

1. A Brief Review of Chemical Analytical Methods

2. Some Results for Moisture, Protein, Ash and Falling Number

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# The Measurement Process

- Simple
  - weight
- Complex
  - concentration

- An Analytical Procedure is an orderly step-by-step instruction designed to ensure operational uniformity and to minimize uncertainty

# Terminology

- True Value – what is actually there
- Measurement Result – your estimate of the True Value
- Error – the difference between the True Value and your estimate

# Reasons for Variation

- 1) Sampling
  - What is the weight of:
    - A specific kernel of wheat?
    - An average kernel of wheat?
- 2) The Measurement Process
  - Sample prep
  - Instrument calibration
  - Time, temperature, humidity, reagents
  - other

# Performance Attributes of a Method

- Linearity
- Specificity
- Sensitivity
- Precision
- Accuracy
- Repeatability
- Reproducibility

# Terminology

- **Linearity** – The ability of a method to perform across a range of concentrations
- The range of an analytical method is the range of concentrations across which the method has been tested successfully.
- (many methods tend to become unstable as the concentration nears zero)

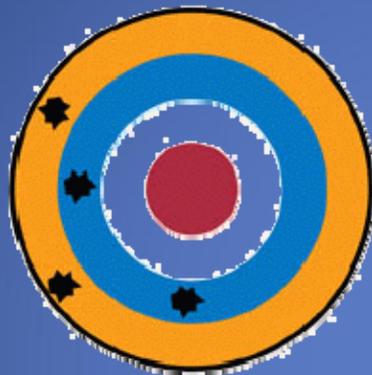
# Terminology

- **Selectivity / Specificity** - The ability to measure an analyte accurately in the presence of interference
- *Material/Matrix* - the medium or material that may contain the target analyte(s).

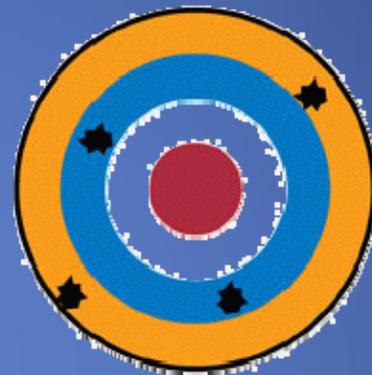
# Terminology

- Precision - The extent to which individual tests of the same material agree
- Accuracy – The extent to which the test results differ from the True Value

