Newsletter for November 2014

Magruder Check Sample Program Review from 2001 to 2014

Products in Survey: DAP, MAP and Potash (50-62%)

Best Laboratories in the Magruder Check Sample Program for Total Nitrogen, Total Phosphate as P_2O_5, Available Phosphate and Soluble Potash.

How many laboratories consistently analyze DAP, MAP and Potash within 1 standard deviation between the periods of 2001 to 2014 for total nitrogen, total phosphate, available phosphate and potash? The table below shows the number of times a laboratory was within 1 standard deviation out of 13 samples over the thirteen years (13*) Note: During this period some labs have been added and some labs have been dropped, but looking for consistent laboratories. There are very few laboratories consistently within 1 standard deviation among the estimated 100 – 110 member laboratories.*

Table 1 – Number and Percentage of Laboratories within 1 Standard Deviation for TN, Total Phosphate as P_2O_5, AP and K_2O from 2001 to 2014 (A total of 13 samples)

No. of Times Within 1 STD	Total Nitrogen, No. & %	Total Phosphate, No. & %	Available Phosphate, No. & %	Potash, No. & %
13/13	0, 0.00%	0, 0.00%	0, 0.00%	1, 1.06%
12/13	4, 4.17%	3, 3.80%	2, 2.99%	3, 3.19%
11/13	7, 7.29%	1, 1.27%	4, 5.97%	2, 2.13%
10/13	4, 4.17%	4, 5.06%	2, 2.99%	3, 3.19%
9/13	8, 8.33%	1, 1.27%	3,4.48%	4,4.26%
8/13	2, 2.08%	2,2.53%	0, 0.00%	3, 3.19%
7/13	3, 3.13%	1, 1.27%	5,7.46%	9,9.57%
6/13	7, 7.29%	6,7.59%	3, 4.48%	10,10.64%
5/13	12,12.50%	8,10.13%	6,8.96%	12,12.77%
4/13	15,15.63%	9,11.39%	4, 5.97%	14,14.89%
3/13	6, 6.25%	14,17.72%	16,23.88%	12,12.77%
2/13	14,14.58%	18,22.78%	10,14.93%	14,14.89%
1/13	14,14.58%	12,15.19%	12,17.91%	7,7.45%
No. of Samples	13	13	13	13
No. of Analysis	13	13	13	13
% of Labs > 6/13	36.4%	22.8%	28.3%	26.6%
% of Labs < 6/13	63.6%	77.2%	71.7%	73.4%
Total No. of Labs	96	79	67	94

Samples used in the study: 200110B, 200306AB, 200310B, 200101, 200501, 200512B, 200711, 200804B, 201001AB, 201009, 201103AB, 201203, 201205B, 201207, 201209A, 201307AB, 201310AB, 201311AB, 201402AB

Table 2 - How does the bottom quartile of laboratories perform within one standard deviation in the Magruder Program within one (1) standard deviation from 2001 to 2014?

No. of Labs	Type of Lab	Times 1 STD	No. of Labs	Type of Lab	Times 1 STD
1	Commercial	1/52	3	Foreign	1/52
1	Industry	1/52	20*	Unknown Labs	1/24
2	Commercial	2/52	1 **	Foreign	2/52
22*	Unknown Labs	2/24	1**	Commercial	3/52
1 **	Foreign	4/52	1**	State	6/39

* Joined before 2007 with no record kept ** Dropped from Program

Which type of laboratory (commercial, foreign, industry and state) is at the top and consistently within 1 standard deviation greater than 10 out of 13 samples during the period 2001 to 2014 for total nitrogen, total phosphate, available phosphate and potash?

Table 3 – Number of Laboratories within one (1) standard deviation greater than 10 out of 13 samples for TN, TP, AP and K_2O from 2001 to 2014 (A total of 13 samples)

Type of Laboratory	Total Nitrogen	Total Phosphate	Available Phosphate	Potash
Industry	1	3	1	1
Commercial	0	4	0	1
State	11	2	7	4
Foreign	0	1	0	3

Which type of laboratory (commercial, foreign, industry and state) is consistently at top and within 1 standard deviation for total nitrogen, total phosphate, available phosphate and potash? Thirteen samples with 52 chemical analyses between 2001 and 2014?

