

# An Evaluation of the ICP-PK Method Performance (AOAC 2015.18) based upon Magruder Check Sample Data

*-first draft-*

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# Objectives

- Determine if Magruder data generated over the past three years is suitable for method validation purposes.
- Process was described at AAPFCO WA 2020 Magruder meeting.
  - Focused on the process, but not on results
- This presentation will focus on the method performance.
- *Is this data acceptable for validation purposes or do we need to initiate a “traditional” collaborative study?*
- *Is this a method acceptable?*

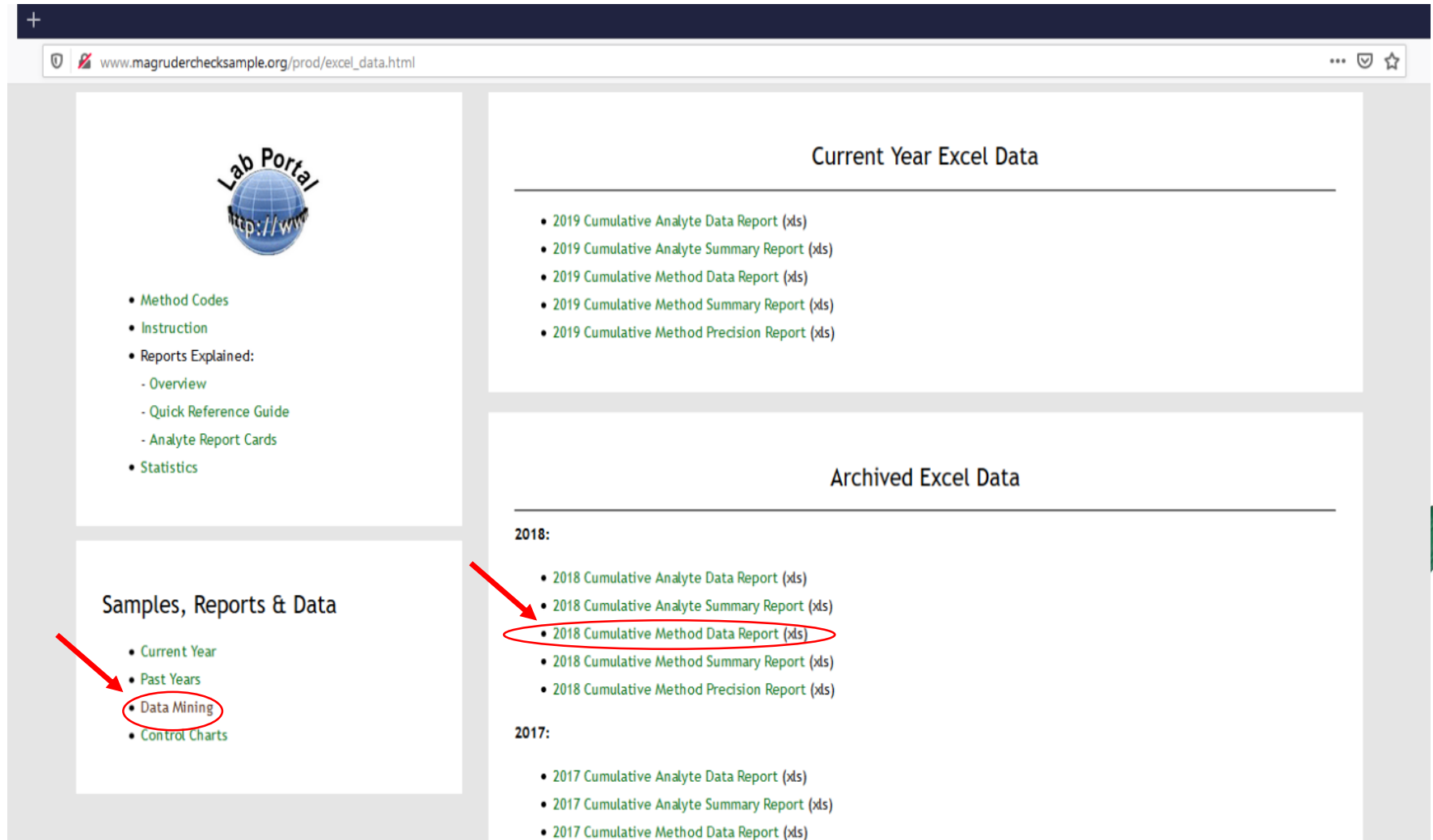


# Data Collection Process

- Downloaded data from the Magruder website
- Method Codes:
  - **041.51** Direct Available P2O5, ICP, Citrate-EDTA Ext
  - **050.51** Soluble K2O, ICP (Citrate-EDTA)
- Entered data into AOAC Spreadsheet
  - *AOAC International Study Workbook Blind (Unpaired) Replicates*
  - *Copyright 2006, 2012 by AOAC International, all rights reserved*
- Entered data into ISO TC-134 Spreadsheet
  - *Not as comprehensive as AOAC's*
  - *Used AOAC spreadsheet to remove outliers*
  - *ISO reports a few statistics/parameters differently than AOAC*