# Bias and Precision



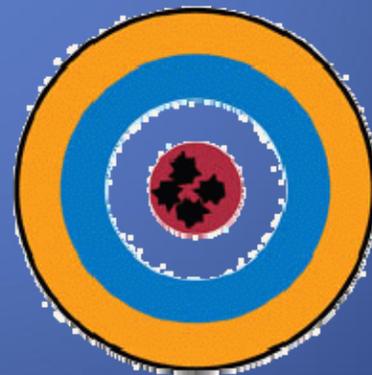
Exp. I



Exp. II

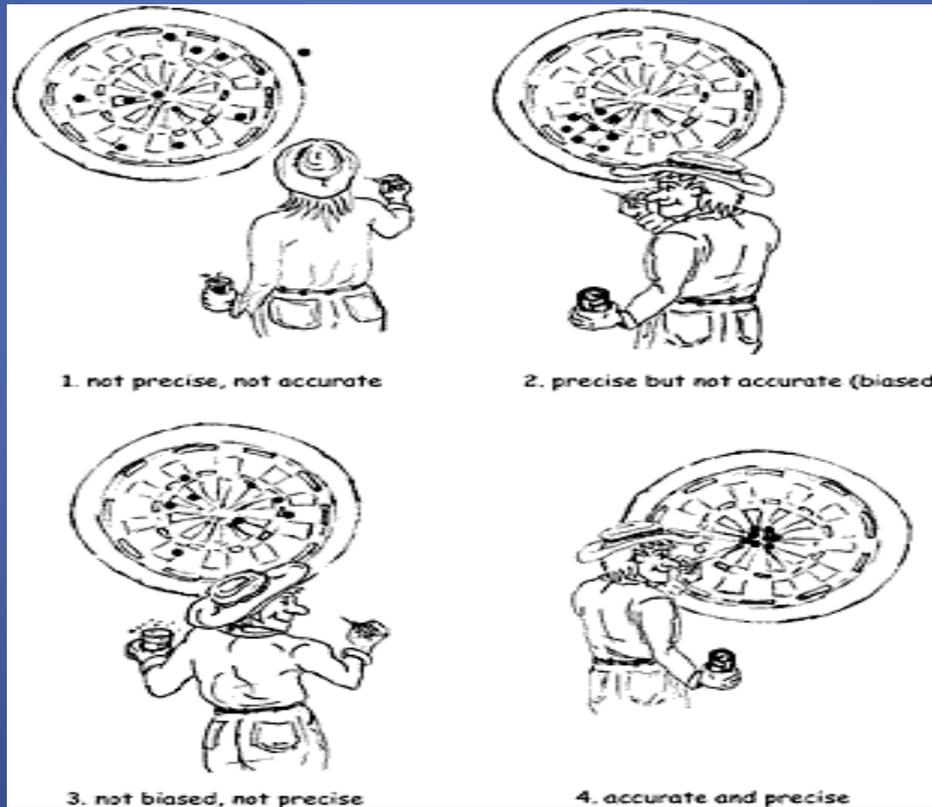


Exp. III



Exp. IV

# Bias and Precision



# Repeatability

- Internal Precision
- $r$  - Two single results obtained within a laboratory under repeatability conditions should not differ by more than  $r$ .
- Repeatability Conditions = same technician, same instruments, same laboratory, same time
- $r = 2.8 \times s_r$

# Reproducibility

- External Precision
- R - Two single results obtained by two different laboratories under reproducibility conditions should not differ by more than R.
- Reproducibility Conditions = different technicians, different instruments, different laboratories, different times
- $R = 2.8 \times s_R$

# Official Methods

- A role of the Official Methods Committee is to ensure that proposed analytical methods have been tested for all performance parameters

# Interlaboratory Studies

Collaborative Studies, Ring Tests, Round-Robins

- Categories
  - 1. Method Performance
  - 2. Material Performance
  - 3. Laboratory Performance

IUPAC, AACC, AOAC, IDF, CIPAC, ISO

“Harmonization”

# Performance Attributes of a Method

- Linearity
- Specificity
- Sensitivity
- Precision
- Accuracy
- Repeatability
- Reproducibility

# Outliers

- An Outlier is a number off by itself



# Conclusions I: Method Acceptability

- Estimate Parameters
- Compare to similar methods
  - Costs
  - Time
  - Safety
  - Stability
  - Range, Materials, Familiarity

**Check Sample and Proficiency Testing  
Service**

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# AACC Check Samples

- Lab subscribes to an AACC check sample series
- At specified times test samples are sent
- Lab analyzes sample(s) and returns its results to AACC
- AACC provides a statistical evaluation of the results of all labs
- Labs check to see how they compare

# AACC Check Samples

- Analytical Series
- Physical Testing Series
- Food Safety Series

# Check Sample Series "A"

- Hard Wheat Flour
  - Moisture
  - Protein
  - Ash
  - Falling Number
  - (Gassing Power)

# Example from Series “A”

## Protein Methods

- B1 - AACCC 46-10
- B2 - AACCC 46-11A
- B3 - AACCC 46-12
- B4 - AACCC 46-30
- B5 - AOAC 991.20
- B6 - Any NIR method
- B7 - Any proprietary method, Tecator, Buchim, etc.,

## Falling Number Methods

- D1 - AACCC 56-81B
- D2 - Perten, FN 1400, etc.
- DX - None of the above.