Table 4 – Type and Number of Laboratories with the highest percentage within one (1) standard deviation for TN, TP_2O_5, AP and K_2O from 2001 to 2014 (A total of 13 samples with 52 total analyses)

Laboratory Type	Number of Labs	Percentage of Time Within 1 Standard Deviation
Industry	1	76.9%, or 40/52
State	1	69.2%, or 33/52
State	1	61.5%, or 32/52
State	1	57.6%, or 30/52
State	1	46.2%, or 24/52
State, Commercial & Foreign	1 Each	44.2% or 23/52
Commercial and State	2 Each	42.3% or 22/52

*Note: All Lab types listed above are different Labs – corresponding Lab No.'s are confidential

Which type of laboratory (commercial, foreign, industry and state) is consistently at the top and within 1 standard deviation for total nitrogen, available phosphate and potash? Thirteen samples with 39 chemical analyses between 2001 and 2014. Note: Most State Labs do not analyze total phosphate.

Table 5 - Type and Number of Laboratories with the highest percentage within one (1) standard deviation for TN, AP and K_2O from 2001 to 2014 (A total of 13 samples with 39 total analyses)

Laboratory Type	Number of Labs	Percentage of Time Within 1 Standard Deviation
State	1	87.1%, or 34/39
State	1	84.6%, or 33/39
State	1	82.1%, or 32/39
Industry	1	76.9%, or 30/39
State	1	61.5%, or 24/39
State	1	56.4%, or 22/39
State	1	51.3%, or 20/39
State, Industry, Foreign	1 Each	46.2%, or 18/39

Table 6 – Average index for the top eleven laboratories in the Check Program between 2001 - 2014 for total nitrogen, available phosphate and potash

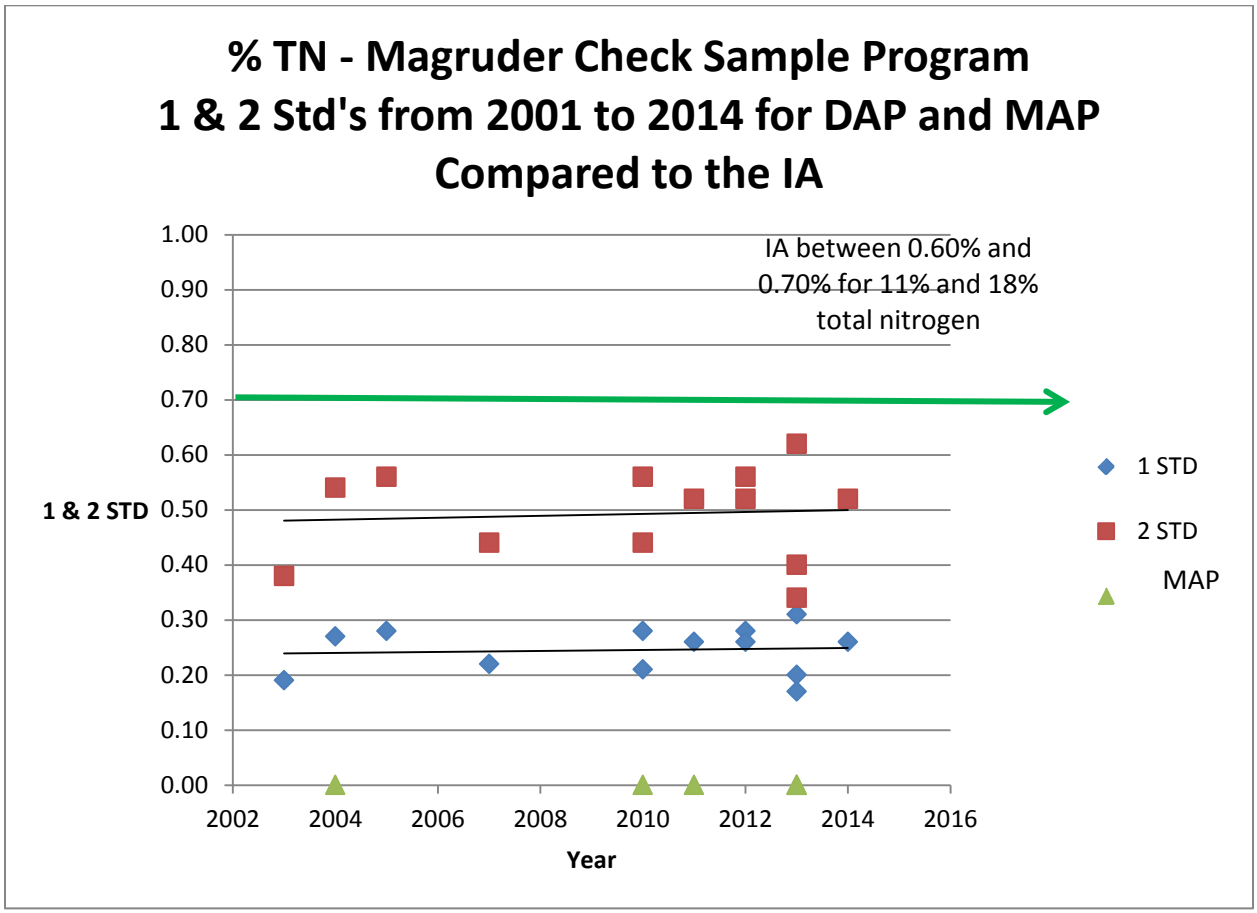
Type Lab	Industry	State	Comm.	State	State	State
Average Index	0.33	0.49	0.52	0.54	0.54	0.55
Type of Lab	State	State	State	State	State	
Average Index	0.56	0.59	0.62	0.94	1.82	

