Determining the Ethanol Content of Denatured Fuel Ethanol Using Near Infrared

Gulf Coast Conference

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PAC LP

Global Ethanol Use

- Consumption of fuel-grade ethanol is on the rise

- Produced from bio- or renewable sources

- Advantages of Using Ethanol as Fuel or Fuel Additive

  – Imparts high octane in relation to its cost

  – Its molecule is 35% oxygen

    • Aids in engine combustion

    • Lowers harmful emissions

  – Alternative to petroleum-based components

ASTM D4806

ASTM D4806 - Standard Specification for Denatured Fuel Ethanol for Blending with Gasoline for Use as Automotive Spark-Ignition Engine Fuel

- Ethanol Concentration by D5501
  - GC Analysis
  - Ethanol concentration determined from 93 to 97% (m/m).
    - Proposal to Expand Scope (from 93-97% to 20-99%).
  - Methanol concentration determined 0.1 to 0.6% (m/m).
- Water Concentration by ASTM E203 (volumetric Karl Fischer titration) and E1064 (coulometric KF titration).

GC Analysis

- Good resolution between ethanol and methanol
- Good accuracy and precision with detailed information about the denaturant composition

- No information about water concentration
- Not suitable for portable field use
- Not a fast analysis
- Trained analyst

KF Analysis

- Good accuracy at low concentration

- No information about ethanol concentration
- Hazardous materials used for the titration
  - Chemical exposure risk
  - Disposal of spent titration chemicals
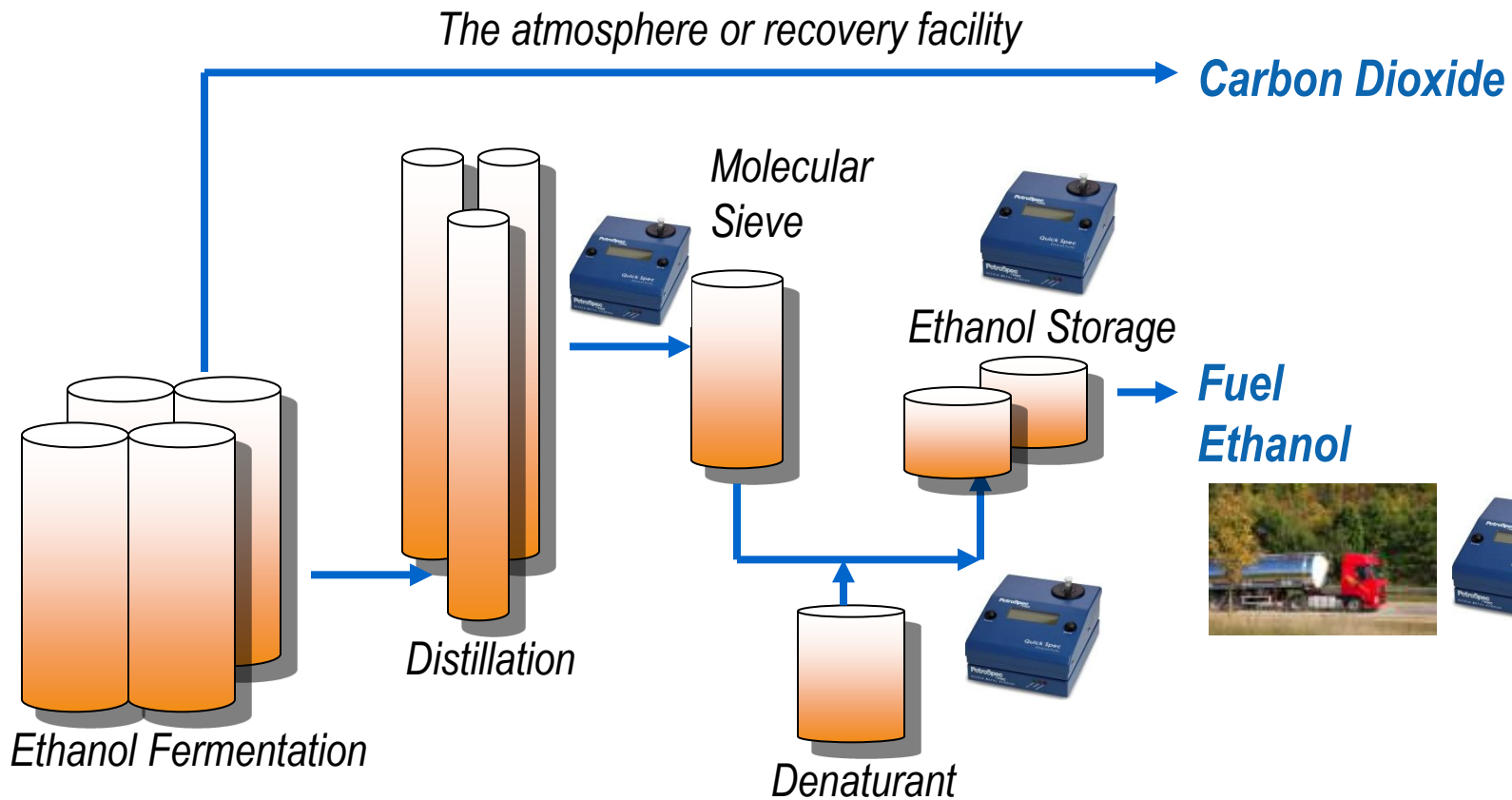- Some instrument and sample preparation required
- Trained analyst