# Downloading data from Magruder website



The screenshot shows a web browser window with the URL [www.magruderchecksample.org/prod/excel\\_data.html](http://www.magruderchecksample.org/prod/excel_data.html). The page is titled "Lab Portal" and features a navigation menu on the left and two main content sections on the right.

**Lab Portal**  
[http://www](http://www.magruderchecksample.org)

- Method Codes
- Instruction
- Reports Explained:
  - Overview
  - Quick Reference Guide
  - Analyte Report Cards
- Statistics

**Samples, Reports & Data**

- Current Year
- Past Years
- **Data Mining**
- Control Charts

**Current Year Excel Data**

- 2019 Cumulative Analyte Data Report (xls)
- 2019 Cumulative Analyte Summary Report (xls)
- 2019 Cumulative Method Data Report (xls)
- 2019 Cumulative Method Summary Report (xls)
- 2019 Cumulative Method Precision Report (xls)

**Archived Excel Data**

**2018:**

- 2018 Cumulative Analyte Data Report (xls)
- 2018 Cumulative Analyte Summary Report (xls)
- **2018 Cumulative Method Data Report (xls)**
- 2018 Cumulative Method Summary Report (xls)
- 2018 Cumulative Method Precision Report (xls)

**2017:**

- 2017 Cumulative Analyte Data Report (xls)
- 2017 Cumulative Analyte Summary Report (xls)
- 2017 Cumulative Method Data Report (xls)

Red arrows point from the "Data Mining" link in the left menu to the "2018 Cumulative Method Data Report (xls)" link in the Archived Excel Data section. The "2018 Cumulative Method Data Report (xls)" link is also circled in red.



# P205 Samples – Method Code 041.51

#	Sample #	Sample Name/Grade	# of labs	Analyte P205 value
1	190511	Complex fertilizer / 16-1-0	9	1.22
2	180911	<b>Organic solid</b> / 3-1-3	8	2.73
3	180611	Lawn w/slow N 18-3-6	9	3.11
4	181111	17-6-18 and micros	8	6.64
5	181211	11-11-21 and micros	10	10.69
6	190311	<b>Organic solid</b> /12-12-2.5	10	12.34
7	160711	12-12-12 + Micros	7	12.39
8	190211	14-14-14	10	14.45
9	180211	14-14-14 + micros	9	14.40
10	171211	5-15-30	9	15.12
11	180411	12-24-12	11	25.16
12	170911	<b>MAP+</b> /12-40-0	7	39.37
13	190911	<b>Water soluble</b> /10-45-10	7	45.06
14	180512	<b>TSP</b>	9	45.40
15	171012	<b>TSP</b> / 0-45-0	7	45.72
16	191011	<b>DAP</b> / 18-46-0	11	46.05
17	170111	<b>DAP</b> / 18-46-0	7	46.51
18	190811	<b>MAP</b> / 11-52-0	7	52.11

- **Several samples dating back to 2016**
- **Good range of concentrations**
- **Decent range of matrices**
  - *Could have used a few more liquids, others?*
- **Limited number of labs routinely reporting**
  - *Did not list samples with < 7 labs reporting*



