



WATER DETERMINATION IN CRUDE OIL

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- **An improved technique for measuring the water content of crude oil**
- **Obtaining ASTM/API approval for the method**
 - I. **In-house study**
 - II. **Inter-lab Round Robin**
 - III. **ASTM ILS**

CURRENT METHODS



Test Method	Time Required for Test (Minutes)	Method
Centrifuge	30	ASTM D4007
Distillation	120	ASTM D4006
Karl Fischer Titration	5	ASTM D4928



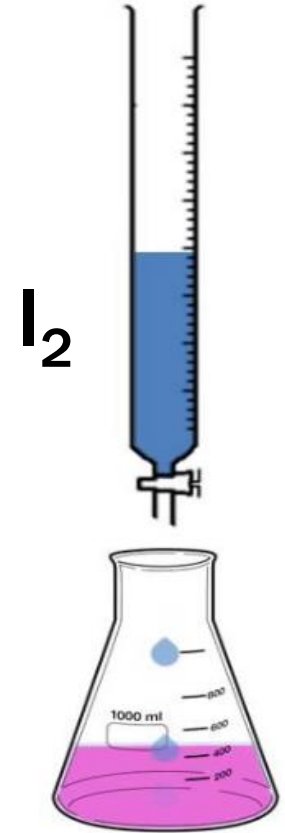
The Karl Fischer method appears to have overwhelming advantages with regards to speed and precision when compared to the other, currently available water measurements for crude oil. The COQA, dedicated to quality, endorses efforts on the part of the industry to use Karl Fischer, noting the disadvantages which include costs and a lack of sediment determination.

COQA 2003

THE MEASUREMENT OF WATER IN CRUDE OIL

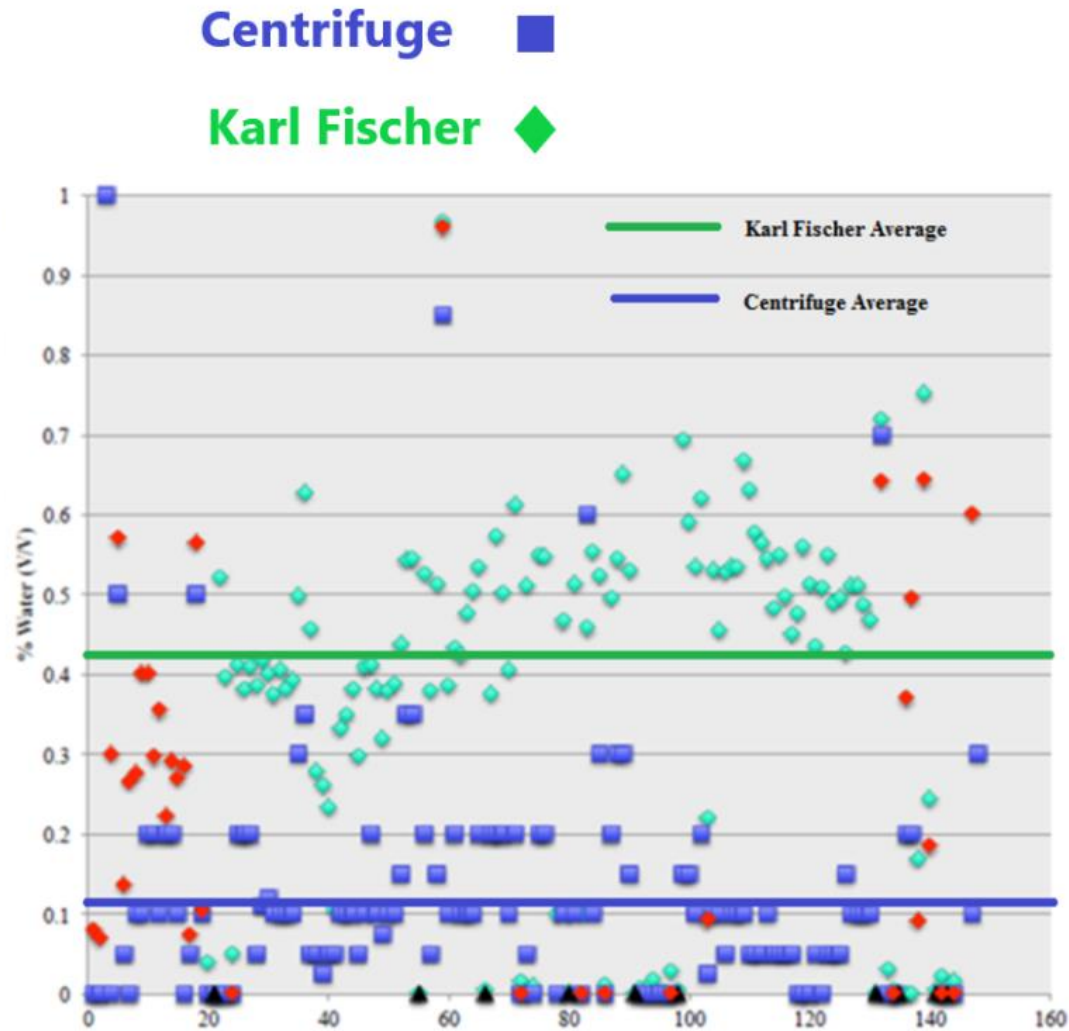


Karl Fischer Titration



SO_2 + Sample

WATER IN CRUDE METHOD COMPARISON

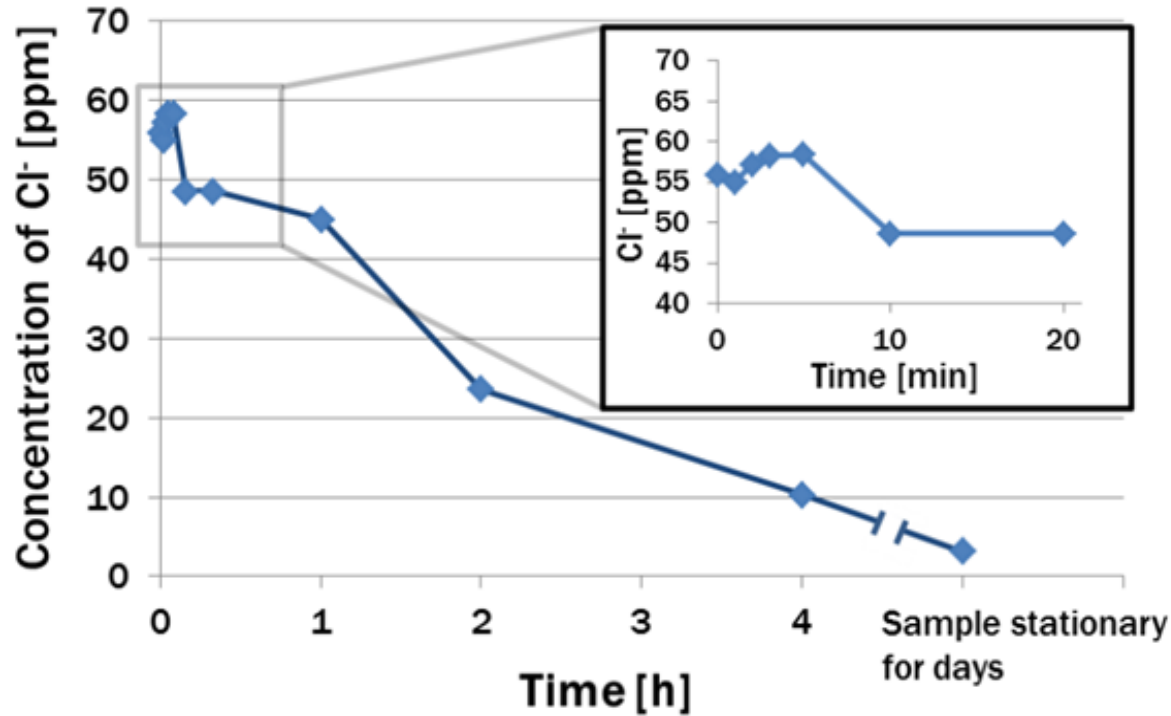


- Clear bias
- Datasets are not fully the same
- Numerous studies (ASTM, COQA etc.) show similar results