Alternative – Near IR

- Portable and rugged design allows ethanol analysis 'in the Field'

- Highly accurate analysis results in less than 20 seconds

- Fully automated, easy to use

- Low cost (investment, operation, maintenance)

- (QuickSpec™) Delivered fully calibrated for 0% to 100% Ethanol & 0.01% - 5% water

Portable IR Can Expand Range of Testing

The atmosphere or recovery facility

Carbon Dioxide

Molecular Sieve

Ethanol Storage

Fuel Ethanol

Distillation

Ethanol Fermentation

Denaturant

Users Needing Quick and Simple Analysis

- Ethanol Producers – Process Monitoring
- Terminals – Fuel Ethanol and Oxygenated Gasoline Verification
- Independent Testing Labs
- Government Compliance Agencies
- Ethanol/Gasoline End-users:
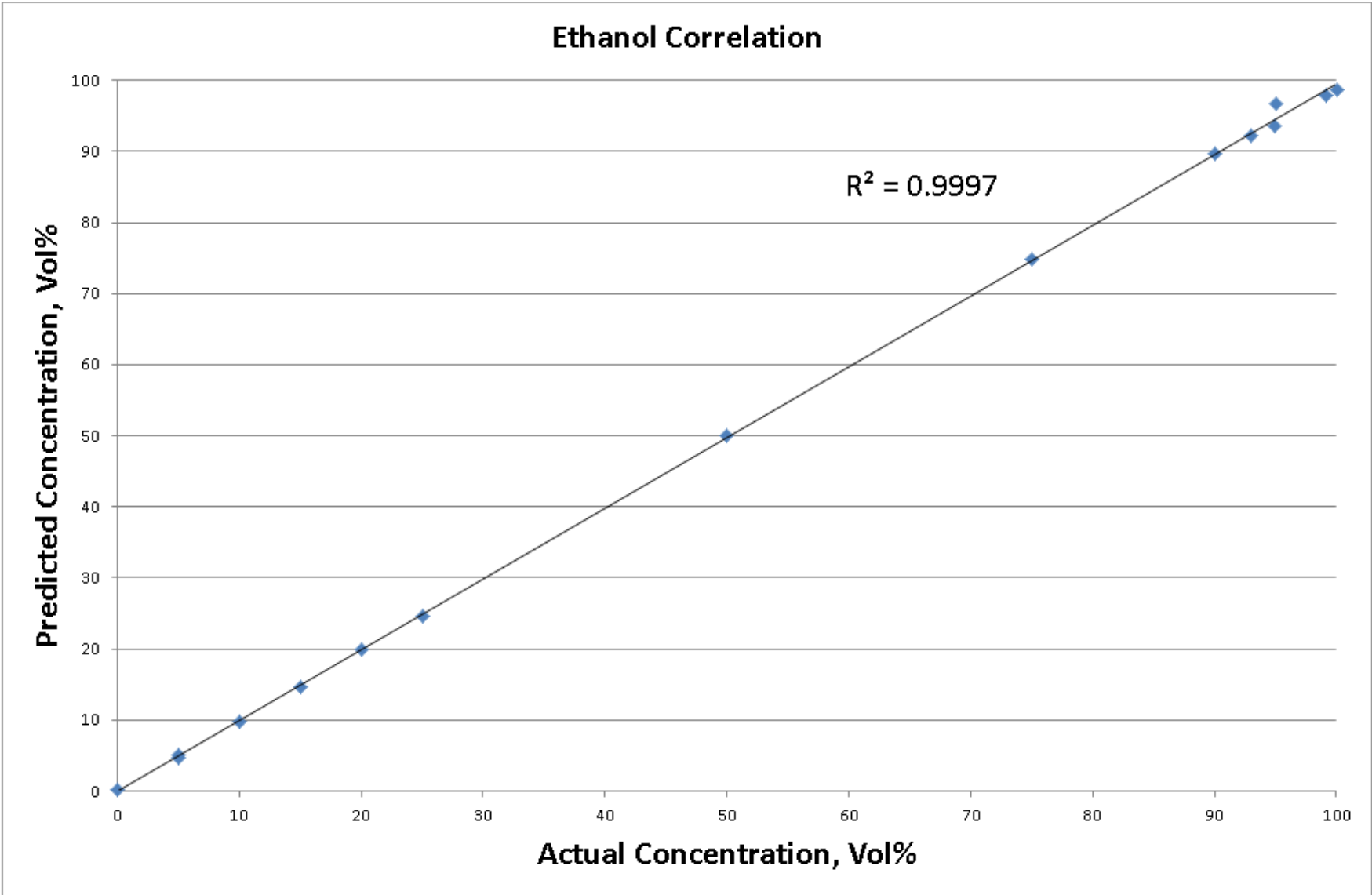 - Car Manufacturers
  - Military