Magruder ID	Sample ID	Lab A	Lab B	Lab C	Lab D	Lab E	Lab F	Lab G	Lab H	Lab I	Lab J	Lab K	Lab L	Lab M	Lab N	Lab O	Lab P	Lab Q	Lab R	Avg	
190511	Complex fertilizer 16-1-0	1,32			1,10	1,17		1,29		1,27	1,31		1,21	1,35	1,16						1,27
		1,40			1,20	1,27		1,29		1,33	1,34		1,24	1,36	1,19						
180911	Organic solid 3-1-3	2,82	2,76		2,70	2,72		2,61			2,84		2,73		2,53		2,39 <sub>a</sub>				2,75
		2,96	2,79		2,70	2,81		2,74			2,92		2,78		2,60		2,83 <sub>a</sub>				
180611	Lawn w/slow N 18-3-6	3,24	3,14		3,20	3,01		3,09		2,38 <sub>a</sub>	3,01	3,24	3,06		3,11						3,15
		3,28	3,18		3,20	3,06		3,12		2,52 <sub>a</sub>	3,08	3,28	3,21		3,18						
181111	17-6-18 and micros		6,90	6,66	6,70	6,76	7,06				6,86		6,76		6,41		6,51 <sub>a</sub>				6,80
			7,02	6,75	6,80	6,87	7,11				6,88		6,80		6,48		7,02 <sub>a</sub>				
181211	11-11-21 and micros	10,88	8,37 <sub>a</sub>	10,60	10,60	10,81	10,89	10,78			11,06	10,92	10,73		9,28 <sub>a</sub>	10,55					10,80
		10,92	8,43 <sub>a</sub>	10,62	10,70	10,82	10,94	10,80			11,08	10,96	10,81		9,47 <sub>a</sub>	10,60					
190311	Organic solid 12-12-2.5		12,60		12,20	12,48		11,85			13,03	11,80	12,78		12,06	12,49	12,51				12,43
			12,70		12,30	12,50		11,96			13,03	12,08	12,82		12,18	12,60	12,67				
160711	12-12-12 + Micros		12,26					12,00			12,21		12,42		12,02		12,67	11,87			12,26
			12,31					12,02			12,23		12,64		12,09		13,01	11,87			
190211	14-14-14		14,50		14,60	14,04	14,05	14,29			14,62	14,07	13,45			14,88	14,23				14,35
			14,90		14,60	14,12	14,12	14,31			14,67	14,40	13,49			14,96	14,64				
180211	14-14-14 + micros	14,38	14,6	14,81	14,40	14,09		14,19			14,61		14,15		12,85 <sub>a</sub>		14,10 <sub>a</sub>	14,02			14,42
		14,41	14,67	15,07	14,60	14,12		14,46			14,85		14,19		13,11 <sub>a</sub>		14,91 <sub>a</sub>	14,02			
171211	5-15-30		15,00	14,95	15,10		14,84	15,23			15,26	14,73	15,14		14,85						15,12
			15,39	15,25	15,60		15,04	15,29			15,40	14,77	15,30		15,00						
180411	12-24-12	26,29	25,69	24,89	24,70	25,03		25,57			24,88		25,46		22,63		25,37			23,73	25,04
		26,42	25,87	25,77	24,70	25,13		25,77			24,91		25,49		22,76		25,99			23,83	
170911	12-40-0		37,51					39,56		37,26	38,52		38,81		39,50		39,40				38,99
			38,82					40,19		39,27	39,05		38,88		39,64		39,46				
190911	Water soluble 10-45-10	45,10	44,70			43,88 <sub>a</sub>		45,28	43,20		45,69		44,52			43,87					44,81
		45,80	45,10			46,16 <sub>a</sub>		45,51	43,60		46,51		44,63			43,88					
180512	TSP		45,44			46,75	45,69	44,75		47,73	45,37	45,01			42,50		45,04				45,59
			46,11			47,24	45,82	45,59		48,14	45,37	45,70			42,55		45,75				
171012	TSP/0-45-0	45,17	46,32					45,61		42,53 <sub>a</sub>	45,55		46,57		44,68		45,36				45,92
		46,24	47,16					45,89		46,51 <sub>a</sub>	46,17		46,68		44,78		46,70				
191011	DAP/ 18-46-0	46,40	45,50		45,60	45,42		44,63	44,00		45,94		45,07		44,45	46,17	45,55				45,64
		46,50	45,70		46,10	45,91		45,36	45,50		46,24		45,38		45,28	46,40	46,88				
170111	DAP/ 18-46-0	46,51		46,23	45,40			45,95					46,40		44,56		46,38				46,03
		46,58		46,52	45,90			46,06					46,64		44,90		46,41				
190811	MAP/ 11-52-0	52,45	52,00		51,90	49,62		52,27			51,69		50,76								51,78
		52,46	53,10		52,10	51,32		52,39			51,97		50,82								

a - outliers

## P2O5 Example

### Good:

- There were 18 different labs reporting some data
- Only 2 labs with a high percentage of outliers
  - Lab I (50%)
  - Lab P (25%)

### Bad:

- Some labs only reported for a few samples
- “Dynamic” data versus static?
- Yellow = gaps
- Impact on experimental error?