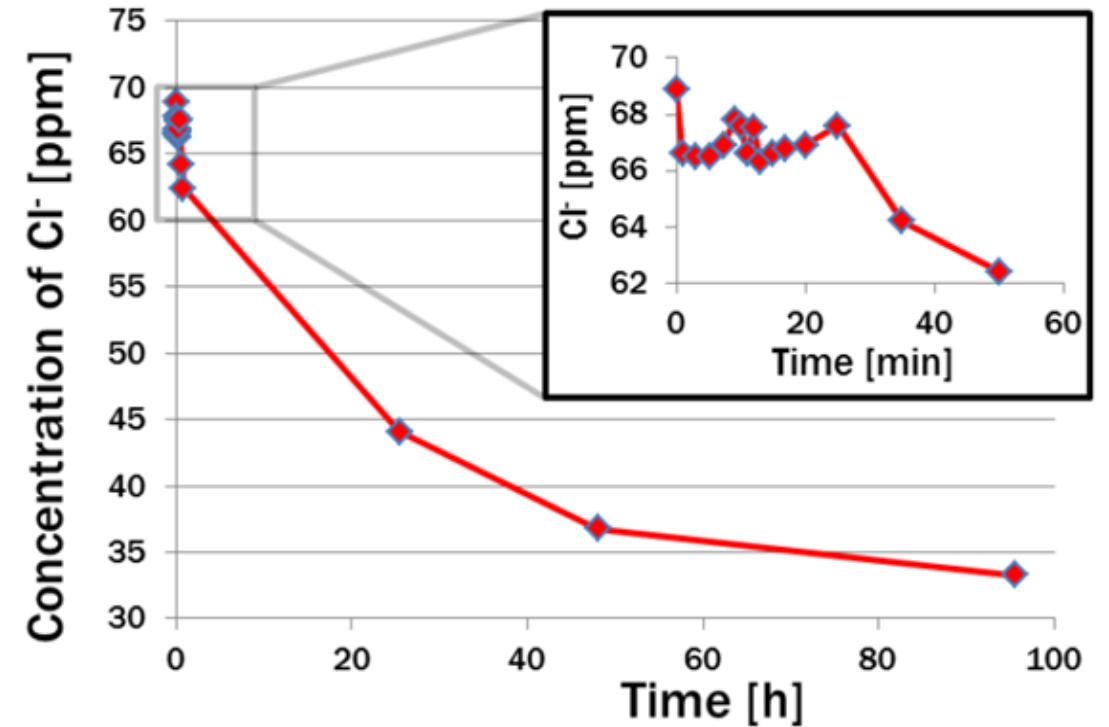
THE IMPORTANCE OF SAMPLING



API 40° Crude Oil



API 20° Crude Oil



* Samples drawn from the top of 500ml bottles.