# Check Sample Results

## *Subscriber*

*Number*    *Moisture(%)*    *Protein (%)*    *Ash (%)*    *Falling Number*

..

50            11.53 A1            11.50 B7            0.487 C2            653 D2

54            12.16 A1            11.45 B4            0.469 C2            355 D2

55            11.92 A3            11.40            0.506 C2            438

56            11.80 A1            11.10 B1            0.501 C2            493 D1

58            11.46 A3            11.29 B4            0.491 C2            467 D2

...

***Subscriber***

**Number   Moisture(%)   Protein (%)   Ash (%)   Falling Number**

<b>N</b>	<b>46</b>	<b>39</b>	<b>40</b>	<b>38</b>
<b>Mean</b>	<b>11.63</b>	<b>11.27</b>	<b>0.491</b>	<b>495</b>
<b>Min</b>	<b>10.78</b>	<b>10.64</b>	<b>0.450</b>	<b>341</b>
<b>Max</b>	<b>12.24</b>	<b>11.68</b>	<b>0.563</b>	<b>653</b>
<b>Std</b>	<b>0.32</b>	<b>0.21</b>	<b>0.021</b>	<b>70</b>

Calculate z-value = (reported value – mean)/std

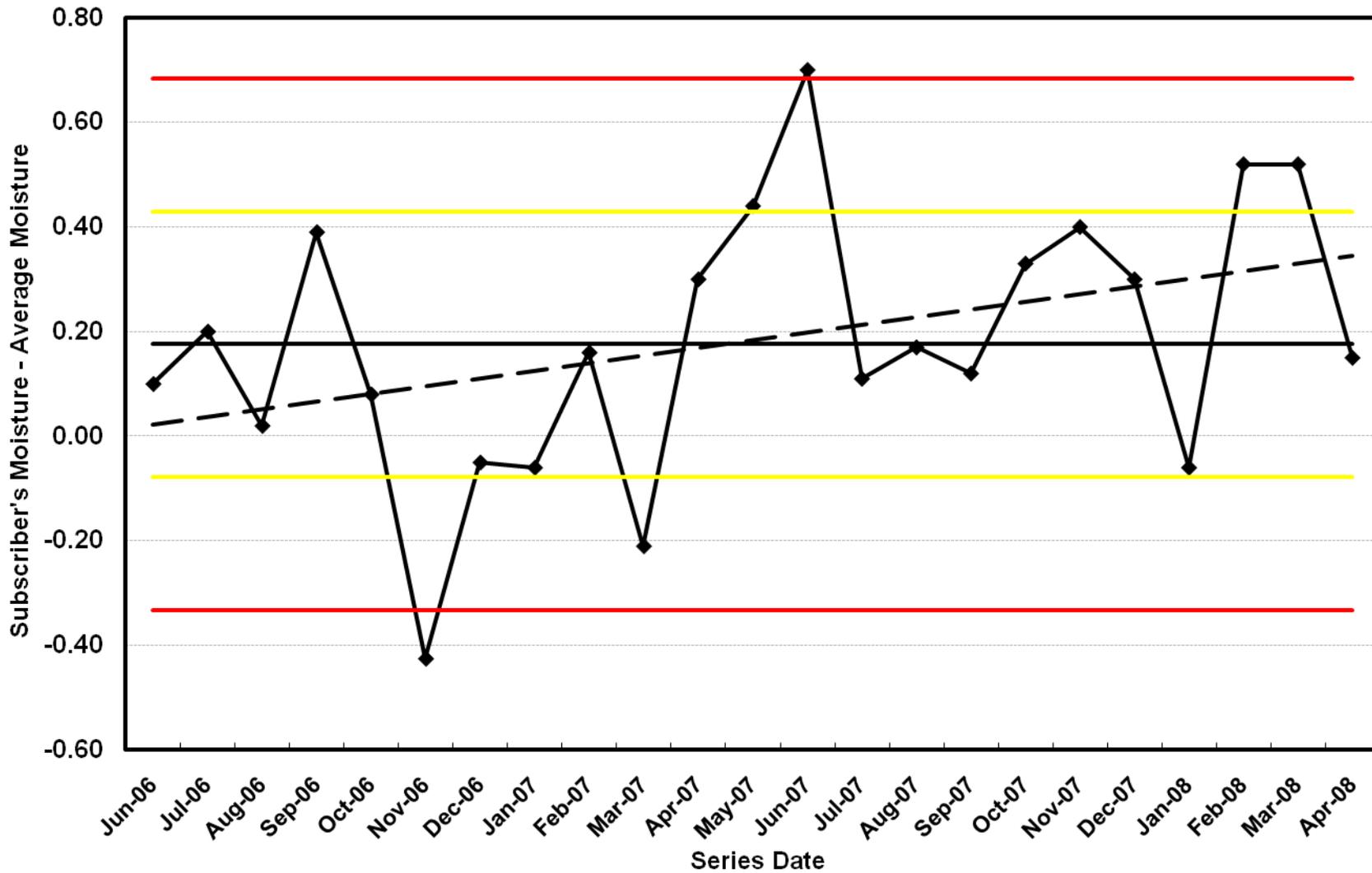
# Calculated z-values

<u>Sub #</u>	<u>Moisture z-values</u>	<u>Protein z-values</u>	<u>Ash z-values</u>	<u>Falling Number z-values</u>
...				
50	0.32	1.10	0.18	2.26
54	1.68	0.86	1.04	2.01
55	0.92	0.63	0.72	0.82
56	0.54	0.78	0.49	0.03
58	0.54	0.11	0.01	0.41
...				

