Measuring or Calculating Phase Diagrams?

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Motivation

- Phase-diagram calculations are used routinely in the industry
  - Various software packages are available
- Phase calculations are used to
  - satisfy custody transfer tariffs on hydrocarbon dew point
  - Design processes and equipment
  - Design sampling equipment
- Errors in the phase diagrams can cause numerous problems

Previous Research (not an exhaustive list)

The Need For Accurate Hydrocarbon Dew Point Determination, Darin L. George, Ph.D., Andy M. Barajas and Russell C. Burkey

Hydrocarbon Dew Point Measurement and Model Evaluation of Synthetic and Real Natural Gases
Pu Zhang, Li Zhou, Wenping Zeng, Gang Xiong, Hongfa Huang, Li Cai, Huiyan Ye, and Shanshan Qu*

Development of Accurate Methods for Predicting Hydrocarbon Dew Points, Darin L. George, Ph.D.

Comparative Study of the Consistency of C6+ Composition Splits of Pipeline Gas for Hydrocarbon Dewpoint Determination, *Livinus Aniefi*

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Previous Research

- A wealth of data from work by others
- Most indicate significant errors when using C6 or C9 GCs
  - >70F for C6+
  - >40F for C9+
  - Depends on a lot of factors
- Errors in the phase diagrams can cause numerous problems
- We aim to further study sources of errors

Methodology

- The ECOFISK blend was prepared gravimetrically at SPL
- Several C12 analysis was performed
  - Pressure regulation at different temperatures
- Phase diagrams were calculated for each analysis
  - Used two different software packages
- Phase diagram was analytically measured
  - Using automated spectroscopic chilled-mirror instrument
- Field data from GCs and chilled-mirrors were also compared.

SUMMARY of RESULTS

- Calculations of Phase Diagrams *Can* Have Significant Errors
  - Multiple sources of errors
- Calculations Based on GC-C6+ Data Have Uncertainty in Excess of 50°C (90 °F)
- Calculations Based on C9+ Are Only Marginally Better
  - They reduce only one source of error
- C12 analysis is needed for calculation of phase diagrams
  - Pressure regulation can add significant errors
  - Choice of software is important

Sources of Error When Calculating Phase Diagrams

1. Heavy Distribution error
   - When using a C6+ or a C9+ heavy distribution is assumed
     - The assumptions may or may not be true
     - Uncertainty contribution >20 °C (~35 ° F)
2. Pressure regulation error
   - GCs work at near atmospheric pressure
   - Pressure regulation from line to 20 psi can introduce significant errors
3. GC uncertainty
   - GCs have errors, particularly for heavier components
   - Heavier components influence the HCDP most
   - Uncertainty contribution ~20-30 °C

Sources of Error When Calculating Phase Diagrams

4. Equation of State Error
   - Different Software packages give different answers
   - Uncertainty contribution as high as 20 °C
5. Compounding of Uncertainty
   - Any calculations compounds the uncertainty of individual measurements
   - Calculation of HC dewpoints have a large number of independent measurement that contribute to the calculation.
6. Sampling error
   - When sampling, significant changes to the composition can occur

The ECOFISK Gravimetric Mixture

N2	0.8992
C1	85.5505
C2	8.3705
C3	2.796
iC4	0.8377
nC4	0.7314
iC5	0.338
nC5	0.1575
C6	0.1988
C7	0.0709
C8	0.0287
C9	0.01
C10	0.007
C11	0.003
C12	0.001

