Targeted Signal Enhancement (TSE)

A Powerful Means of Boosting Process GC Detection Limits by 1-2 Orders of Magnitude

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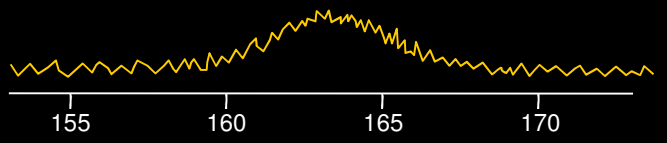
Presented at IFPAC® 2007, Baltimore, MD, USA

What's the Problem?

- Some Process GC Applications Require More Sensitivity than what Conventional GC can Deliver
  - Ambient Air Monitoring



  - Trace analysis of feed streams for catalyst poisons
  - Trace water analysis for corrosion prevention
  - Finished Product Quality
  - Water Quality/Environmental

What's the Problem?

- Need a means to achieve lower detection limits
  - Sample enrichment techniques: P/T, SPME, Headspace, etc.
  - New detector technologies: PDD, DMD, DBD etc.
- These solutions often lack the ruggedness, stability & low maintenance needed for a process analyzer
- Need a Simple & Rugged Solution

What is TSE?

- A process whereby a broad GC peak is cryotrapped & then vapourized into a narrower, taller peak
- The Result:
  - Increased signal-to-noise ratio
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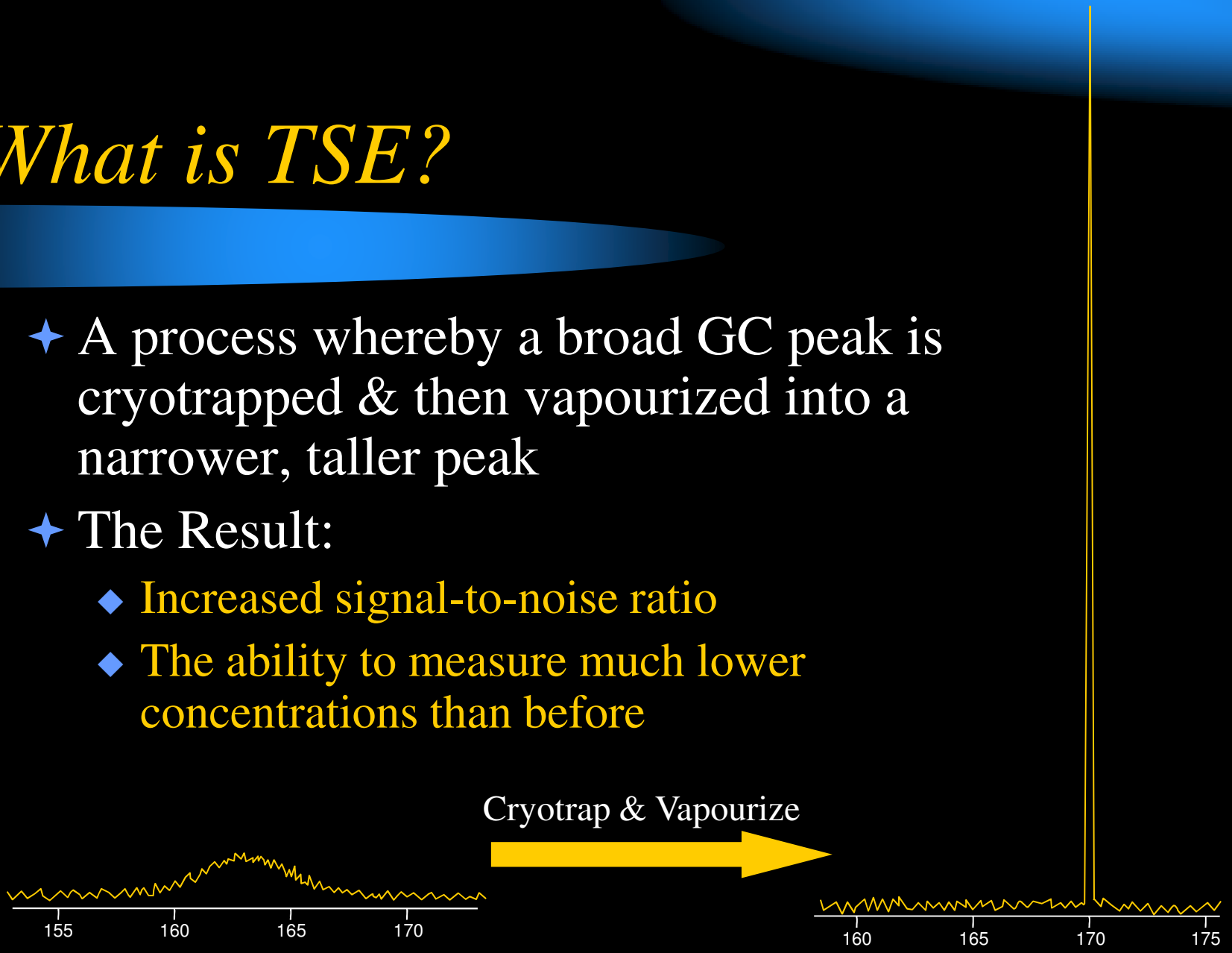

TSE Background

- TSE concept demonstrated in ‘97 by Marriott & Kinghorn
  - Required Liquid Cryogen
- Not widely used in process GC’s for continuous use
  - Due to Need for Liquid Cryogen
    - Expensive, High Maintenance
  - Need for Hazardous Area Classification
- Great concept, but need it to be rugged for on-line use
  - Eliminate the Need for Liquid Cryogen
  - Low Maintenance, Rugged

TSE Design for On-line Use

"Things should be made as simple as possible, but no simpler.“

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TSE Design for On-line Use

- Eliminate the Need for Liquid Cryogen
- Employ Vortex Cooling for Cryotrapping
  - Requires only 80-100 psig Compressed Air
  - Typically in abundant supply in process environments
  - Achieves -40°C temperatures
  - Encased & Insulated – Quiet Operation
- Employs GC Oven-Heated Air for Vapourizing
  - No additional heat source required
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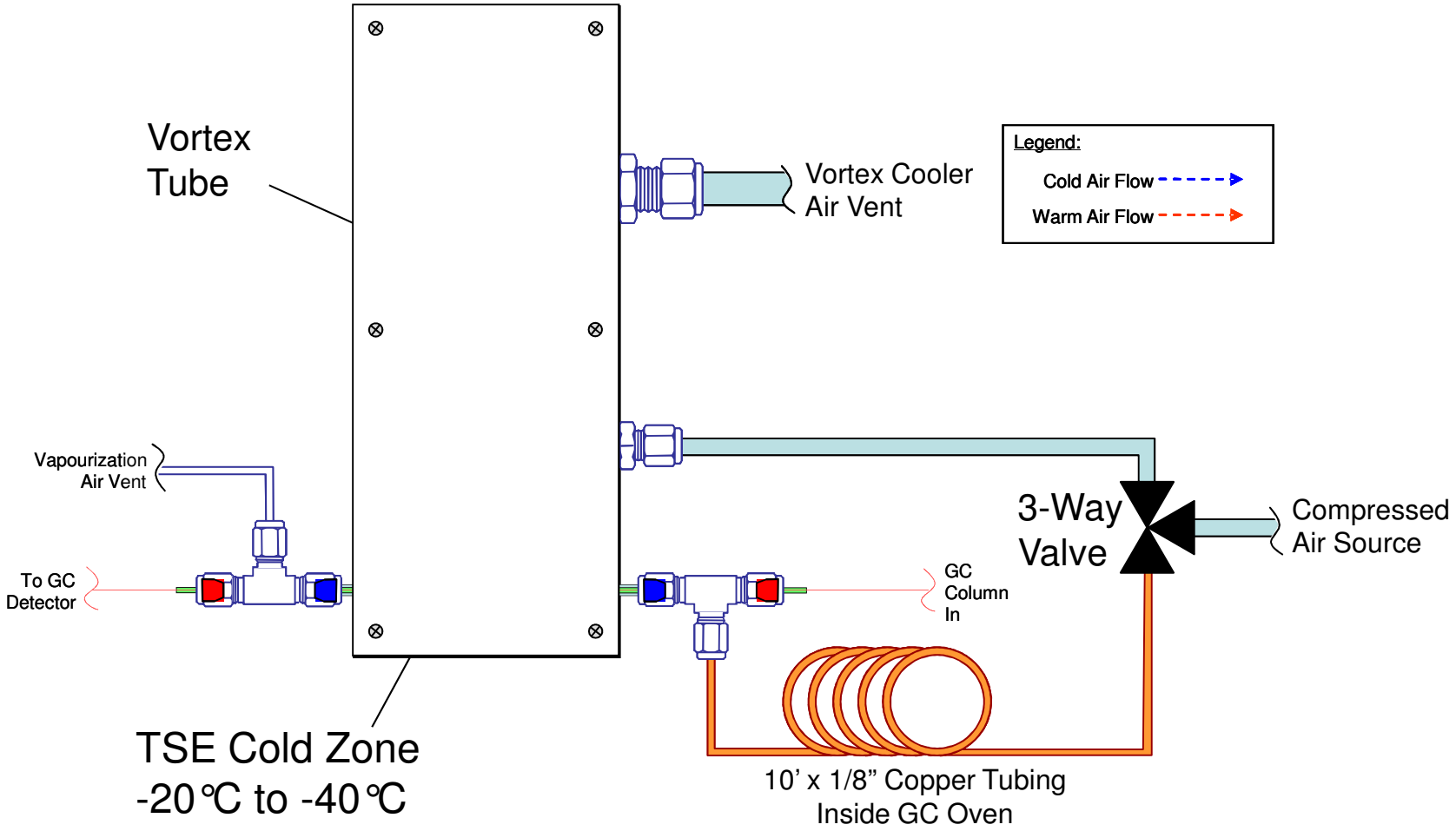
- Capillary column phases used as the trapping medium
- Assembled with mostly off-the-shelf parts

