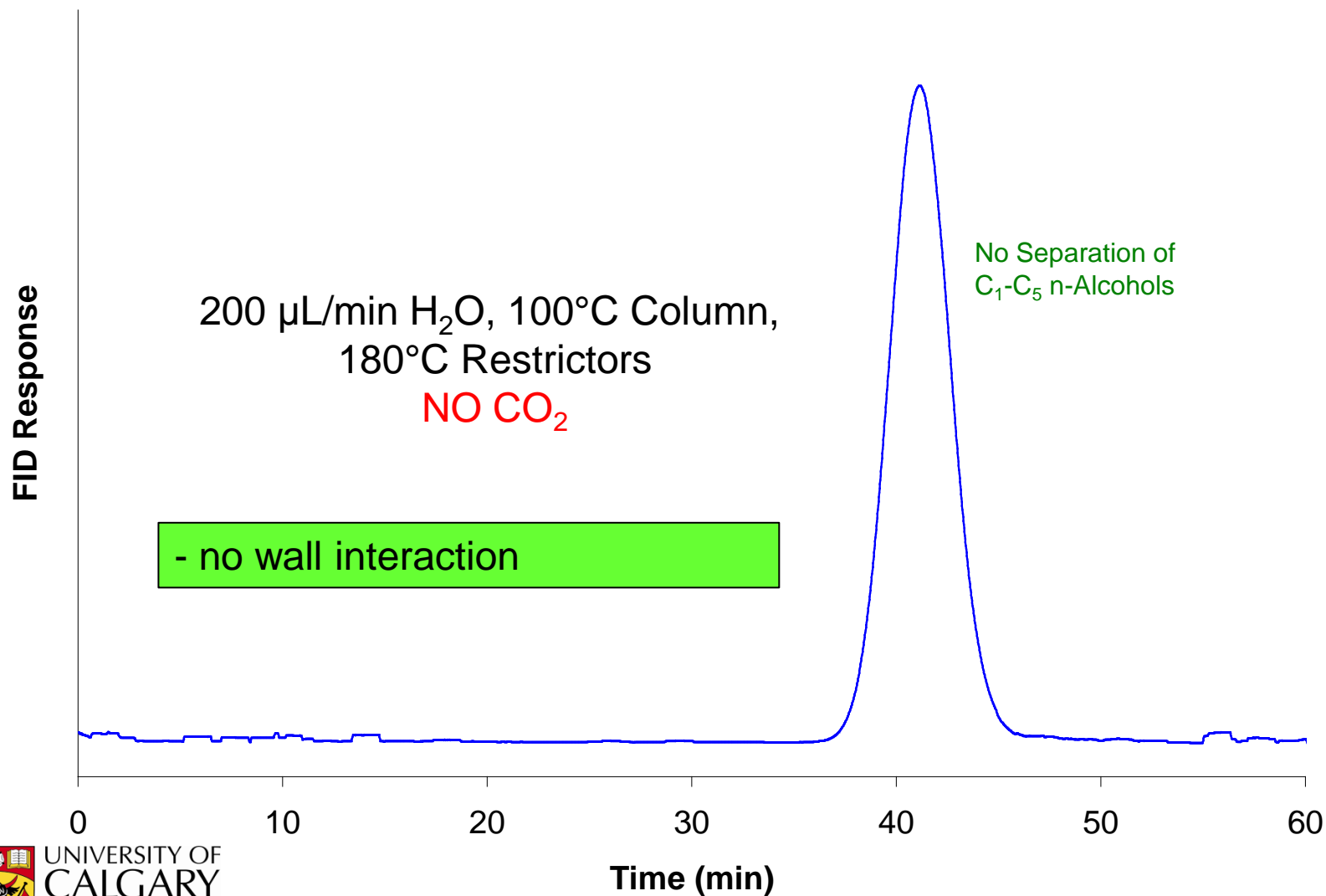
Water Phase Properties



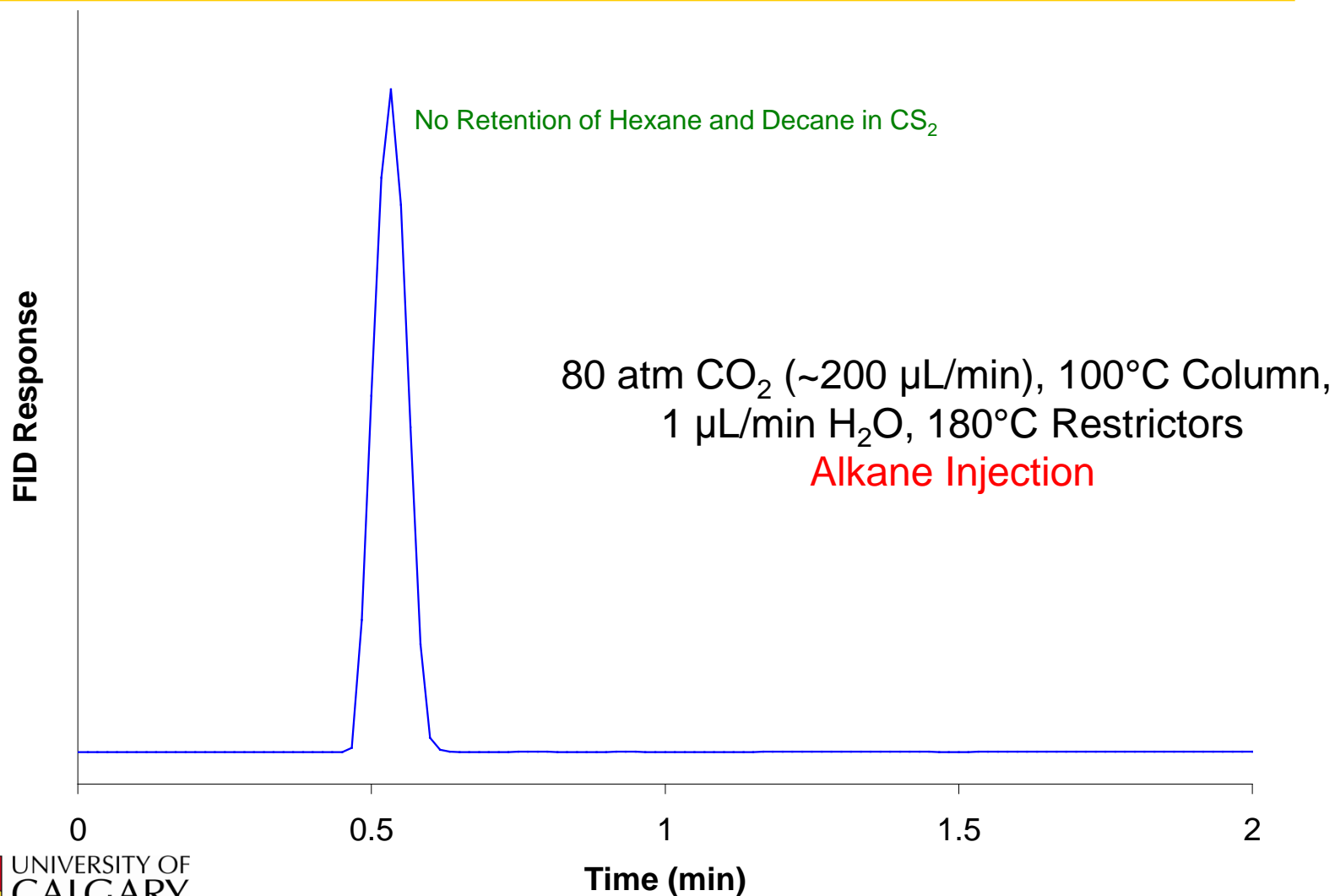
Separation Mechanism



