Magruder Check Sample Program What's new? What to look for?

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2015 Fertilizer Administrator's Seminar

James Bartos Office of Indiana State Chemist

What is this?

- "Round-Robin" or Proficiency (like) Program
 - Compare your lab results to others
 - Help identify which labs/methods/products are doing well/poorly
 - Differences from a "full" proficiency program?
 - Self-monitoring, results are anonymous, no disqualification, less cost
- Membership cost is \$300 per year (see Jamey)
- Approx. 100 participating labs
- Receive at least one sample per month
- Run sample twice by your methods & report results

History:

• Established in 1922 by Dr. E. W. Magruder

- F.S. Royster Guano Company
- Dr. Magruder ran program 36 years; been in place for <u>93 years</u>
- 1958 sponsorship transferred to AAPFCO & TFI
- Only AAPFCO committee that grants full membership privileges to industry
 - 14 committee members (fixed #)
 - 7 regulatory
 - 7 industry
 - Current chair: Bill Hall, Mosaic
 - Current vice-chair: Keith Wegner (Colorado)

What's new?

• March 2015

- Changed to new statistical and reporting format (similar AAFCO)
- Program Administrator Dr. Frank Sikora (KY)
- Statistician Andy Crawford (uses IHS)
- Web host FASS (Federation of Animal Science Societies)
- Submit results and receive reports electronically
 - <u>www.magruderchecksample.org</u>
- Unique aspects
 - Data linked to Investigational Allowance (IA)
 - Box and Whisker Plots
 - Magruder Newsletter

Historical Reports (pre-2015)

Results Report (Soluble Potash example):

MAGRUDER - Fertilizer Check Sample No. - 200710 Grade 16-4-8

- Pass 1 Results for 79 Labs - - Pass 2 Results for 78 Labs -

Metho	d	AOAC Ref.	Method _Code	No. of <u>Labs</u>	Grand Avg.	Std. Dev.	Average Range <u>of Dups</u>	No. of <u>Labs</u>	Grand Avg.	Std. Dev.	Average Range <u>of Dups</u>
Soluble Potash,	STPB Oxalate	958.02	050.00	14	7.80	0.17	0.08	14	7.80	0.17	0.08
Soluble Potash,	STPB Citrate	969.04	050.10	1	7.80	0.24	0.34	1	7.80	0.24	0.34
Soluble Potash,	AA (Oxalate)		050.30	12	7.58	0.39	0.09	12	7.58	0.39	0.09
Soluble Potash,	AA (Citrate)		050.31	1	8.64	0.04	0.05	1	8.64	0.04	0.05
Soluble Potash,	ICP (Oxalate)		050.50	6	7.86	0.40	0.07	6	7.86	0.40	0.07
Soluble Potash,	ICP (Citrate)		050.51	8	7.77	0.24	0.11	8	7.77	0.24	0.11
Soluble Potash,	Flame (Oxalate)	983.02(a	050.60	7	7.91	0.38	0.03	7	7.91	0.38	0.03
Soluble Potash,	Flame (Citrate)	983.02(b	050.61	7	7.75	0.19	0.10	6	7.74	0.18	0.06
Soluble Potash,	Other		050.99	16	7.63	0.35	0.09	15	7.65	0.36	0.07

Grade Report:

Printed: November 26, 2007

MAGRUDER Sample 200710 Laboratory Performance & Z Values Based on the Current Report ONLY Only methods which have 5 or more labs reporting in Pass 2 are included in the rankings.