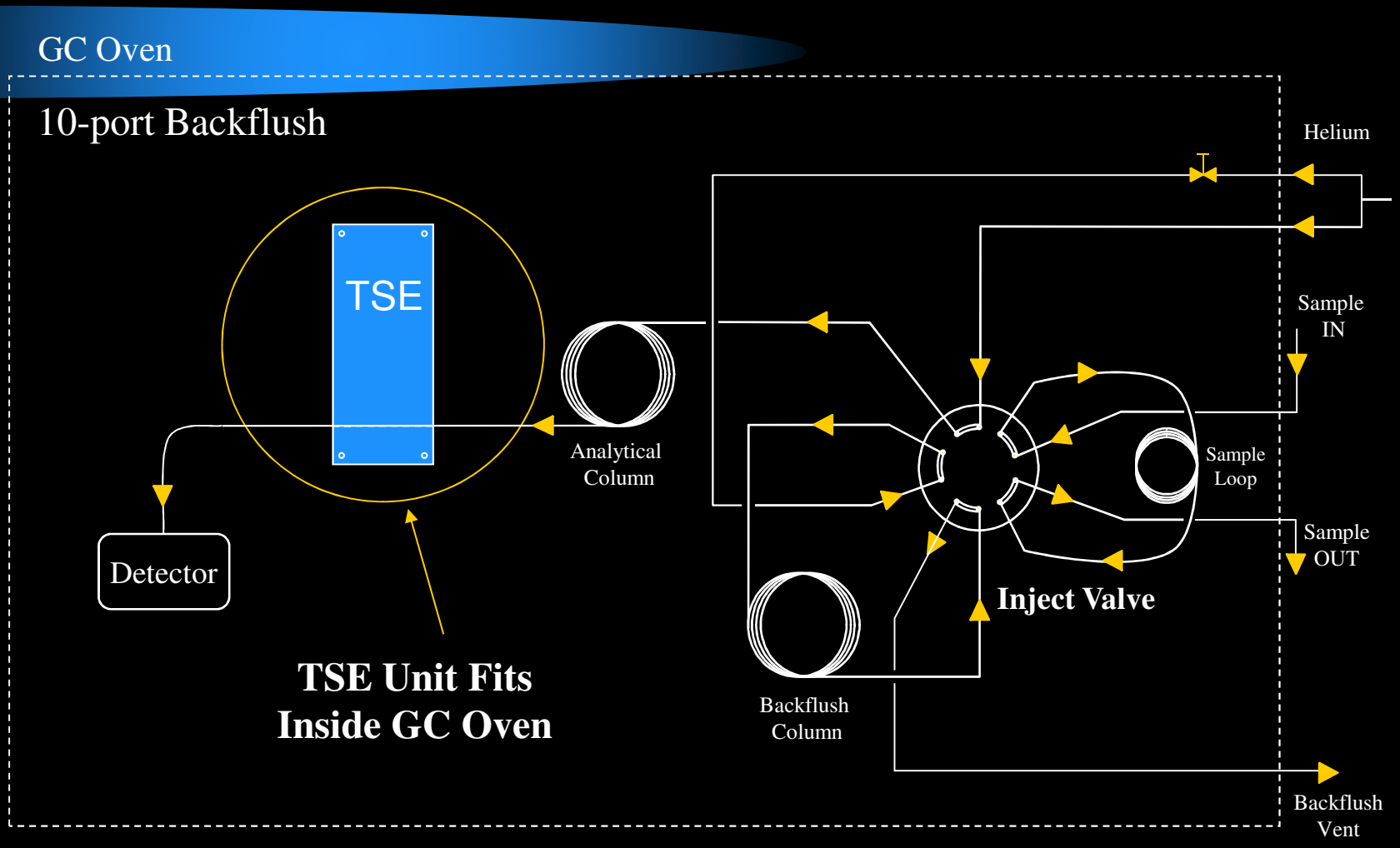
TSE Design



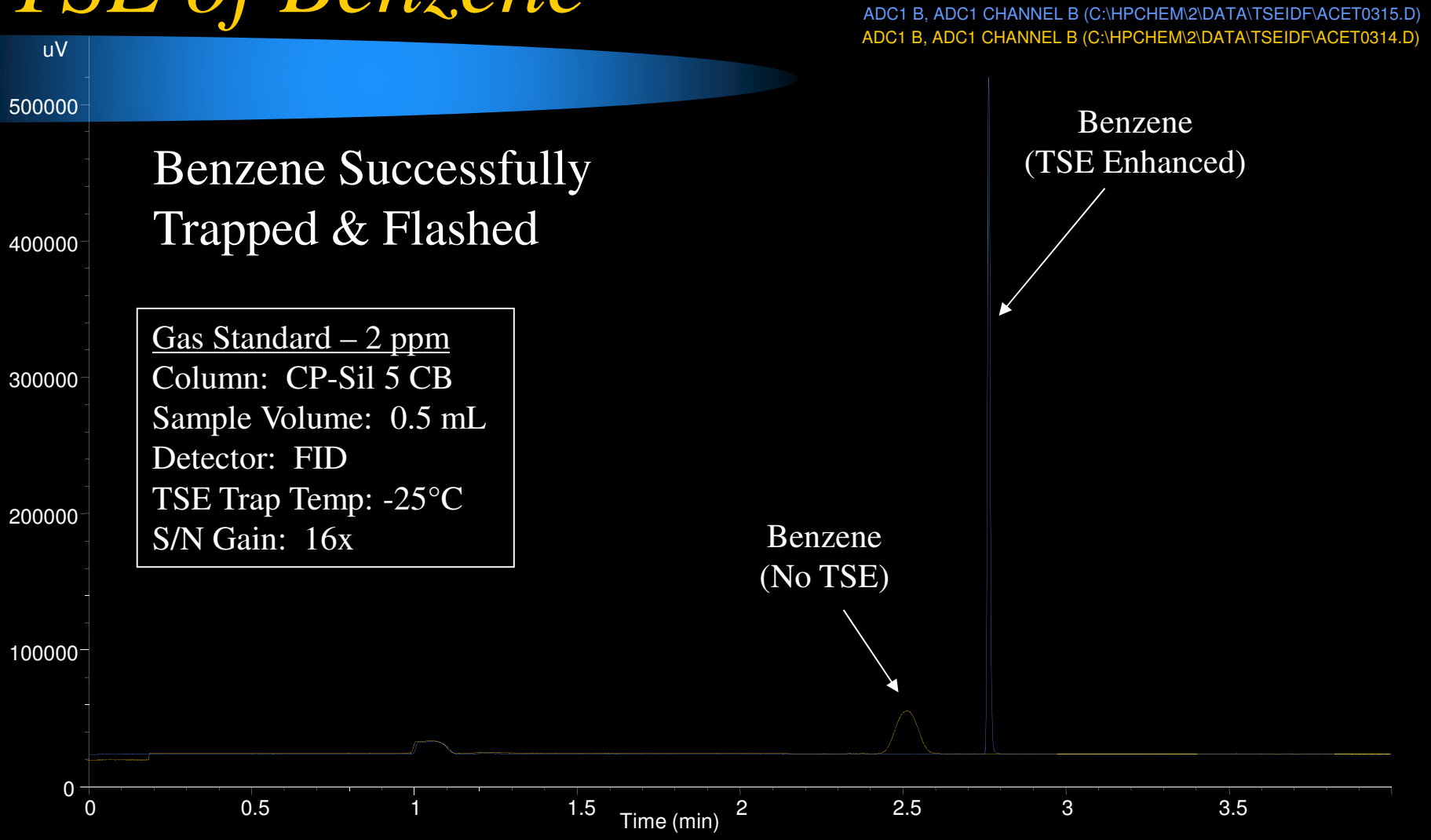
TSE Design Advantages

- 100% Pneumatic (no Hazard Class. Barriers)
- Retrofittable to most any GC
- Absurdly Simple
  - One Moving Part: 3-way valve to redirect air flow
  - Virtually Maintenance Free
- Small – Can fit inside a Process GC Oven
  - Dimensions: 6.5” x 3.5” x 2”
- Quiet Operation
- Economical

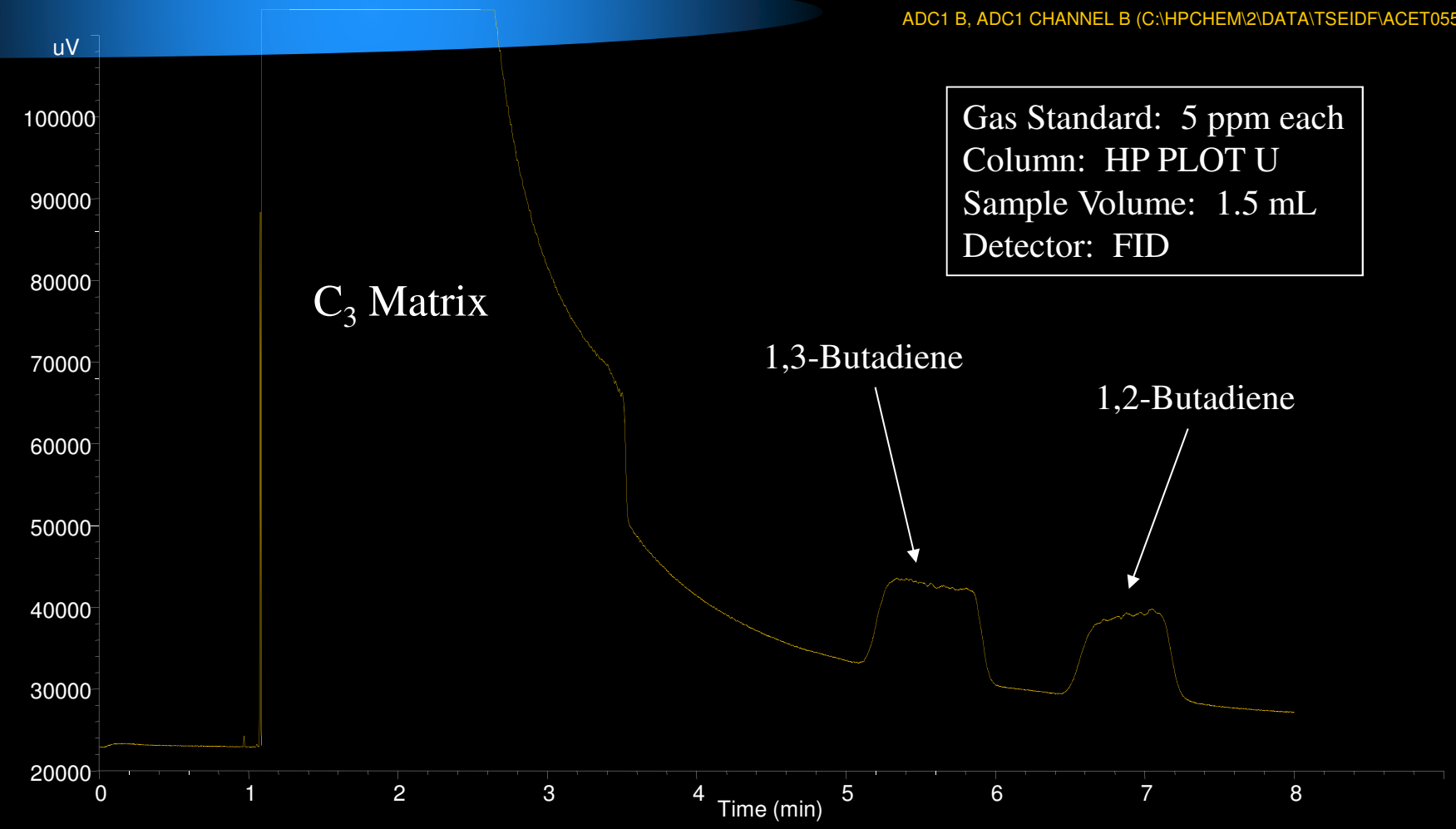
GC/TSE Oven Schematic



TSE of Benzene



TSE of C_4 Hydrocarbons



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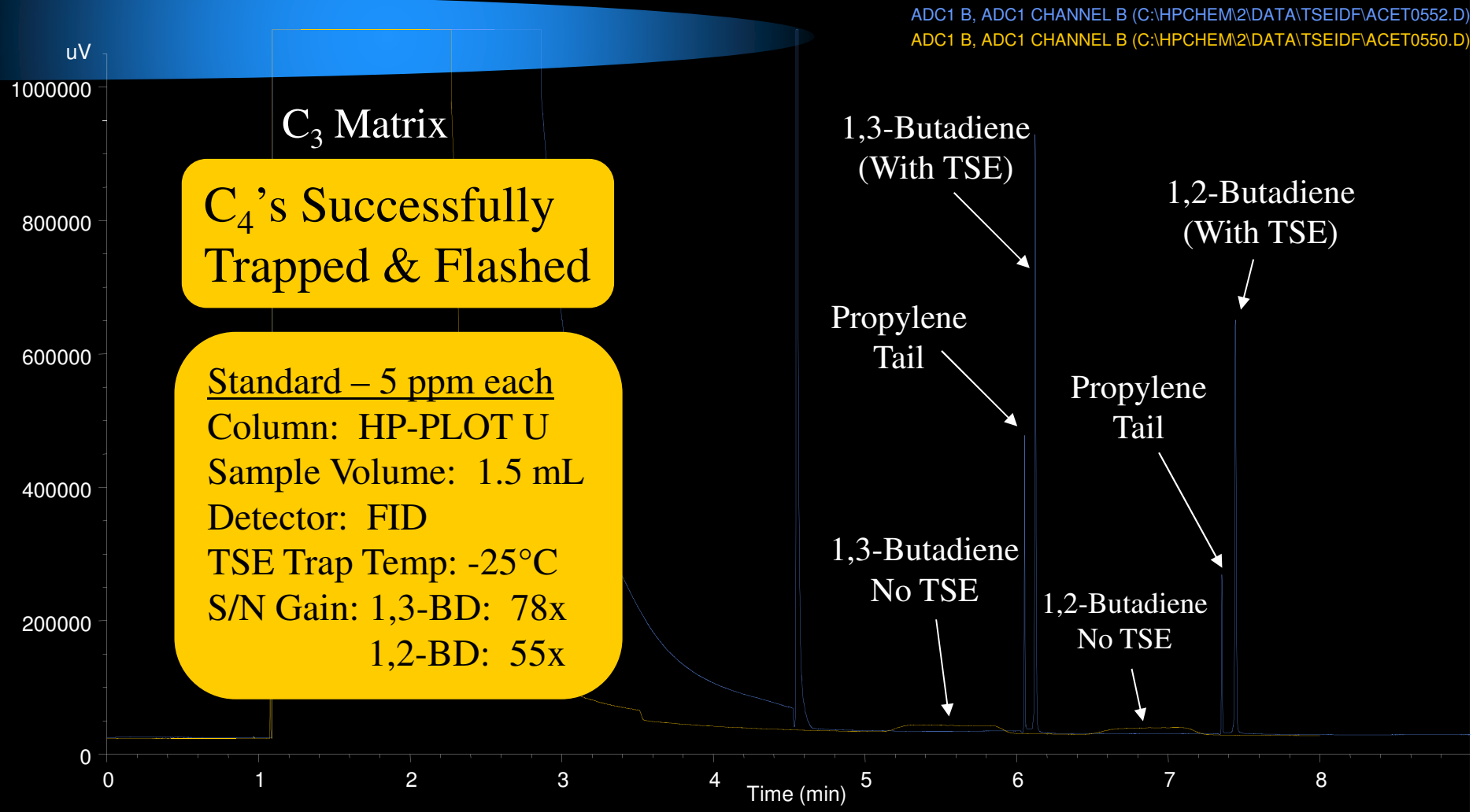

