Calidus – Palarus System

Fast Gas Chromatography using Heated Headspace Gas Auto Sampling Techniques: Ethylene Oxide and 1,4-Dioxane in Fatty Acids

Jonathan Blackwell, Eric Wise – Lonza

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Lonza

Abstract

Fast Gas Chromatography using Heated Headspace Gas Autosampling Techniques: Ethylene Oxide and Dioxane in Fatty Acids -1:30-1:50 pm

Jonathan Blackwell, Eric Wise - Lonza, Derrick Saul, Joe Perron - Falcon Analytical

Sampling is often the most difficult part of an analytical method even for micro and Fast Gas Chromatography. In some cases the analytes of interest cannot be separated and measured with a column system that can survive the balance of the sample matrix. Determination of low boiling oxides in fatty acids is an excellent example of this problem. The solution is to heat the fatty acid sample driving the low boiling analytes into the headspace gas. The autosampler using a gas tight syringe can then sample and introduce the resultant sample into the GC.

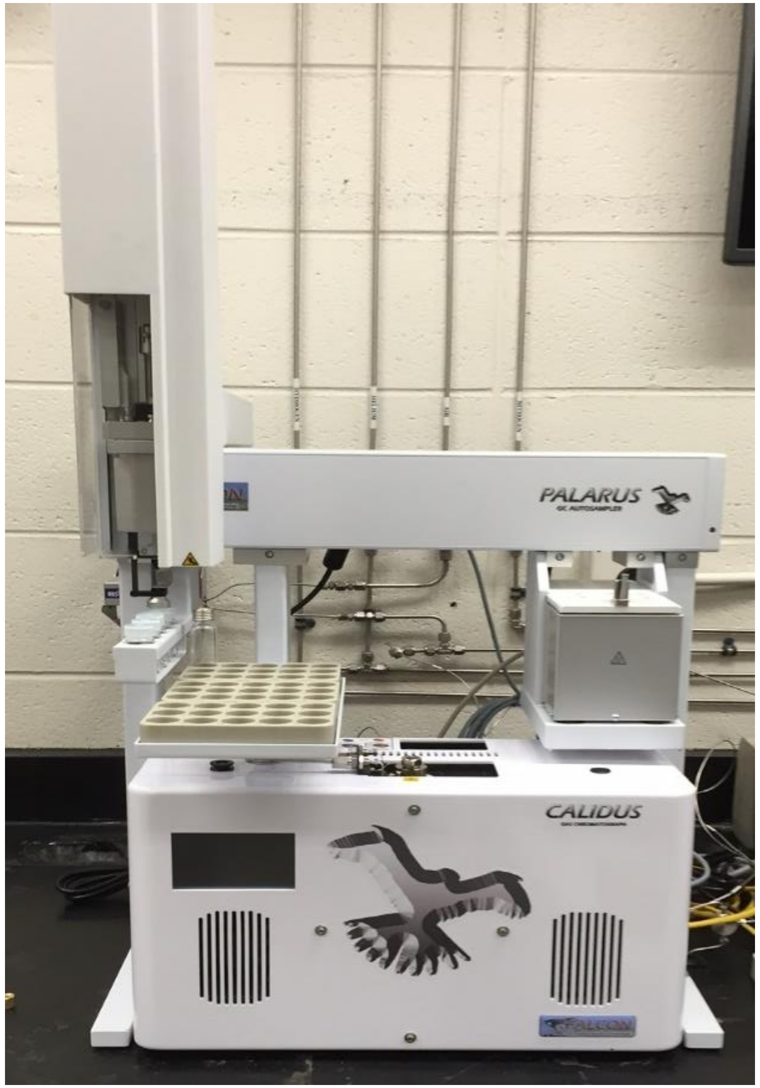
This paper will describe the system and the methods developed for this analysis. In addition, we will discuss other potential applications for this technique, for example analysis for residual monomer in polymer pellets.

Analytical Design

- Sample introduction is just as important as the analytical technique used.
- Difficulties with sample introduction can include, but are not limited to:
  - Analyte/Matrix column phase incompatibility
  - “Non-Injectable” sample matrix
  - Sample extraction/preparation may degrade target analytes, may not be effective, or may not be practical.