Total Nitrogen Results:

The total nitrogen analyses for DAP and MAP on all thirteen (13) samples from 2001 to 2014 are all within the Investigational Allowance of AAPFCO of 0.60% and 0.70% for 11.0% and 18.0% nitrogen, respectively. Note: Most labs (80%) are using combustion analysis. One (1) standard deviation and two (2) standard deviations for DAP and MAP are 0.26, 0.52 and 0.21, 0.42, respectively.

See graph 1 below showing all thirteen samples of DAP and MAP below the IA of AAPFCO

Graph 1 – One (1) & Two (2) Standard Deviations for Total Nitrogen Compared to AAPFCO's IA in the Magruder Check Sample Program from 2001 to 2014

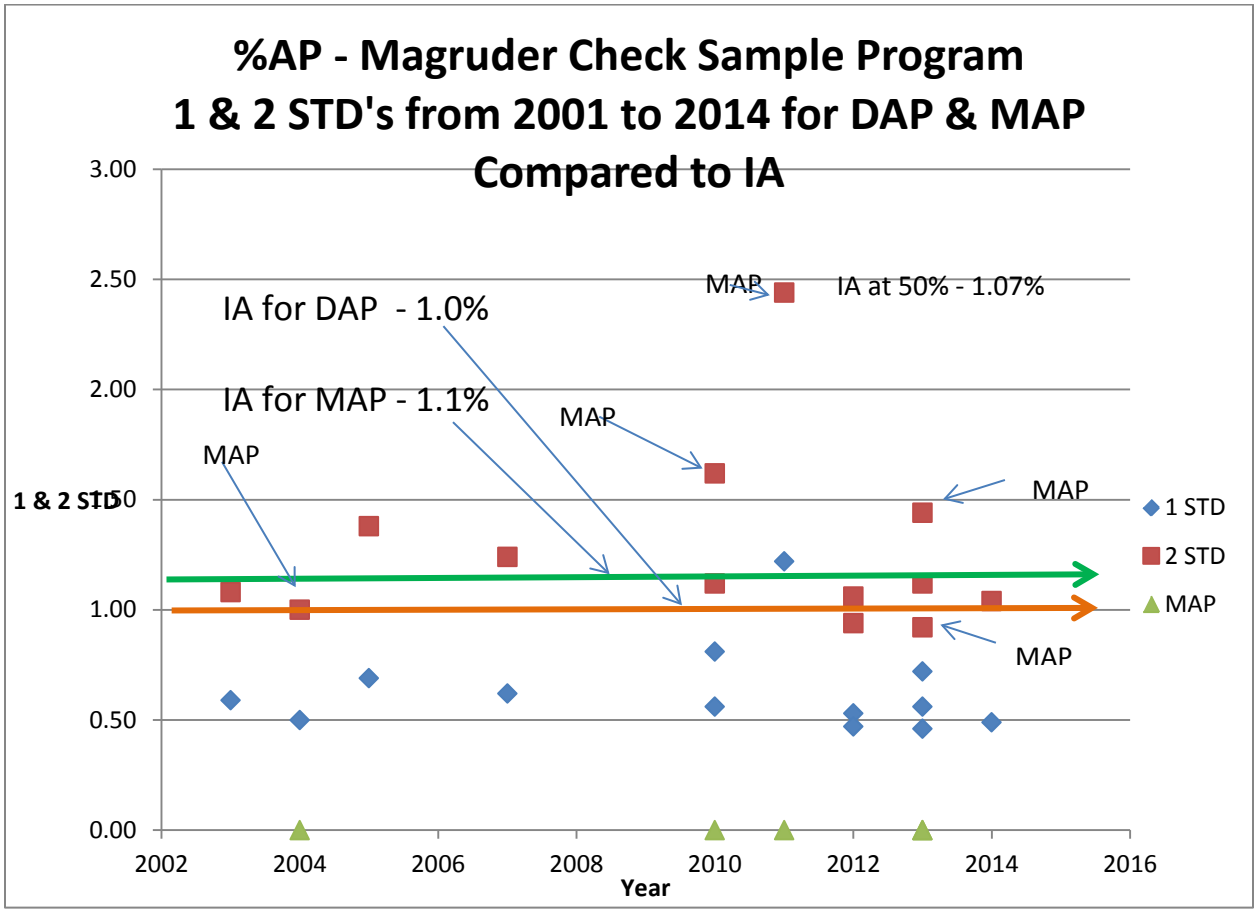


Available Phosphate Results:

Available Phosphate found 7/8 samples of DAP and 3/5 samples of MAP two (2) standard deviations were over the Investigation Allowance of AAPFCO. The IA's for DAP and MAP are 1.0 and 1.1% for 46.0% and 52.0%, respectively. The average standard deviation for DAP on all samples between 2001 and 2014 was 0.56% (2 STDs 1.12%). The average standard deviation for MAP on all samples between 2001 and 2014 was 0.74% (2 STDs 1.48%).

Note: The method consistently with higher standard deviations and overall lower average AP results was ICP. The one standard deviation for ICP for AP analysis was 0.86% or 1.72% (2 standard deviations). The best method is the Gravimetric Quinolinium Molybdophosphate Method (AOAC 2.3.03 or 962.02). One standard deviation for gravimetric method was 0.40% with 2 standard deviations at 0.80%.

Graph 2 - One (1) & Two (2) Standard Deviations for Available Phosphate (AP) Compared to AAPFCO's IA in the Magruder Check Sample Program from 2001 to 2014