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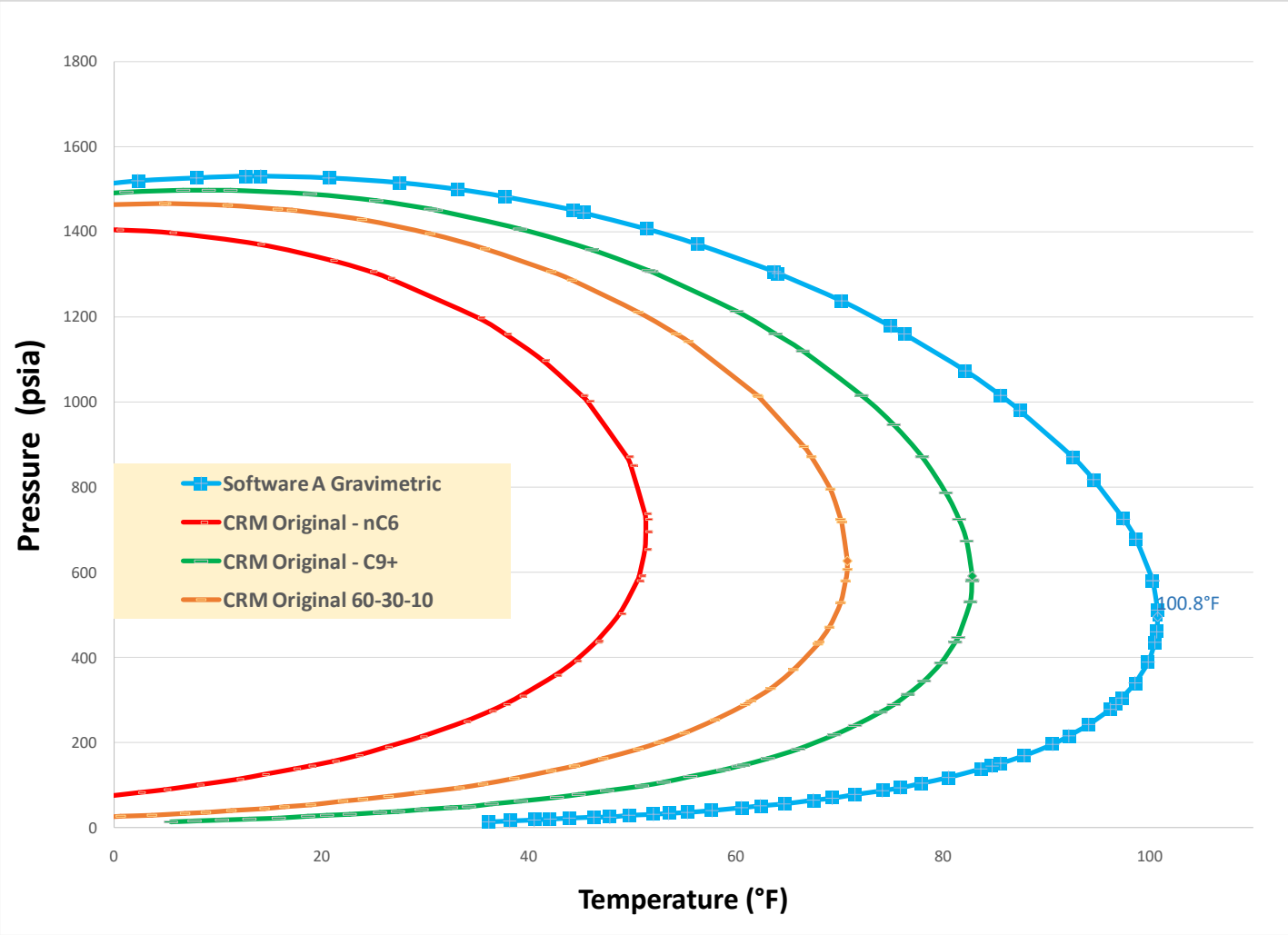
Effect of Distribution Assumption

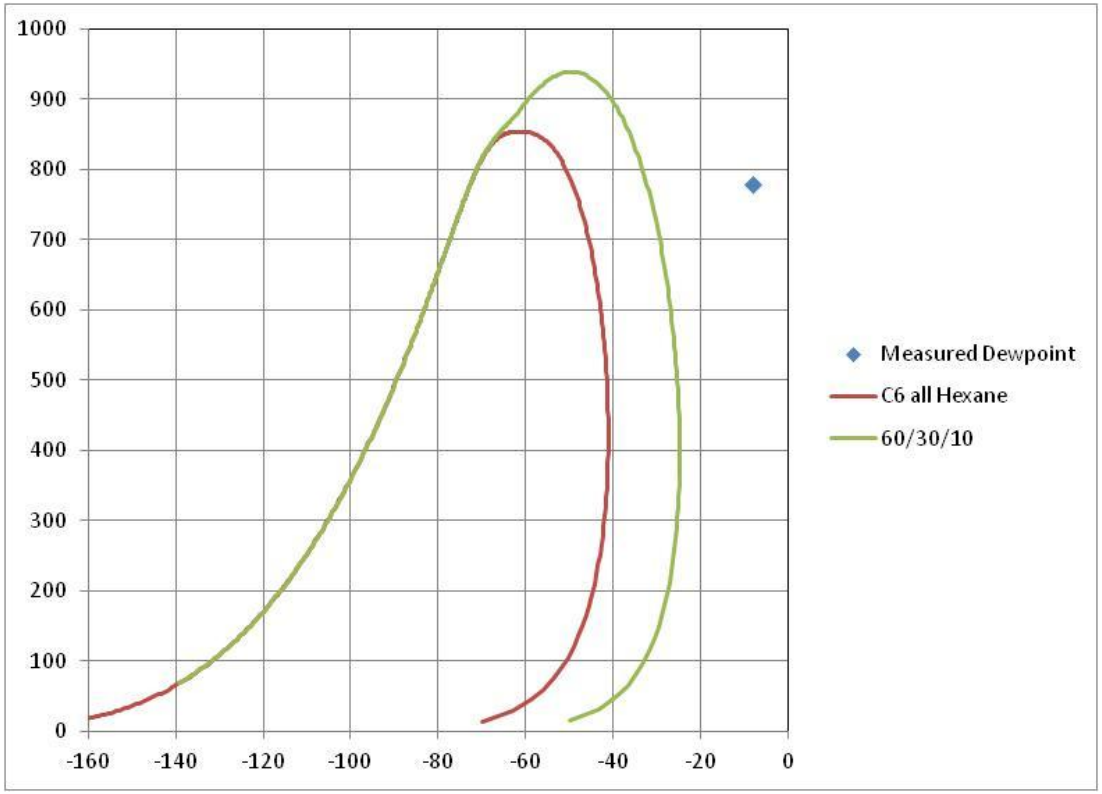
C12 GC Laboratory Analysis (Software Package A)