SAMPLE COLLECTION : VIALS AND CAPPING DEVICE



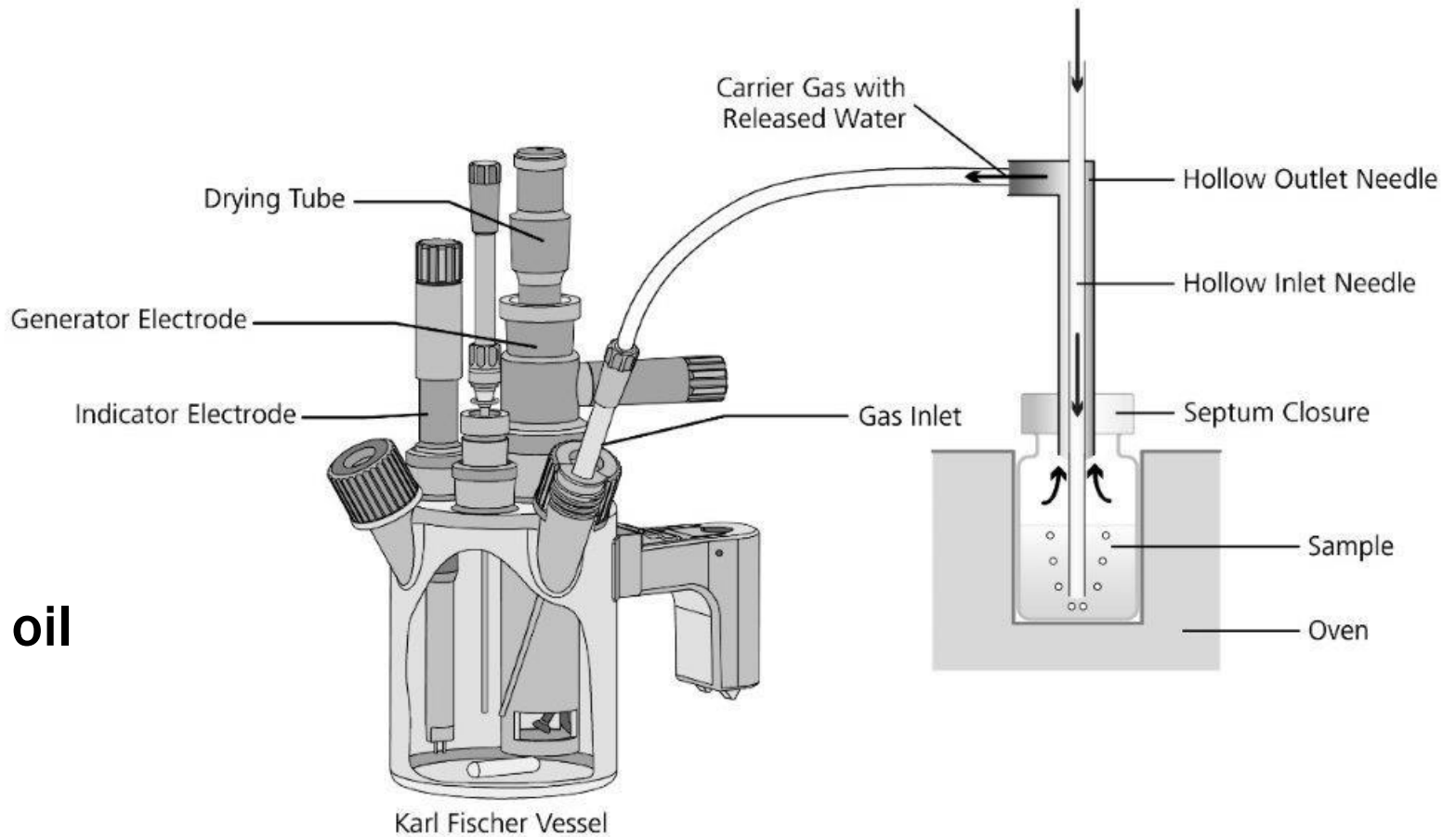
Image from Mettler Toledo

COULOMETRIC TITRATION WITH SAMPLE PRE-EVAPORATION



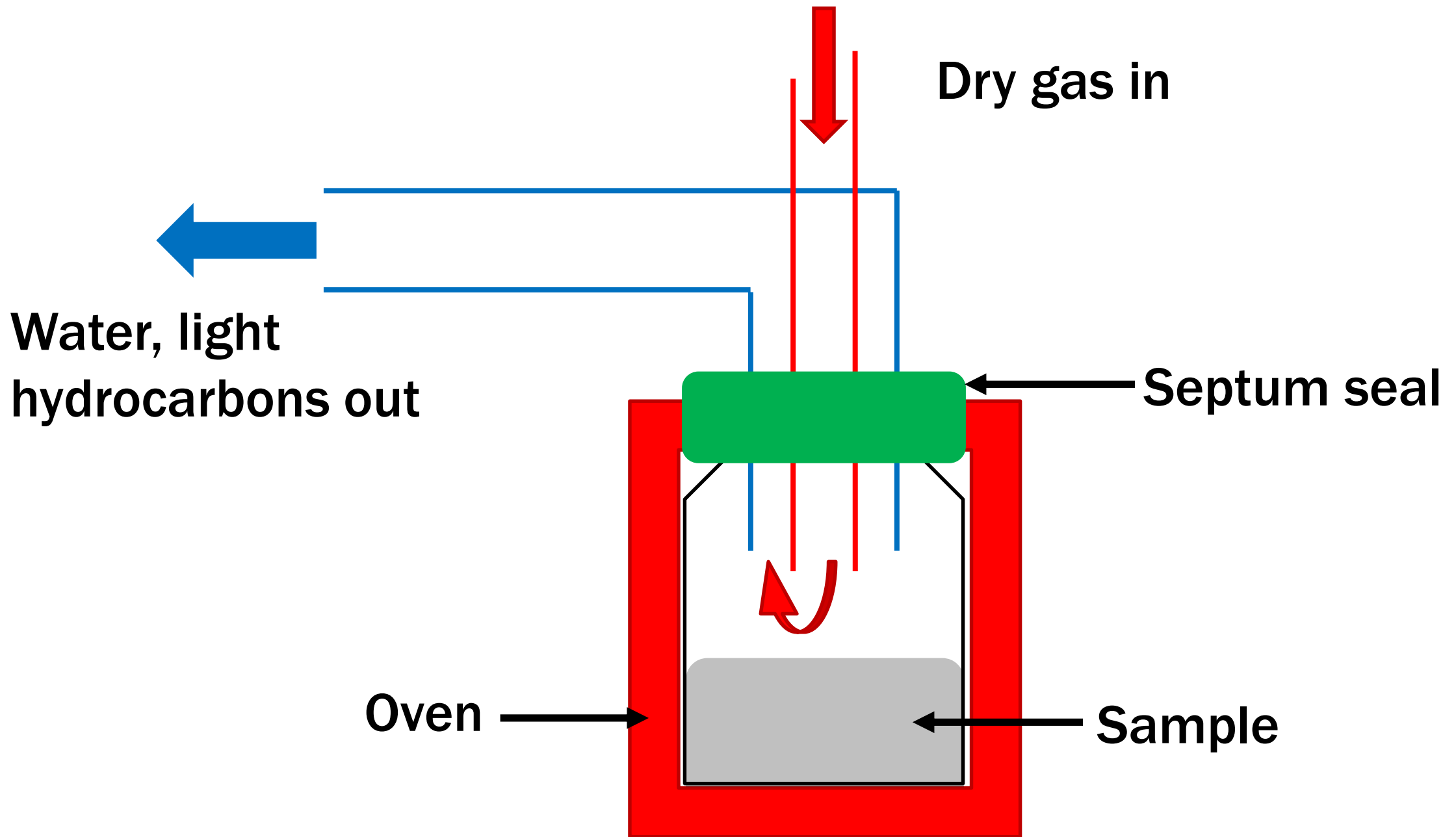
Not approved by ASTM for crude oil

Approved as D6304

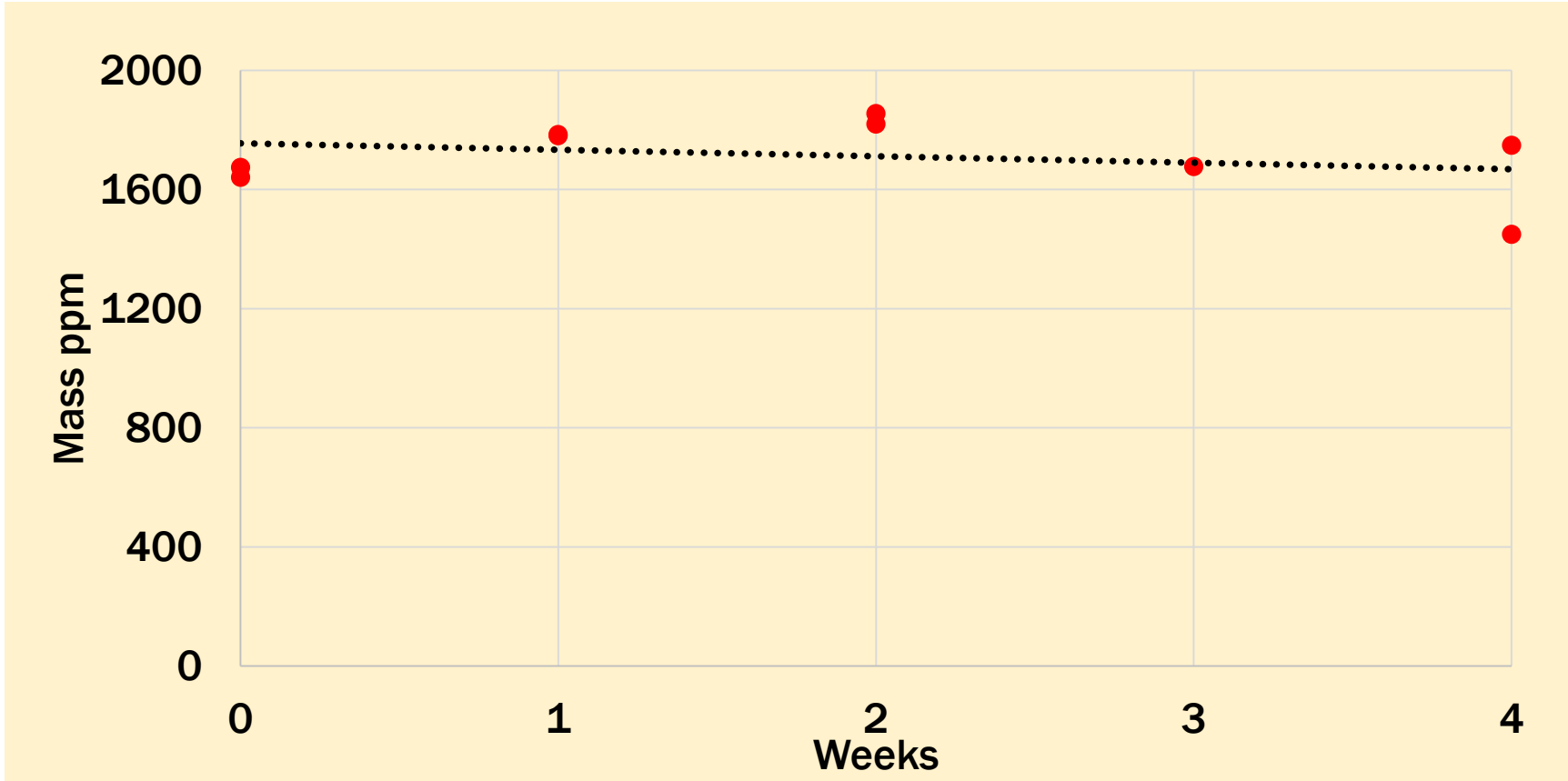


Titration

Sample Evaporation



EFFECT OF VIAL STORAGE TIME ON MEASURED WATER CONTENT



Crude homogenized, added to vials and sealed

Left to stand at room temperature

- 12.9 ppm/day loss, 95% lower confidence limit
- 3.1 ppm/day loss, estimate
- 6.7 ppm/day gain, 95% upper confidence limit

WHY PRE-EVAPORATION OVER CENTRIFUGE?