NIR Technology

- **Detection Method: Near Infrared Spectroscopy**
  - Highly accurate
  - Uses light to probe a denatured ethanol sample
- **Optical Design: LED/Bandpass Filter Photometric Technique**
  - Measures absorbance at selected wavelengths
  - 1950 nm / 1550 nm

**Denatured Ethanol
5 mm Cell Pathlength**

Ethanol
97.1 Vol.%

H_2O
0.4 Vol.%
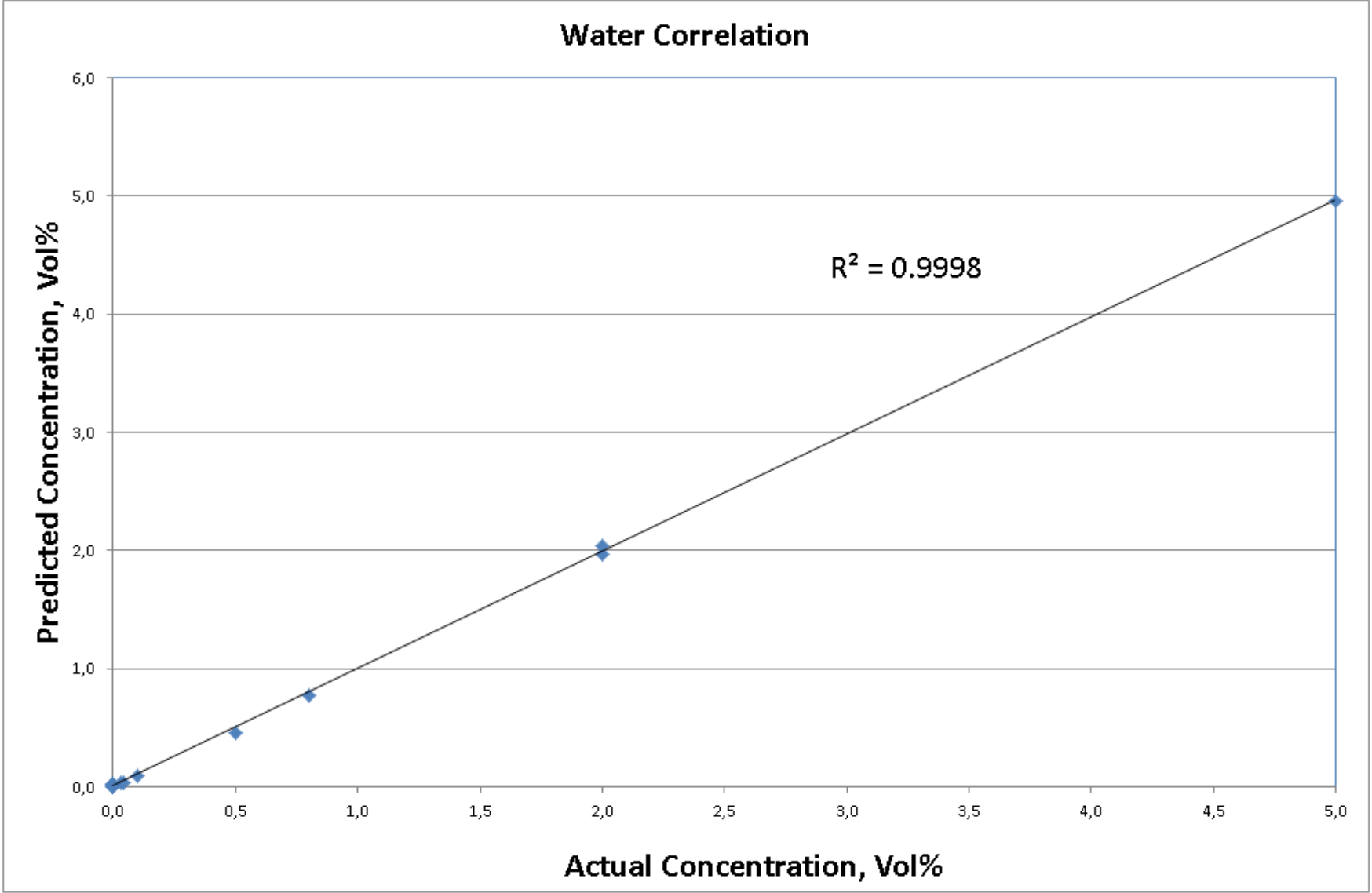
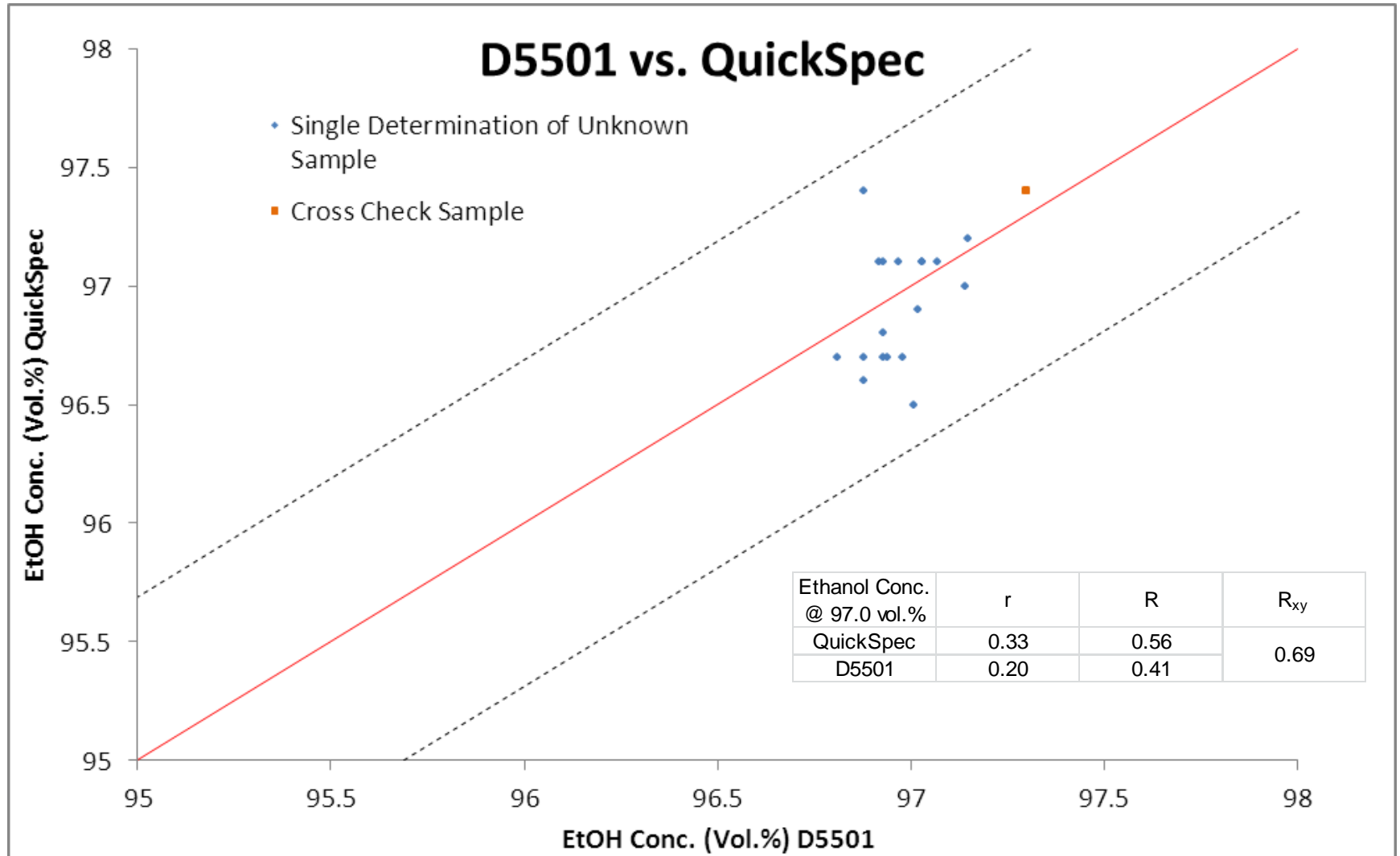Absorbance