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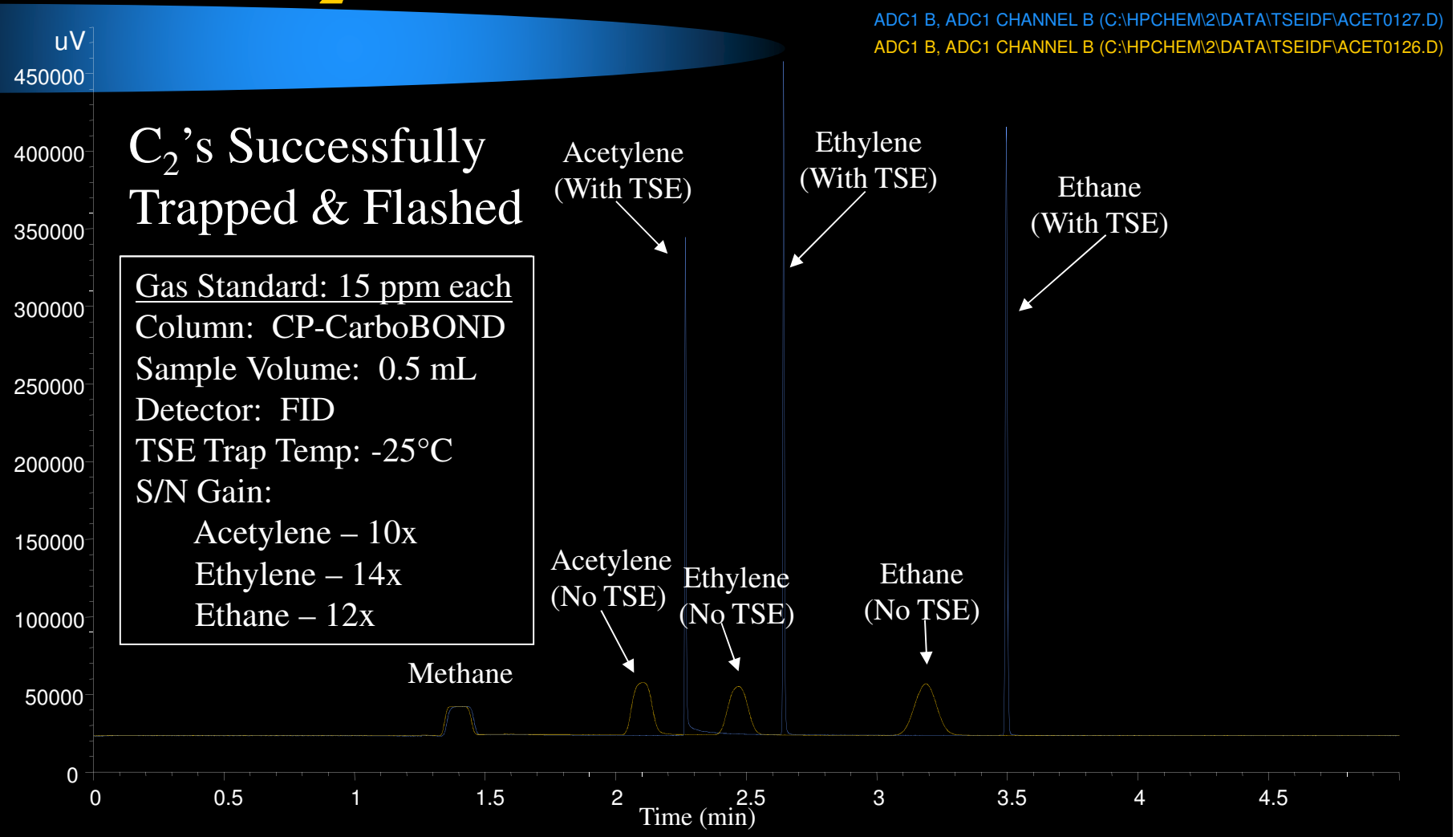
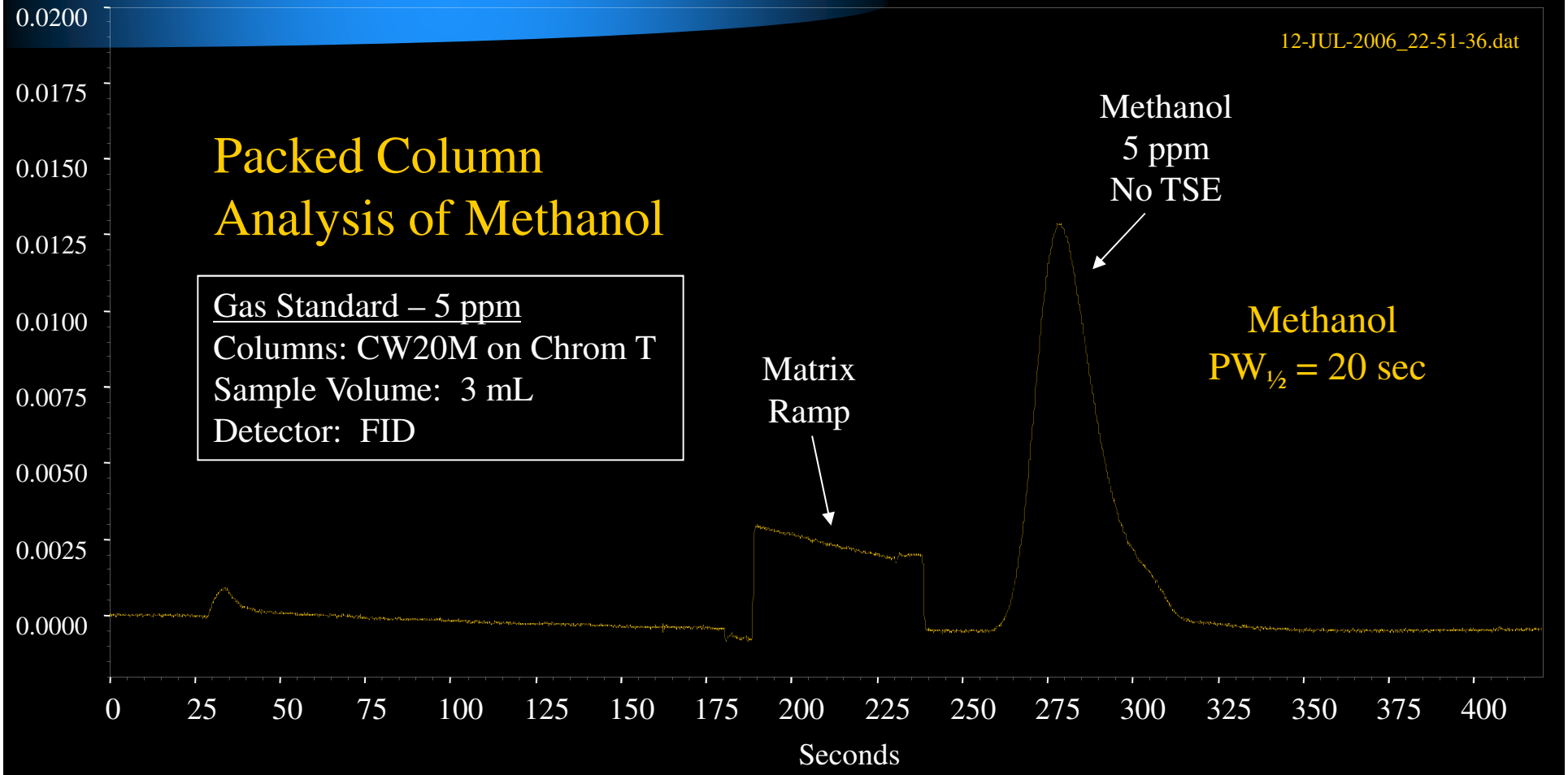


TSE of Methanol



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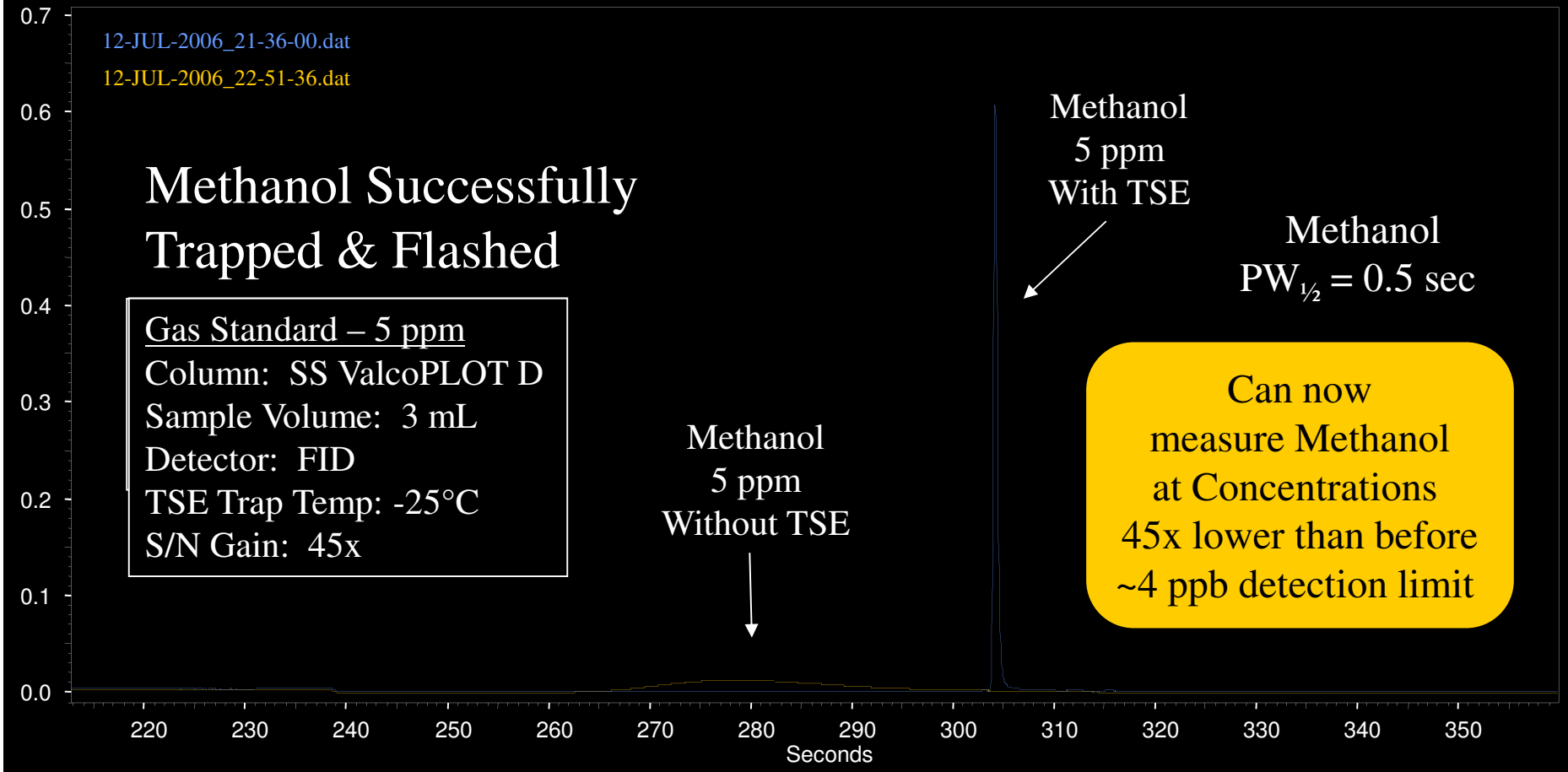
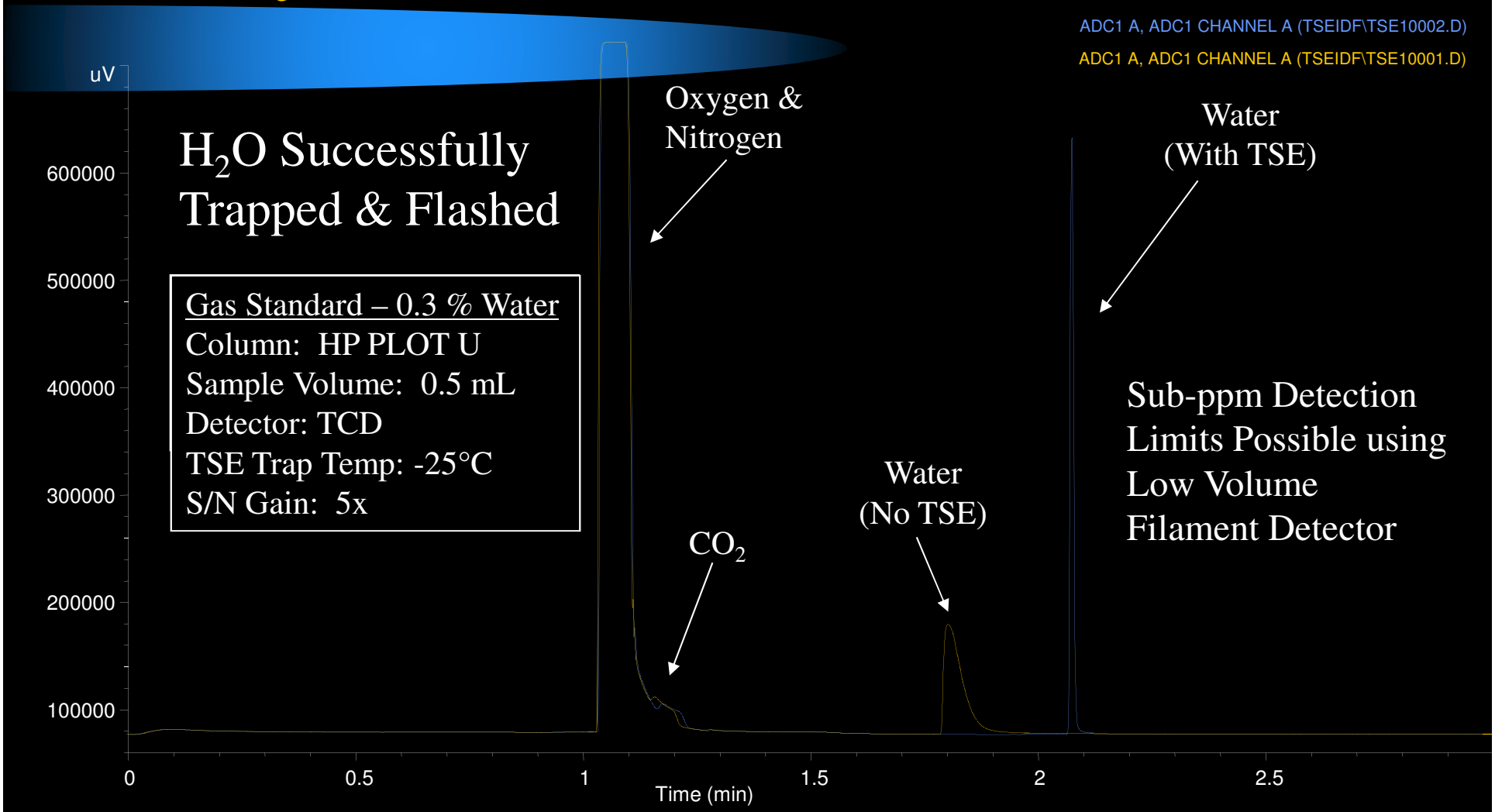
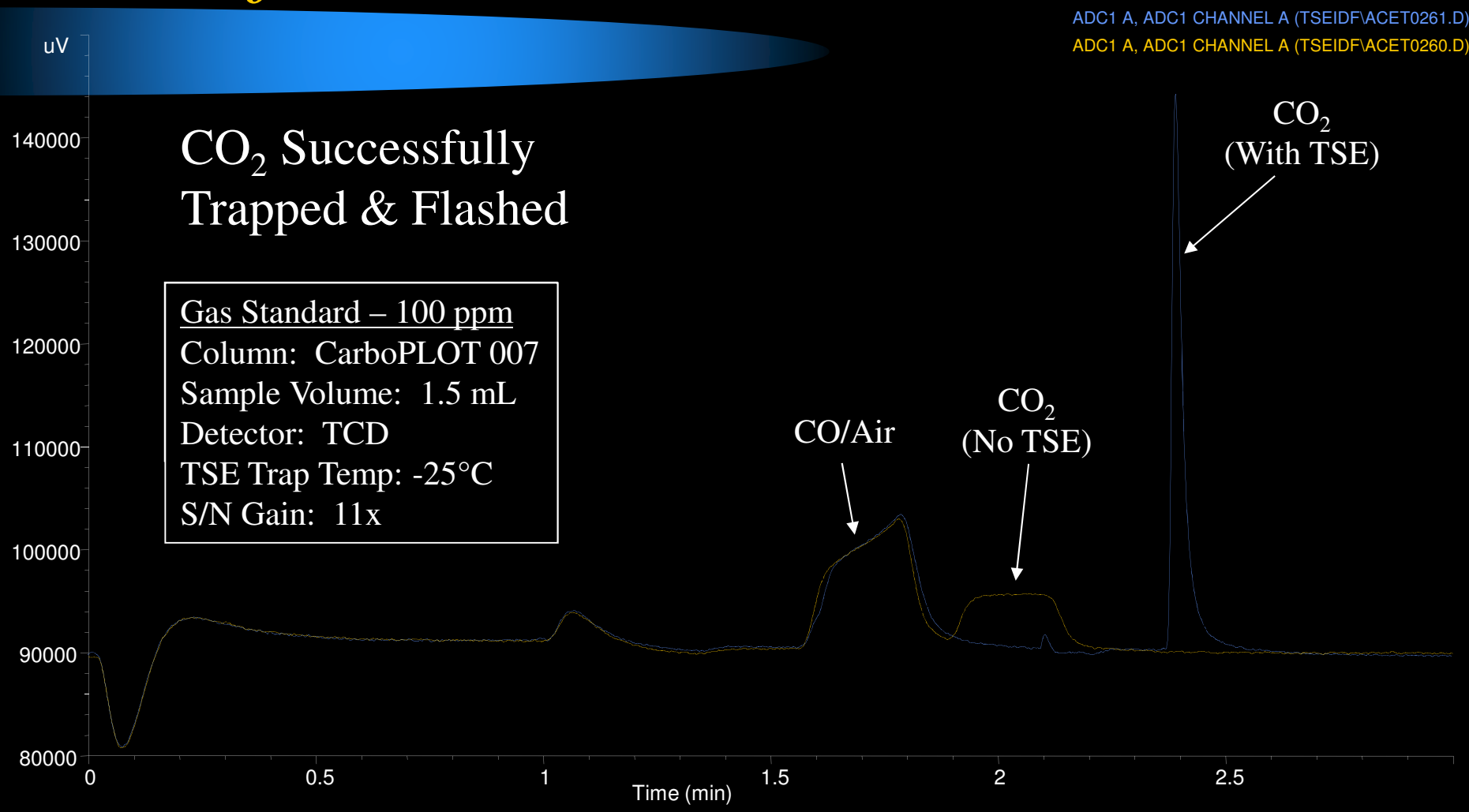