Method	B	ias	Preci	sion	Acc	uracy	Method	Bias	Precision	Accuracy
010.XX	+A	.20	A	.17	A	.26				
041.XX	+B	.64	в	.79	С	1.02				
050.XX	-A	09	A	.14	A	.17				
121.XX	+A	.15	A	.08	A	.17				
144.XX	+A	.34	A	.04	A	.35				
191.XX	-A	16	A	.06	A	.17				
261.XX	-B	86	^ A	.37	в	.93				
291.XX	-B	76	A	.15	B	.77				
321.XX	+A	.29	A	.09	A	.31				

Historical Reports (pre-2015)

- Grand Average, Standard Deviation, Average Range of Duplicates for each method
 - No interpretation, just for relative comparison
- Received letter grade: A, B, C or D for each method
 - $A = 1/3^{rd}$ of labs with results <u>closest</u> to the average and most repeatable
 - $B = 1/3^{rd}$ of labs whose results were next closest
 - $C = 1/3^{rd}$ of labs whose results were <u>furthest</u>
 - D = (few) screened outlier; range too large; result > 3 SD from average
- "Index" values bias/accuracy/precision and combined?
 - Not well understood
- Problems?
 - Letter grade is arbitrary (always grading on a "curve")
 - Sometimes got low grade when did well or good grade when did bad
 - Only compared to participating population
 - No comparison with IA
 - Interpretation was subjective not universal

Letter Grade – Good Example

Grade	Lab Avg	Mean Dev	
Α	46.47	0.15	
Α	46.48	0.16	
Α	46.32	0.00	
Α	46.43	0.11	
Α	46.45	0.13	
Α	46.44	0.12	
Α	46.41	0.09	
Α	46.29	-0.03	
Α	46.29	-0.03	
Α	46.31	-0.01	
Constant			
Grand	46.32	Avg	
A	46.32 46.27	Avg -0.05	
A A A	46.32 46.27 46.22	Avg -0.05 -0.10	
A A A A	46.32 46.27 46.22 46.22	Avg -0.05 -0.10 -0.10	
A A A A A	46.32 46.27 46.22 46.22 46.18	Avg -0.05 -0.10 -0.10 -0.14	
A A A A A A	46.32 46.27 46.22 46.22 46.18 46.18	Avg -0.05 -0.10 -0.10 -0.14 -0.14	
A A A A A A A	46.32 46.27 46.22 46.22 46.18 46.18 46.25	Avg -0.05 -0.10 -0.10 -0.14 -0.14 -0.07	
A A A A A A A	46.32 46.27 46.22 46.22 46.18 46.18 46.25 46.15	Avg -0.05 -0.10 -0.10 -0.14 -0.14 -0.07 -0.17	
A A A A A A A A	46.32 46.27 46.22 46.22 46.18 46.18 46.25 46.15 46.15	Avg -0.05 -0.10 -0.14 -0.14 -0.14 -0.07 -0.17 -0.17	
A A A A A A A A A	46.32 46.27 46.22 46.22 46.18 46.18 46.25 46.15 46.15 46.13	Avg -0.05 -0.10 -0.14 -0.14 -0.14 -0.07 -0.17 -0.17 -0.19	

Grade	Lab Avg	Mean Dev	
В	46.75	0.43	
В	46.70	0.38	
в	46.63	0.31	
в	46.69	0.37	
В	46.68	0.36	
В	46.65	0.33	
В	46.61	0.29	
В	46.60	0.28	
В	46.45	0.13	
В	46.55	0.23	
Grand	46.32	Avg	
Grand B	46.32 46.18	Avg -0.14	
Grand B B	46.32 46.18 46.15	Avg -0.14 -0.17	
Grand B B B	46.32 46.18 46.15 46.09	Avg -0.14 -0.17 -0.23	
Grand B B B B	46.32 46.18 46.15 46.09 46.02	Avg -0.14 -0.17 -0.23 -0.30	
Grand B B B B B	46.32 46.18 46.15 46.09 46.02 45.99	Avg -0.14 -0.17 -0.23 -0.30 -0.33	
Grand B B B B B B	46.32 46.18 46.09 46.02 45.99 45.98	Avg -0.14 -0.17 -0.23 -0.30 -0.33 -0.34	
Grand B B B B B B B	46.32 46.18 46.09 46.02 45.99 45.98 45.97	Avg -0.14 -0.17 -0.23 -0.30 -0.33 -0.34 -0.35	
Grand B B B B B B B B B	46.32 46.18 46.09 46.02 45.99 45.98 45.97 45.91	Avg -0.14 -0.17 -0.23 -0.30 -0.33 -0.34 -0.35 -0.41	
Grand B B B B B B B B B B	46.32 46.18 46.09 46.02 45.99 45.98 45.97 45.91 45.90	Avg -0.14 -0.17 -0.23 -0.30 -0.33 -0.34 -0.35 -0.41 -0.42	