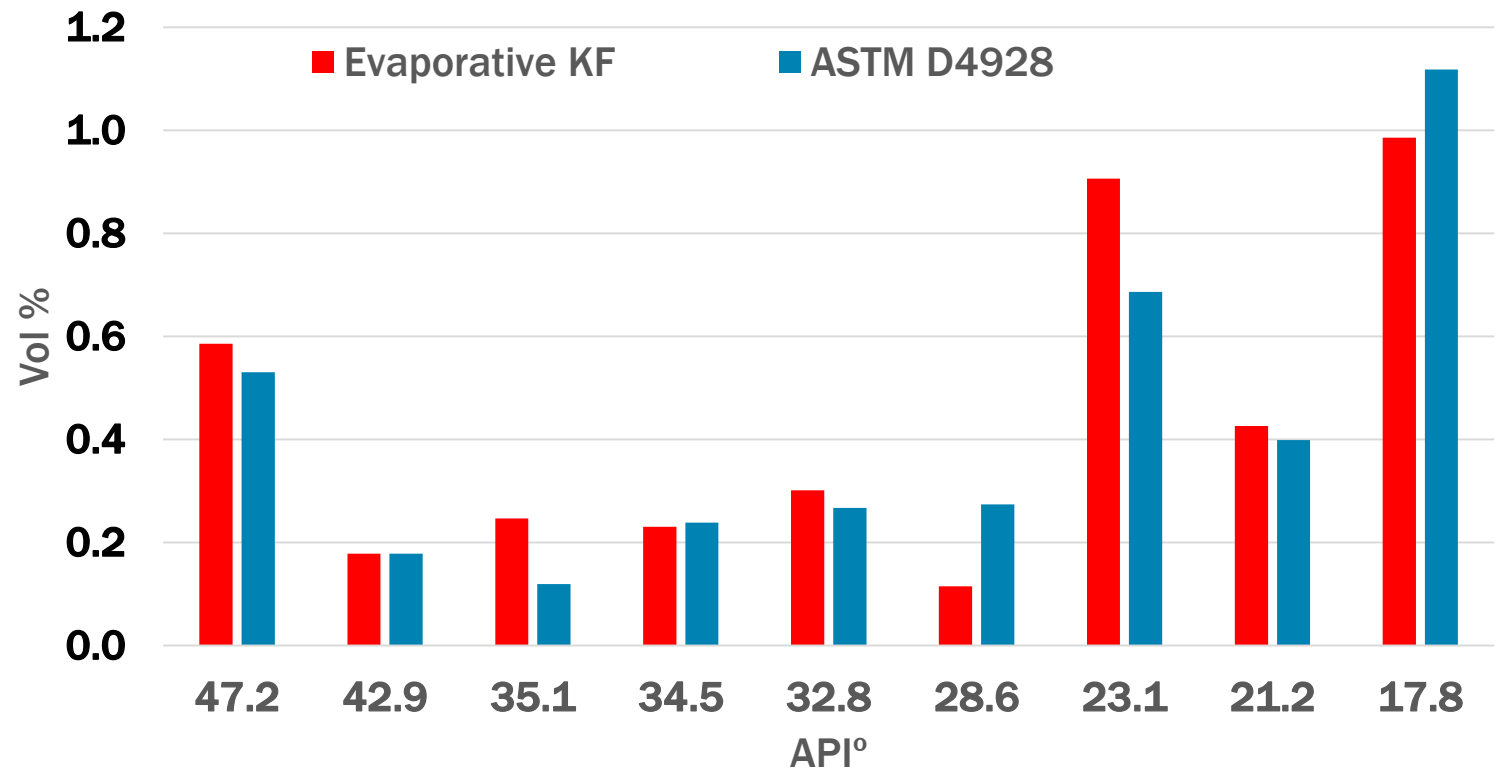
	KF	Centrifuge
Field Equipment Needed	Vial, pipette, optional crimper	Centrifuge, electricity, sample heater, water-saturated toluene, emulsion breaker
Accuracy	High	Low
Data recording	Automated	Manual
Time per sample	5 minutes	25 minutes
Field Technician skill level	Lower	Higher
Safety	Lower risk	Higher risk



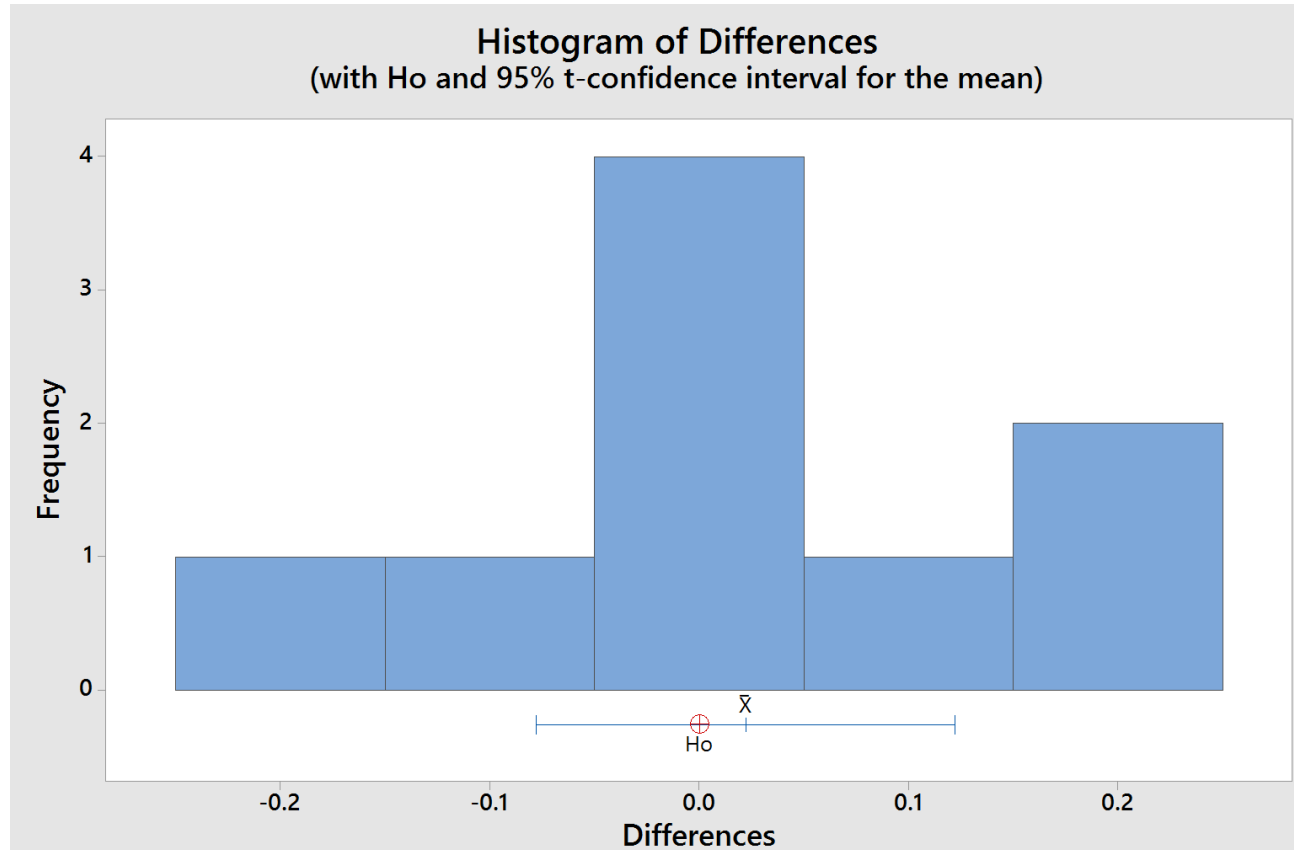
ASTM APPROVAL

Step 1: In Shop evaluation

Evaporative v Coulometric KF



STEP 1: COMPARISON OF EVAPORATIVE KF VERSUS D4928 FOR NINE CRUDE OILS



Paired T-Test and CI: Evaporative KF, ASTM 4928

Descriptive Statistics

Sample	N	Mean	StDev	SE Mean
Evaporative KF9		0.499	0.340	0.113
ASTM 4928	9	0.477	0.332	0.111