TSE of Water


ADC1 A, ADC1 CHANNEL A (TSEIDF\TSE10002.D)
ADC1 A, ADC1 CHANNEL A (TSEIDF\TSE10001.D)
uV
600000
500000
400000
300000
200000
100000
0
0.5
1
1.5
2
2.5
Time (min)
H_2O Successfully Trapped & Flashed
Gas Standard – 0.3 % Water
Column: HP PLOT U
Sample Volume: 0.5 mL
Detector: TCD
TSE Trap Temp: -25°C
S/N Gain: 5x
Oxygen & Nitrogen
CO_2
Water (No TSE)
Water (With TSE)
Sub-ppm Detection Limits Possible using Low Volume Filament Detector

TSE of Carbon Dioxide



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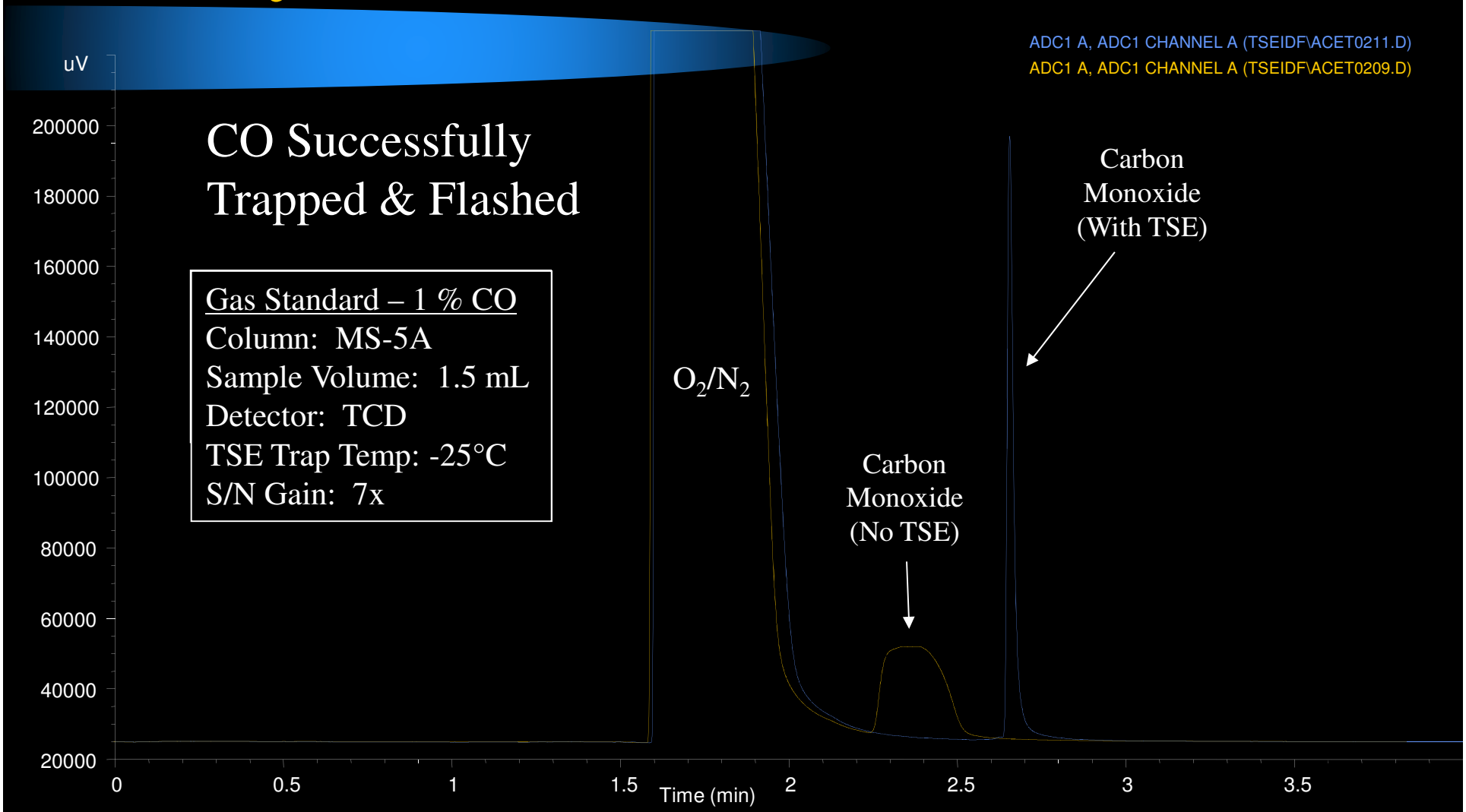
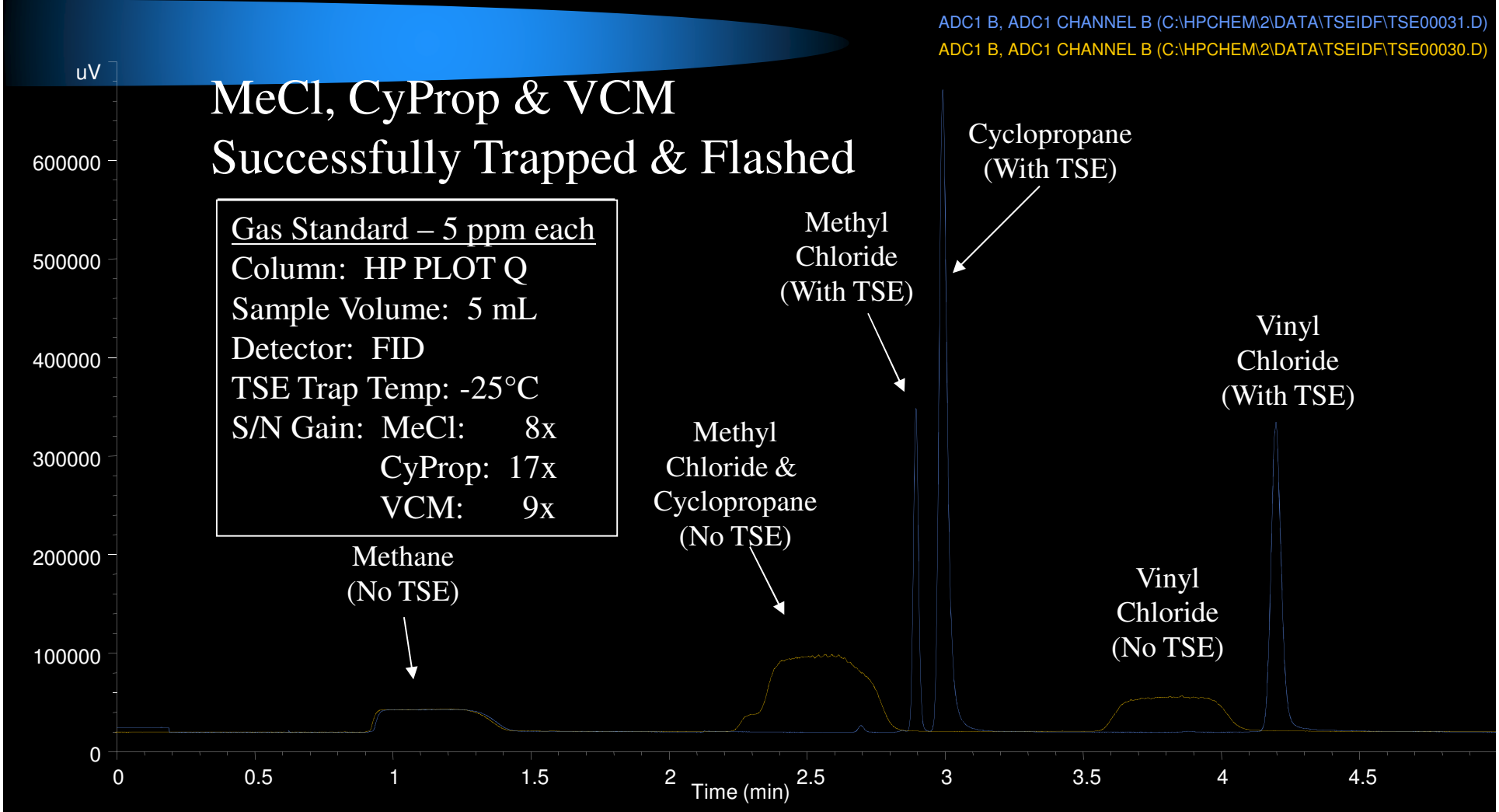


TSE at Column Head



TSE Capabilities

- Almost Any GC Analyte Can Be Signal-Enhanced by TSE

Some Analytes Successfully Enhanced by TSE:		
Acetylene	1,3-Butadiene	Hydrogen Sulphide
Ethylene	1,2,-Butadiene	Carbonyl Sulphide
Ethane	Isobutylene	Mercaptans
Cyclopropane	Ethyl Acetylene	Sulphides
Propane	n-Pentane	Formaldehyde
Propylene	n-Hexane	Acetaldehyde
n-Butane	Benzene	Ethylene Oxide
iso-Butane	Methyl Chloride	Methanol
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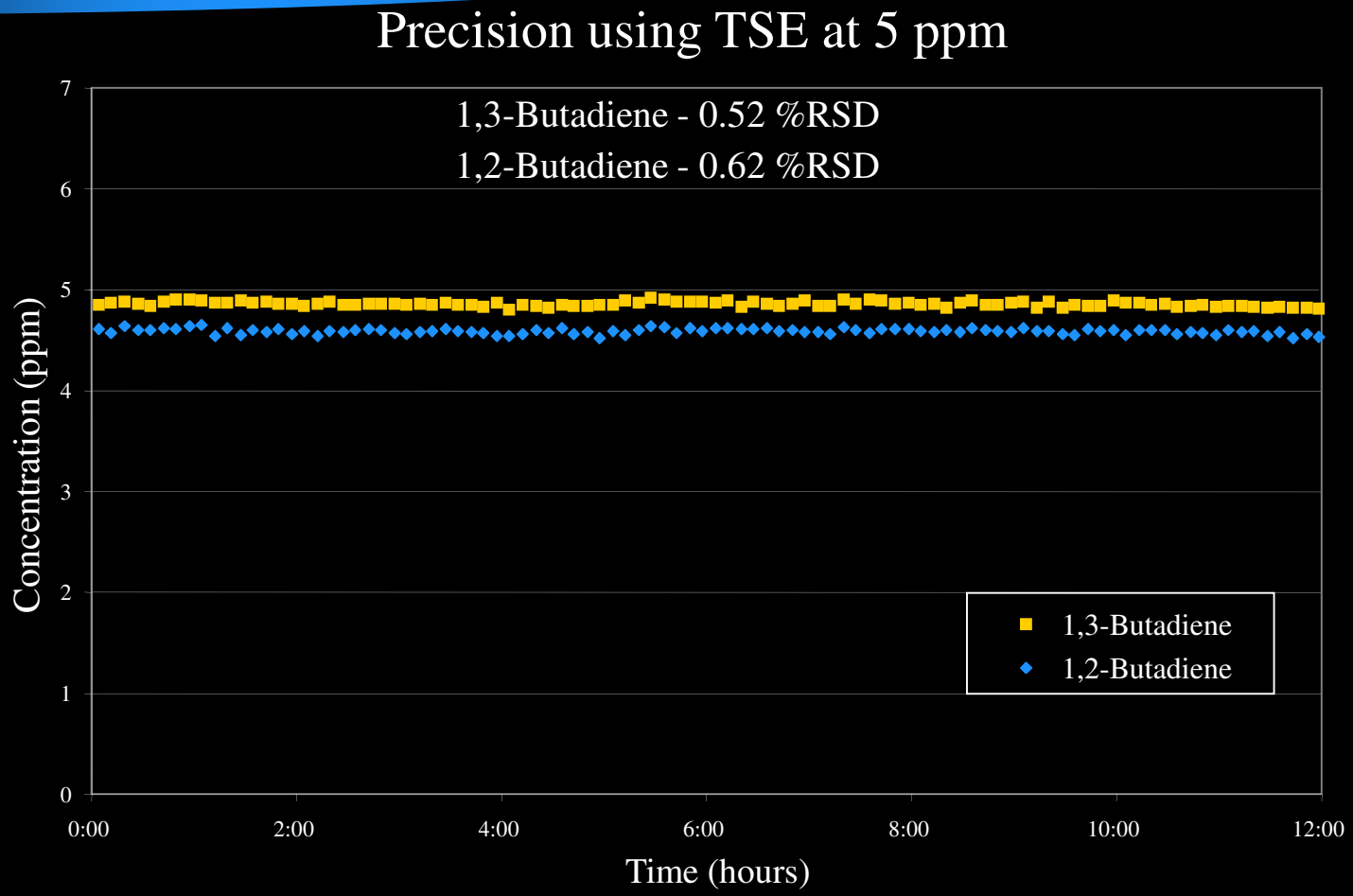
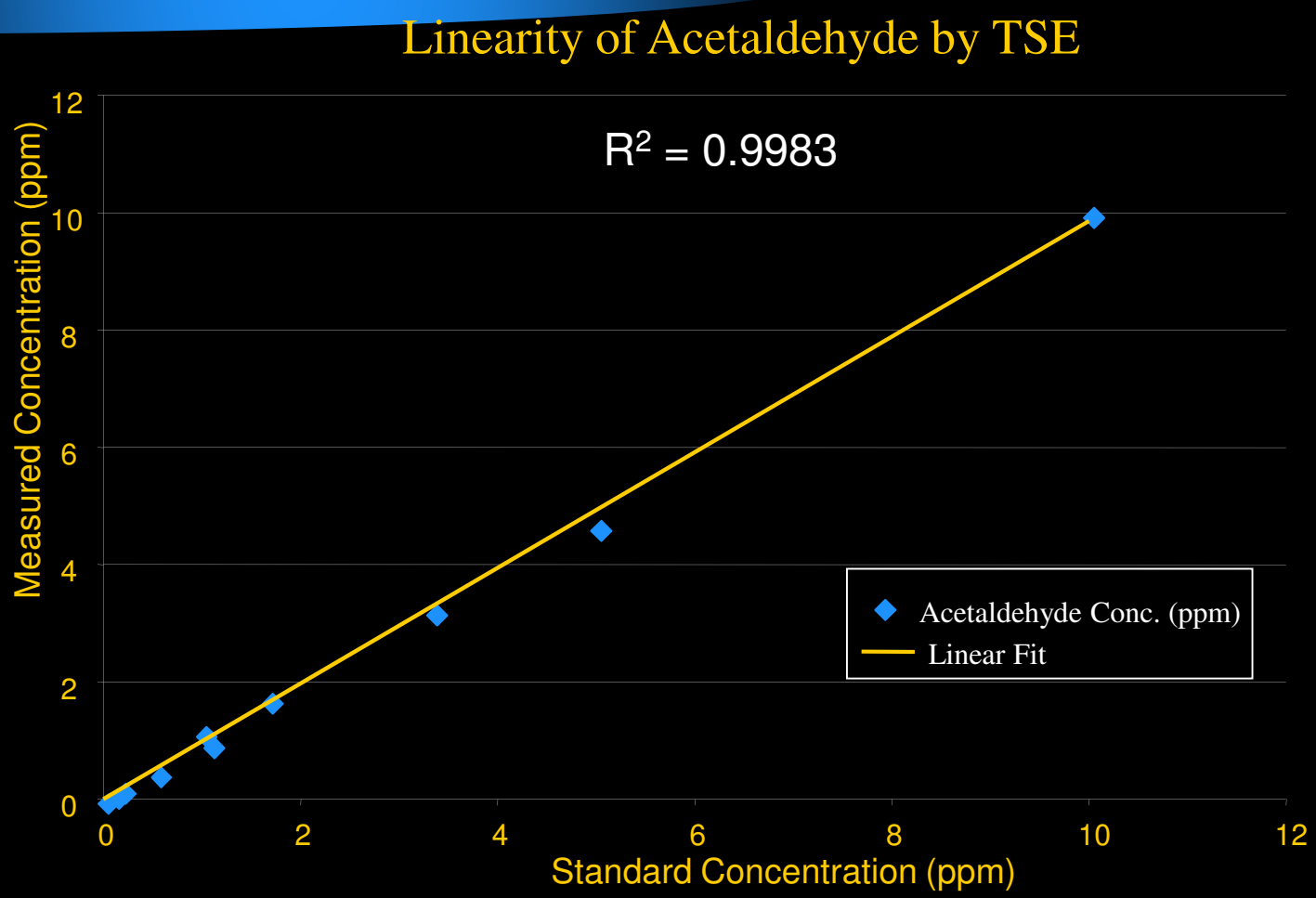
cis-2-Butene	Ethyl Chloride	Carbon Dioxide
trans-2-Butene	Carbon Tetrachloride	Water