Grade	Lab Avg	Mean Dev
С	47.54	1.22
С	47.15	0.83
С	47.00	0.68
С	46.95	0.63
С	46.92	0.60
С	46.83	0.51
С	46.85	0.53
С	46.84	0.52
С	46.80	0.48
Grand	46.32	Avg
С	45.88	-0.44
C C	45.88 45.84	-0.44 -0.48
C C C	45.88 45.84 45.79	-0.44 -0.48 -0.53
с с с с	45.88 45.84 45.79 45.74	-0.44 -0.48 -0.53 -0.58
0 0 0 0	45.88 45.84 45.79 45.74 45.74	-0.44 -0.48 -0.53 -0.58 -0.58
с с с с с с	45.88 45.84 45.79 45.74 45.74 45.70	-0.44 -0.48 -0.53 -0.58 -0.58 -0.62
с с с с с с с с	45.88 45.84 45.79 45.74 45.74 45.70 45.69	-0.44 -0.48 -0.53 -0.58 -0.58 -0.62 -0.63
с с с с с с с с с	45.88 45.84 45.79 45.74 45.74 45.70 45.69 45.60	-0.44 -0.48 -0.53 -0.58 -0.58 -0.62 -0.63 -0.72
с с с с с с с с с	45.88 45.79 45.74 45.74 45.70 45.69 45.60 45.35	-0.44 -0.48 -0.53 -0.58 -0.58 -0.62 -0.63 -0.72 -0.97

• Sample 2012-01

• Urea 46-0-0, *IA* = 0.88

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- Combustion method
- Relative to IA:
 - some labs doing better than letter grade
 - some labs doing worse than letter grade
- Overall good example:
 - good method
 - good sample
 - few results outside IA
 - system mostly worked

Letter Grade – Bad Example

Grade	Lab Avg	Mean Dev	Grade	Lab Avg	Mean Dev	Grade	Lab Avg	Mean Dev
Α	36.34	-0.02	В	38.33	1.98	С	43.25	6.89
Α	36.31	-0.05	В	38.25	1.89	С	41.81	5.45
Α	35.76	-0.60	В	37.75	1.39	С	39.43	3.07
Α	35.75	-0.61	В	37.52	1.16	С	39.21	2.85
Α	35.72	-0.64	В	36.77	0.41	С	39.05	2.69
Α	35.80	-0.56	в	36.45	0.09	С	39.03	2.67
Grand	36.36	Avg	Grand	36.36	Avg	Grand	36.36	Avg
Grand A	36.36 35.59	Avg -0.77	Grand B	36.36 35.23	Avg -1.13	Grand C	36.36 34.25	Avg -2.11
Grand A A	36.36 35.59 35.60	Avg -0.77 -0.76	Grand B B	36.36 35.23 34.95	Avg -1.13 -1.41	Grand C C	36.36 34.25 33.92	Avg -2.11 -2.44
Grand A A A	36.36 35.59 35.60 35.50	Avg -0.77 -0.76 -0.86	Grand B B B	36.36 35.23 34.95 34.84	Avg -1.13 -1.41 -1.52	Grand C C C	36.36 34.25 33.92 33.15	Avg -2.11 -2.44 -3.21
Grand A A A A	36.36 35.59 35.60 35.50 35.80	Avg -0.77 -0.76 -0.86 -0.56	Grand B B B B	36.36 35.23 34.95 34.84 34.69	Avg -1.13 -1.41 -1.52 -1.67	Grand C C C C	36.36 34.25 33.92 33.15 32.50	Avg -2.11 -2.44 -3.21 -3.86
Grand A A A A A	36.36 35.59 35.60 35.50 35.80 35.35	Avg -0.77 -0.76 -0.86 -0.56 -1.01	Grand B B B B B	36.36 35.23 34.95 34.84 34.69 34.70	Avg -1.13 -1.41 -1.52 -1.67 -1.66	Grand C C C C C	36.36 34.25 33.92 33.15 32.50 29.66	Avg -2.11 -2.44 -3.21 -3.86 -6.70