True for Lean Gases Too

- 20 °F Error even in a very lean gas assuming 60/30/10 distribution

propane	0.005373
isobutane	0.000581
butane	0.000671
isopentan	0.000236
pentane	0.000092
nitrogen	0.006025
methane	0.9401
CO2	0.010761
ethane	0.035872
C6+hexan	0.000285



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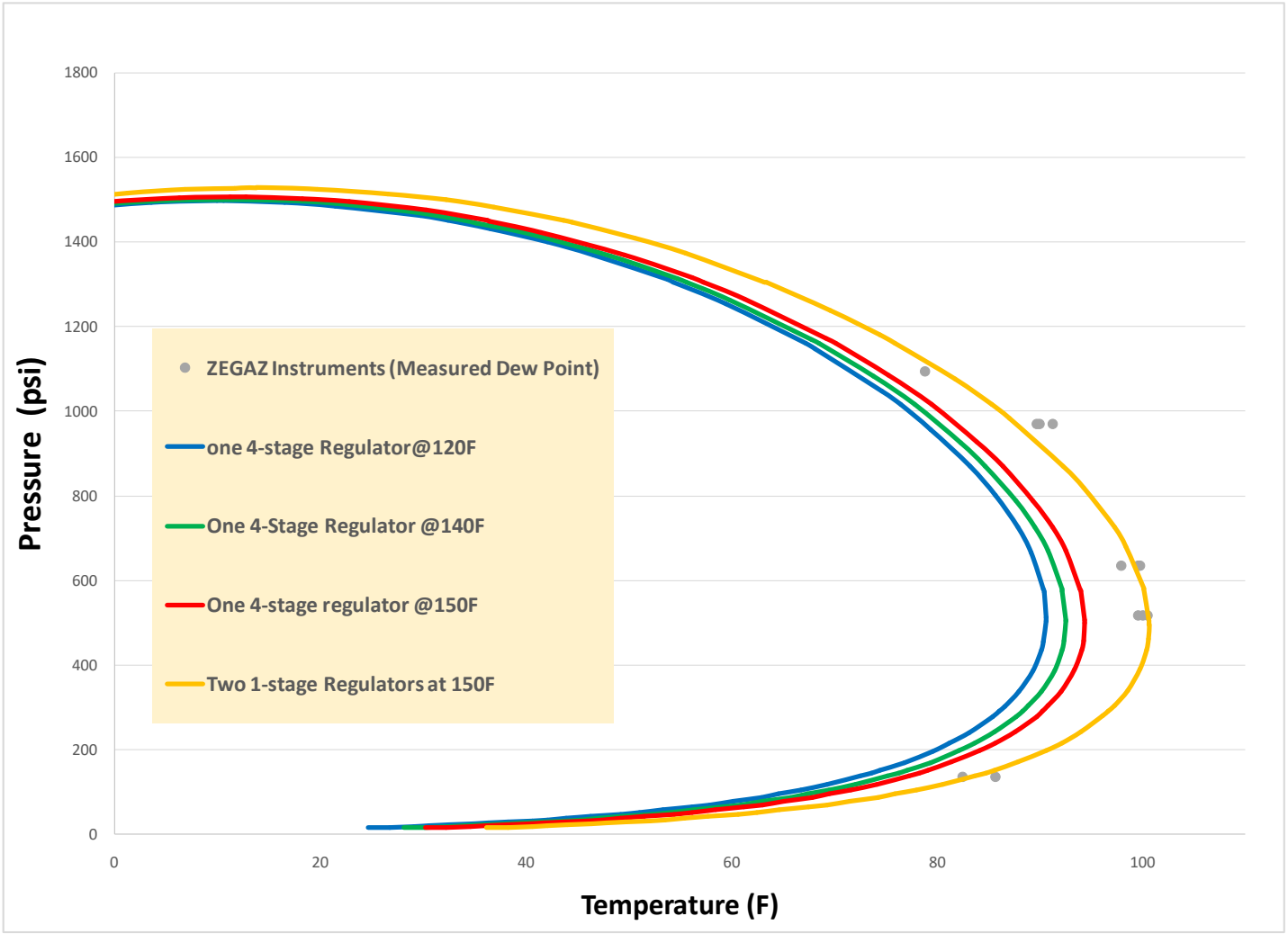
Effect of Pressure Regulation on Phase Calculations

C12 GC Laboratory Analysis (Software Package A)