Nanometers
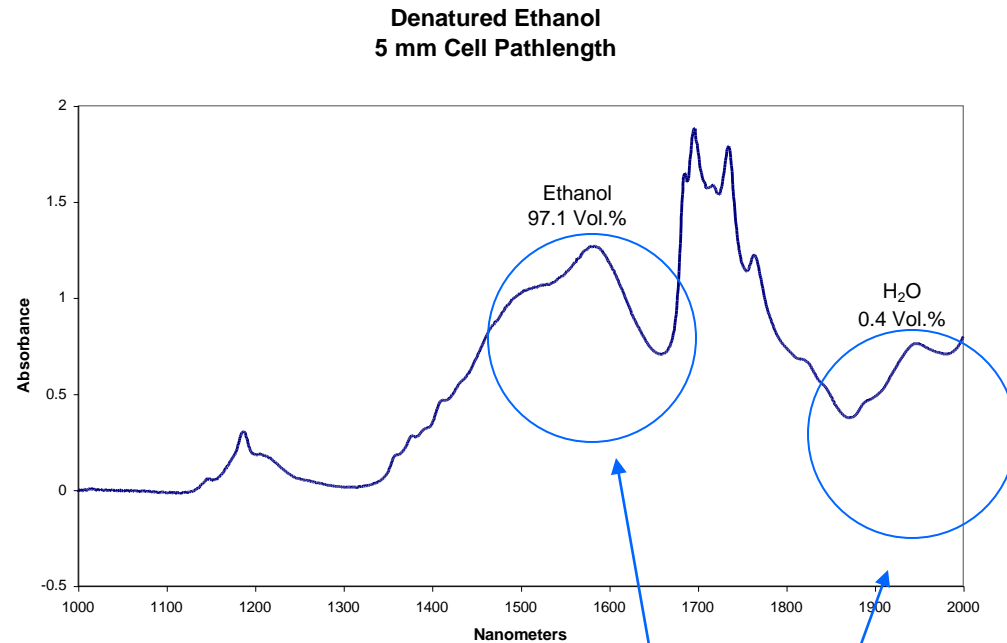
Distinct differences between ethanol and water absorption peaks

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NIR Ethanol Calibration

NIR Water Calibration

Independent Laboratory Data

Independent Laboratory Data

E1064 vs. QuickSpec

- Single Determination of Unknown Sample
- Cross Check Sample

Water Conc. @ 0.50 vol.%	r	R	R_{xy}
QuickSpec	0.018	0.031	0.091
E1064	0.020	0.086	