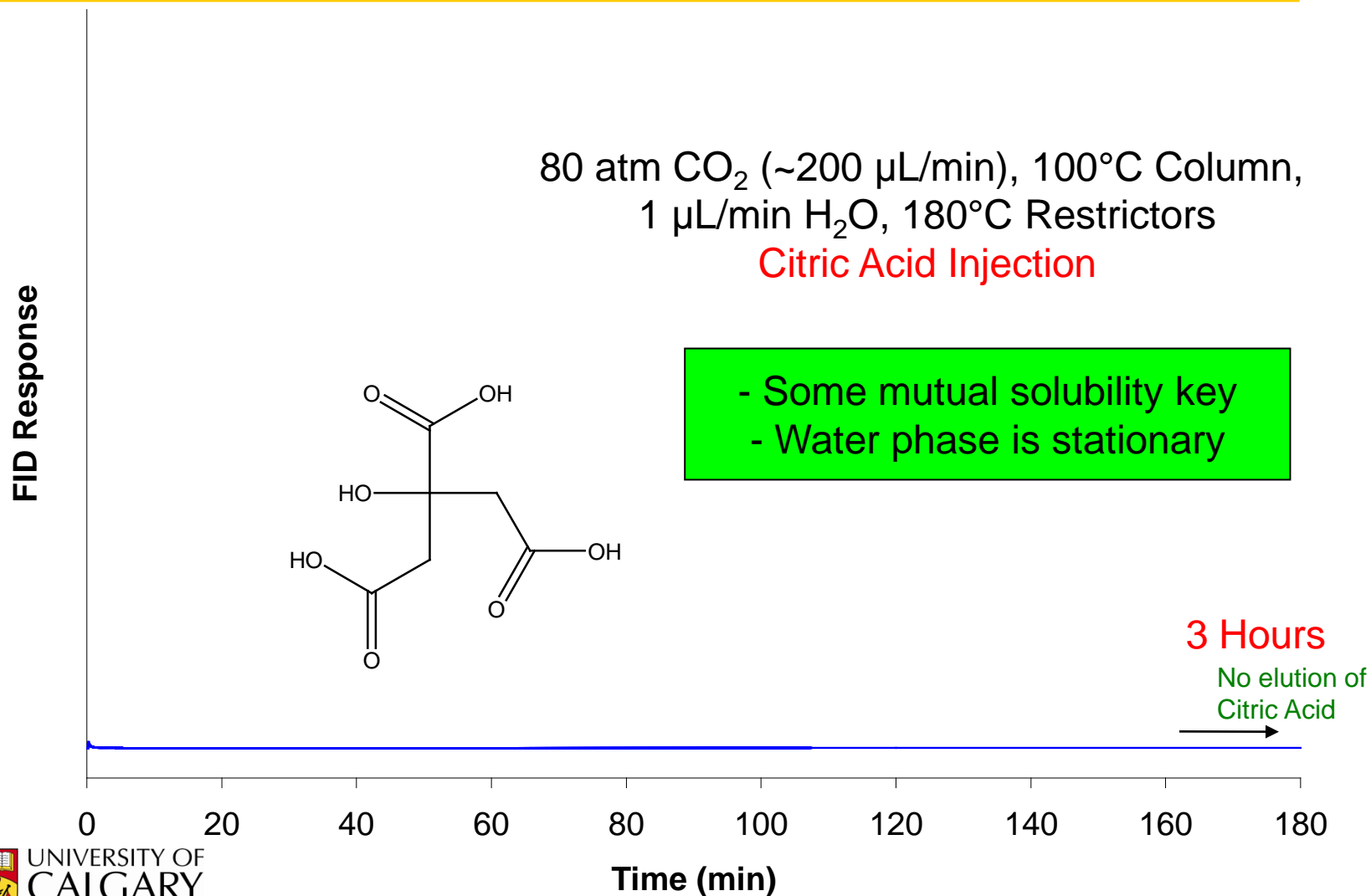
Separation Mechanism



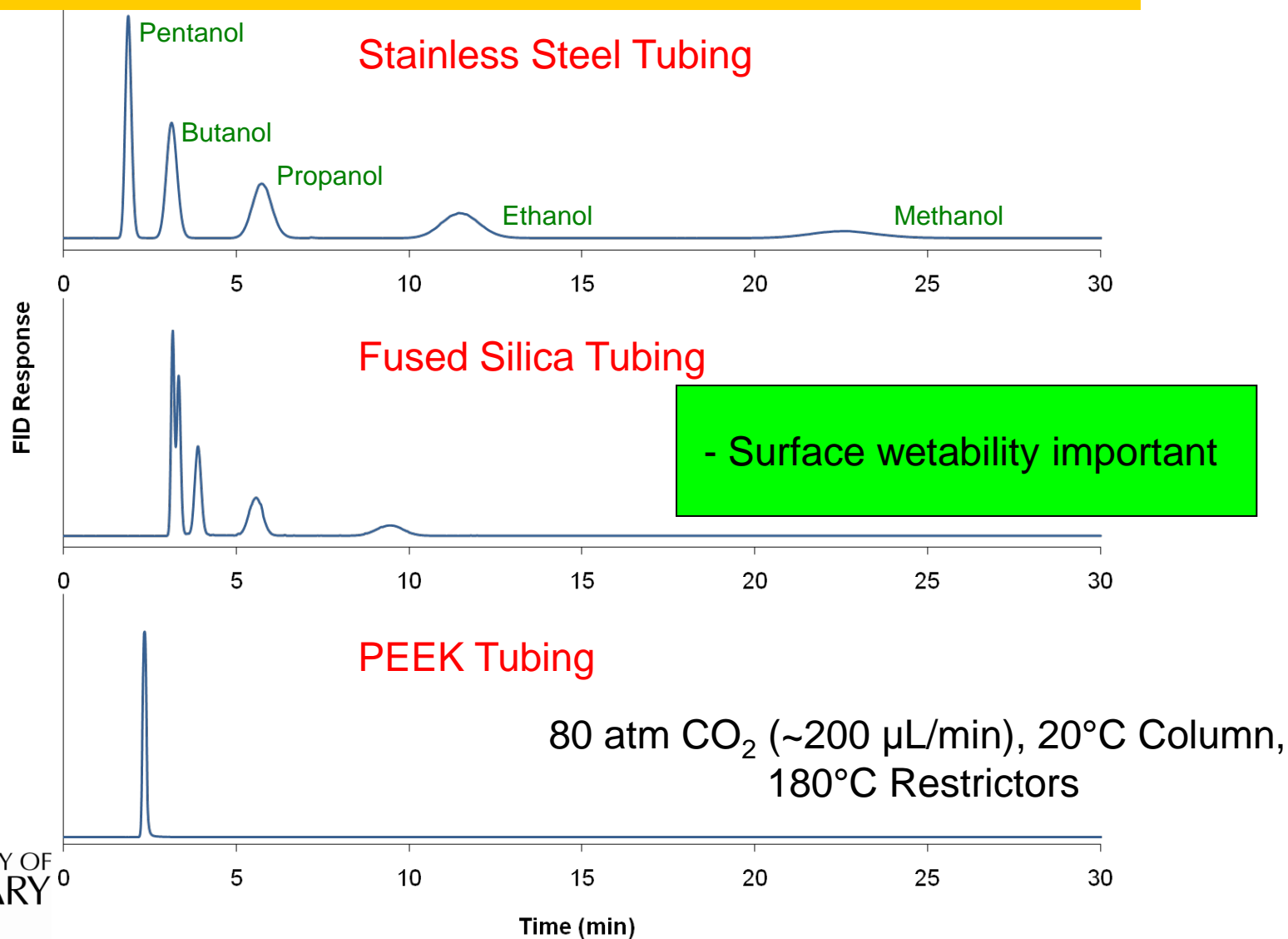
Separation Mechanism



Separation Mechanism