Gravimetric vs Best GC result

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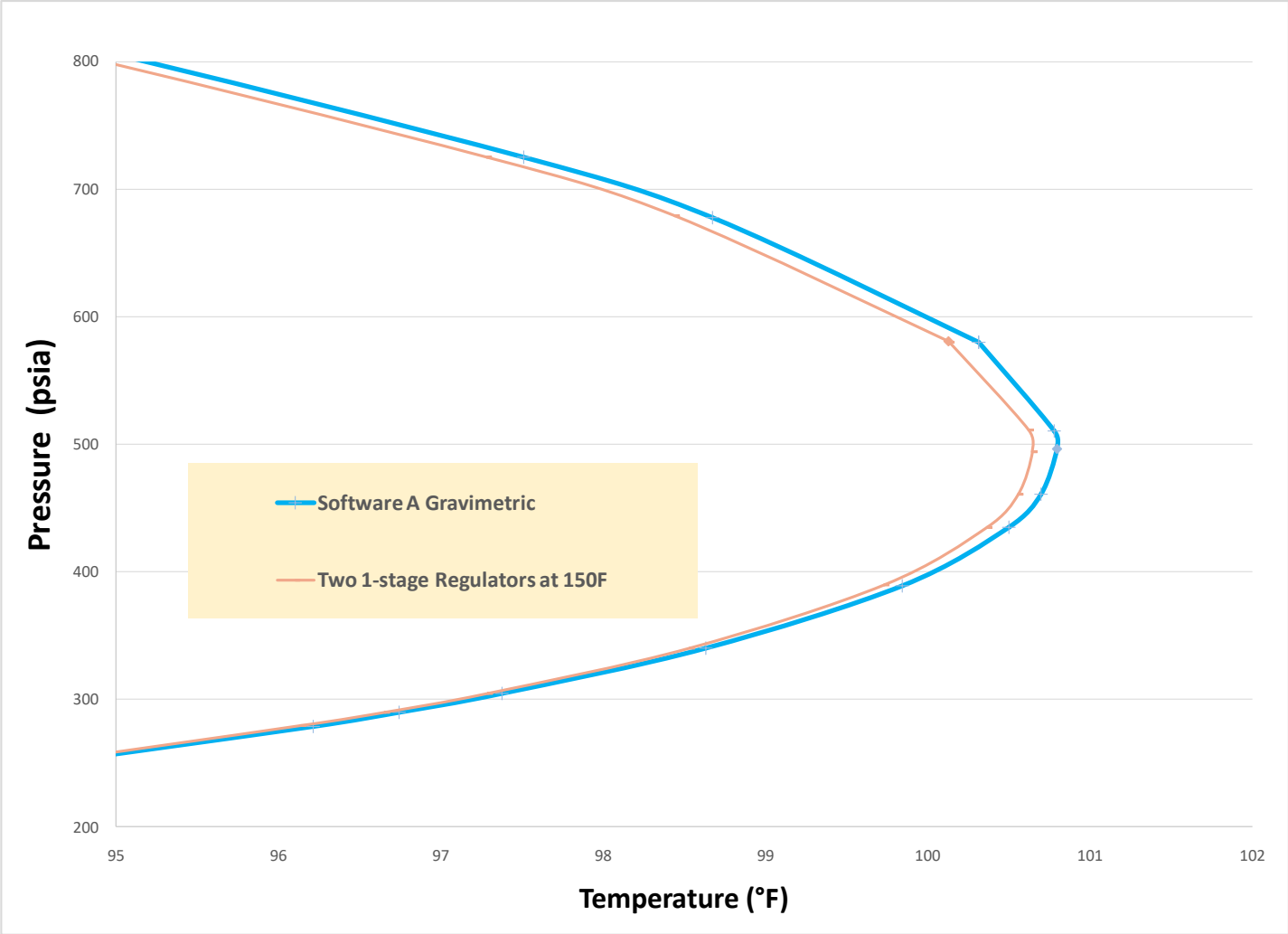

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Analysis of Error
From Distribution of Heavy Components