Falcon Analytical's Calidus 101 Paired with the Palarus RSI Auto Sampler

- Based on the PAL XYZ robot platform
- Modular System
- UHP Purge Gas Input
- Magnetic Vial Transfer
- Variable Speed, Temperature, Duration Agitator
- Interchangeable Tool – Headspace, Liquid, and SPME injections possible with the same Auto Sampler
- Supports a wide range of Injection volumes
- Virtual Interface Terminal (Physical Terminal Interface Available)

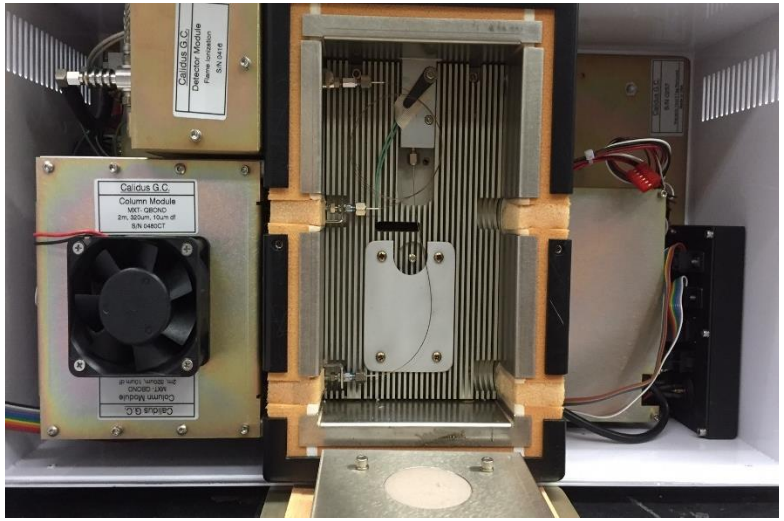


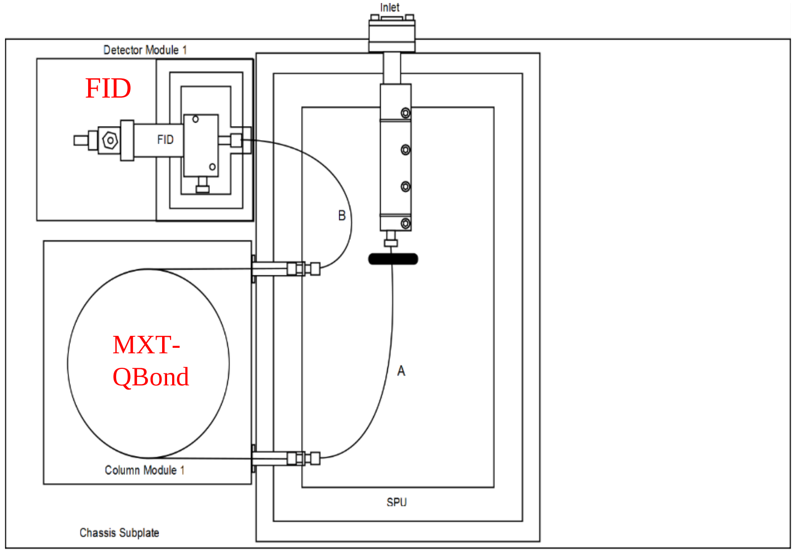
Operation

- Automated Vial Movement/Agitation
  - Controlled by XML within Chromperfect Data Acquisition Software
- Pre/post-injection Purge
- Fully Adjustable Injection Volume and Speed
- Differences from traditional headspace sampling
  - – No vial pressurization
  - – Mobile Syringe vs. Stationary Syringe