Sample 2012-09; Zinc Sulfate; 36% Zn, IA = 1.0; Method ICP

Couple labs with A's near the IA

Most labs with B's and C's <u>well</u> outside the IA

Std Dev = 2.55 (<u>needs to be < 0.5</u> for IA); Accepted Range = 31.26 to 41.46

Most labs getting good letter grades, so assume they have no problem

System broken = bad method and bad data

"Normal Distribution" and Z-Score



- z-score is your deviation from the average compared to the standard deviation
- example: a z-score of 1 means your result is exactly one SD from the average
- A positive z-score means your result was higher than average, while a negative score means your result was lower than average
- z-score < +/- 1 : <u>VERY GOOD</u>; your score within top 68.2% of data
- +/- 1 < z-score < +/- 2 : OK; outside top 68%, but within next 27.2% (13.6 + 13.6)</p>
- +/- 2 < z-score < +/- 3 : WARNING; your results in bottom 4.2% (false penalties)</p>
- z-score > +/- 3 : <u>ACTIONABLE</u>; your results in bottom 0.2% (99% CI)

Analyte Report (NEW)

Analyte		Lab	Lab D	ata	M	ethod Value	s		Magruder CS	Your	
Group	Analyte (Units)	Code	Value	Range	Rob Mean	Rob SD	R-bar	# Labs	Z Score	Method	Flag
041	Direct Available Phosphorus as P2O5 (46%)	0368	43.58*	0.3300	46.55	0.7703	0.2989	36	-3.86	041.50	0
041	Direct Available Phosphorus as P2O5 (46%)	0325	44.75*	1.500	46.55	0.7703	0.2989	36	-2.34	041.50	0
041	Direct Available Phosphorus as P2O5 (46%)	0504	45.03*	0.1200	46.55	0.7703	0.2989	36	-1.98	041.20	0
041	Direct Available Phosphorus as P2O5 (46%)	0007	45.45*	0.9000	46.55	0.7703	0.2989	36	-1.43	041.50	0
041	Direct Available Phosphorus as P2O5 (46%)	0043	45.62	0.1400	46.55	0.7703	0.2989	36	-1.21	041.50	0
041	Direct Available Phosphorus as P2O5 (46%)	0397	45.81	0.0900	46.55	0.7703	0.2989	36	-0.97	041.60	0
041	Direct Available Phosphorus as P2O5 (46%)	0095	46.00	0.0900	46.55	0.7703	0.2989	36	-0.72	041.40	0
041	Direct Available Phosphorus as P2O5 (46%)	0043	46.26	0.1200	46.55	0.7703	0.2989	36	-0.38	041.60	0
041	Direct Available Phosphorus as P2O5 (46%)	0360	46.29	0.6500	46.55	0.7703	0.2989	36	-0.35	041.50	0
041	Direct Available Phosphorus as P2O5 (46%)	0049	46.42	0.2700	46.55	0.7703	0.2989	36	-0.18	041.10	0
041	Direct Available Phosphorus as P2O5 (46%)	0055	46.43	0.1300	46.55	0.7703	0.2989	36	-0.16	041.50	0
041	Direct Available Phosphorus as P2O5 (46%)	0185	46.53	0.2300	46.55	0.7703	0.2989	36	-0.03	041.10	0

• Sample 150111; 18-46-0; for 46% phosphate IA = 1.0

- Results arranged from lowest to highest
- Analyte = combined results for all direct "available" phosphate methods
 - grav(41.10), manual(41.20), auto(41.50), citrate-EDTA(41.60), ICP(41.50) & other(41.99)
- z-scores identified that labs 368 and 325 are outside "main population"
- z-score alone did not identify that labs 504 and 7 are outside the IA
- * symbol now indicates their value is below the IA value