Analysis

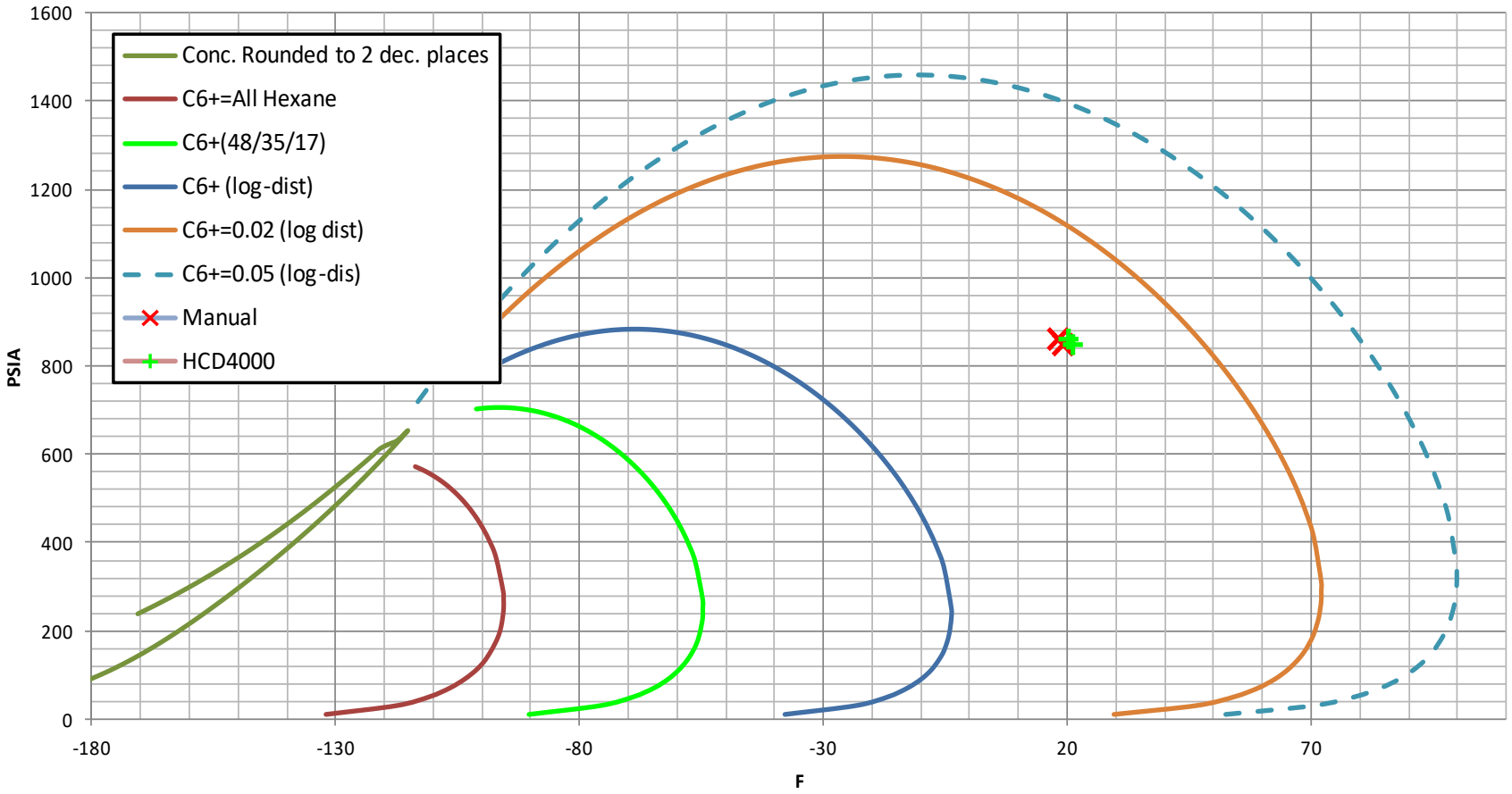
Date-Time: 01/06/12 16:10 Analysis Time: 345 Cycle Time: 360
Stream: 3 Stream 3 Mode: ANLY Cycle Start Time: 16:04
Analyzer: 78008 Strm Seq:1,1,1,2,2,2,3,3,3

Component Name	Mole Percent	Weight Percent	LiqVol Percent	Gallons/ 1000 SCF	BTU Gross	Relative Density
C6+ 47/35/17	33.3 PPM	0.0196	87.7 PPM	0.0015	0.18	0.0001
PROPANE	0.0317	0.0858	0.0514	0.0087	0.80	0.0005
i-BUTANE	39.2 PPM	0.0140	75.6 PPM	0.0013	0.13	0.0001
n-BUTANE	32.5 PPM	0.0116	60.2 PPM	0.0010	0.11	0.0001
NEOPENTANE	0.0000	0.0000	0.0000	0.0000	0.00	0.0000
i-PENTANE	12.0 PPM	53.1 PPM	25.9 PPM	0.0004	0.05	0.0000
n-PENTANE	9.07 PPM	40.1 PPM	19.4 PPM	0.0003	0.04	0.0000
NITROGEN	0.3285	0.5642	0.2127	0.0361	0.00	0.0032
METHANE	98.6299	97.0238	98.4273	0.0000	998.47	0.5463
CARBON DIOXIDE	0.5063	1.3664	0.5087	0.0864	0.00	0.0077
ETHANE	0.4910	0.9053	0.7730	0.1313	8.71	0.0051
TOTALS	100.0000	100.0000	100.0000	0.1446	1008.47	0.5631