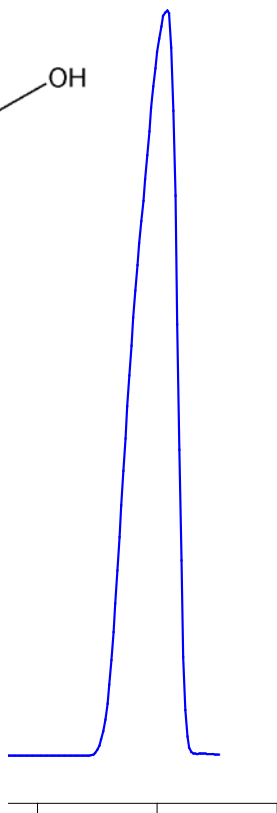
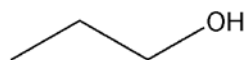


Column Material

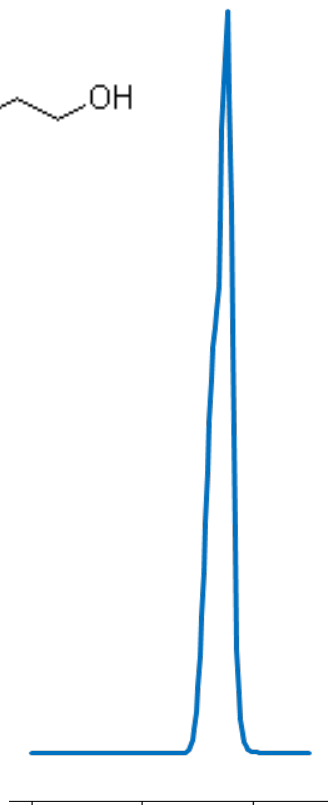