The Calidus 101

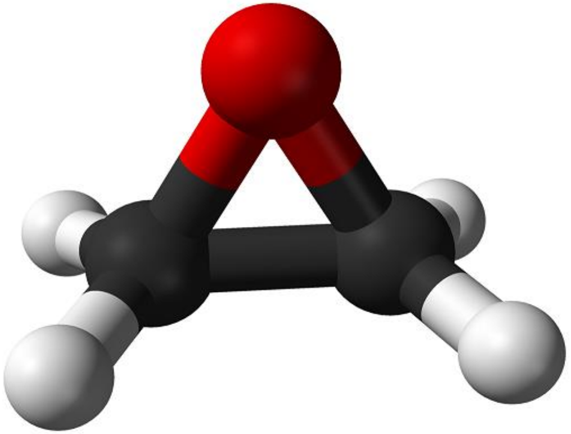
- Sample Processing Unit (SPU) – Single Split/Splitless Injector
- Program Temperature Column Module (PTCM) – 2m, 320µm ID, 10µm df, MXT-QBond phase.
- Detector Module (DM) – Micro Flame Ionization

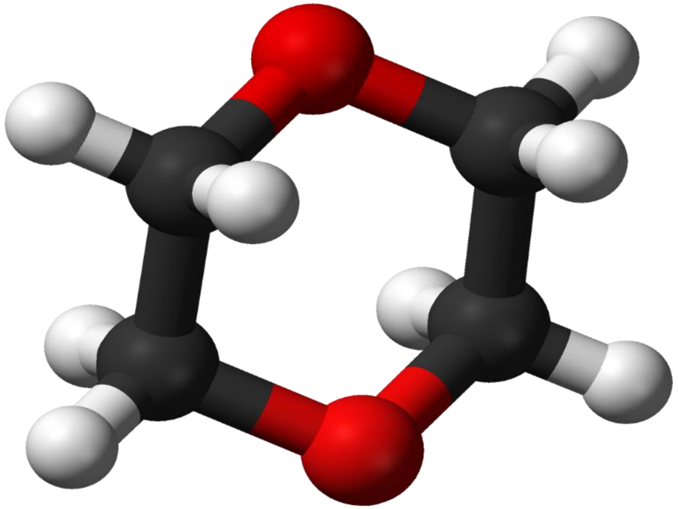




Method Development

- **Started with Client's "current" SOP**
  - 2g sample size, 100μL DI Water, Heated Zones, Standard Concentrations
- **Target Analytes in PEG 400**
  - To emulate sample matrix, as closely as possible.
- **Adding Ethylene Oxide to Analytical Method**
  - Previously only analyzing 1,4-Dioxane.





PALARUS
GC AUTOSAMPLER

Experimental Procedure

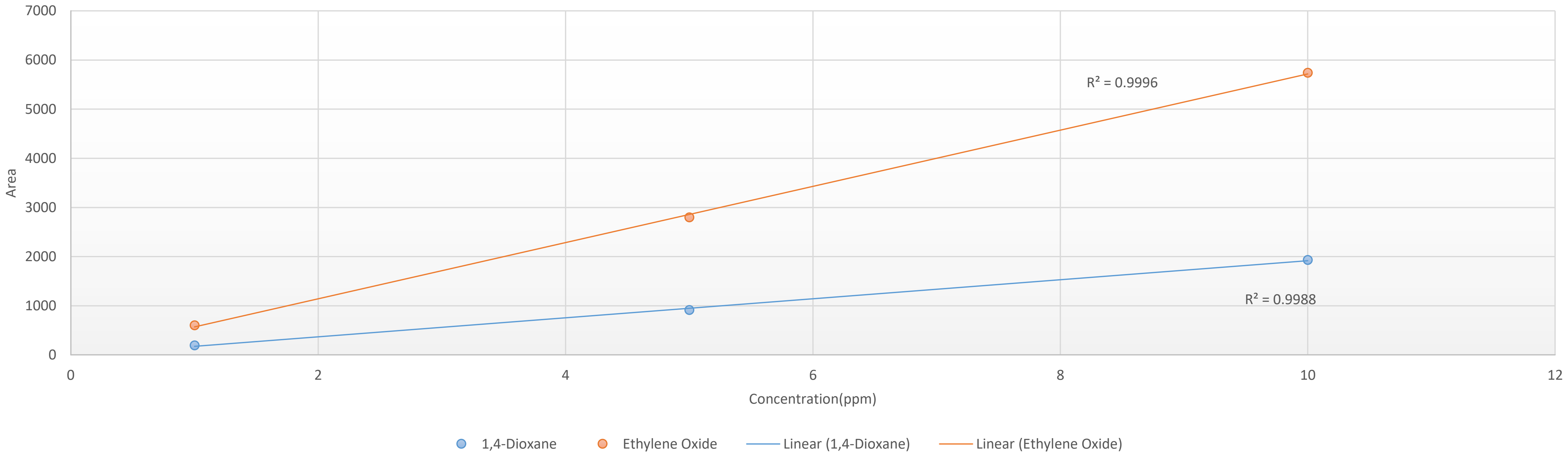
- 2g Solid sample –w- 100μL DI water
- Sample heated/agitated at 120°C and 500 rpm for 1min.
  - Syringe at 120°C, as well.
- Pre-Injection Syringe Purge – 5s
- 300μL Headspace Injected @ 3mL/min
- Post-Injection Syringe Purge – 10s
- UHP Nitrogen used as purge gas.