'*' indicates user-defined components

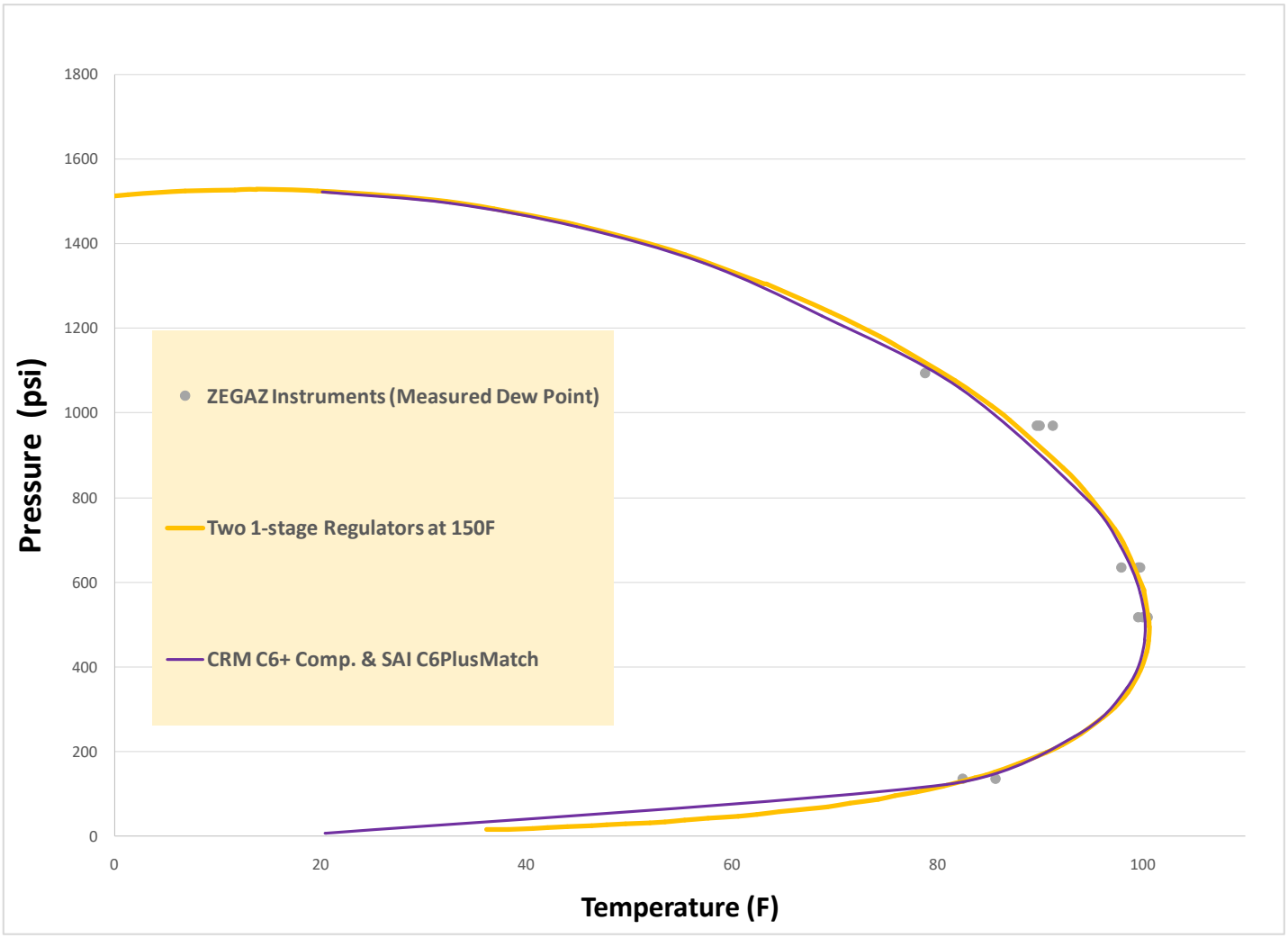
Compressibility Factor (1/Z) @ 14.73000 PSIA & 60.0 DEG.F= 1.00200

Analysis of Error From Distribution



One Can **Choose!** the HC dewpoint based on inherent assumptions in calculations