Sample Capacity

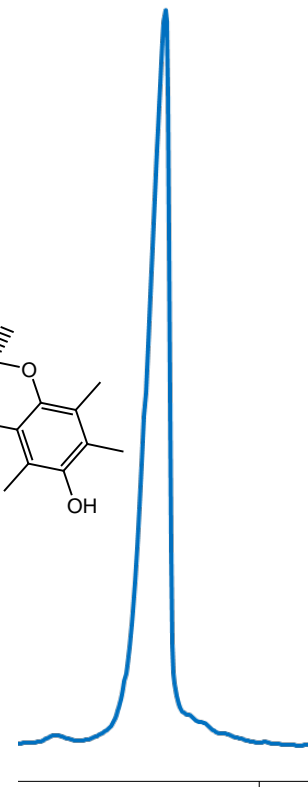
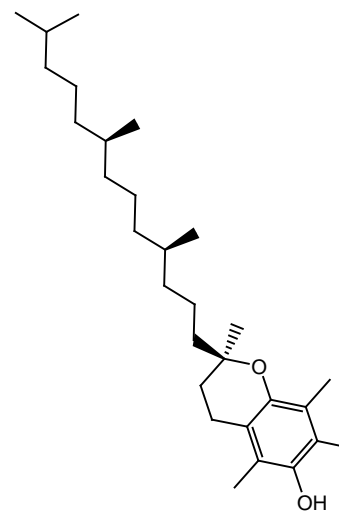
1-Propanol 400 μg