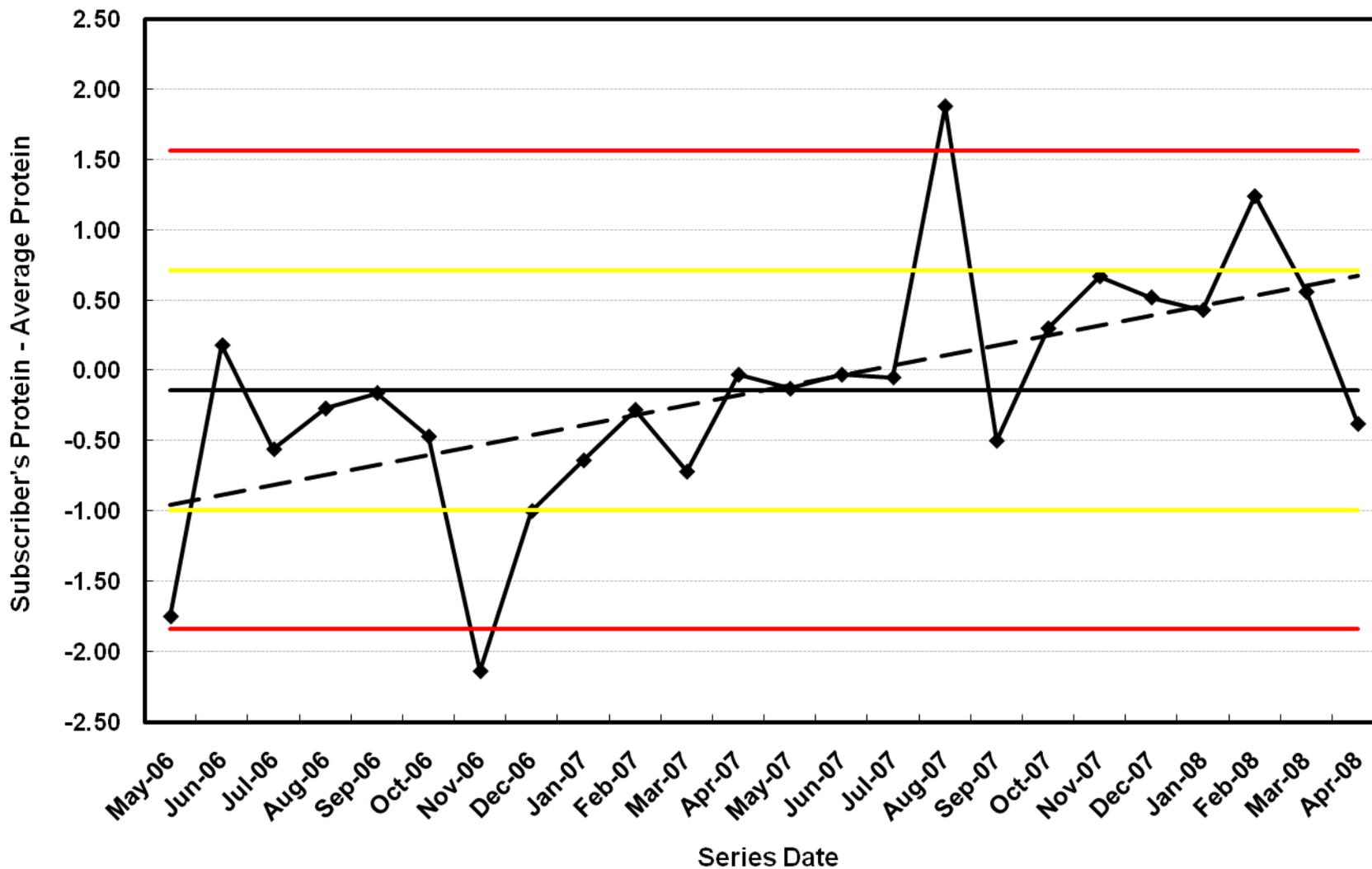
# Check Sample Results

- Current Result is a “snapshot”
- An Excel spreadsheet is now available to look at long term accuracy and possible trends
- Questions or suggestions – contact Terry Nelsen or Wayne Moore