Method Report (NEW)

Method		Lab	Lab [)ata	M	ethod Value	s		Magruder CS	Threshold	
Code	Analyte Name and Method (Units)	Code	Value	Range	Rob Mean	Rob SD	R-bar	# Labs	Z Score	%RSD	Flag
041.50	Direct Available Phosphorus as P205, ICP (48%)	0368	43.58*	0.3300	46.24	1.172	0.3882	11	-2.28	3%	0
041.50	Direct Available Phosphorus as P205, ICP (46%)	0325	44.75*	1.500	46.24	1.172	0.3882	11	-1.27	2%	0
041.50	Direct Available Phosphorus as P205, ICP (48%)	0007	45.45*	0.9000	46.24	1.172	0.3882	11	-0.68	1%	0
041.50	Direct Available Phosphorus as P205, ICP (48%)	0043	45.62	0.1400	46.24	1.172	0.3882	11	-0.53	1%	0
041.50	Direct Available Phosphorus as P205, ICP (46%)	0360	46.29	0.6500	46.24	1.172	0.3882	11	0.04	0%	0
041.50	Direct Available Phosphorus as P205, ICP (48%)	0055	46.43	0.1300	46.24	1.172	0.3882	11	0.16	0%	0
041.50	Direct Available Phosphorus as P205, ICP (48%)	0137	46.54	0.1700	46.24	1.172	0.3882	11	0.25	0%	0
041.50	Direct Available Phosphorus as P205, ICP (48%)	0377	46.60	0.2000	46.24	1.172	0.3882	11	0.31	0%	0
041.50	Direct Available Phosphorus as P205, ICP (48%)	0452	47.24	0.0200	46.24	1.172	0.3882	11	0.85	1%	0
041.50	Direct Available Phosphorus as P2O5, ICP (46%)	0023	47.53	0.0000	46.24	1.172	0.3882	11	1.10	1%	0
041.50	Direct Available Phosphorus as P2O5, ICP (46%)	0423	47.62	0.2300	46.24	1.172	0.3882	11	1.17	1%	0

- Sample 150111; 18-46-0 *(same sample)*
- Method = all results for a single method (e.g. 041.50 = ICP)
- z-score: only identified lab 368 was outside the "main population"
- ICP method robust mean = 46.24% was less than analyte mean = 46.55%
- 3 labs reported results less than the IA value of 1.0
- * symbol now indicates their value is below the IA value
- note: lab 7 may argue that their result of 45.45% result would pass for a 46% DAP guarantee, BUT their result would pass IF the product was over-formulated, as was the case here (i.e. analyte mean = 46.55%)

Methods Comparison

m	check sample pro	Z e gra	m				1				E.	· ·	
STF Method Sample Grade	RIVING FOR EXCELLENCE IN AN d Proficiency For All Labs (Lab Values) e # 150111 18-46-0 (DAP)	ALY	15		Statisti	cal Sur	nmary				Issue (Date : 02	/28/2015
Method Code	Analyte & Method	Total # Labs Submitting	# Labs in Robust Calculations	Raw Mean	Raw SD	Assigned Value Robust Mean	IA at Analyte Value	Robust sd	Robust Uncertainty (U)	Robust % RSD	IA %RSD	Average Range (R-bar)	Horwitz %RSD
040.20	Indirect Available Phosphorus as P2O5, Spectr (46%)	1		46.38									
040.40	Indirect Available Phosphorus as P2O5, Automated (46%)	2	2	46.74	0.0601								
040.50	Indirect Available Phosphorus as P2O5, ICP (46%)	1		46.74									
041.10	Direct Available Phosphorus as P2O5, Gravimet (46%)	8	8	46.60	0.2999	46.65	1.0083	0.2332	0.0583	0.50%	1.08%	0.1353	2.24%
041.20	Direct Available Phosphorus as P2O5, Spectrop (46%)	3	3	46.96	1.670	46.96	1.0083	1.670	0.6819	3.56%	1.07%	0.4033	2.24%
041.40	Direct Available Phosphorus as P2O5, Automated (46%)	1		46.00									
041.50	Direct Available Phosphorus as P2O5, ICP (46%)	11	11	46.15	1.227	46.24	1.0083	1.172	0.2499	2.54%	1.09%	0.3882	2.25%
041.60	Direct Available Phosphorus as P2O5, Citrate (46%)	11	10	46.09	2.151	46.53	1.0083	0.7138	0.1596	1.53%	1.08%	0.3629	2.24%
041.99	Direct Available Phosphorus as P2O5, Other (46%)	3	3	47.14	1.327	47.14	1.0083	1.327	0.5416	2.81%	1.07%	0.1600	2.24%
-												-	