Estimation for Paired Difference

Mean	StDev	SE Mean	95% CI for $\mu_{\text{difference}}$
0.0222	0.1300	0.0433	(-0.0777, 0.1221)

$\mu_{\text{difference}}$: mean of (Evaporative KF - ASTM 4928)

Test

Null hypothesis	$H_0: \mu_{\text{difference}} = 0$
Alternative hypothesis	$H_1: \mu_{\text{difference}} \neq 0$
T-Value	0.51
P-Value	0.622

High confidence that the methods are not different

STEP 2: PRE-STUDY FOR ASTM APPROVAL FOR AN INTER LAB STUDY



Crudes	12
Labs	4
Instrument Suppliers	1
Instrument Set Up	Common protocol
Homogenization	Hand or table shaking

STEP 2: CRUDES AND LABS USED IN ROUND ROBIN



Crude #	API°
1	42.2
2	32.0
3	32.1
4	41.7
5	23.8
6	18.2
7	18.6
8	23.8
9	27.9
10	30.8
11	33.5
12	34.5

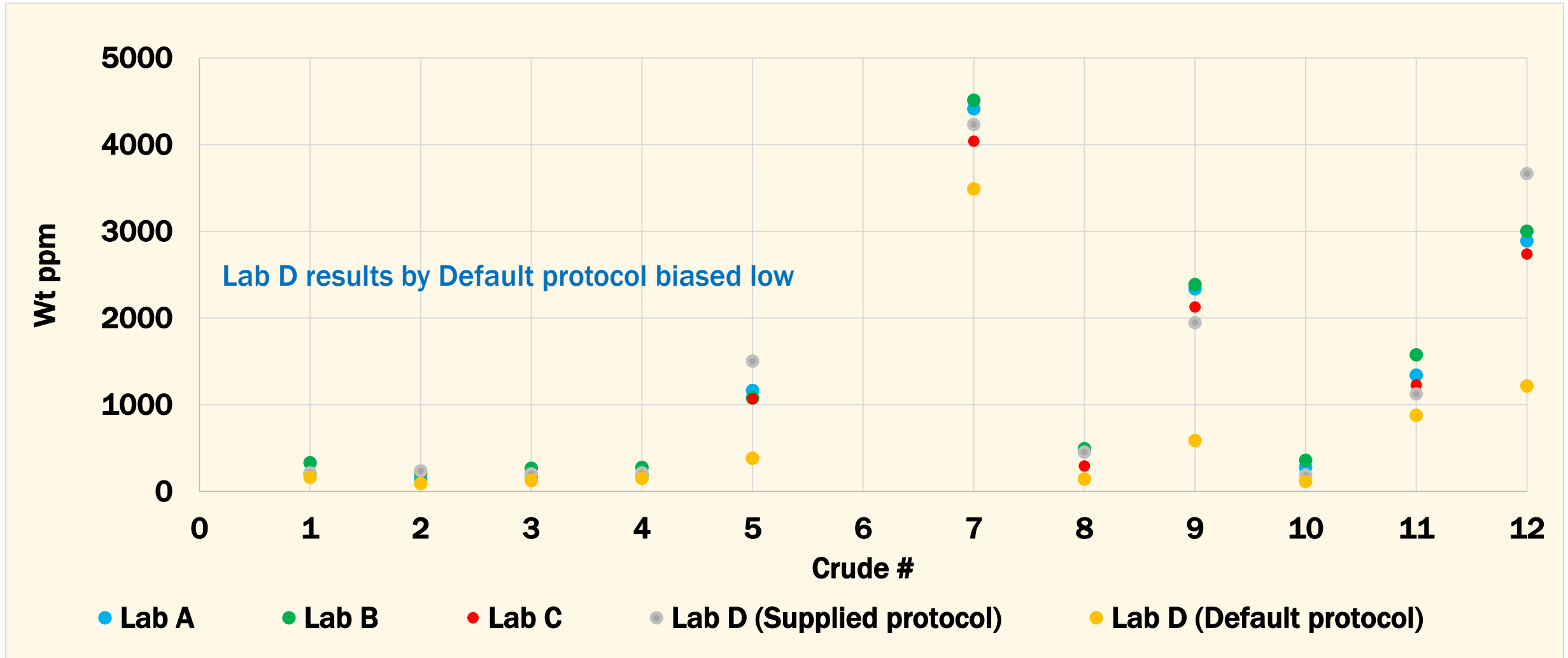
Lab	Location
A	P66 Analytical Sciences, Bartlesville, OK
B	P66 Crude Lab, Bartlesville, OK
C	Instrument Supplier
D	Major Oil Company

WHAT WENT WRONG!