### Difference Between Reported Moisture and Series Average Moisture

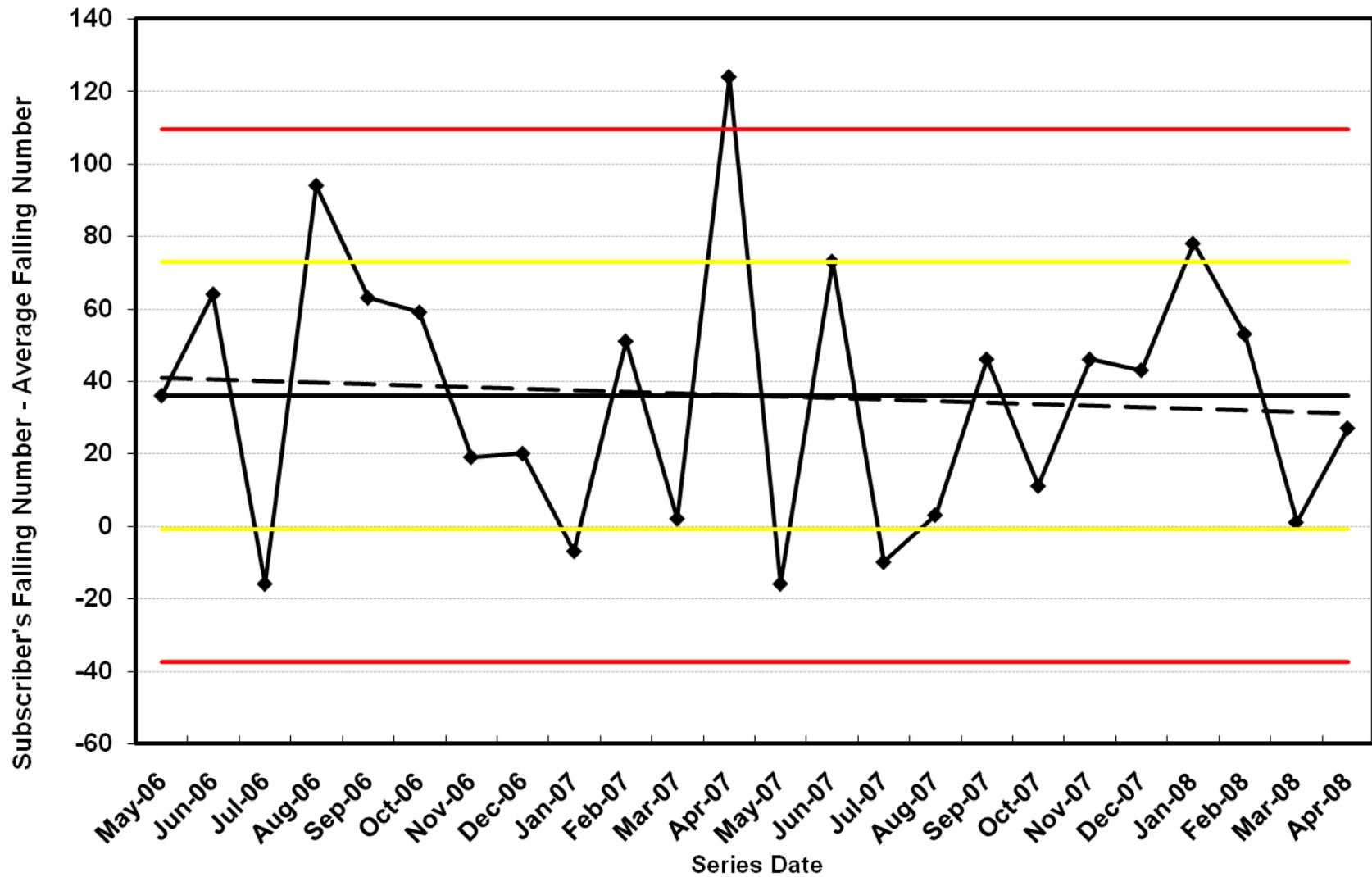


## Difference Between Reported Protein and Series Average Protein



A  
v  
e  
r  
a  
g  
e  
  
T  
r  
e  
n  
d  
+  
/  
-  
1  
S  
i  
g  
m  
a  
+  
/  
-  
2  
S  
i  
g  
m  
a

## Difference Between Reported Falling Number and Series Average Falling Number



A  
v  
e  
r  
a  
g  
e  
  
T  
r  
e  
n  
d  
+  
/  
-  
  
1  
  
S  
i  
g  
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a  
+  
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-  
  