Using the *C6 Match* Method



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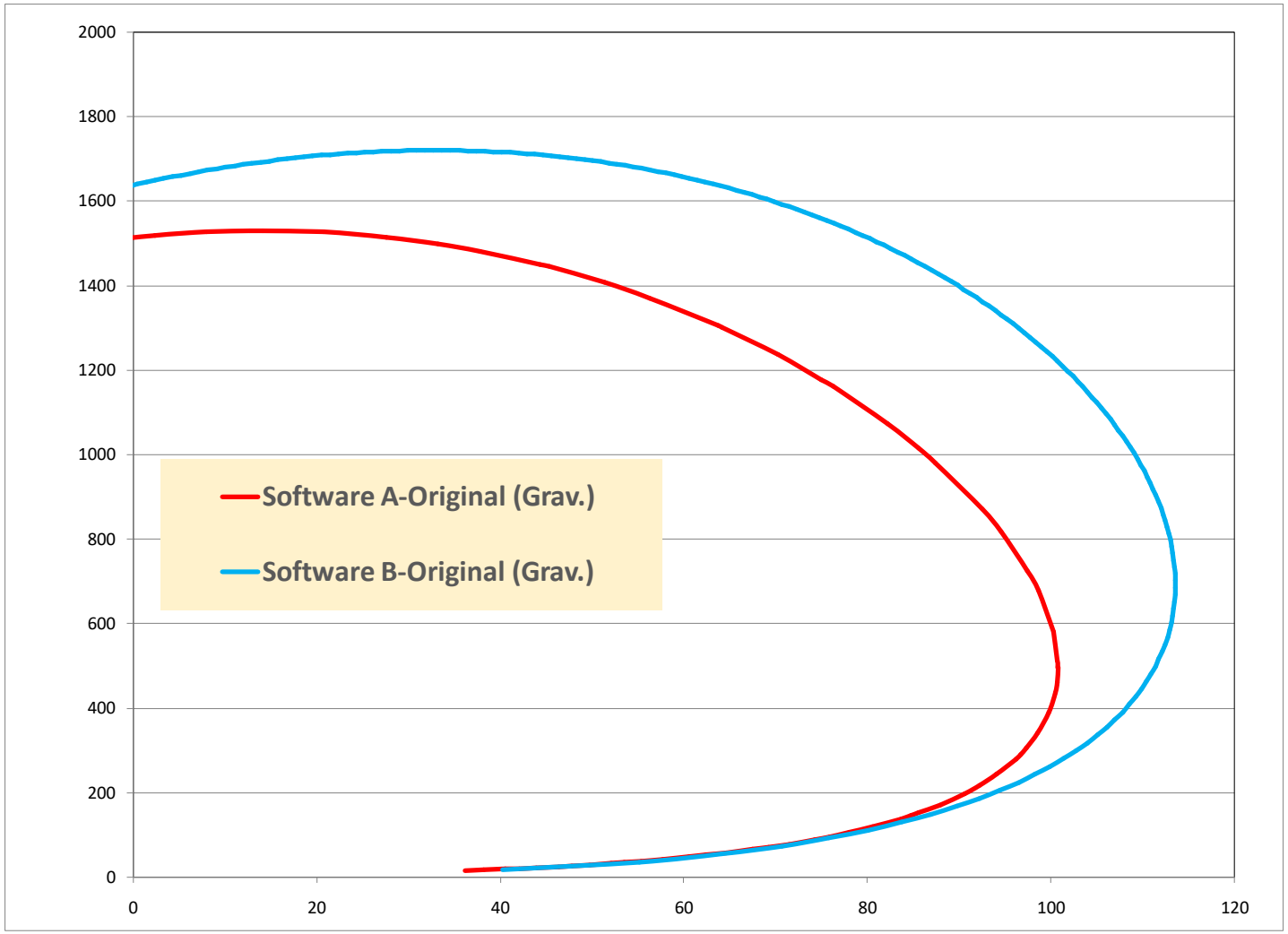
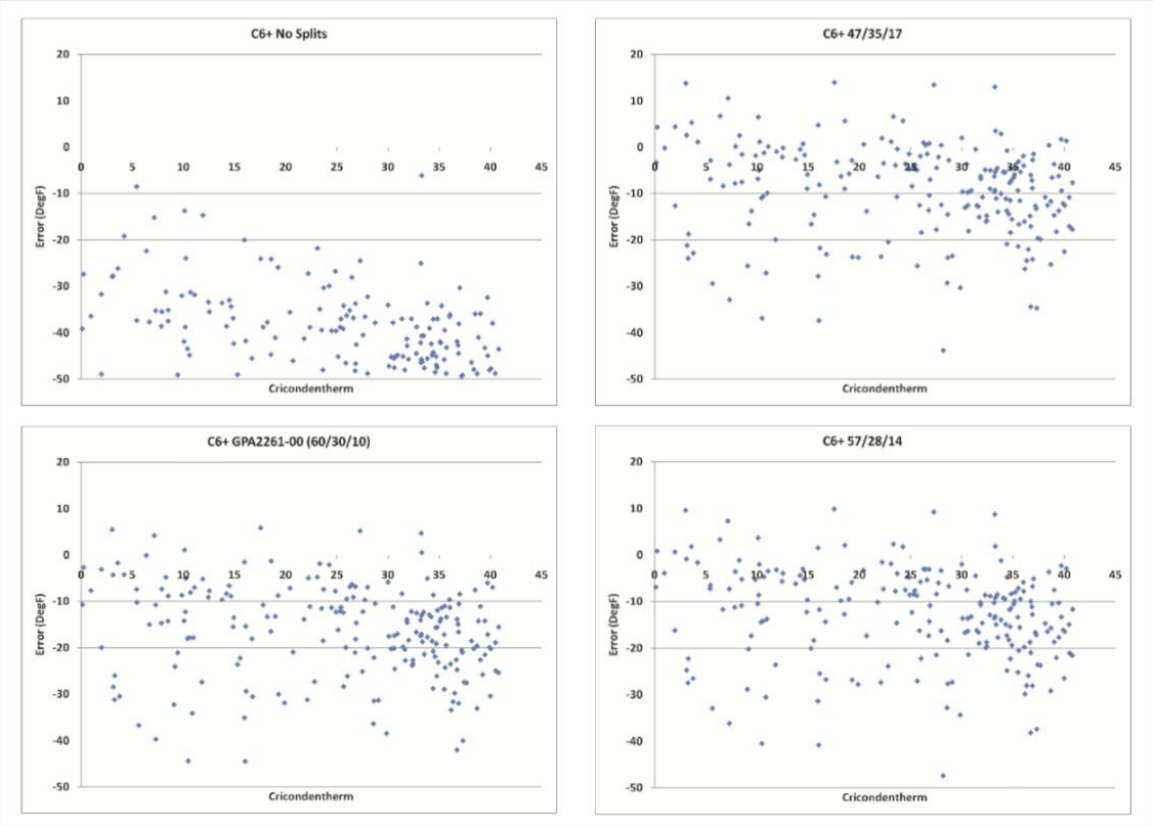
Software A vs Software B



Data from a GC Manufacturer

- This data is from a GC manufacturer (1)
- The error from using a GC-C6+ is in excess of 80 F in this chart
- This chart is the difference between using a GC-C6+ and a GC-C9+.
- The actual error is even higher.



(1) Emerson Technical Note

FIELD DATA ANALYSIS

- Field Data from multiple locations were collected
- GC data was compared to measurements of HC dew points
- Trends were analyzed

Major Finding

Measured dewpoints almost always higher than customers' expectations

Where do expectations come from?