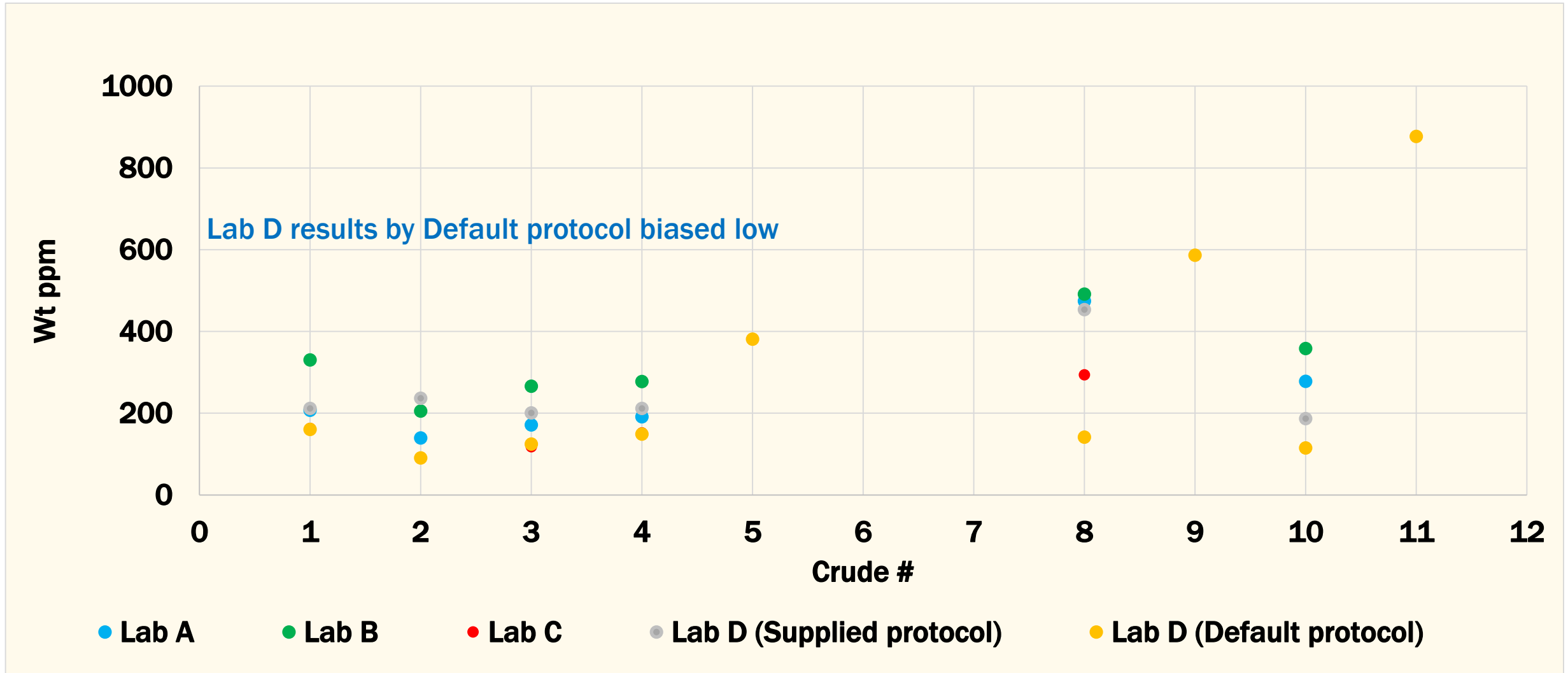


- **Homogenization of high viscosity crude #6**
- **Sample set bias**
- **Issues at Lab D**
 - **Protocols**
 - **Lack of repeats**
 - **Delay in running samples**
- **Offset in results between labs**

KARL FISCHER EVAPORATIVE KF ROUND ROBIN



KARL FISCHER EVAPORATIVE KF ROUND ROBIN





STATISTICAL ANALYSIS PROCEDURE – PRECISION STATEMENT FOR EVAPORATIVE KF: FOLLOW D6300

- **Develop preliminary precision statement (repeatability and reproducibility) for Evaporative KF for crude oil samples**
 - Compare precision with existing D4928 method for crude oils
- **Transform data to make precision independent of measurement level for the statistical analysis**
- **Perform analysis of variance (ANOVA) on transformed data**
- **Calculate repeatability and reproducibility based on variances determined from ANOVA**

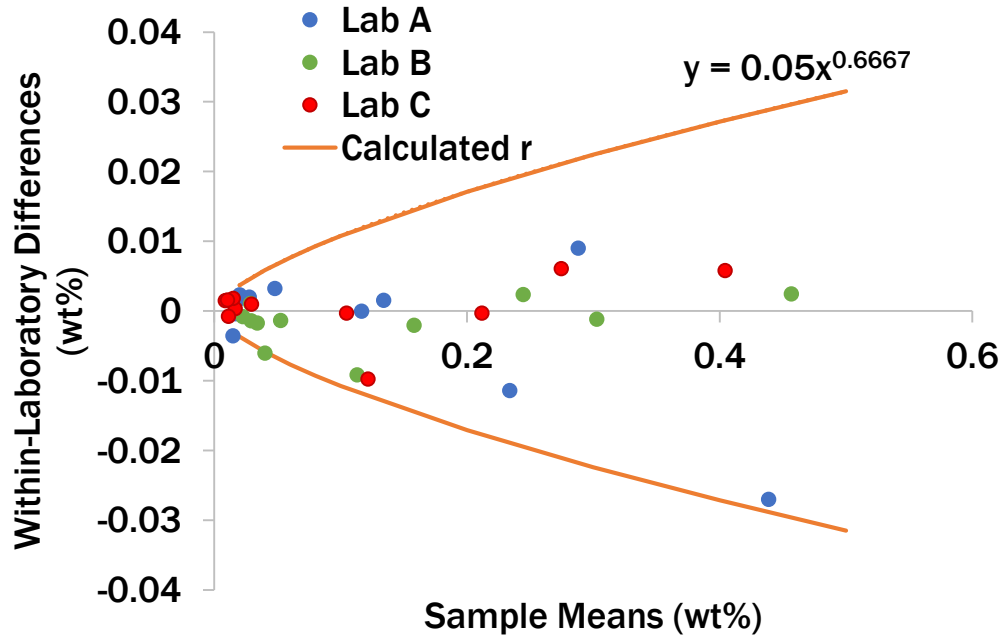
Simplifications and modifications from D6300:

- Use same precision statement format as D4928 for ease of comparison ($aX^{2/3}$)
- Uniformity of precision not examined
- No statistical outlier rejection performed
- Performed ANOVA using Minitab (General Linear Model)

PRECISION FOR EVAPORATIVE KF (11 CRUDES)