1-Pentanol 100 μg

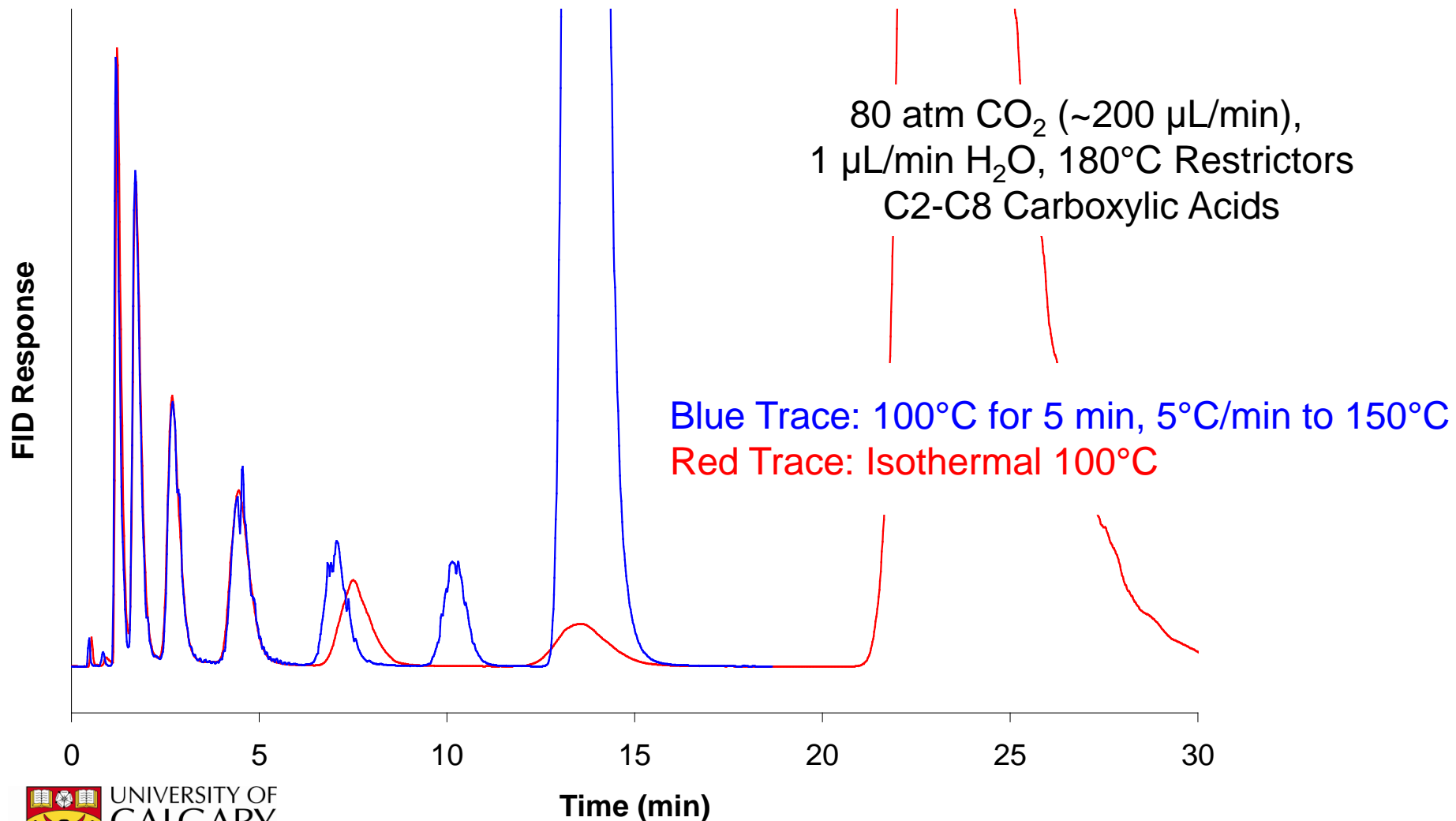


Tocopherol 5 μg

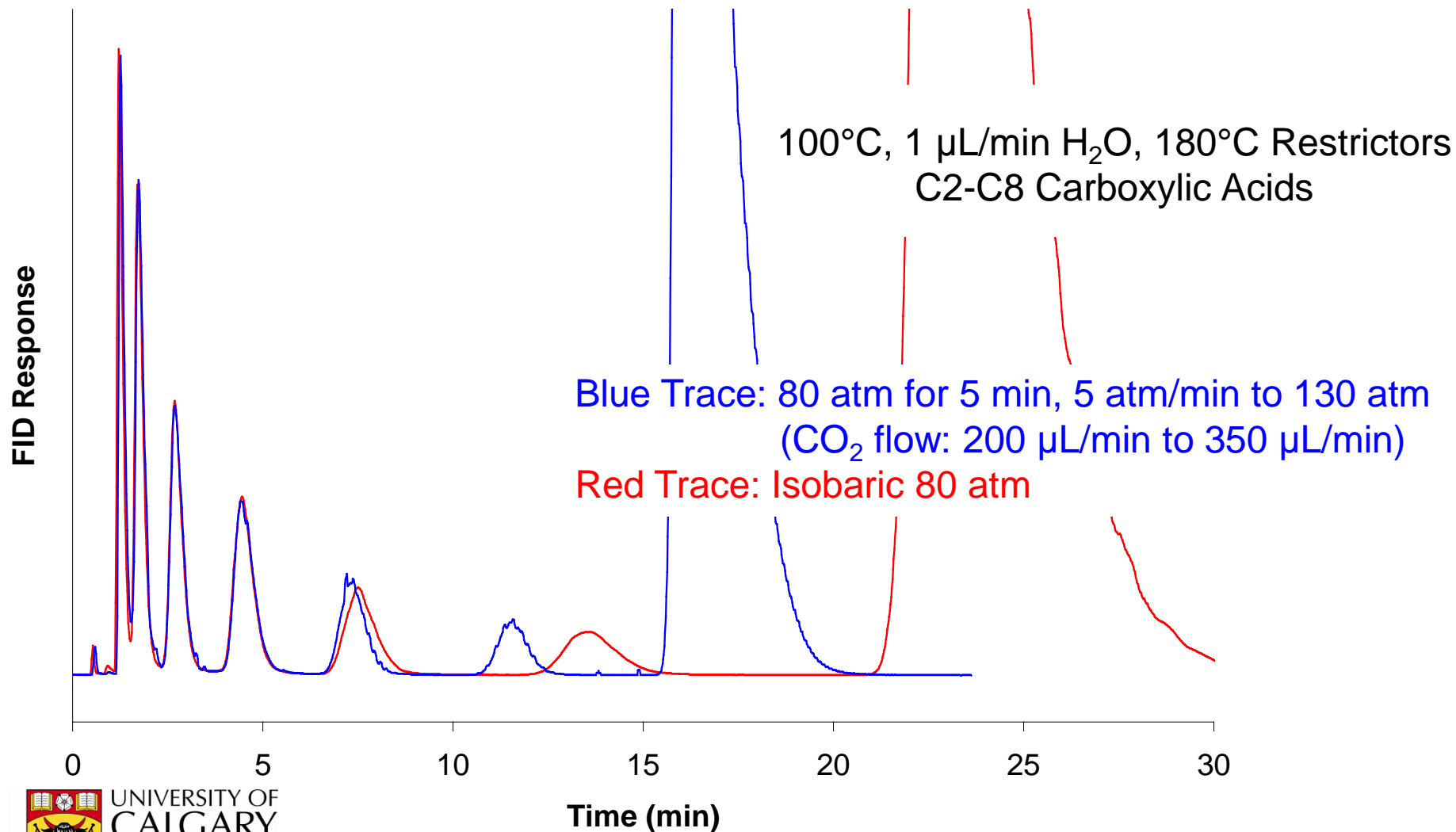


Peak Heights Normalized
Quantitative Recovery

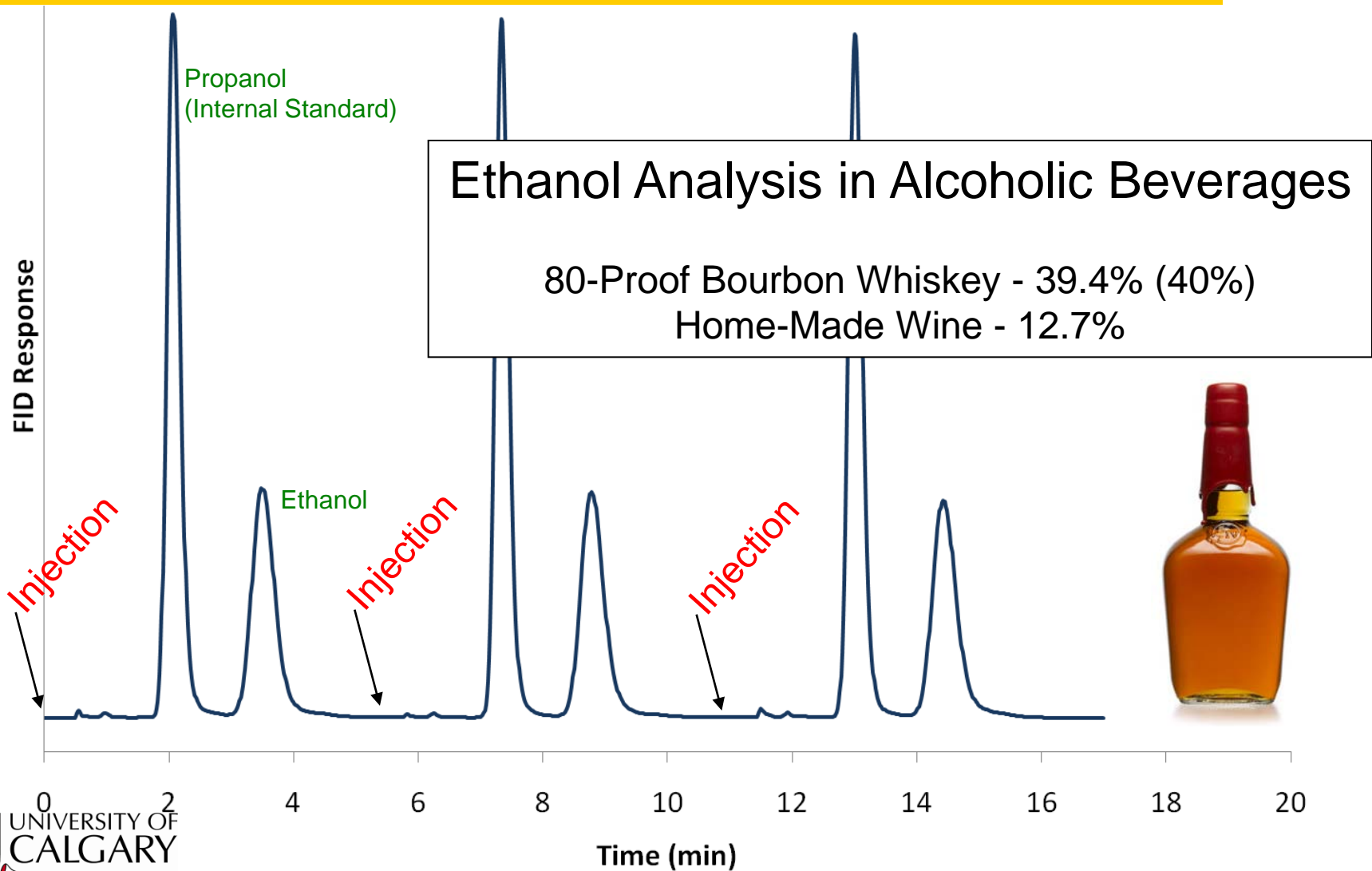