- Can compare Robust Means (ICP lowest result; "Other" highest) bias?
- Can compare Robust SD (i.e. variability, grav has very low SD; spectrop, ICP and Other have higher SD)
- Can compare Average Range
 - Average difference between replicate readings
- Can compare %RSD to Horwitz predicted %RSD
 - Manual spec (41.20), ICP (41.50) and Other (41.99) did worse than Horwitz average
- IA %RSD = (IA / 2) / analyte robust mean
 - ideal for %RSD to be near or below this
 - why is IA divided by 2: need room for sampling/sample variability

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Method Report Card



Sample # 150111: Grade 18-46-0 (DAP) Method Report Card for Lab Code 0007

STRIVING FOR EXCELLENCE IN ANALYSIS

Proficienc	Proficiency For 2 Methods Issue Date : 02/28/201									
Method	Analyte	Lab 000	07 Data	Me	ethod Value	s		Magruder	Threshold	
Code	Name and Method (Units)	Value	range	Rob Mean	Rob SD	R-bar	# Labs	Z Score	%RSD	Flag
010.60	Total Nitrogen, Combustion (18%)	17.70	0.0000	17.77	0.2074	0.0913	44	-0.31	0%	0
041.50	Direct Available Phosphorus as P2O5, ICP (46%)	[45.45]	0.9000	46.24	1.172	0.3882	11	-0.68	1%	0

Interpreting Z Scores: Red indicates a normally distributed Z value >3 or <-3 (requires action), Orange = Z between 2 and 3 or -2 and -3 (warning) and Green = Z < 2 and >-2 (OK at 95%). Flags indicate data usage: 0 = Used, 1 = rejected for duplicates too far apart, 2 = rejected as extreme outlier and a 4 flag indicates rejected due to 0 value/s submitted. Robust statistics not used if < 6 labs reporting, in this case the Z Scores are included for information only (Grey). Square brackets indicate that [your value] is lower than the Robust Analyte value less the Investigational Allowance. Method or Analyte codes in light green indicate a guaranteed analyte. Individual lab values may be below detection limits but are reported solely for the purpose of this Proficiency Testing program.

- Your unique report for just your lab results/methods
- Good z-score for N (i.e. -0.31)
 - In the top 1 SD or 68% of data
 - z-score is negative meaning your result is lower than the average result
 - N result is not bracketed, so your result is within the IA value
- Good z-score for Phosphate (i.e. -0.68)
 - In the top 1 SD or 68% of data
 - z-score is negative meaning your result is lower than the average result
 - Phosphate result is bracketed, so your result is outside the IA value
- How can lab get good z-score but outside IA ??
 - Can if entire population did bad (either bad method and/or bad sample)

Sample # 150311: Grade 6-9-22 Analyte Report Card for Lab Code 0481 Z-Score Box Plot and Guarantees

STRIVING FOR EXCELLENCE IN ANALYSIS

Proficiency Testing For 17 Analytes

Z-Score Box and Whisker Plots for Lab # 0481 <guaranteed analyte>

2 1 Z-Scores 0 -1 -2 -3 68 50 82 20 21 31 56 17 1 24 12 35 18 43 16 59 21 Notes: The Methods you used are indicated above and the # Labs involved are below the Box and Whisker.