GC Program

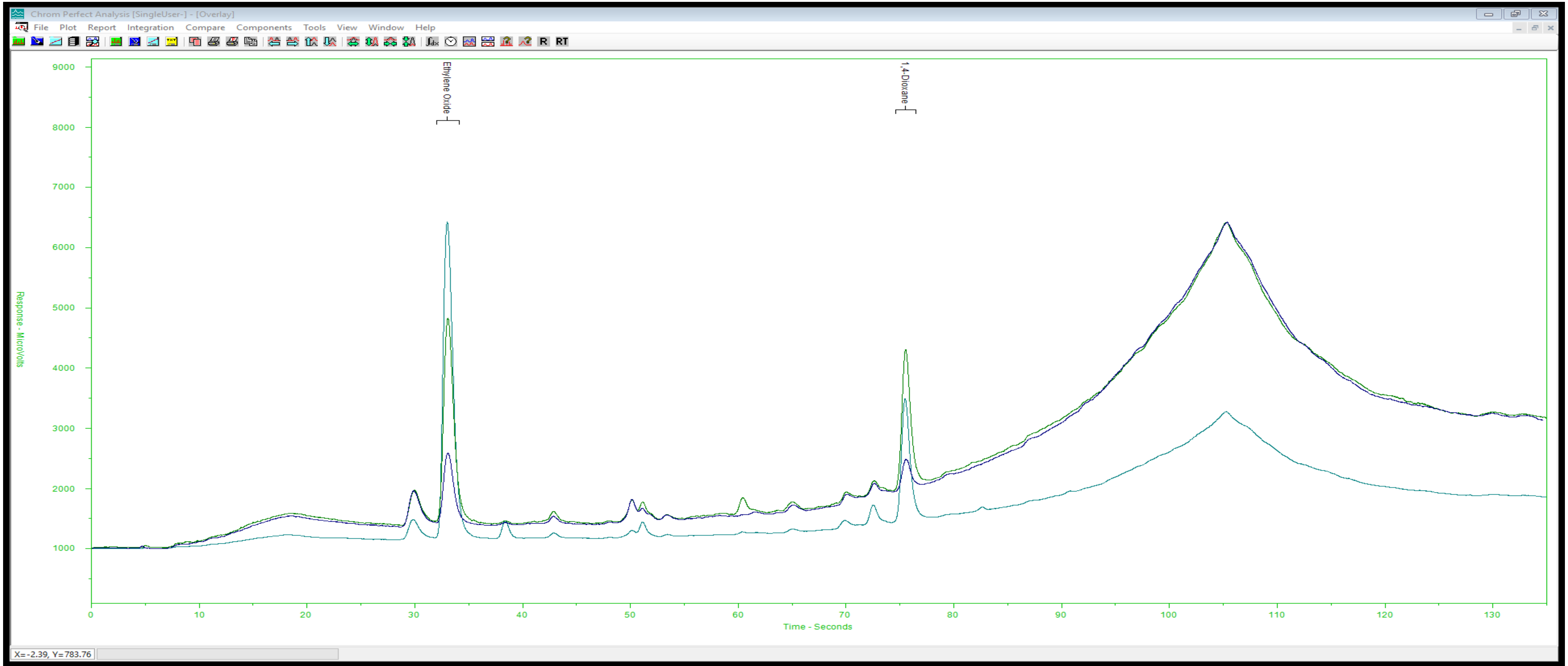
- Inlet Temp - 225°C
- Inlet Pressure – 15psi, Constant Pressure
- Detector Temp - 225°C
- Column Program - 40°C hold 0s, 2°C/sec to 250°C hold 30s
- Total Run Time – 135s
- Total Cycle Time – Less than 5 Min.