# K2O Samples – Method Code 050.51

#	Sample #	Sample Name/ Grade	# of labs	Analyte K2O value
1	170511	Complex Fertilizer / 16-1-0	7	1.73
2	180311	Liquid NOP / 3-1-2	10	3.67
3	180911	Organic solid/ 3-1-3	10	3.73
4	160811	Liquid Organics	8	3.96
5	160211	24-25-4	8	4.13
6	170811	21-0-5	10	5.10
7	180611	Lawn w/slow N / 18-3-6	8	5.84
8	161111	32-0-10	9	10.13
9	180411	12-24-12	15	12.89
10	160711	12-12-12 + Micros	8	12.26
11	190211	14-14-14	9	14.38
12	180211	14-14-14 + micros	11	14.55
13	181111	17-6-18 and micros	10	17.96
14	181211	11-11-21 and micros	10	21.69
15	190411	K ThioS / 0-0-25-17S	10	25.22
16	171211	5-15-30	10	30.49
17	190812	KCl / 0-0-60 Potash	7	61.98
18	180812	KCl / 0-0-60 Potash	10	60.32

- *Several samples dating back to 2016*
- *Good range of concentrations*
- *Good range of matrices*
  - *any critical sample type missing?*
- *Some samples with limited labs reporting*
  - *Did not list samples with < 7 labs reporting*





# P2O5 Precision Results

Sample #	Sample Name/ Grade	# of labs	# outliers removed	ICP, P2O5 mean	s(r)	s(r)^2	s(R)	s(R)^2	r (repeatability)	%RSD(r)	R (reproducibility)	%RSD(R)	HorRat (R)
190511	Complex fertilizer/ 16-1-0	9	0	1.27	0.042	0.0018	0.083	0.0068	0.118	3.32	0.231	6.52	3.75
180911	Organic solid/ 3-1-3	8	1	2.75	0.061	0.0037	0.115	0.0133	0.170	2.20	0.323	4.19	2.71
180611	Lawn w/slow N 18-3-6	9	1	3.15	0.047	0.0022	0.088	0.0078	0.132	1.50	0.247	2.81	1.85
181111	17-6-18 and micros	8	1	6.80	0.058	0.0034	0.193	0.0374	0.163	0.86	0.542	2.84	2.11
181211	11-11-21 and micros	10	2	10.80	0.036	0.0013	0.161	0.0258	0.101	0.33	0.450	1.49	1.18
190311	Organic solid/12-12-2.5	10	0	12.43	0.090	0.0081	0.375	0.1407	0.253	0.73	1.050	3.02	2.45
160711	12-12-12 + Micros	7	0	12.26	0.111	0.0123	0.343	0.1175	0.310	0.90	0.960	2.80	2.26
190211	14-14-14	10	0	14.35	0.151	0.0229	0.427	0.1824	0.424	1.06	1.1958	2.98	2.47
180211	14-14-14 + micros	9	2	14.42	0.117	0.0137	0.317	0.1006	0.328	0.81	0.888	2.20	1.82
171211	5-15-30	9	0	15.12	0.184	0.0337	0.243	0.0592	0.514	1.21	0.681	1.61	1.34
180411	12-24-12	11	0	25.04	0.243	0.0591	1.043	1.0876	0.680	0.97	2.920	4.16	3.75
170911	12-40-0	7	0	38.99	0.679	0.4616	0.813	0.6612	1.902	1.74	2.277	2.09	2.01
190911	Water soluble/10-45-10	7	1	44.81	0.332	0.1104	0.973	0.9459	0.930	0.74	2.723	2.17	2.13
180512	TSP	9	0	45.59	0.378	0.1428	1.492	2.2273	1.058	0.83	4.179	3.27	3.23
171012	TSP/0-45-0	7	1	45.92	0.543	0.2951	0.770	0.5936	1.521	1.18	2.157	1.68	1.66
191011	DAP/ 18-46-0	11	0	45.64	0.523	0.2740	0.707	0.5002	1.466	1.15	1.980	1.55	1.53
170111	DAP/ 18-46-0	7	0	46.03	0.194	0.0375	0.671	0.4509	0.542	0.42	1.880	1.46	1.44
190811	MAP/ 11-52-0	7	0	51.78	0.550	0.3026	0.914	0.8346	1.540	1.06	2.558	1.76	1.77
Averages										1.17		2.70	2.19