TSE Precision at 5 ppm



TSE Linearity



TSE Performance

- TSE operated continuously for over 1 year with zero maintenance required
- Good Precision & Linearity
  - Equal to or better than conventional GC methods for trace analyses
  - Sometimes better due to improved peak shape

TSE Shortcomings

- Vortex cooler requires min. 80 psig air pressure
  - Insufficient cooling = Analyte breakthrough
  - Monitor TSE Trap Temp & Alarm
- Undesirable impurities cryotrapped as well
  - Carrier gas impurities, Column bleed, etc.
  - Requires short length of column after TSE trap
    - Ineffective if impurity is same as analyte (e.g. Water in carrier gas)
- Cannot trap extremely light analytes (yet)
  - O_2, N_2, CH_4, H_2, Ar…
- Generates peaks 0.5-1.0 sec wide
  - Best for enhancing peaks > 2 sec wide
- Potential to overload TSE trap exists

Summary

- Vortex Cooler-Driven TSE:
  - Can signal-enhance almost any process GC analyte
  - Provides the capability to measure process GC analyte concentrations as much as 78x lower than before
  - Is Reliable, Inexpensive & very Low Maintenance
  - Offers the robustness of packed columns with the peak widths of capillary columns
  - Can be retrofitted to most common process GC's
  - Is absurdly simple, yet powerful
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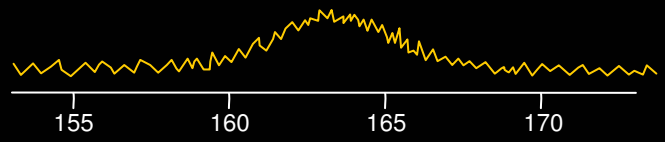

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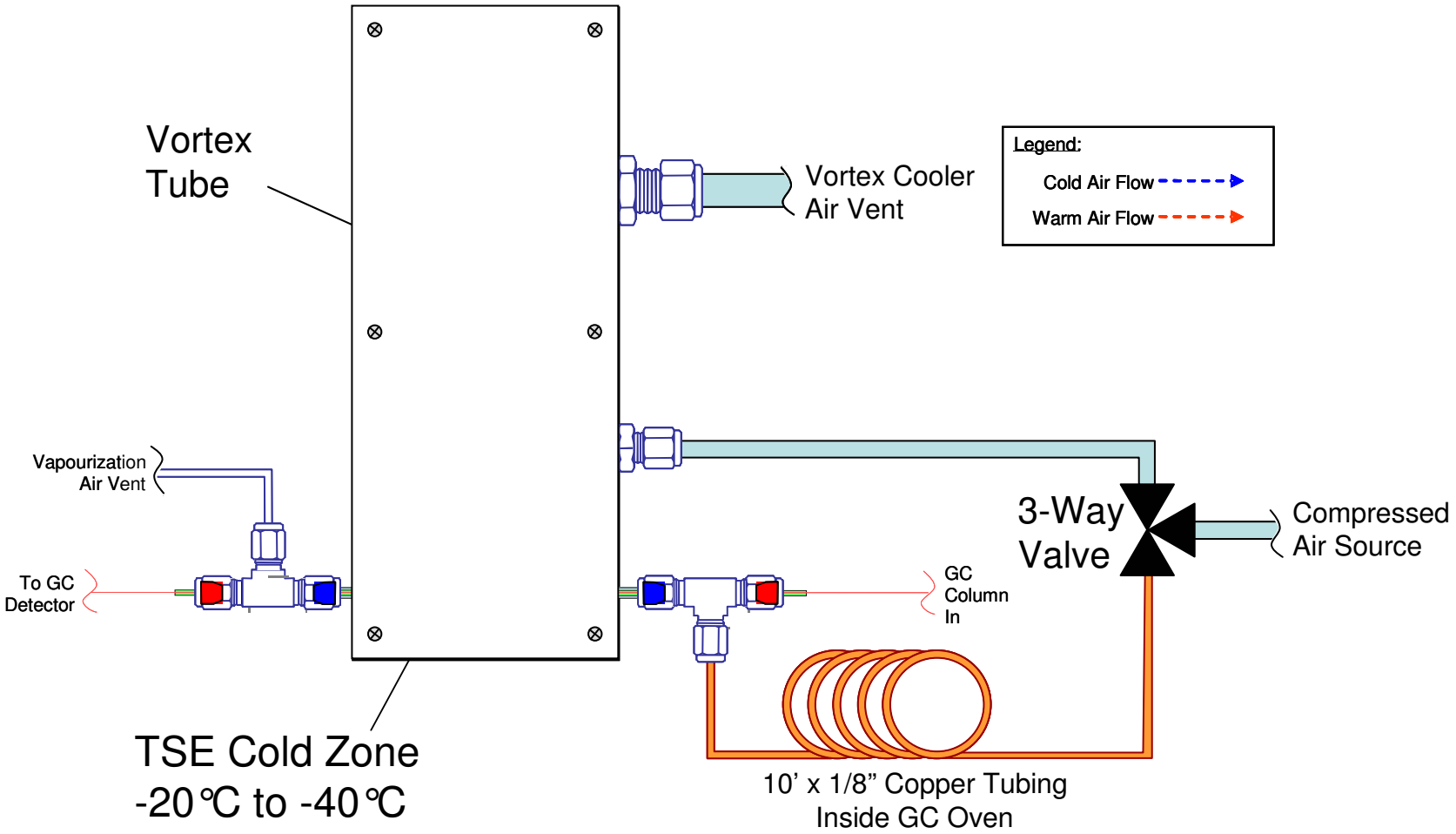

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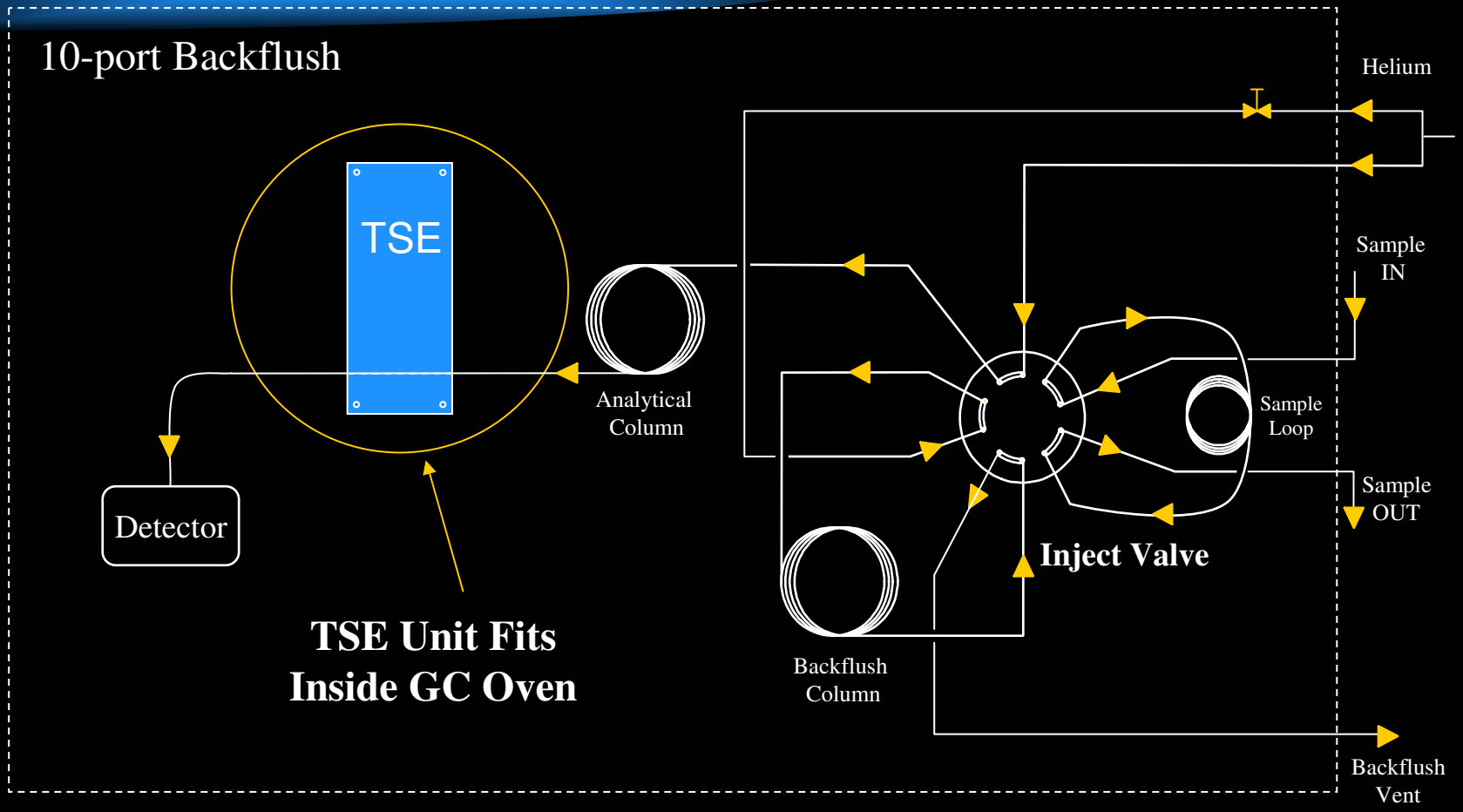

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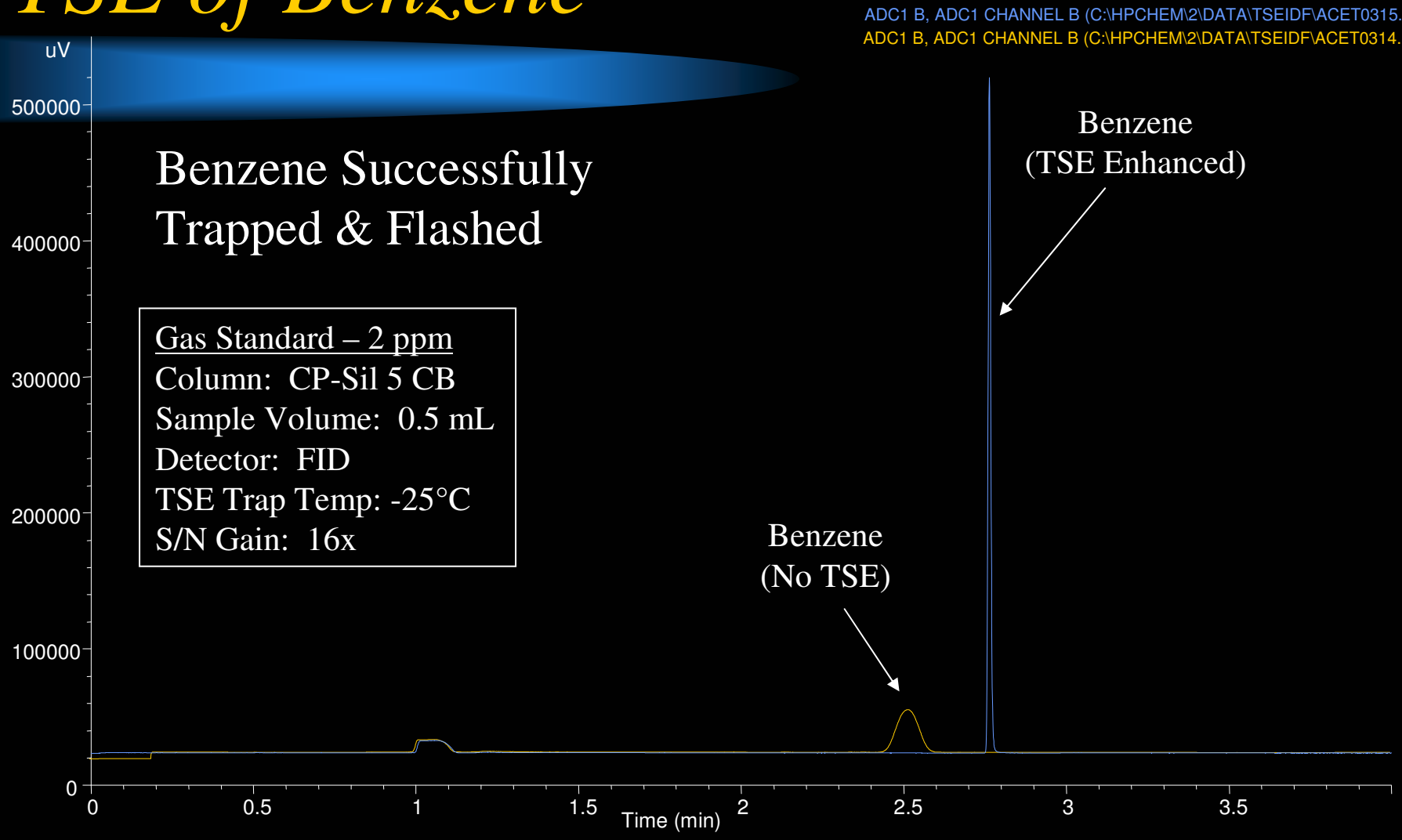