Linearity Results - 10.0ppm, 5.0ppm, 1.0ppm

- Laboratory Control Samples (Spiked Blank Matrix)
- Acceptance Criteria – $R^2 \geq 0.995$



Linearity, 10ppm, 5.0ppm, 1.0ppm



Repeatability Results @ 10ppm

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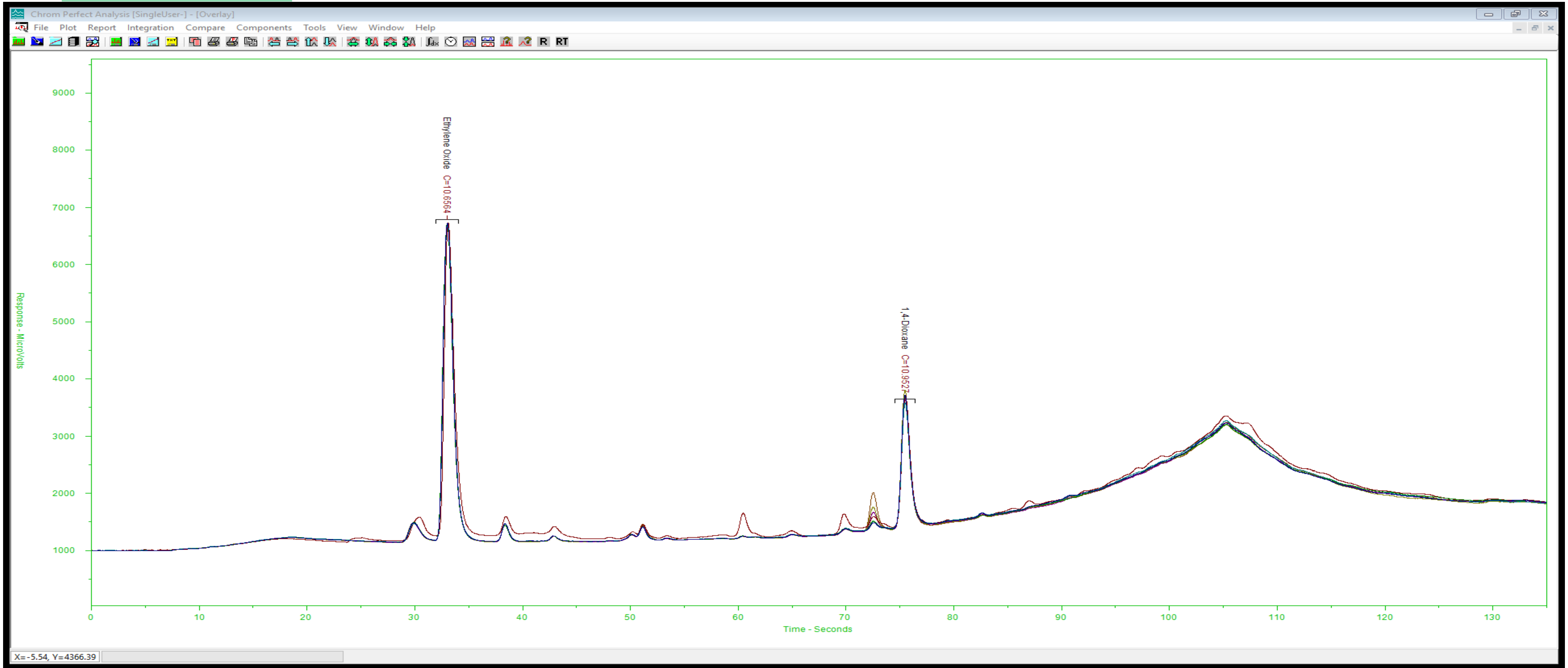
- Laboratory Control Samples
- Acceptance Criteria - %RSD ≤ 5.0%