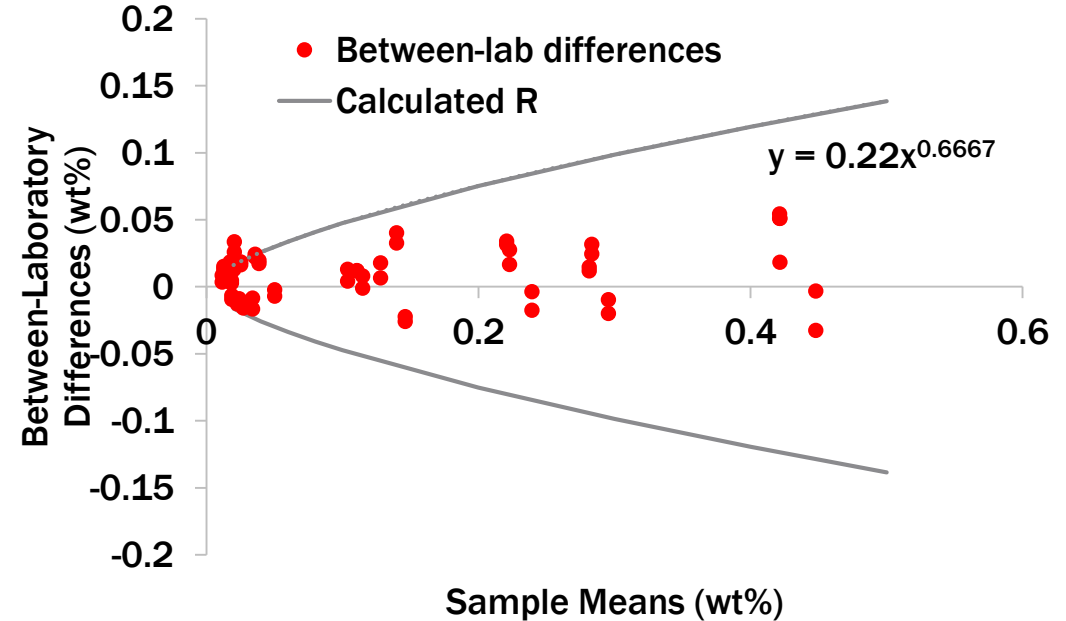


One sample with > 0.5% water removed from analysis



Measured Repeatability, $r = 0.05 X^{2/3}$

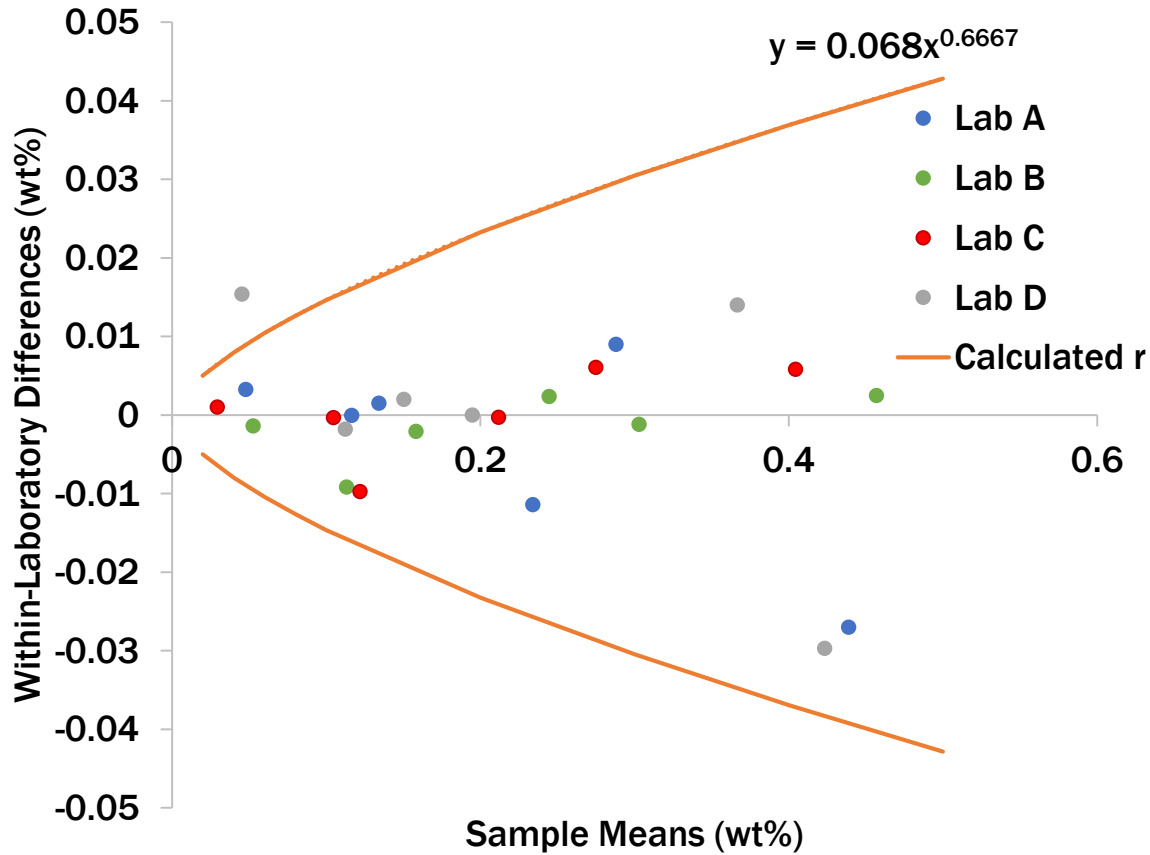
D4928 repeatability, $r = 0.04 X^{2/3}$



Measured Reproducibility, $R = 0.22 X^{2/3}$

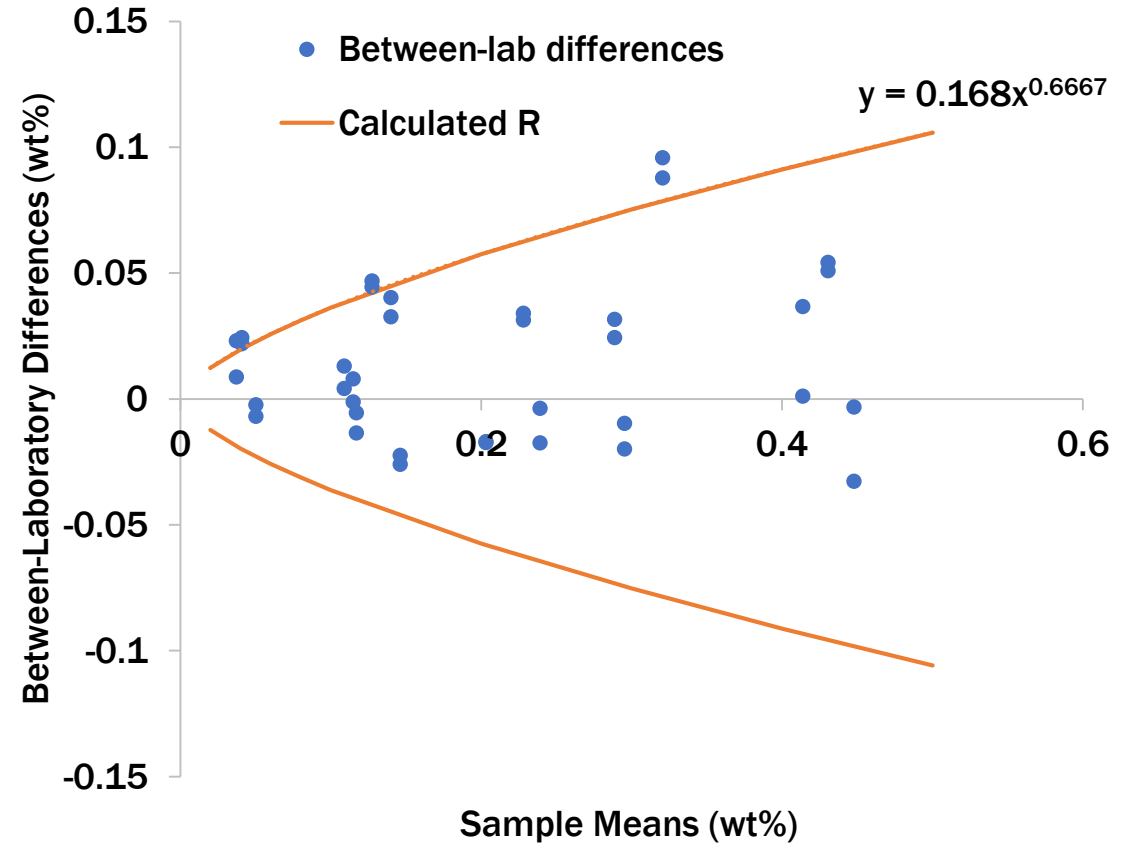
D4928 reproducibility, $R = 0.105 X^{2/3}$