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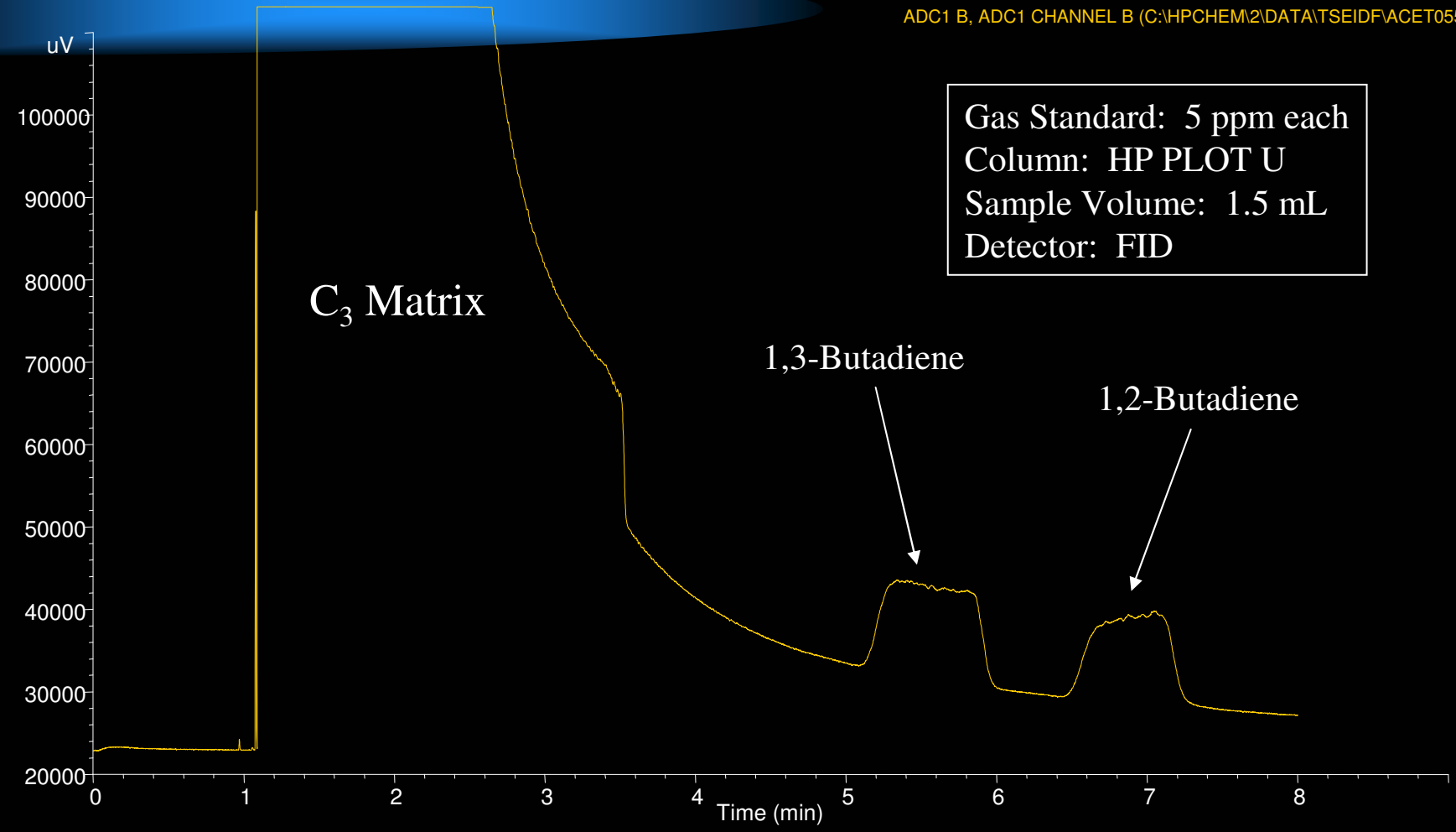

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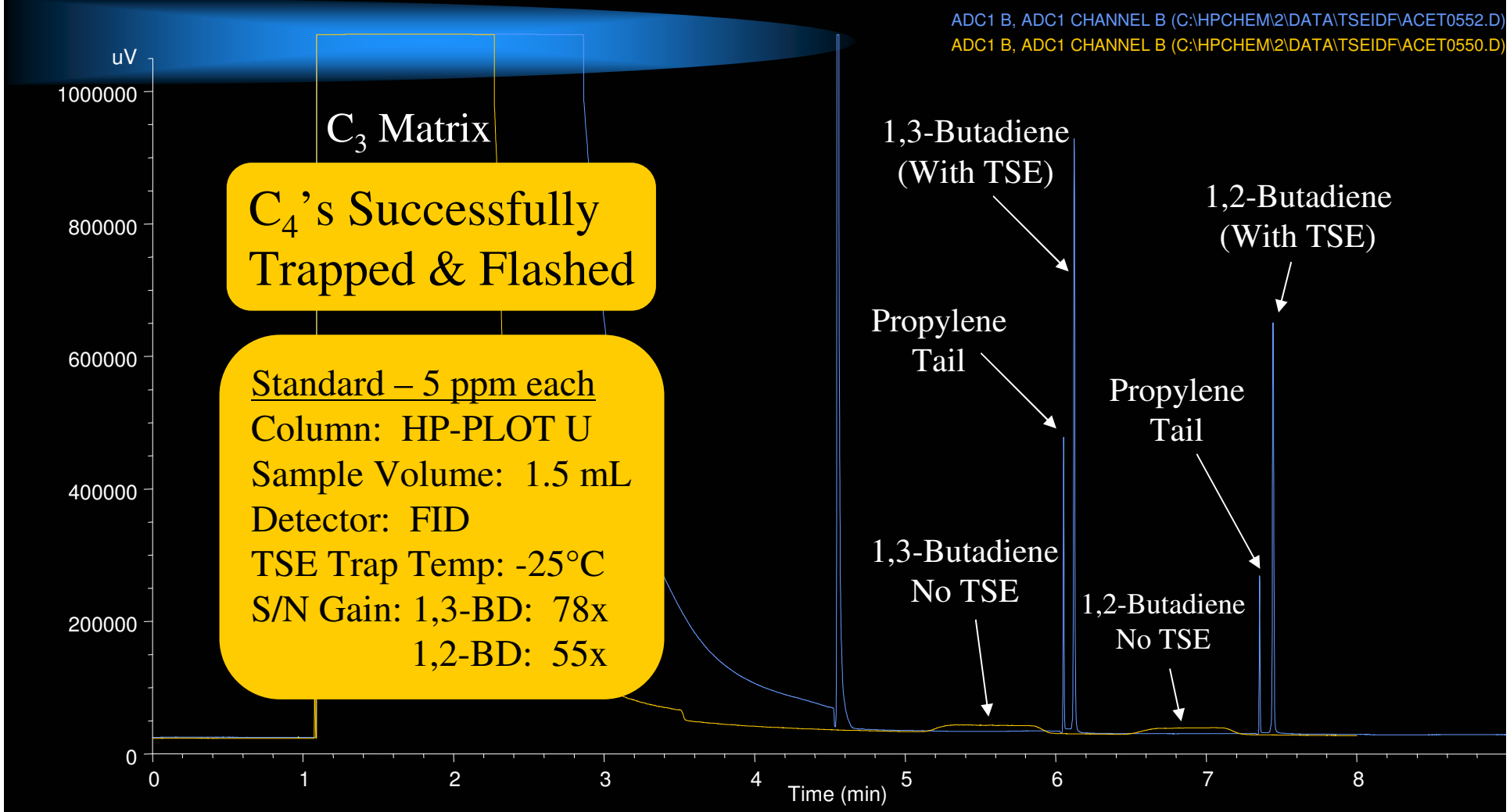

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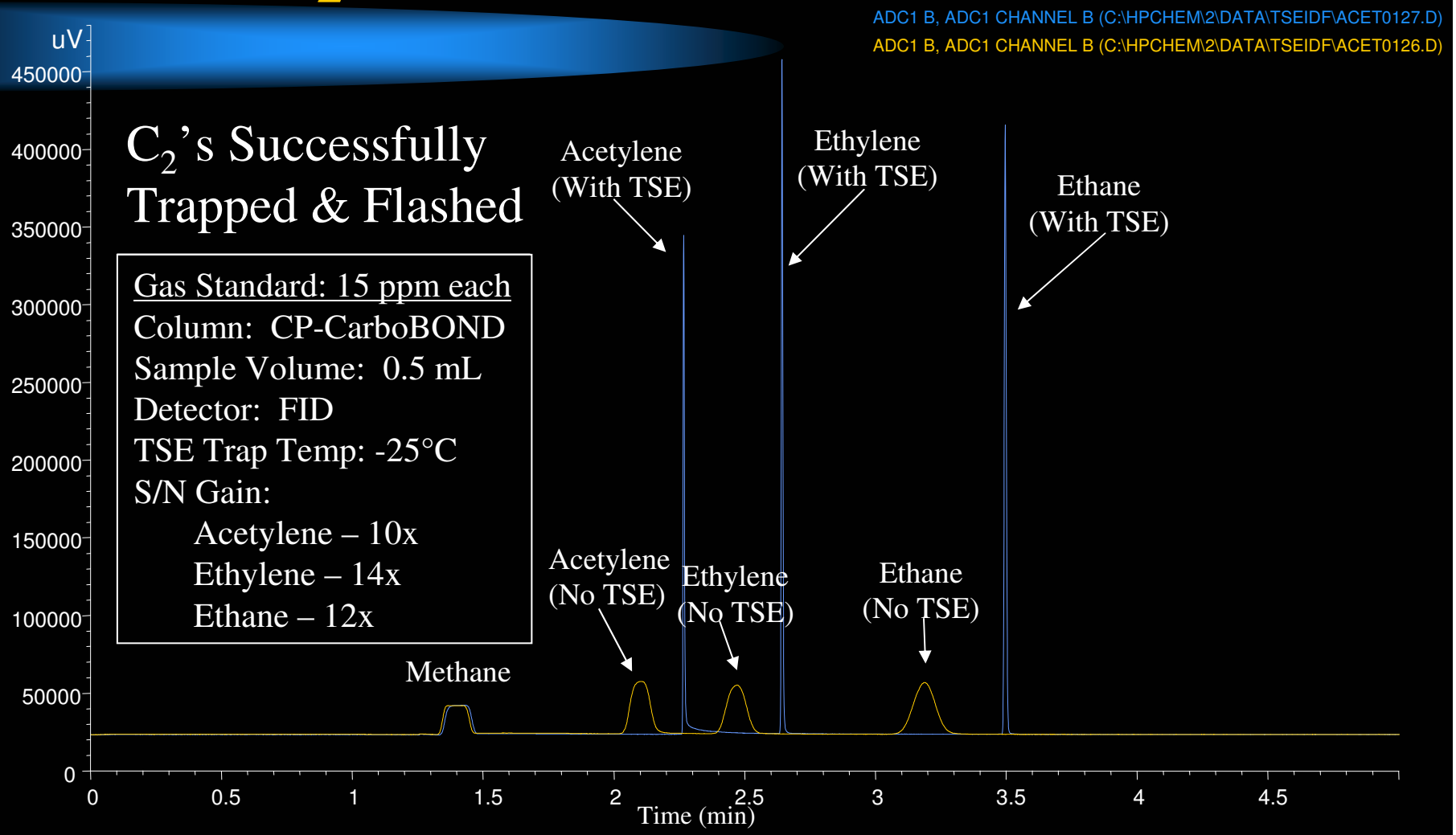