- Limited number of outliers removed
- Average HorRat(R) is **2.19**, or about twice as variable as a “typical” AOAC Collaborative Study
- Data is not horrible, but is not great either; on the edge
- IA for P2O5 is about half Horwitz predicted RSD
  - Some concerns with full regulatory use at this time?
- On average, reproducibility is 2.31 x repeatability, with ~ 2 expected



# K2O Precision Results

Sample #	Sample Name/ Grade	# of labs	# outliers removed	ICP, K2O mean	sr	sr^2	sR	sR^2	r (repeatability)	%RSD(r)	R (reproducibility)	%RSD(R)	HorRat (R)
170511	Complex Fertilizer / 16-1-0	7	0	1.76	0.080	0.0063	0.087	0.0075	0.223	4.53	0.243	4.94	2.98
180311	Liquid NOP / 3-1-2	10	0	3.84	0.055	0.0030	0.290	0.0839	0.153	1.42	0.811	7.55	5.13
180911	Organic solid / 3-1-3	10	1	3.78	0.054	0.0029	0.160	0.0257	0.150	1.42	0.449	4.24	2.87
160811	Liquid Organics	8	0	4.02	0.045	0.0020	0.168	0.0283	0.125	1.11	0.471	4.18	2.86
160211	24-25-4	8	0	4.25	0.084	0.0071	0.221	0.0489	0.235	1.98	0.619	5.20	3.59
170811	21-0-5	10	1	5.10	0.117	0.0138	0.173	0.0300	0.329	2.30	0.485	3.39	2.41
180611	Lawn w/slow N / 18-3-6	8	0	5.90	0.137	0.0188	0.317	0.1005	0.384	2.32	0.888	5.37	3.89
161111	32-0-10	9	0	10.10	0.130	0.0170	0.342	0.1167	0.365	1.29	0.957	3.38	2.66
180411	12-24-12	15	0	13.16	0.269	0.0723	0.589	0.3464	0.753	2.04	1.648	4.47	3.66
160711	12-12-12 + Micros	8	0	12.43	0.124	0.0154	0.249	0.0619	0.347	1.00	0.697	2.00	1.62
190211	14-14-14	9	1	14.49	0.145	0.0210	0.468	0.2192	0.406	1.00	1.311	3.23	2.68
180211	14-14-14 + micros	11	1	14.45	0.240	0.0575	0.470	0.2209	0.672	1.66	1.316	3.25	2.70
181111	17-6-18 and micros	10	1	17.66	0.438	0.1921	0.752	0.5654	1.227	2.48	2.105	4.26	3.64
181211	11-11-21 and micros	10	1	21.57	0.269	0.0722	0.955	0.9117	0.752	1.25	2.673	4.43	3.90
190411	K ThioS / 0-0-25	10	1	25.30	0.295	0.0870	0.421	0.1773	0.826	1.17	1.179	1.66	1.50
171211	5-15-30	10	0	30.84	0.302	0.0912	0.823	0.6780	0.845	0.98	2.306	2.67	2.48
190812	KCl / 0-0-60 Potash	7	1	62.03	0.301	0.0906	1.285	1.6501	0.843	0.49	3.597	2.07	2.14
180812	KCl / 0-0-60 Potash	10	1	60.65	0.725	0.5262	1.076	1.1571	2.031	1.20	3.012	1.77	1.83
Averages										1.65		3.78	2.92

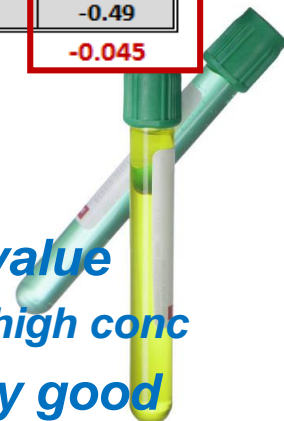
- Limited number of outliers removed
- Average HorRat(R) is **2.92**, or about three times as variable as a “typical” AOAC Collaborative Study
- HorRat(R) above AOAC’s suggested range, so explanation warranted
- IA for K2O is close to Horwitz predicted RSD
  - Concerns with full regulatory use at this time?
- On average, reproducibility is 2.29 x repeatability, with ~ 2 expected