Temperature Programming



Pressure Programming



Application



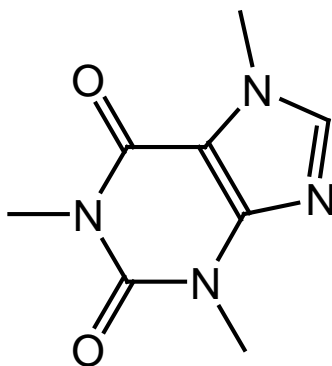
Application

Caffeine Analysis in Beverages

Energy Beverage – 3.81 mg/mL (3.85 mg/mL)
Coffee – 0.392 mg/mL (0.333 mg/mL)

FID Response

Caffeine



Neat Injection!



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5

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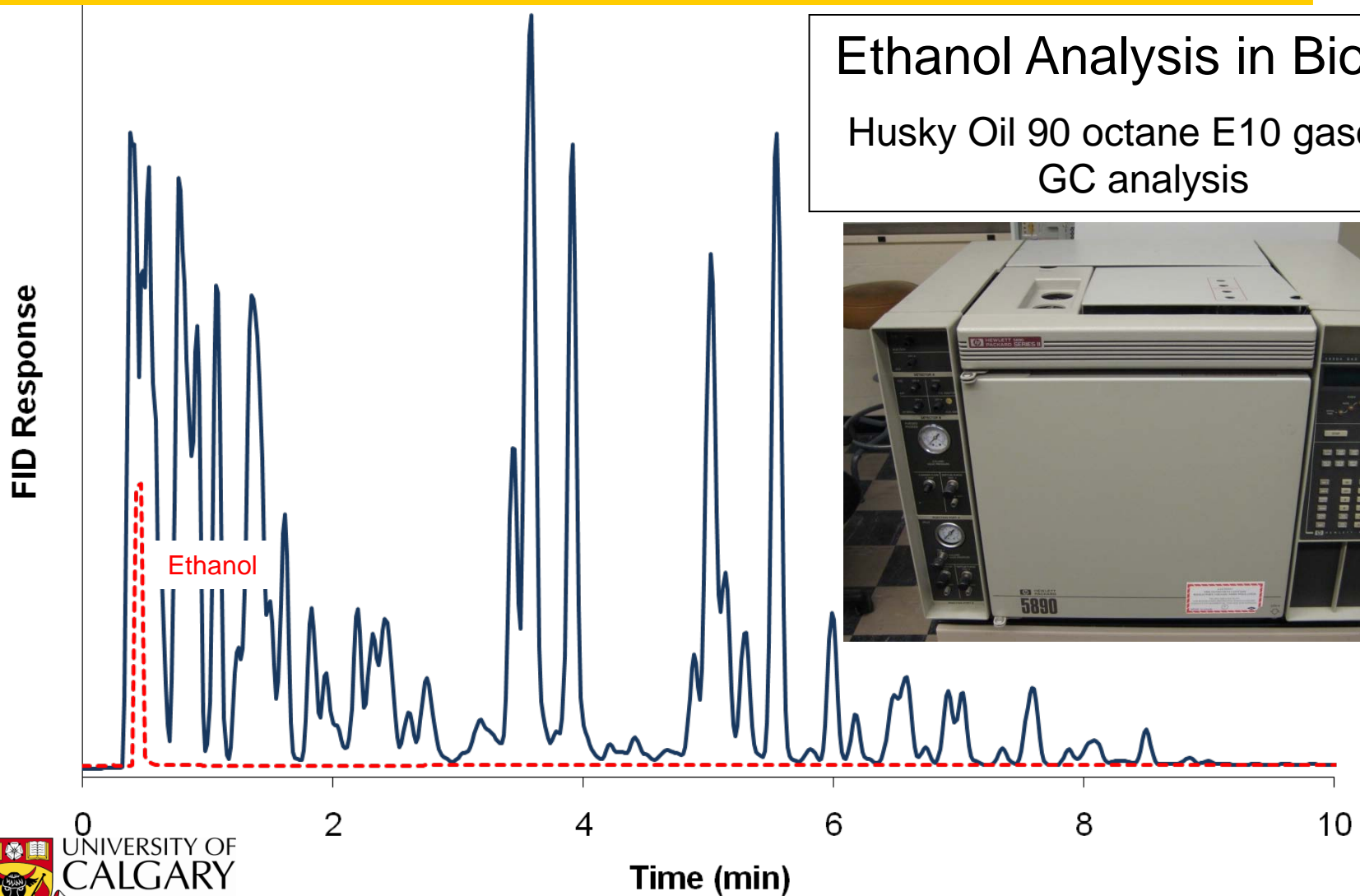
15