Replicate	Ethylene Oxide Area	1,4-Dioxane Area
1	6121.2	2208
2	6152.3	2200.5
3	6202.1	2064.5
4	5688.6	2062.4
5	6063.3	2099.2
6	6162.2	2303.8
7	6208.9	2101.2
Average	6085.5	2148.5
Standard Dev.	181.9	90.8
%RSD	3.0%	4.2%

Repeatability, 7 Replicates of 10ppm



System Precision

- Laboratory Control Samples
- Acceptance Criteria - %RSD Must Be ≤ 10.0%

Replicate	Ethylene Oxide	1,4-Dioxane
1	8563.3	4458.7
2	8387.4	4080.32
3	9456.0	4419.61
4	8928.1	4528.88
5	8598.0	4233.50
Average	8786.5	4344.2
Standard Deviation	422.1	183.6
%RSD	4.80%	4.23%

Method Precision

- Live Samples
- Acceptance Criteria - %RSD of the Results (ppm) Must Be ≤ 5.0%

Replicate	Ethylene Oxide Result (ppm)	1,4-Dioxane Result (ppm)
1	3.02	1.08
2	3.26	1.05
3	3.31	1.14
4	3.30	1.09
5	3.34	1.14
6	3.29	1.09
7	3.19	1.07
8	3.43	1.07
9	3.39	1.07
10	3.29	1.09
Average	3.28	1.09
Standard Deviation	0.11	0.03
%RSD	3.46%	2.72%

Ruggedness

- Two Operators, Running Live Samples Side-By-Side, Across Two Different Days
- Acceptance Criteria - %Difference ≤ 10.0%

Day 1				
Operator	1		2	
	Ethylene Oxide (ppm)	1,4-Dioxane (ppm)	Ethylene Oxide (ppm)	1,4-Dioxane (ppm)
	3.11	1.1	2.98	1.15
	3.05	1.03	3.34	1.09
Average	3.08	1.065	3.16	1.12
% Difference between operators			Ethylene Oxide	1,4-Dioxane
			2.60%	4.67%
Day 2				
Operator	1		2	
	Ethylene Oxide (ppm)	1,4-Dioxane (ppm)	Ethylene Oxide (ppm)	1,4-Dioxane (ppm)
	3.07	1.1	3.18	1.17
	2.82	0.97	2.97	0.98
Average	2.95	1.04	3.08	1.08
% Difference between operators			Ethylene Oxide	1,4-Dioxane
			4.41%	3.36%