2  
  
S  
i  
g  
m  
a

## Number of Positives in 48 Months

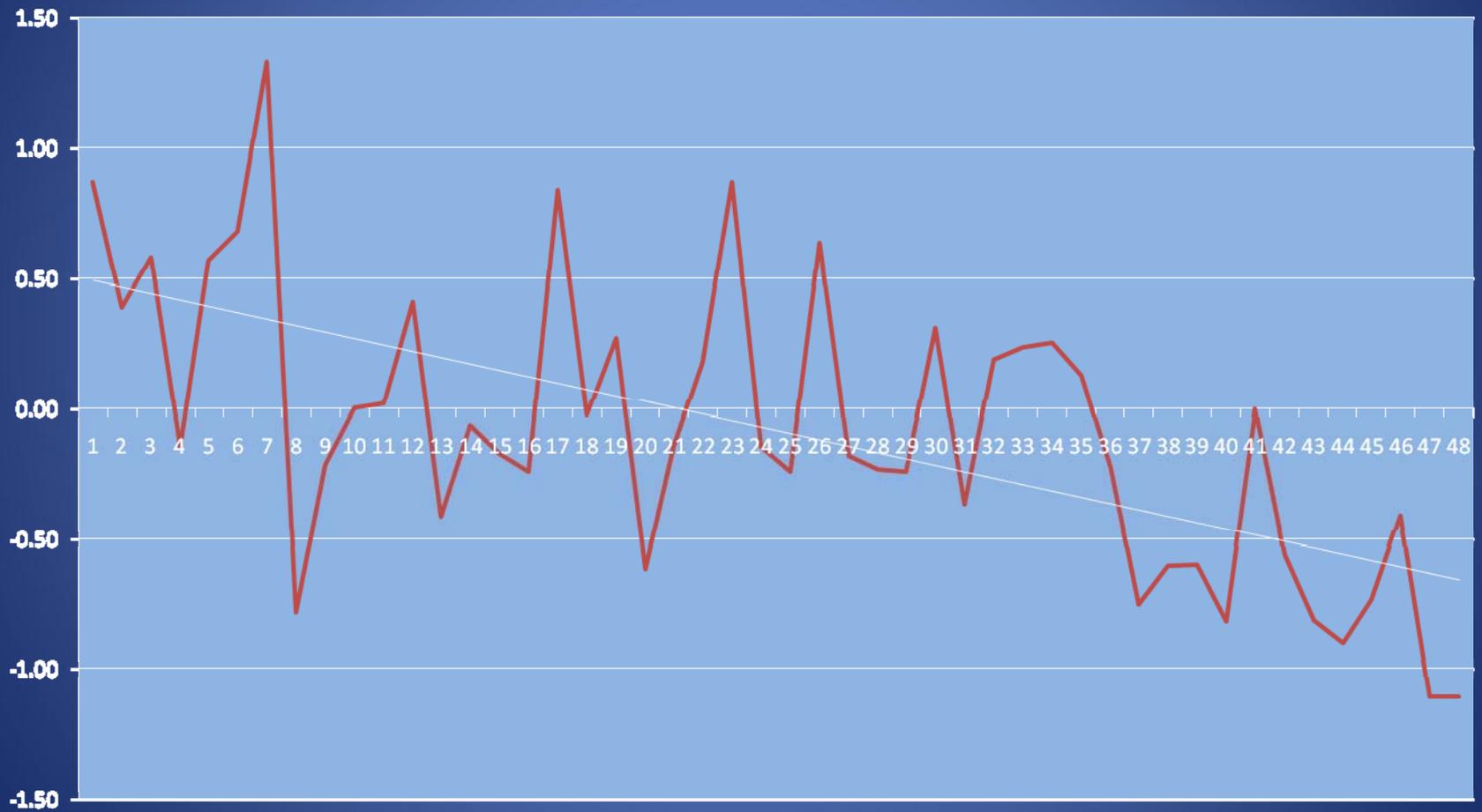
Lab	Moisture	Protein	Ash	Falling Number
A	39	12	25	32
B	17	22	29	47
C	27	31	10	16
D	23	21	24	12
E	32	31	21	30
F	33	37	34	37
G	25	24	28	28
H	39	39	2	19
I	24	27	14	25
J	36	22	42	30
K	27	13	18	45
L	20	24	27	6
M	16	9	18	42
N	21	26	42	20
O	11	0	24	3
P	21	17	20	4
Q	21	25	32	29

# Significant trends over 48 Months

Lab	Moisture	Protein	Ash	Falling Number
A	+	+	-	
B	-			
C	+			
D				
E		-		-
F		-	-	
G	+	-		
H				-
I		+		-
J				
K		-	-	-
L				+
M		-		
N	-	-		-
O				+
P				
Q		+		