- Some based on producer supplied information
- Others based on GC-EOS based
- Some based on historical data

Major Findings

GC-EOS based calculations show significant errors when compared with measurements

- Sources of error
  - EOS embedded errors
  - Heavy distribution error
  - GC uncertainty error
  - Pressure regulation error
- Cumulative errors as high as 80-100 °F !!!

Major Findings

Wide variance between HC dew points in different regions

- Warmer climates show higher HC dew points
- Colder climates show lower HC dew points
- Pipelines with multiple inputs show higher HC dew points
- Pipelines with unmonitored inputs show higher HC dew points with larger variations

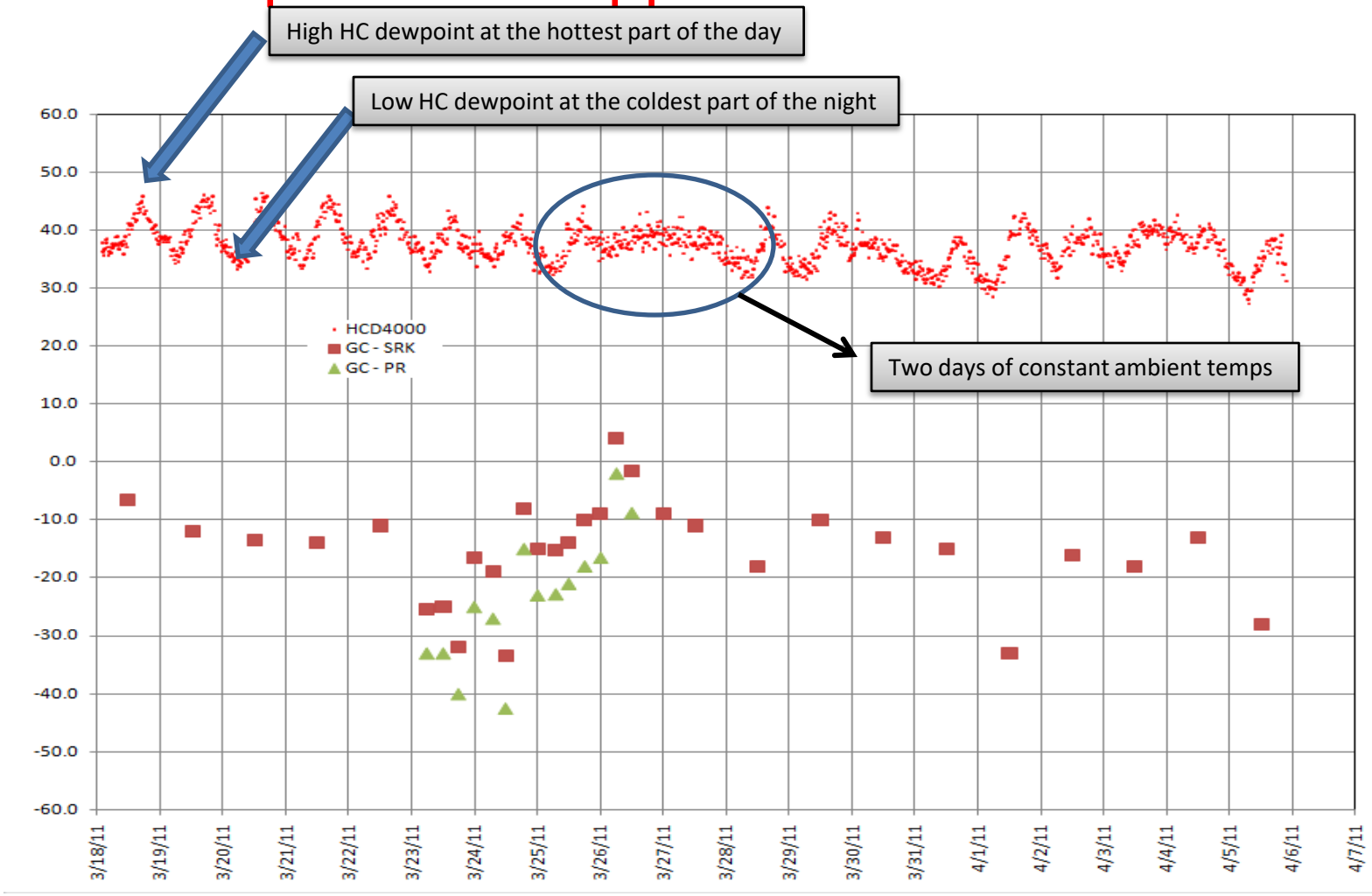
Major Findings

HC dewpoints fluctuate with Pipe Temperature

- This indicates a two-phase flow
- During the day (warmer) more heavies are evaporated in the pipe
  - And sampled by the probe

Fluctuation of HC dewpoint day and night

Indicates a two phase flow in the pipeline



Conclusions and Summary

- Field GC measurements not suitable for calculation of
  - Hydrocarbon dew point
  - Complete phase diagrams
- Only C12 analysis in a lab setting yields acceptable results
  - Within 5-10 degrees
- Sampling and pressure regulation can introduce significant errors.
  - For both water and HC dewpoint
  - If not done properly.
- Phase diagrams can be measured using the right equipment
- There is large, unaccounted for, economic impact due to liquid drop-out in pipelines, compressors, and power plants.