Independent Laboratory Data

D5599 vs. QuickSpec

Single Determination of Unknown Sample

Cross Check Sample

EtOH Conc. (Vol.%) QuickSpec

EtOH Conc. (Vol.%) D5599

Ethanol Conc. @ 10.0 vol.%	r	R	R_{xy}
QuickSpec	0.27	0.32	1.61
D5599	0.23	1.58	
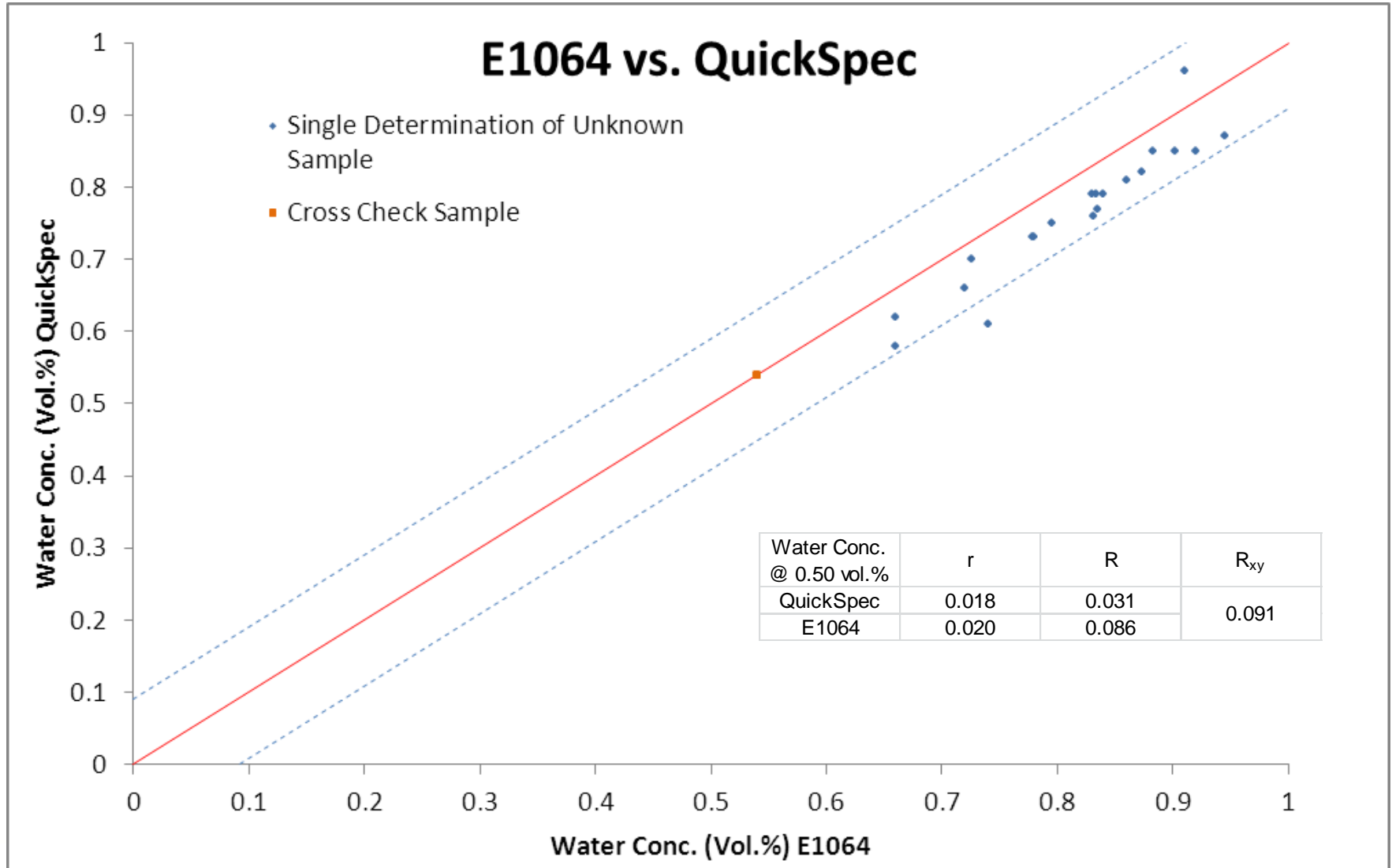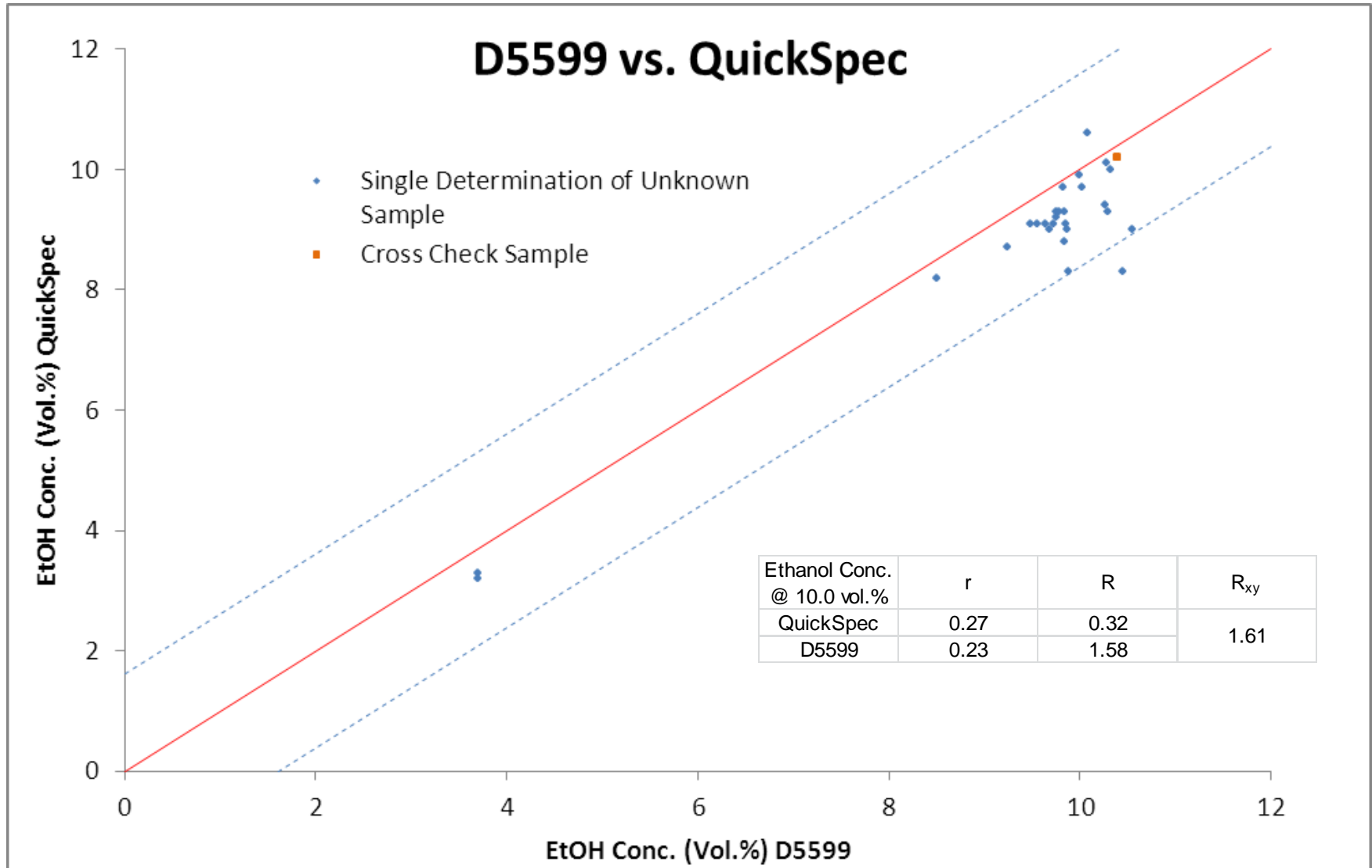
Product Overview – Scope

	Ethanol Vol%		Water Vol%		
	GC D5501	NIR* @97 vol.%	KF E203	KF E1064 @0.5 vol.%	NIR* @0.5 vol.%
Method Range	93% -97%	0% – 100%	>0.05%	0% - 2%	0.01% - 5.0%
Repeatability	0.21%	0.33%	0.008%	0.020%	0.018%
Reproducibilty	0.53	0.56%	0.027%	0.086%	0.031%

*Internal RR at 95% confidence limit.

Summary

- Near IR
  - Good accuracy and precision – Correlates to standard methods
  - Measures ethanol and water (denaturant by difference)
  - Can be made to be portable and rugged. Used where critical decisions are made.
  - Low cost
  - Simple to use
  - Quick analysis with high throughput

Thank you