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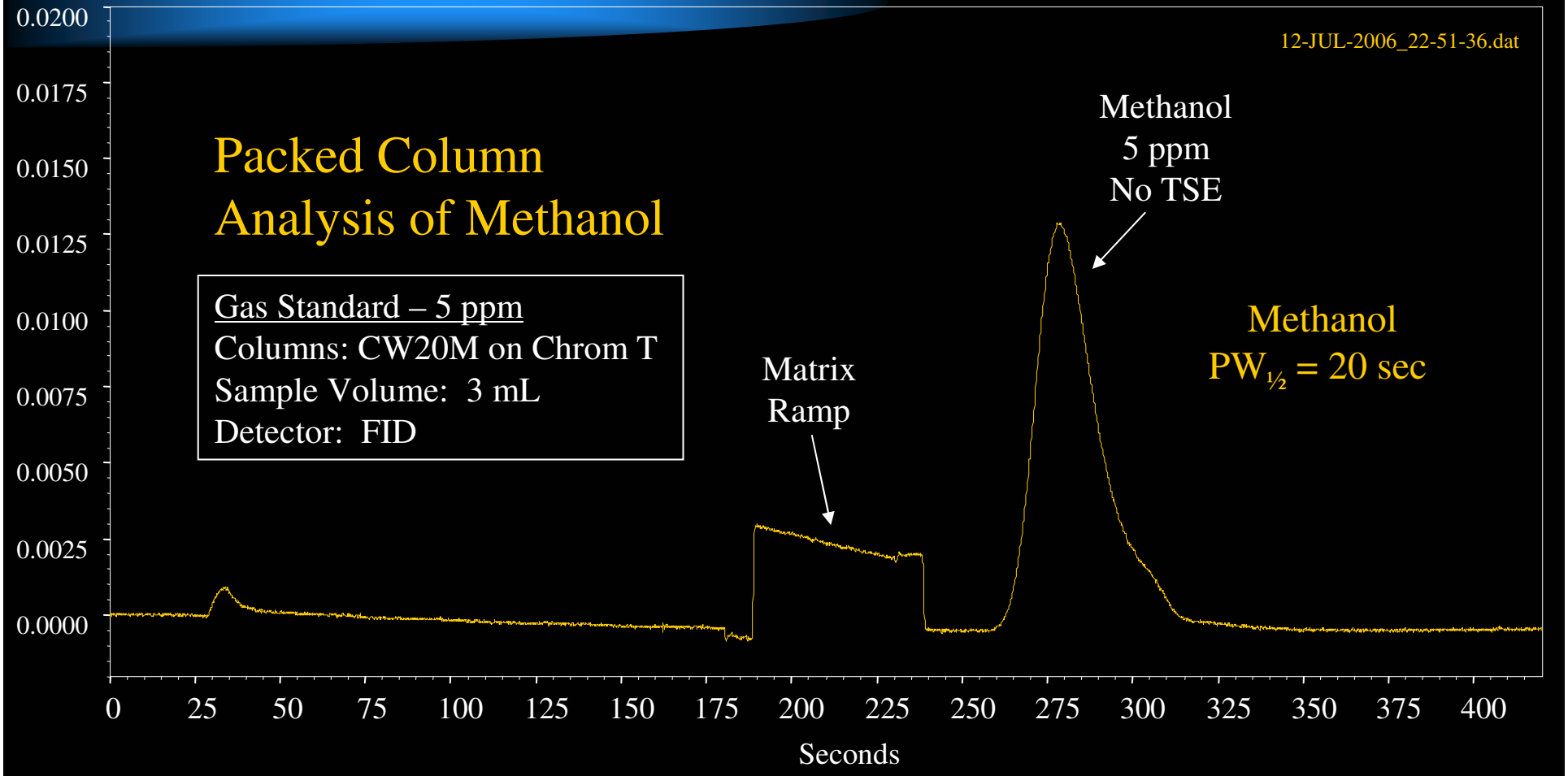

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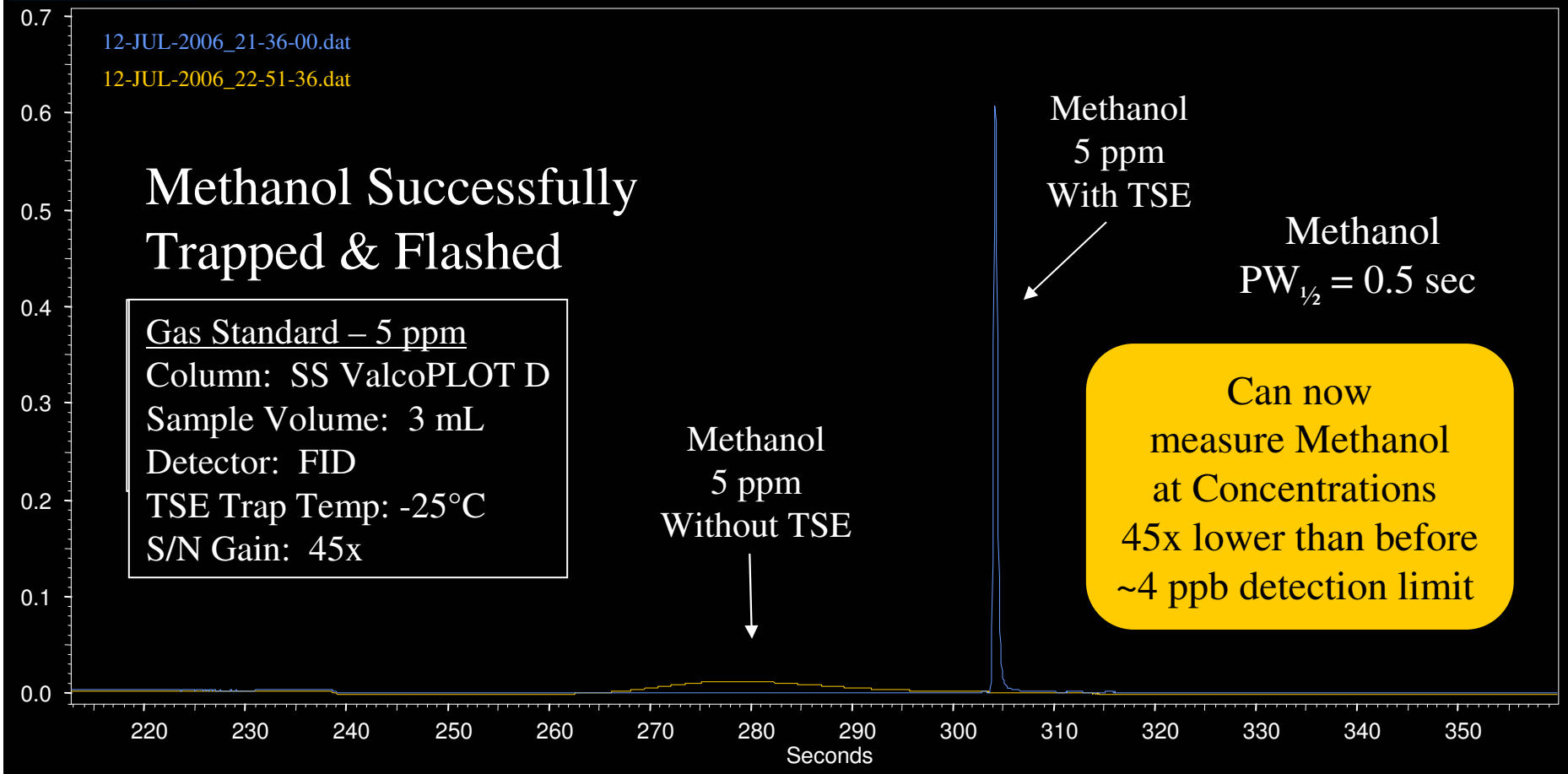
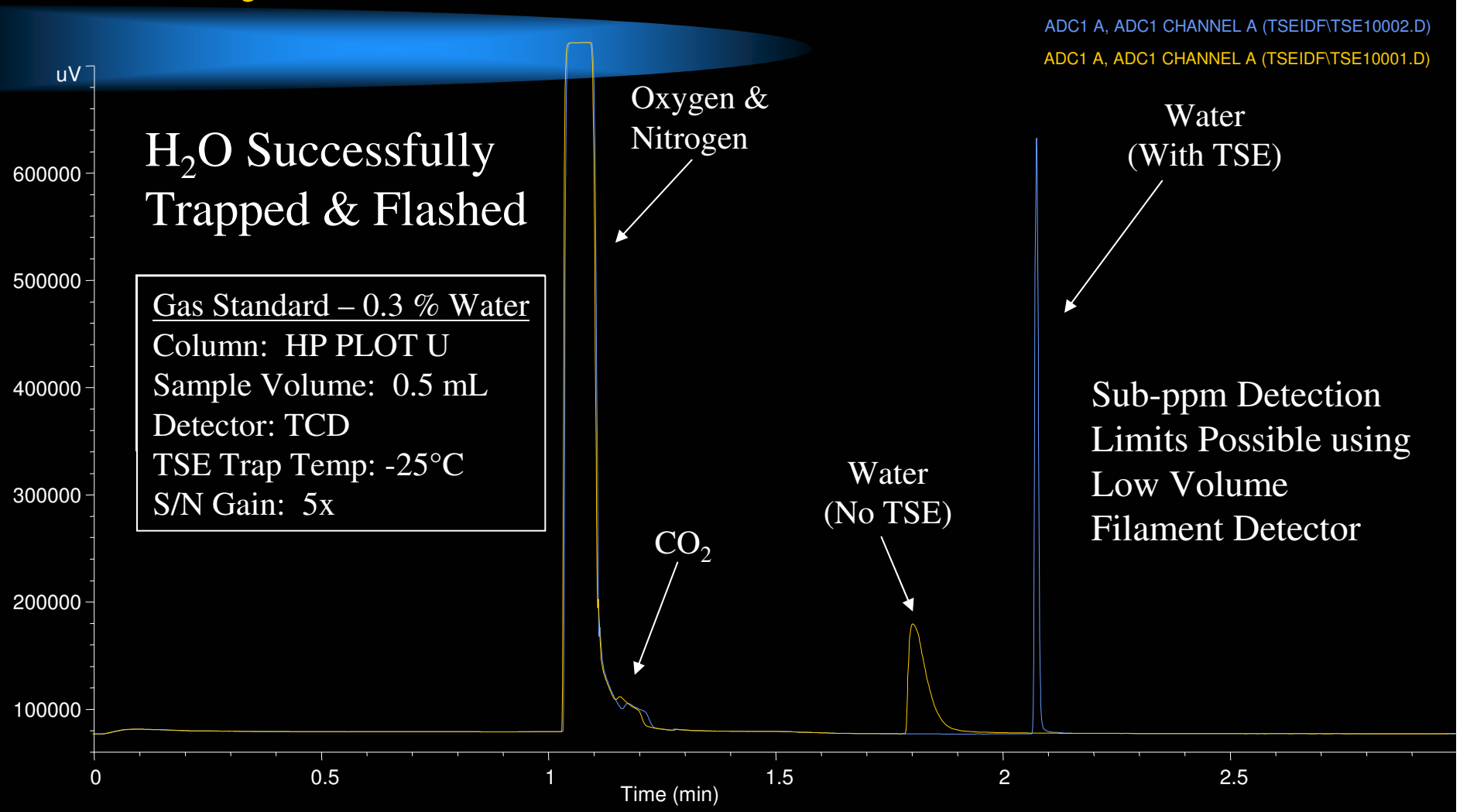


TSE of Water


ADC1 A, ADC1 CHANNEL A (TSEIDF\TSE10002.D)
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uV
600000
500000
400000
300000
200000
100000
0
0.5
1
1.5
2
2.5
Time (min)
H_2O Successfully Trapped & Flashed
Gas Standard – 0.3 % Water
Column: HP PLOT U
Sample Volume: 0.5 mL
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Oxygen & Nitrogen
CO_2
Water (No TSE)
Water (With TSE)
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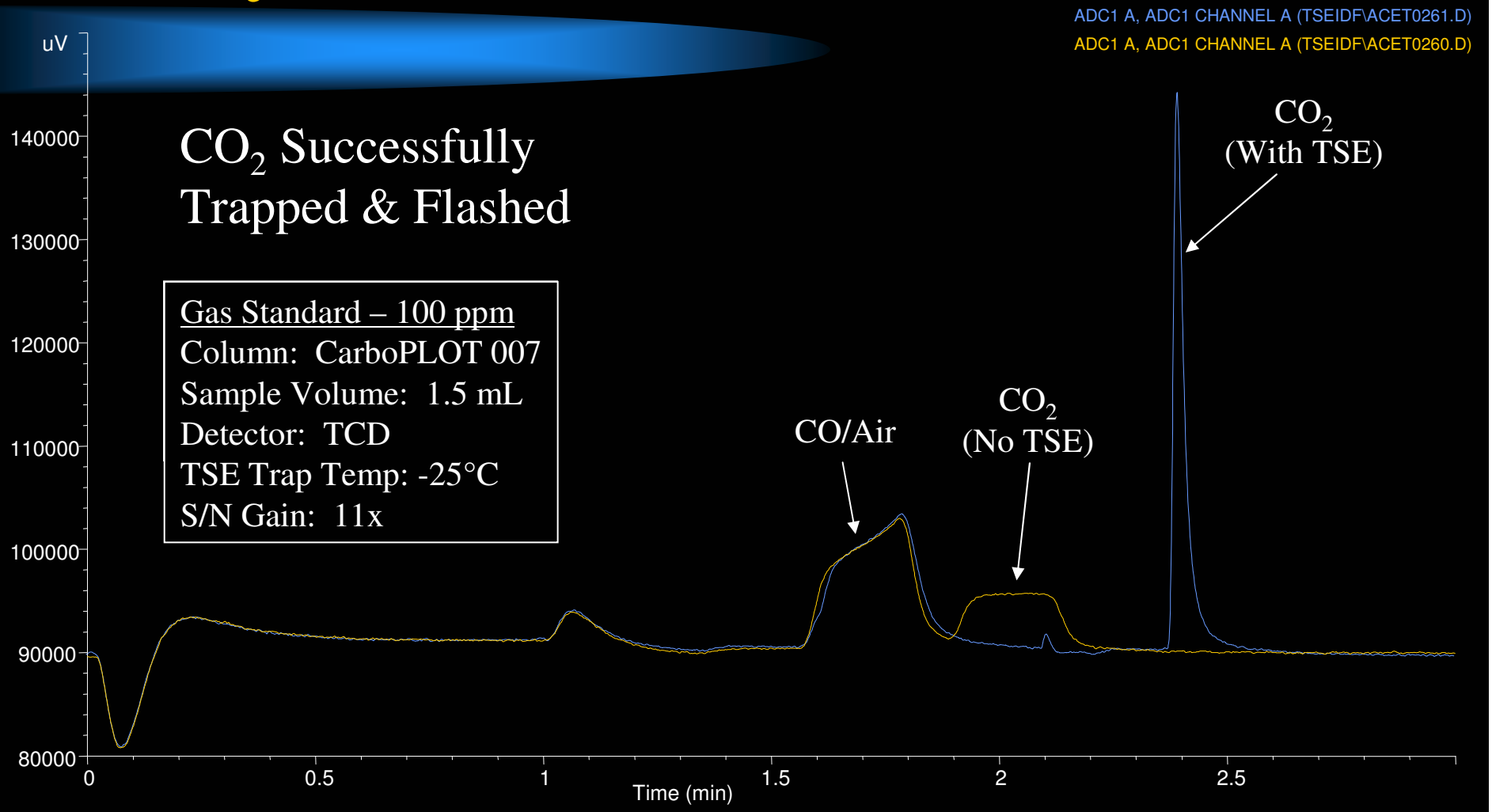