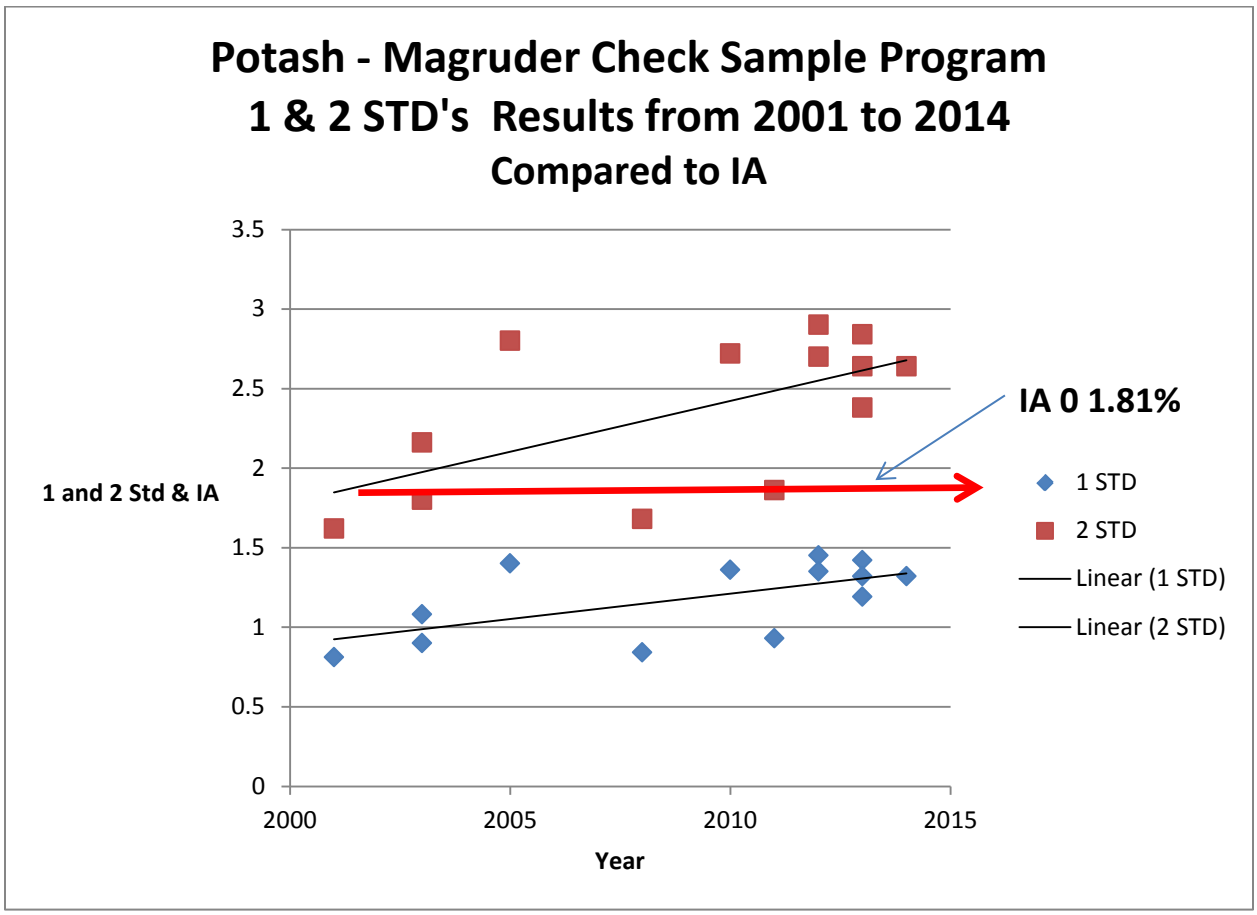


Potash Results:

For the thirteen (13) potash samples from 2001 to 2014, 11/13 times were found to be above the AAPFCO IA of 1.81%. The average one standard deviation of all samples for potash (50-62%) was 1.18% (2 STDs 2.36%).

Note: The two highest standard deviations came from ICP and AA. One standard deviation for ICP and AA was 1.19 and 1.45% respectively. Standard deviation (2 STD) was 2.38 and 2.90%, respectively. The best method for analyzing potash at 60 to 62% is STPB (Sodium Tetraphenylboron Method). The average 1 standard deviation for STPB was 0.60% with 2 standard deviations at 1.20%.