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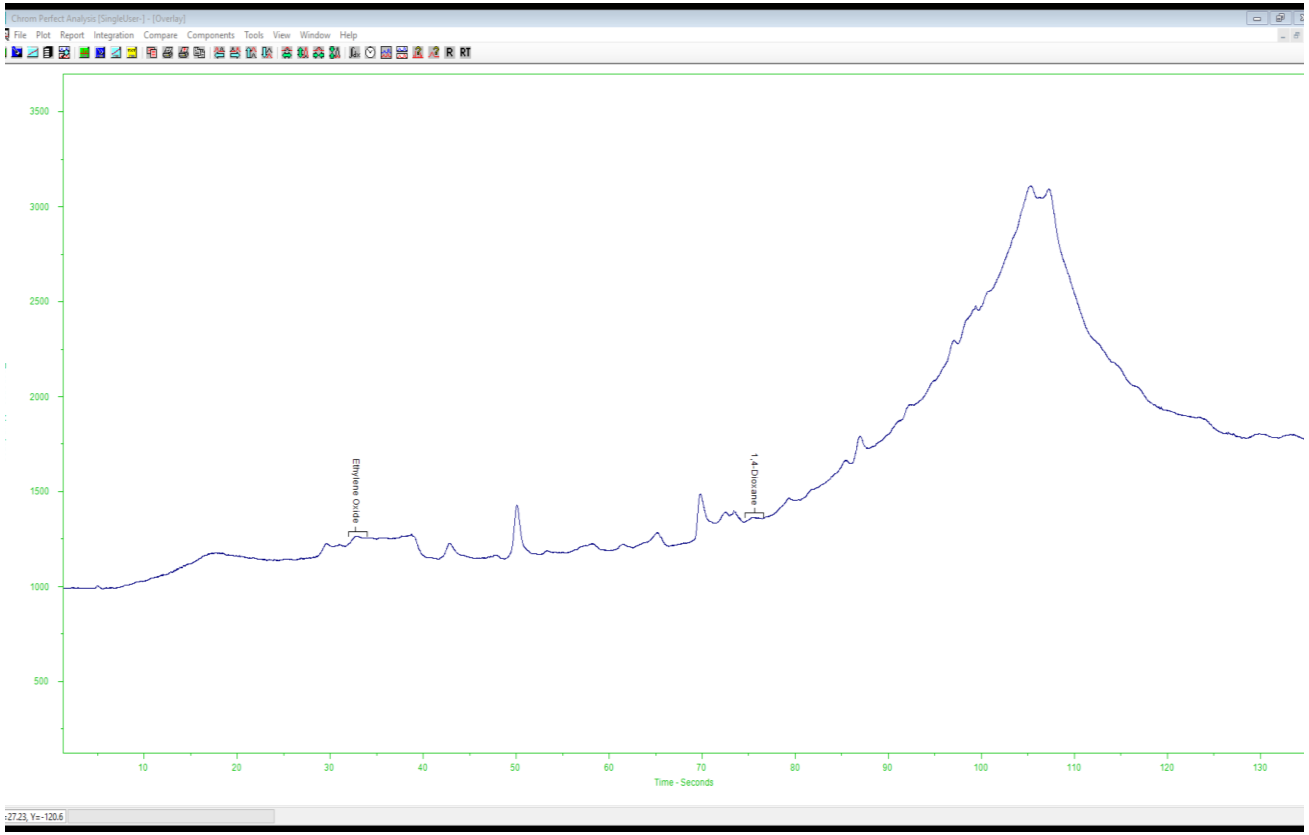
Specificity

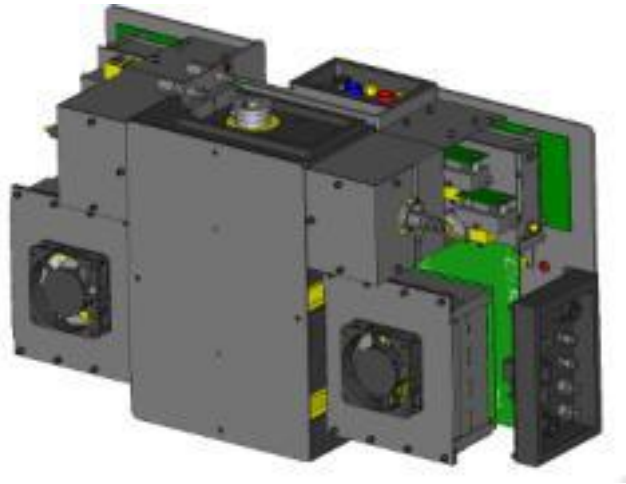
- The chromatograms must show little to no interferences with the peak(s) of interest. Some standards, by product nature, may contain some levels of trace Ethylene Oxide or 1,4-Dioxane.
- No significant or observable interferences from DI Water or PEG 400 standard.



CALIDUS
GAS CHROMATOGRAPH

Other Potential Applications

- Monomers in Polymer Pellets
  - ASTM 4322-96
- Ripening Agents in Food Industry Applications
  - Ethylene in Apples
- Residual Solvents in Pharmaceuticals
  - USP, General Chapters Residual Solvents
- Low Boiling Environmental Contaminants in Soil/Water
  - RSK-175 Methane, Ethane, Ethylene in Water
  - SW846 8015 Alcohols in Soil/Water
- And Many More!



Thank You

Any Questions?

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