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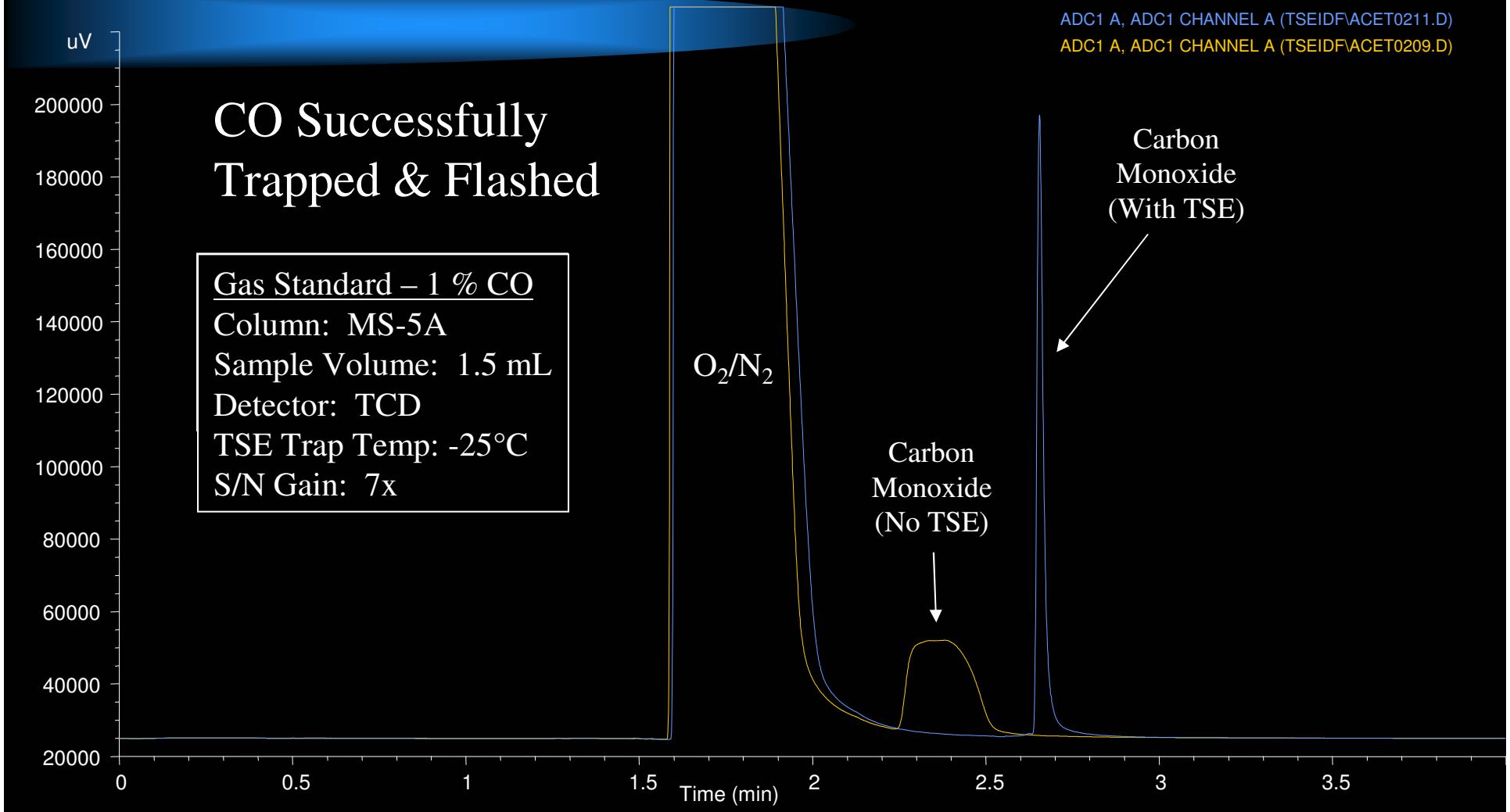

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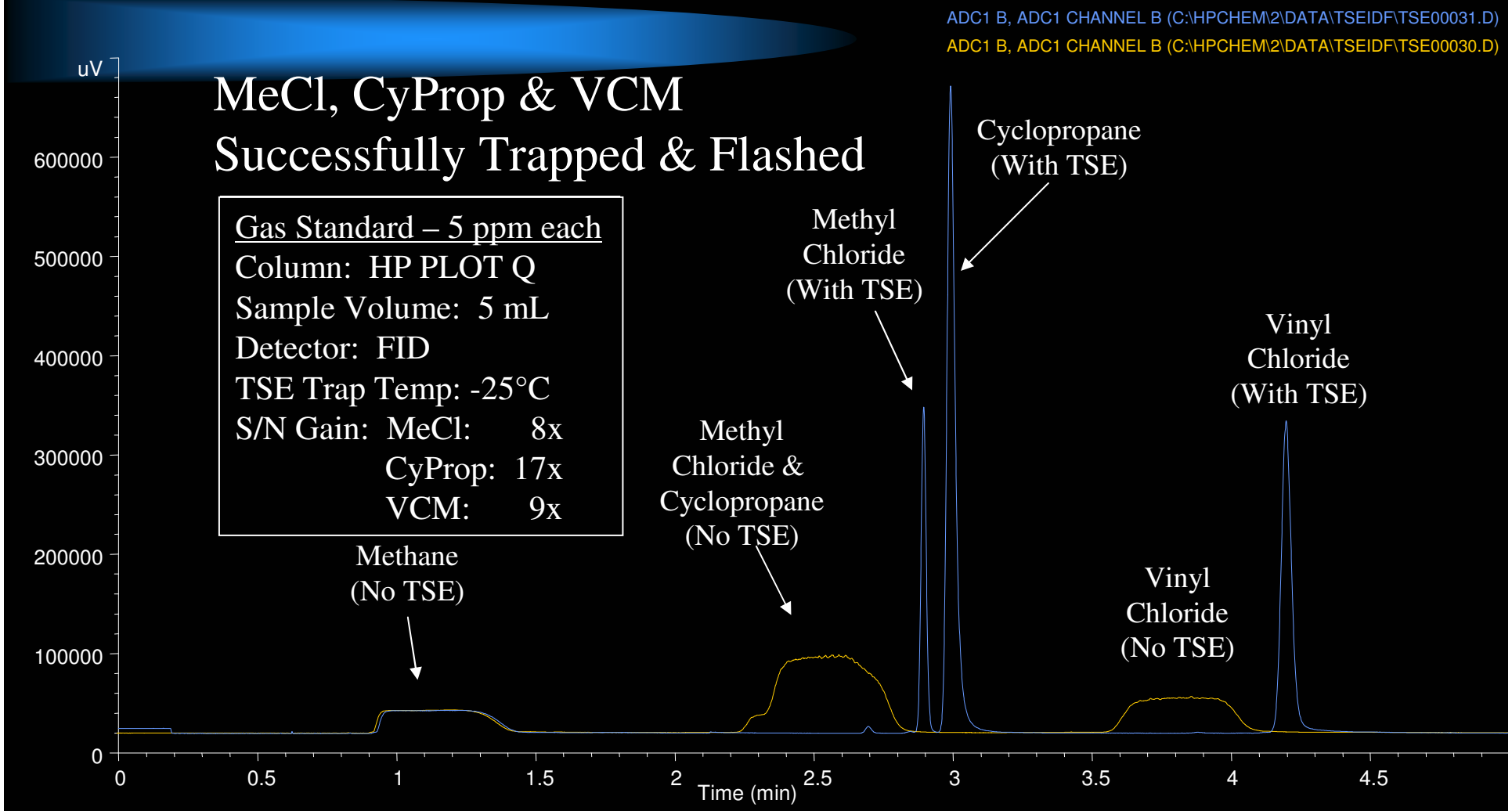

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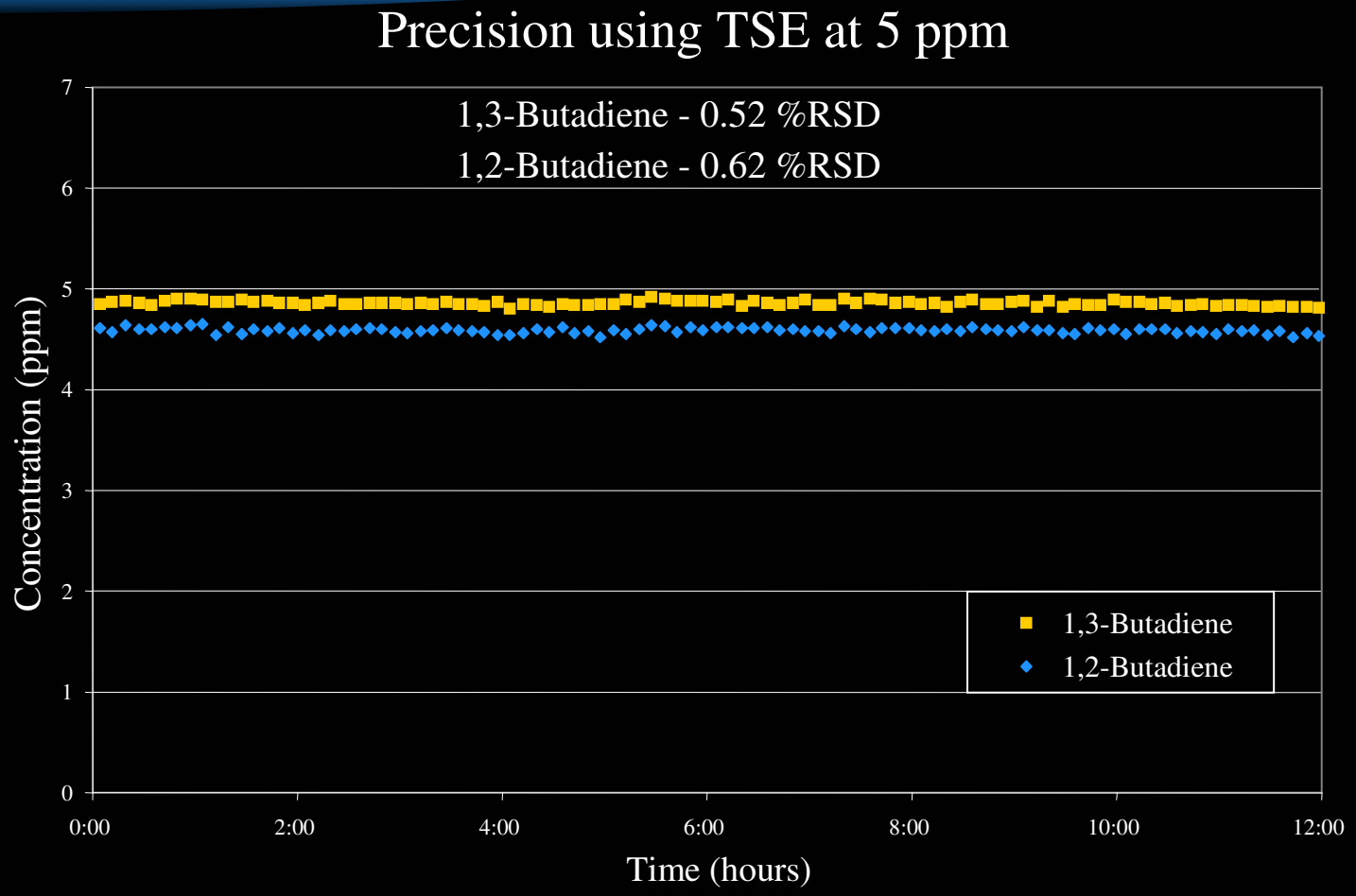
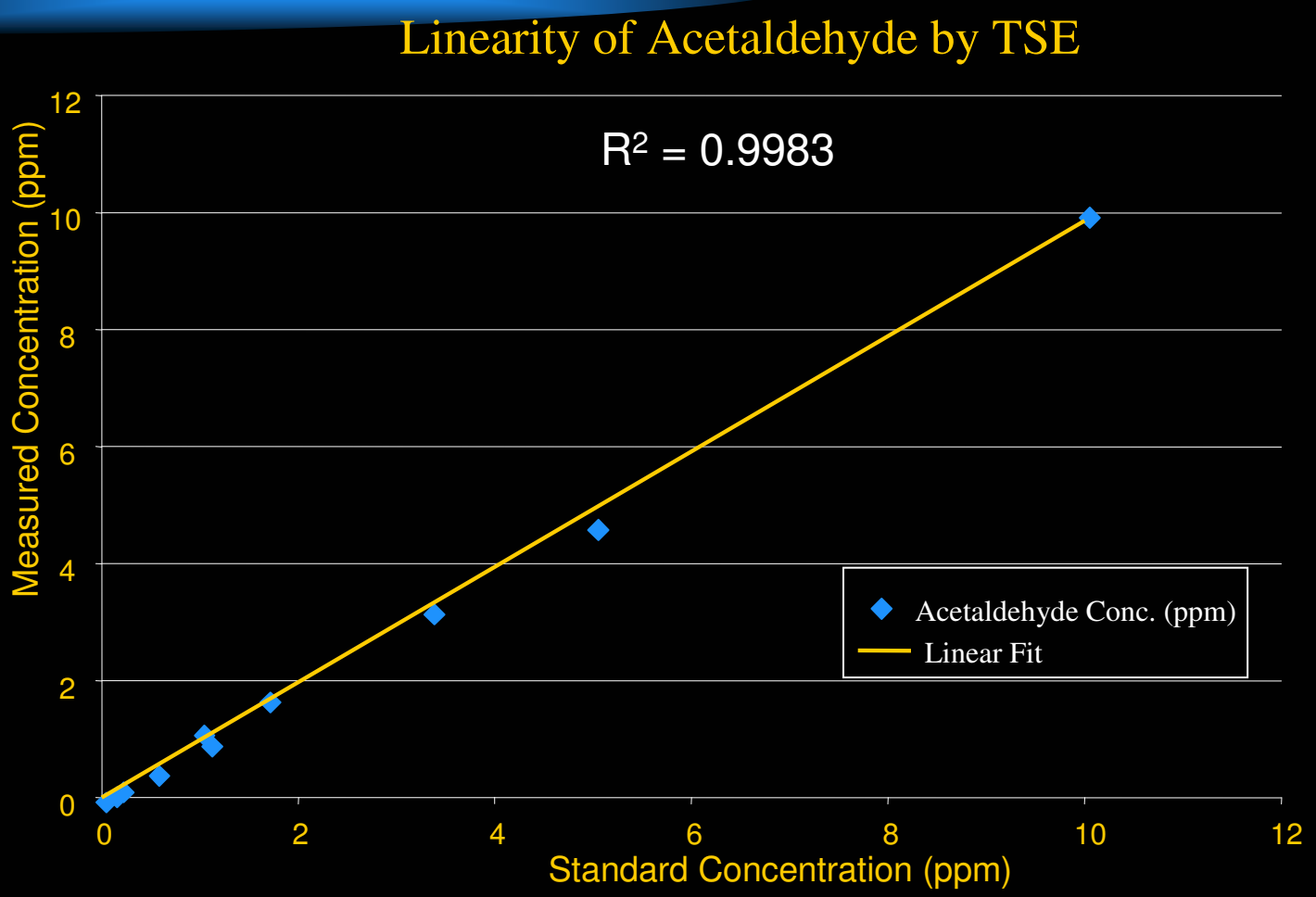


TSE Linearity



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