Graph 3 - One (1) & Two (2) Standard Deviations for Potash (K_2O) Compared to AAPFCO's IA in the Magruder Check Sample Program from 2001 to 2014



Recommendations to improve performance by laboratories to be consistently within one standard deviation and below the AAPFCO's Investigational Allowance

1. ICP method (unofficial and not approved by AOAC) has numerous problems for phosphate and potash

a. Use Sc/Be for internal standard for all types of fertilizer samples
b. Use Cs or Li for ionization standard for all types of fertilizer samples
c. Do not use Y as the internal standard – DAP and MAP contain Y as does most mixed fertilizers
d. Standards for phosphate should use NIST 194a or equivalent
    i. *Compare any other manufacturer of pure MAP to NIST 194a before use*
    ii. Analyze and compare at least six times and take average
    iii. Samples are to be dried at 110°C for 2 hours and stored in a desiccator with drying agent.
e. When using Potassium Phosphate with no organic present (no ammonium citrate and EDTA) as the primary standard found the correct value using a and b conditions above/ and no conditions were found when using Yttrium (Y) with the correct value - all the values found when using Y were low compared to the standard value.
f. When using MAP with organics present (ammonium citrate and EDTA) as the primary standard the correct values were found when the conditions were meet as in a and b above for DAP, MAP and MicroEssentials. All other conditions including using potassium phosphate found low values for all high concentrate products for available phosphate.
g. For potash samples use a pure KCl sample from NIST 999b with a 99.977% purity
    i. Compare any other manufacturer of pure KCl to SRM 999b before use
    ii. Analyze and compare at least six times and take average
    iii. Dry sample for 4 hours at 500°C in a Pt or fused silica crucible before use and store in a desiccator with drying agent
h. Organics in the plasma is a concern and the best solution will be to remove them before analyzing with the ICP.

2. P recoveries using ICP sometimes improve with higher power settings, diluting the citrate matrix, and/or slowing the pump speed down slightly to reduce the amount of citrate and phosphate loading of the plasma. This aspect with different settings needs more study as a possible way to remove the interference from the organic matrix..

3. Work out the problems with the ICP and re-write the procedure. Labs not following the procedure should not be allowed to participate in the collaboration of the official method.

4. Previous Magruder standards of DAP, MAP and Potash should be compared to the unknowns for the future samples and compared to the pure MAP and KCl. You can purchase additional samples from Magruder at a reasonable price.

5. Use good laboratory practices for cleaning glassware and certify the volume of the flask being used. Long periods of time (2 months) digesting in the sample flask can distort or etch the flask and change the mark for dilution.

6. In the calibration curve for ICP, AA and Colorimetric analysis five (5) standards should be used to cover the sample range.
    a. The sample range **should not** be from 0 to 62% for potash or 0 to 52% for P_2O_5. The range should be a linear range covering a smaller range such as 0 to 10% or in the case of P_2O_5 curve for colorimetric it could be 17 to 27 % (zero is 17%) or 680 to 1080 ppm. The ICP P_2O_5 should be from 800 to 1120 ppm for DAP or MAP prepared from NIST 194a or equivalent MAP.
    b. Lower curve standards like 1 to 10 ppm for ICP would not be recommended. The dilution would be too great and error would be significant at lower concentration on high grade DAP, MAP or Potash.
    c. In the setup of standards and samples, you should have several other known standards place throughout the analytical run. Duplicates of the samples and standards should be used occasionally. Standards curve should be used in every analytical run and do not assume the curve does not change between analytical runs. One example: If the temperature changes during a colorimetric run the curve for P_2O_5 will change with the temperature change. ICP needs to maintain stable temperature during the run.
    d. Two standards only for a P_2O_5 or any other parameter run (e.g. 0 and 30%) should never be used. With two standards and one being at zero the slope of the curve could change up or down causing high or low results.
    e. Preparation of all type of standards for P_2O_5 and K_2O should be made fresh every two weeks.