20

Time (min)



Application



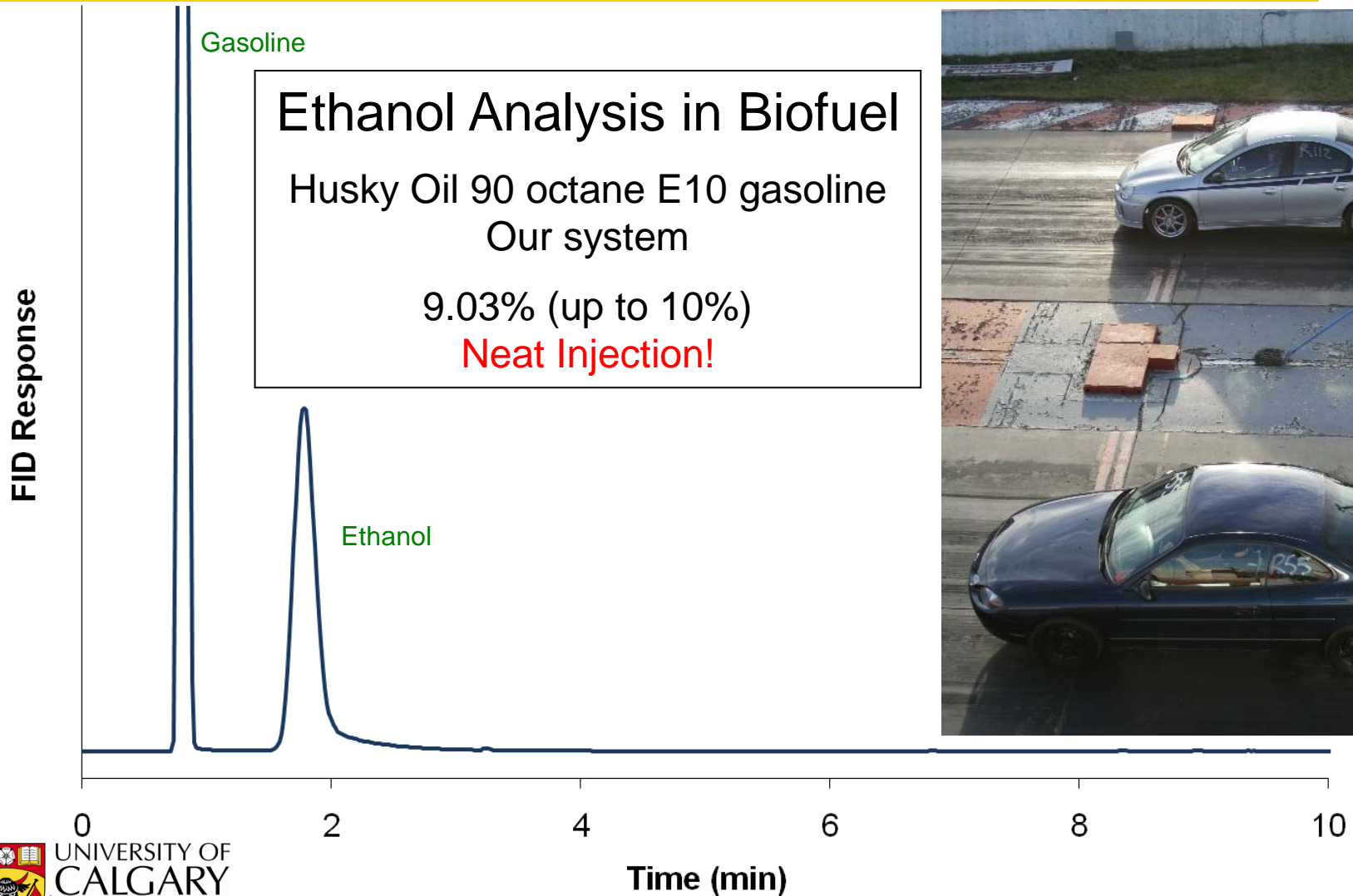
Ethanol Analysis in Biofuel

Husky Oil 90 octane E10 gasoline
GC analysis



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Application



Conclusions

- CO₂/H₂O provide useful and efficient separations within an empty capillary
- Interesting and unique properties
- Flexible tuning parameters
- Sensitive Universal Detection
- Requires no organic solvents/materials

Acknowledgement



NSERC
CRSNG

• Project Funding from NSERC