# P2O5 “Accuracy” (Trueness) & Bias

Sample #	Sample Name / Grade	# of labs	# outliers removed	ICP, P2O5 mean	Consensus P2O5 value	Consensus # of Results	% Recovery Consensus	Analyte SD	Z score
190511	Complex fertilizer/ 16-1-0	9	0	1.27	1.22	21	104.2	0.1322	0.38
180911	Organic solid/ 3-1-3	8	1	2.75	2.73	80	100.8	0.1910	0.12
180611	Lawn w/slow N 18-3-6	9	1	3.15	3.11	77	101.3	0.1115	0.37
181111	17-6-18 and micros	8	1	6.80	6.64	76	102.4	0.3332	0.48
181211	11-11-21 and micros	10	2	10.80	10.69	80	101.1	0.3258	0.35
190311	Organic solid/12-12-2.5	10	0	12.43	12.34	91	100.7	0.3406	0.27
160711	12-12-12 + Micros	7	0	12.26	12.39	79	98.9	0.3135	-0.42
190211	14-14-14	10	0	14.35	14.45	82	99.3	0.3544	-0.29
180211	14-14-14 + micros	9	2	14.42	14.40	97	100.2	0.3396	0.07
171211	5-15-30	9	0	15.12	15.12	85	100.0	0.3013	0.00
180411	12-24-12	11	0	25.04	25.16	87	99.5	0.7238	-0.17
170911	12-40-0	7	0	38.99	39.37	92	99.0	0.8280	-0.46
190911	Water soluble/10-45-10	7	1	44.81	45.06	88	99.5	0.7172	-0.34
180512	TSP	9	0	45.59	45.40	88	100.4	0.5836	0.32
171012	TSP/0-45-0	7	1	45.92	45.72	90	100.4	0.7807	0.26
191011	DAP/ 18-46-0	11	0	45.64	46.05	80	99.1	0.6852	-0.60
170111	DAP/ 18-46-0	7	0	46.03	46.51	84	99.0	0.7268	-0.66
190811	MAP/ 11-52-0	7	0	51.78	52.11	84	99.4	0.6851	-0.49
<b>Average</b>							<b>100.3</b>		<b>-0.045</b>

- Consensus P2O5 value = Analyte mean from *all* methods
- Analyte SD = standard deviation for all method data
- Average recovery was very good @ 100.3% of consensus value
  - Slightly higher recovery at low conc & slightly lower recovery at high conc
- ICP-P z-score relative to consensus mean and SD were very good
- Overall, the data accuracy is better than the precision



# K2O “Accuracy” (Trueness) & Bias

Sample #	Sample Name / Grade	# of labs	# outliers removed	ICP, K2O mean	Consensus K2O value	Consensus # of Results	% Recovery Consensus	Analyte SD	Z score
170511	Complex Fertilizer / 16-1-0	7	0	1.76	1.73	21	101.74	0.082	0.37
180311	Liquid NOP / 3-1-2	10	0	3.84	3.67	80	104.54	0.255	0.65
180911	Organic solid / 3-1-3	10	1	3.78	3.73	77	101.38	0.348	0.15
160811	Liquid Organics	8	0	4.02	3.96	76	101.52	0.226	0.27
160211	24-25-4	8	0	4.25	4.13	80	102.89	0.261	0.46
170811	21-0-5	10	1	5.10	5.10	91	100.09	0.188	0.03
180611	Lawn w/slow N / 18-3-6	8	0	5.90	5.84	79	101.10	0.303	0.21
161111	32-0-10	9	0	10.10	10.13	82	99.69	0.329	-0.10
180411	12-24-12	15	0	13.16	12.89	97	102.07	0.562	0.48
160711	12-12-12 + Micros	8	0	12.43	12.26	85	101.35	0.370	0.45
190211	14-14-14	9	1	14.49	14.38	87	100.73	0.451	0.23
180211	14-14-14 + micros	11	1	14.45	14.55	92	99.29	0.531	-0.19
181111	17-6-18 and micros	10	1	17.66	17.96	88	98.30	0.453	-0.67
181211	11-11-21 and micros	10	1	21.57	21.69	88	99.46	0.756	-0.16
190411	K ThioS / 0-0-25	10	1	25.30	25.22	90	100.33	0.496	0.17
171211	5-15-30	10	0	30.84	30.49	80	101.16	0.730	0.48
190812	KCl / 0-0-60 Potash	7	1	62.03	61.98	84	100.07	1.65	0.03
180812	KCl / 0-0-60 Potash	10	1	60.65	60.32	84	100.55	0.99	0.34