7. There are labs in the Magruder program consistently high or low results with each check sample during the period of investigation (2001 to 2014). They show no improvement over time. Many Labs are consistently higher than the theoretical value for 60-62% potash (as many as 12 labs above theoretical of 63.15% on samples 2005-12B, 2013-10B and 2014-02B. Laboratories which are consistently analyzing erratic results should be noted by the statistician and maybe a note on their report card should be sent to the laboratory for an explanation from them, including standards being used, written procedure on method being used, etc. If the statistician needs help in understanding the method being used they can forward to someone to look over without names or laboratory number. Maybe there is something obvious and recommendations from the reviewer can be sent to statistician and then forwarded to the lab in question.

8. Final recommendations - if the 2 standard deviations continue to stay at current levels or above compared to the AAPFCO's IA for DAP at 1.0%, MAP at 1.1% and 1.81% for Potash with no improvement:
    a. Move the IA for DAP and MAP from 1.0 to 1.1 and 1.1 to 1.5% for AP
    b. Move the IA for 60-62% K_2O from 1.81 to 2.40%
    c. Keep the IA for nitrogen the same for 11 and 18% at 0.60 and 0.70%.
    d. Note: AFPC Check Sample Program between 2010 to 2014 with 45 samples of DAP, MAP and MicroEssentials found the following standard deviations:

i. Indirect available phosphate average one (1) standard deviation was 0.27% and 0.74% for direct available phosphate for all samples. A three to one ratio.
ii. DAP & MicroEssentials found the indirect available phosphate 1 STD to be 0.28% and 0.67% for direct available phosphate.
iii. MAP found the indirect available phosphate 1 STD to be 0.28% and 0.88% for direct available phosphate.
iv. Based on the AFPC the recommendations changes to the IA would be 1.34% for DAP & MicroEssentials and 1.76% IA for MAP. (slightly higher than Magruder)
v. Indirect AP Methods are used by Industrial and Commercial Laboratories
vi. Direct AP Methods are used by State Laboratories
vii. Optional: Based on a low citrate insoluble for these products (DAP, MAP, MicroEssentials and Blends) a total phosphate is recommended for States to verify the guarantee which will save considerable time in analysis. (How much time will be saved – a total vs. available analysis could save 3-4 hours). The wide range of standard deviations of 0.67% to 0.88% for these products (DAP, MAP and MicroEssentials) with the citrate insoluble portion would not be found in the analysis. If a product is found below the IA of 1.0 to 1.1% or a new IA an official AOAC method should be used to verify the analysis.
    a. Analyzing totals on ICP will improve
    b. Save time in analysis of products
    c. Reduce chemical supplies
    d. Save cost of analyzing samples

Table 7 – Comparing Two Different Labs in the Magruder Program from 2001 to 2014

	TN	AP	Potash	TN	AP	Potash
Avg. Index Score 13 yrs.	0.32	0.33	0.31	1.10	1.26	1.12
1 STD of method (13 yr. avg.)	0.23	0.67	1.15	0.23	0.67	1.15
1 STD x Avg. Index Score = (difference from average for Laboratory)	0.07	0.22	0.36	0.26	0.90	1.18
IA (Investigation Allowance)*	0.65	1.05	1.79	0.65	1.05	1.79
LAB Number	X	X	X	Y	Y	Y
Diff. from Average/ IA	0.11	0.21	0.20	0.24	0.86	0.66
Diff. from Average / IA/2	0.21	0.42	0.40	0.47	1.71	1.31

*IA's were calculated from 11 & 18% TN (0.60 + 0.70)/2, 46 & 52% AP (1.00 +1.10)/2 and 60 -62 % Potash (1.78 + 1.80)/2

Difference from Average / IA / 2 = ESIPP Ratio (Excellent, Satisfactory, Improvement, Poor Performance)

< 1 = good score or <0.5 Excellent and >0.5 <1 good

>1 <2 = OK score or Approaching IA and needs improvement

>2 = outside or IA or needs major improvement

What does all this data tell us about each Laboratory? Next Newsletter will try to explain the meaning of all this data – and how to improve your index and standard deviations.