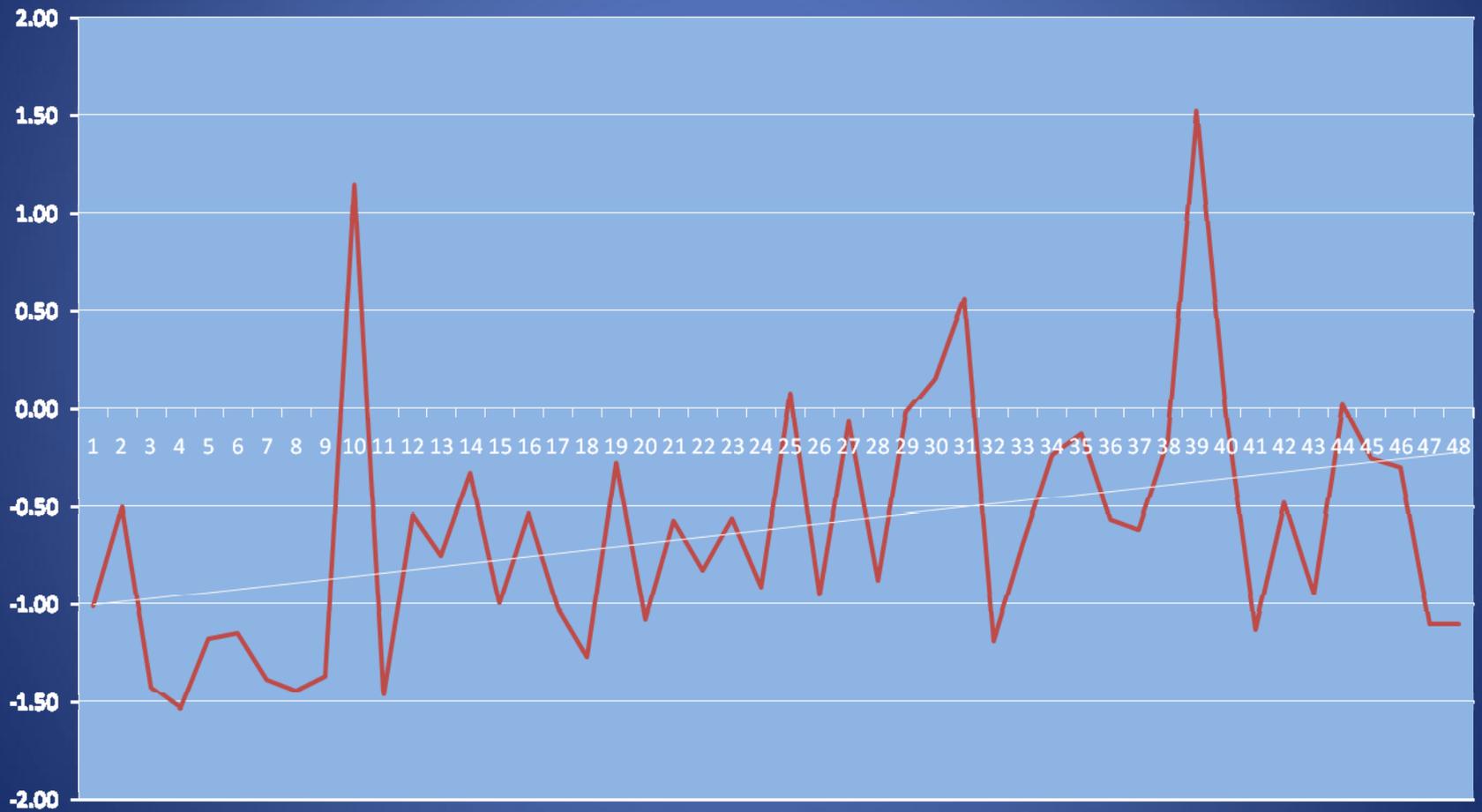
# Lab H

## Falling Number z-scores



# Lab L

## Falling Number z-scores



# Conclusions

- Some accepted methods can have biases
- Check your results over time
- For a good time – talk to a statistician

# References

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- Use of Statistics to Develop and Evaluate Analytical Methods (1985) Grant T. Wernimont (Ed. By William Spendley)
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