Average 100.90

0.177

- Consensus K2O value = Analyte mean from **all** methods
- Analyte SD = standard deviation from all method data
- Average recovery was good @ 100.9% of consensus values
  - Average nearly 1% higher recoveries across conc range
- ICP-K z-score relative to consensus mean and SD were very good
- Overall, the data accuracy is better than the precision



# ISO: %r and %R for ICP-P

Sample #	Sample Name / Grade	# of labs	# outliers removed	ICP, P205 mean	sr	sr <sup>2</sup>	sR	sR <sup>2</sup>	r (repeatability)	R (reproducibility)	r%	R%
190511	Complex fertilizer/ 16-1-0	9	0	1.267	0.0421	0.0018	0.0826	0.0068	0.118	0.231	9.31	18.25
180911	Organic solid/ 3-1-3	8	1	2.750	0.0606	0.0037	0.1153	0.0133	0.170	0.323	6.17	11.74
180611	Lawn w/slow N 18-3-6	9	1	3.149	0.0472	0.0022	0.0884	0.0078	0.132	0.247	4.20	7.86
181111	17-6-18 and micros	8	1	6.801	0.0582	0.0034	0.1935	0.0374	0.163	0.542	2.40	7.97
181211	11-11-21 and micros	10	2	10.804	0.0361	0.0013	0.1606	0.0258	0.101	0.450	0.94	4.16
190311	Organic solid/12-12-2.5	10	0	12.432	0.0902	0.0081	0.3751	0.1407	0.253	1.050	2.03	8.45
160711	12-12-12 + Micros	7	0	12.258	0.1108	0.0123	0.3427	0.1175	0.310	0.960	2.53	7.83
190211	14-14-14	10	0	14.346	0.1515	0.0229	0.4271	0.1824	0.424	1.1958	2.96	8.33
180211	14-14-14 + micros	9	2	14.424	0.1170	0.0137	0.3172	0.1006	0.328	0.888	2.27	6.16
171211	5-15-30	9	0	15.119	0.1836	0.0337	0.2434	0.0592	0.514	0.681	3.40	4.51
180411	12-24-12	11	0	25.040	0.2430	0.0591	1.0429	1.0876	0.680	2.920	2.72	11.66
170911	12-40-0	7	0	38.991	0.6794	0.4616	0.8131	0.6612	1.902	2.277	4.88	5.84
190911	Water soluble/10-45-10	7	1	44.814	0.3323	0.1104	0.9726	0.9459	0.930	2.723	2.08	6.08
180512	TSP	9	0	45.586	0.3779	0.1428	1.4924	2.2273	1.058	4.179	2.32	9.17
171012	TSP/0-45-0	7	1	45.920	0.5432	0.2951	0.7705	0.5936	1.521	2.157	3.31	4.70
191011	DAP/ 18-46-0	11	0	45.635	0.5235	0.2740	0.7073	0.5002	1.466	1.980	3.21	4.34
170111	DAP/ 18-46-0	7	0	46.031	0.1937	0.0375	0.6715	0.4509	0.542	1.880	1.18	4.08
190811	MAP/ 11-52-0	7	0	51.775	0.5501	0.3026	0.9136	0.8346	1.540	2.558	2.97	4.94

- r and R relative to the mean, but not sr and sR which is %RSD
  - %r < 2.5 and %R < 10 preferred
  - %r > 2.5 and %R > 10 warning
  - %r > 5.0 and %R > 20 undesirable
- Several warning values
- Couple undesirable, but low conc and an organic (more variable)
- Not sure how ISO TC-134 will respond