SIX CRUDES, FOUR LABS



Measured Repeatability, $r = 0.07 X^{2/3}$

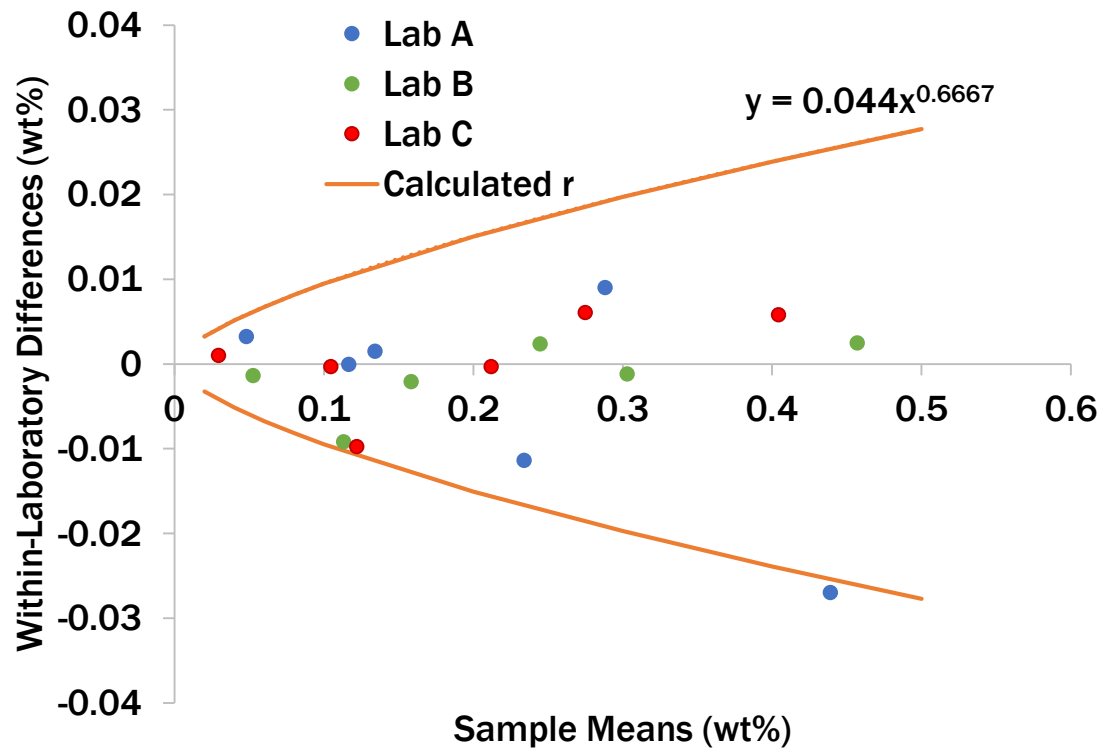
D4928 repeatability, $r = 0.04 X^{2/3}$



Measured Reproducibility, $R = 0.17 X^{2/3}$

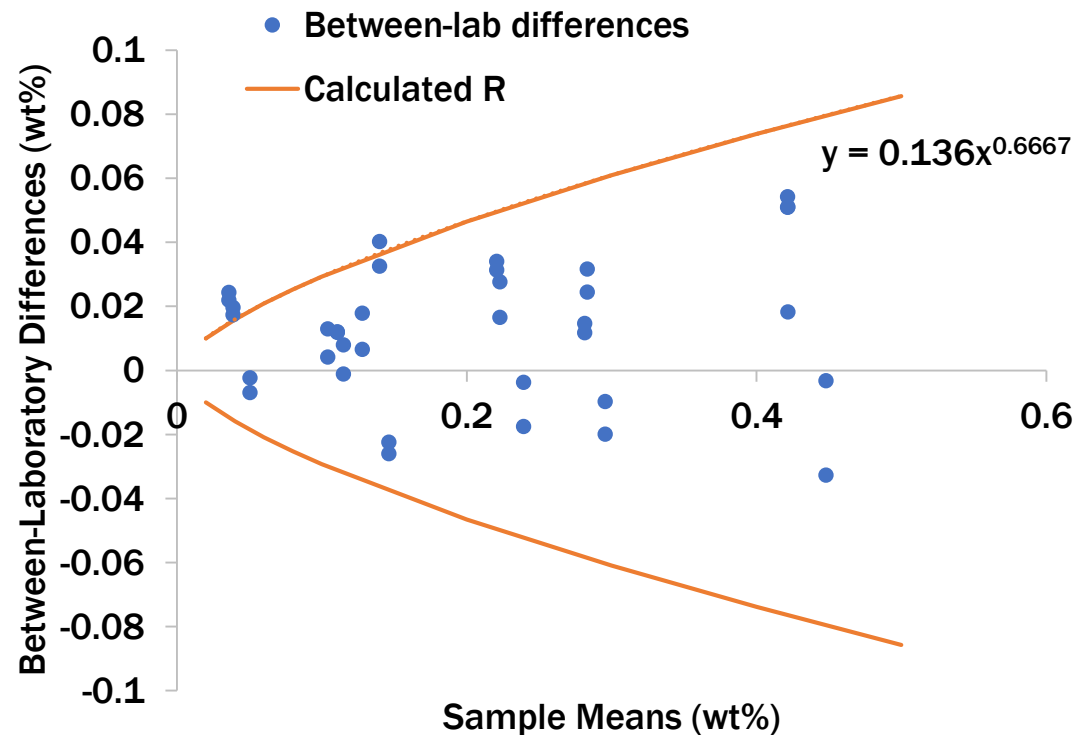
D4928 reproducibility, $R = 0.105 X^{2/3}$

SIX CRUDES, 3 LABS



Measured Repeatability, $r = 0.04 X^{2/3}$

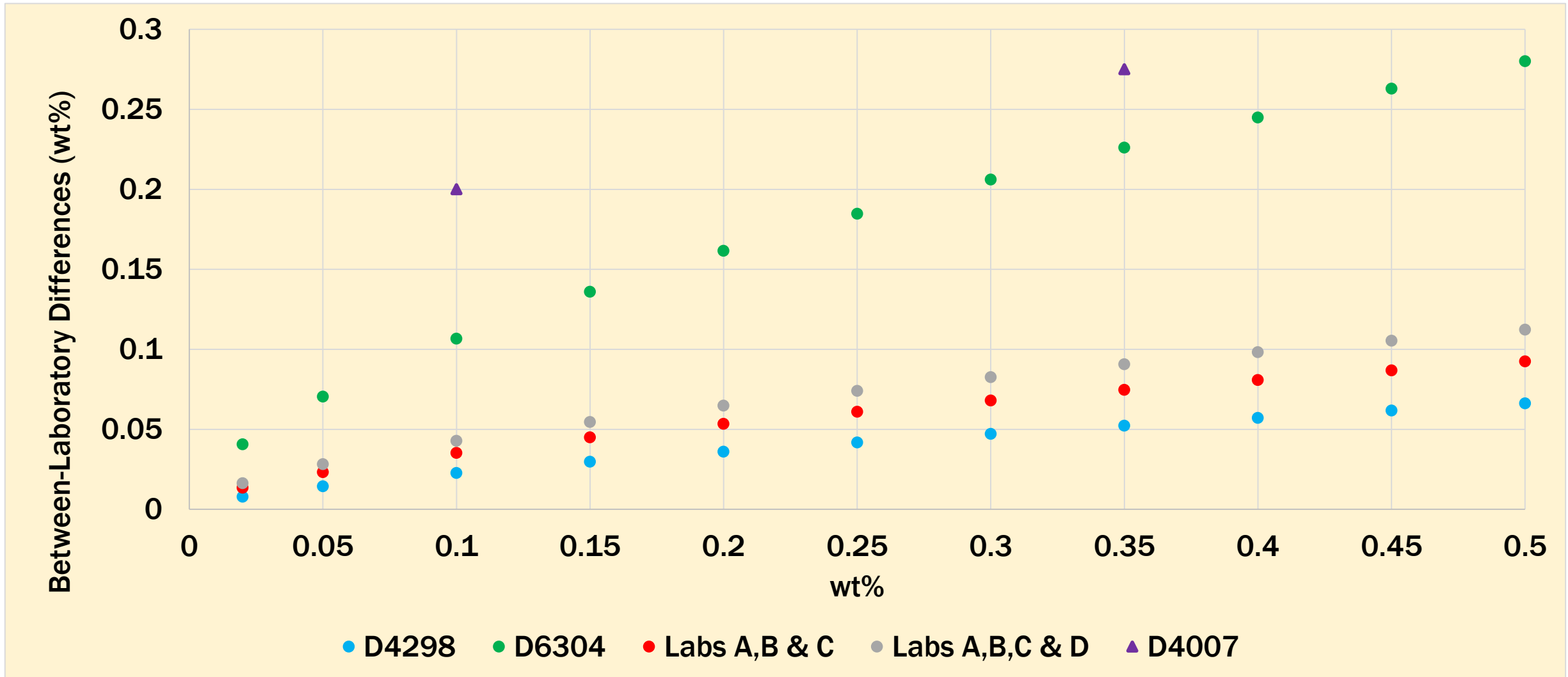
D4928 repeatability, $r = 0.04 X^{2/3}$



Measured Reproducibility, $R = 0.14 X^{2/3}$

D4928 reproducibility, $R = 0.105 X^{2/3}$

ROUND ROBIN REPRODUCIBILITY V ASTM STANDARDS



CONCLUSIONS AND RECOMMENDATIONS



- **Oven based KF has significant advantages for field samples**
- **A full interlaboratory study has been approved so that the pre-evaporation method can gain ASTM approval**
- **More work needed to optimize homogenization for high viscosity crudes**

ACKNOWLEDGEMENTS



- **Larry Tucker (Metrohm)**
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