CI 190 16.190 1.000 Fe 241 0.441 0.049 Mn 261 0.036 0.009 Zn 321 1.393 0.144 Value is the Robust Analyte Value

Guaranteed in This Sample

Analyte Code

010

041

050

121

148

165

N

P2O5

K20

Mg

s в

estimated using the primary Analyte Codes for this sample.

Your Z-Score is indicated by the Dot. If you do not see a Dot your score is off the chart. Dots between the Green lines are acceptable Z-Scores. Dots outside the Red lines are actionable.

The Bar, Box and Whisker represent Median, 25% to 75% percentile and 5% to 95% percentile respectively.

Did well on: ammonical, N, S, B, Cd, Cl, Cr, Cu and Ni

Could improve on: total P2O5, K2O, WS Mg, As, Fe and Mn



magruder fertilizer check sample program

Issue Date : 04/30/2015

Value*

4.795

8.048

20.995

1.273

10.230

0.342

IA

0.506

0.680

1.115

0.264

0.711

0.054

Summary

- Completely new system with much more information
- What to look for (<u>quick</u> <u>visuals</u>):
 - want z-scores less than +/- 2 (Green)
 - don't want z-scores greater than +/- 2 Orange or +/- 3 Red
 - don't want * and [] notations that suggest your results outside of IA
 - probably bad lab result (but maybe a bad method and/or sample)
 - Box and whisker plots
 - box is 25 to 75 percentile from median (good)
 - whisker is 5 to 95 percentile from median (ok)
 - don't want dot outside box and whisker (bad)
 - Interpretation is provided <u>on reports</u> but more detail at:
 - www.magruderchecksample.org



Special Recognition

- Dr. Frank Sikora (UK) Program Administrator
 - donates countless hours to program
- Andy Crawford Statistician
 - compensated, but goes way beyond expectations

Graphite as a Fertilizer/Carbon Source?

• Article: "Graphite could be the next best fertilizer"

- <u>http://www.mining.com/web/graphite-could-be-the-next-best-fertilizer/?utm_source=digest-en-potash-150901&utm_medium=email&utm_campaign=digest</u>
- A rare form of graphite is currently being researched in <u>South Australia</u> as a <u>potential soil</u> <u>conditioner</u>.
- Initial research ... has shown this particular type of graphitic carbon <u>contains critical slow</u> release macro and micronutrients essential for healthy plant growth.
- ... similarities to another form of carbon <u>found in Russia</u> that has been <u>used to fertilise</u> soils for quite some time.
- ... an exploration target of 40-70 million tonnes of <u>10-12% total carbon</u> that could be converted to a resource...
- The research project has also tested the <u>impact of graphene coatings on conventional</u> <u>fertilisers</u>. These molecular <u>coatings significantly reduced the release rates of the</u> <u>nutrients</u>.







Graphite





- Minerals.net:
- Graphite is a mineral <u>composed exclusively of the</u> <u>element carbon</u>.
- Geology.com:
 - ... forms when <u>carbon is subjected to heat and pressure</u> ...pressures in the range of 75,000 psi and temperatures in the range of 750°C are needed to produce graphite.
- The heat of metamorphism destroys the organic molecules ...volatilizing the oxygen, hydrogen, nitrogen and sulfur. What remains is a nearly pure carbon material ...
- Some Uses of Graphite:
- "lead" in pencils, lubricants, paints, batteries, brake linings, rolled graphene sheets are 100X stronger than steel and 10X lighter – used to make light weight sports equipment
- Interesting:
- Graphite and diamond are identical chemically (*both composed of carbon*), but physically, they are very different.
- Graphite hexagonal layers; Diamond tetrahedron

Thoughts:

- "... exploration target of 40-70 million tonnes of <u>10-12% total carbon</u>"
- Pure graphite is nearly 100% carbon; so this contains 88%+ of something else; this 88% would have to be the source of nutrients or soil amendment properties and its not clearly stated what this is?
- "impact of graphene coatings on conventional fertilisers" this might work as a Controlled Release mechanism (<u>if purified</u>), but would "protect" fertilizer rather than a source of nutrients itself.
- Watch out for "source of Carbon" claims (true but misleading)
 - Carbon is a plant essential nutrient
- Graphite is not in a form available to plants
- CO₂ is the recognized plant source of Carbon, and it *comes from the air*6CO₂ + 6H₂O --(energy/light)-- > C₆H₁₂O₆ + 6O₂
- Graphite is probably not a good source of C for soil microbes either
- Conclusion: very suspect claims, supporting data essential

Tolerance vs. Investigational Allowance?

• Tolerance:

- Definition: ISO 2.1.41 tolerance <u>permitted</u> <u>deviation</u> of the measured value of a nutrient content <u>from its declared value</u>
- Commonly used term in many parts of the world
- Tolerances vary in different countries/regions
- Many fertilizers now manufactured and/or distributed worldwide, so there is confusion about AAPFCO's "tolerances"
- Some manufacturer's/distributors assume the investigational allowance is their tolerance
- Many folks do not understand what an investigational allowance is

Examples:

- EU tolerances for fertilizer: <u>www.nutricarefertilisers.com</u> (might be outdated)
- 29.5.2003 EN C 127 E/319 Official Journal of the European Union
- Different for different products and not always proportionate to the guarantee/concentration
 - I don't yet know if these tolerances accommodate for sampling/laboratory errors?
 - I don't yet know if these tolerances apply just to deficiencies or also to overages?

Fertilizer	EU Tolerance	IA
Urea	0.4 unit	0.88
Ammonium Nitrate	0.6 unit	0.88
Ammonium Sulfate	0.3 unit	0.74
Phosphatic Fertilizers	0.8 unit	~ 1.0
Muriate of Potash	0.5 unit	~ 1.8
Potassium Magnesium Sulfate	1.5 unit	~ 1.1
Binary Fertilizers (NK, NP, PK)	1.5 total	variable
Ternary Fertilizers (NPK)	1.9 total	variable
Micros (> 2%)	0.4 unit	variable
Micros (< 2%)	0.2% of declared value	variable

What is an Investigational Allowance?

- AAFPCO Definition:
 - is an allowance for variations inherent in the taking, preparation and analysis of an official sample or soil amendment
- Main sources of variability/statistical uncertainty:
 - 1. **Sampling** variation in sampling (*note expect product to be essentially uniform*)
 - 2. Intra (within) lab variability "analytical" get a slightly different result each time your lab tests the sample
 - 3. Inter (among) lab variability differences in test results from different labs (different methods, instruments, analysts, etc.)
- Combine the sampling, intra-lab and inter-lab variation to estimate the uncertainty and that value is the IA
- Once the IA value is exceeded, we have a high confidence/certainty (CI 95%) that the reported value is statistically different from its guarantee

Considerations

- Misconception: if a company argues their 46% DAP product is not 44.90% (failing IA) but rather is really 45% (passing IA), then this is a flawed argument, not tolerating 45%, rather "enforcing" the guaranteed value of 46%
 - Difference:
 - We have sufficient confidence that 44.90% is not really 46%
 - We don't have sufficient confidence that 45% is not possible 46%
 - Simply moved result from a "black-and-white" area to a "gray" area
- Important consideration:
 - Because of product/manufacturing variability, some companies build in slight overages for added insurance; this should be taken into consideration when enforcing overages

AAPFCO Investigational Allowance

- Pop Quiz:
- Is the AAPFCO Investigational Allowance a Tolerance?
 NO
- What is AAPFCO's Tolerance? *Hint looking for numeric value* ZERO
 - unless otherwise stated: T-76 <u>No Phosphate</u> Fertilizer means fertilizer products with phosphate levels <u>below 0.5%</u> intended for established urban turf or lawns. (Official 2009)
- Is it safe to tell a company they can sell a product they known is below the guarantee by a value < to the IA?
 NO

Congratulations – You are now an IA expert !