# ISO: %r and %R for ICP-K

Sample #	Sample Name / Grade	# of labs	# outliers removed	ICP, K2O mean	sr	sr <sup>2</sup>	sR	sR <sup>2</sup>	r (repeatability)	R (reproducibility)	r%	R%
170511	Complex Fertilizer/ 16-1-0	7	0	1.757	0.0795	0.0063	0.087	0.0075	0.223	0.243	12.68	13.83
180311	Liquid NOP/ 3-1-2	10	0	3.835	0.0545	0.0030	0.290	0.0839	0.153	0.811	3.98	21.15
180911	Organic solid/ 3-1-3	10	1	3.783	0.0537	0.0029	0.160	0.0257	0.150	0.449	3.97	11.87
160811	Liquid Organics	8	0	4.023	0.0448	0.0020	0.168	0.0283	0.125	0.471	3.12	11.71
160211	24-25-4	8	0	4.251	0.0841	0.0071	0.221	0.0489	0.235	0.619	5.54	14.57
170811	21-0-5	10	1	5.101	0.1174	0.0138	0.173	0.0300	0.329	0.485	6.44	9.50
180611	Lawn w/slow N/ 18-3-6	8	0	5.903	0.1371	0.0188	0.317	0.1005	0.384	0.888	6.50	15.04
161111	32-0-10	9	0	10.095	0.1304	0.0170	0.342	0.1167	0.365	0.9566	3.62	9.48
180411	12-24-12	15	0	13.159	0.2689	0.0723	0.589	0.3464	0.753	1.648	5.72	12.52
160711	12-12-12 + Micros	8	0	12.426	0.1239	0.0154	0.249	0.0619	0.347	0.697	2.79	5.61
190211	14-14-14	9	1	14.489	0.1450	0.0210	0.468	0.2192	0.406	1.311	2.80	9.05
180211	14-14-14 + micros	11	1	14.447	0.2399	0.0575	0.470	0.2209	0.672	1.316	4.65	9.11
181111	17-6-18 and micros	10	1	17.656	0.4383	0.1921	0.752	0.5654	1.227	2.105	6.95	11.92
181211	11-11-21 and micros	10	1	21.569	0.2687	0.0722	0.955	0.9117	0.752	2.673	3.49	12.39
190411	K ThioS/ 0-0-25-17S	10	1	25.299	0.2949	0.0870	0.421	0.1773	0.826	1.179	3.26	4.66
171211	5-15-30	10	0	30.839	0.3020	0.0912	0.823	0.6780	0.845	2.306	2.74	7.48
190812	KCL/0-0-60 Potash	7	1	62.028	0.3010	0.0906	1.285	1.6501	0.843	3.597	1.36	5.80
180812	KCL/0-0-60 Potash	10	1	60.653	0.7254	0.5262	1.076	1.1571	2.031	3.012	3.35	4.97

- Many **warning** values
- Several **undesirable** values
- Most of the undesirable values are repeatability
  - Variation within lab is more objectionable than among labs
- Not sure how ISO TC-134 will respond, but will likely be concern



# Thoughts

- *Using Magruder data and available tools seems viable*
- *Advantages & disadvantages given in different presentation*
- *Not sure what impact “dynamic” dataset has on statistics?*
  - *Different combination of labs for nearly every sample*
  - *Data collected over time (possible change in instruments, analysts, standards, etc.)*
  - *May better reflect “real world”*
- *Method still in relative infancy stage*
- *Number of method users is currently increasing over time*
- *LOTS of areas for labs to deviate as method is unconventional*
- *Data on edge of AOAC acceptance, but they may find added value in the collaborative process and be more accepting?*
  - *May be acceptable for First Action*
  - *Will need to improve before Final Action*
- *ISO TC-134 is interested in method, but data below average*
  - *Industry may be rightfully concern about regulatory use of method*





- ***Method better suited for screening than imposing violations at this time***
  - ***Variability exceeding IA's***
  - ***Could be passing some failing sample?***
    - ***rerun samples near the IA?***
  - ***Improvement is necessary***
    - ***or else expand IAs or "surplus" method?***
- ***Inability to work directly with "collaborators" presents limitations for improvement***
- ***How to communicate with anonymous labs?***
  - ***We know which labs are participating***
  - ***How could we inform them or program participants of concerns?***
- ***Is more information through Magruder website possible.***
  - ***List SOP and/or method improvements?***
  - ***Provide some watch areas?***
  - ***Give a contact person(s) for technical support?***
  - ***Could list by method as may more than one study in place?***
  - ***Could apply process to old methods as well?***



# Summary / Guidance

- *For P and K, able to collect sufficient data over a few year's time period*
- *Downloading data from Magruder website was quick and easy*
- *Spreadsheets are straightforward and worked adequately*
- *Method complexity/challenges are above average*
- *Process (currently) limits guidance by a Study Director*
- *Data is below average relative to other AOAC and ISO methods*
  - *Should authors use data for AOAC method collaboration/publication?*
  - *Should authors use data for ISO ring study/publication?*
  - *Is a traditional collaborative/ring study recommended instead?*
  - *At what level should method be used?*
    - *Screening?*
    - *Compliance?*
  - *How to work with method users to improve performance?*
- *Can relatively quickly/easily re-evaluate data after adjustments made*
- *Any thoughts or suggestions ?*

