Magruder Newsletter October 2013

Continued dialog with Laboratories in the Magruder Check Sample Program

1. Comparing two standard materials for calibration of phosphate using the Technicon® (AOAC 958.01 or AFPC *3C* - (colorimetric method) - Two different standards (MAP and KH_2PO_4) compared for six different standards for the calibration curve for phosphate analysis. In this table the MAP is compared to the Potassium Hydrogen Phosphate showing a low bias for the Potassium Phosphate for LQCRM 11-52-0. Rock QA and DAP 2006-07. The MAP standard shows a high bias for MAP/S 2012-07 and Check Rock 22.

Sample	Certified Value	MAP Calibrants	KH_2HPO_4 Calibrants	MAP range Calibrants	KH_2HPO_4 Range Calibrants
LQCRM 11-52-0	52.78	52.83	52.35	0.05	-0.43
	52.78	52.67	52.29	-0.11	-0.49
	52.78	52.81	52.41	0.03	-0.37
std(reproducibility)	0.00	0.09	0.06		
MAP/S 2012-07	40.97	41.27	40.97	0.30	0.00
	40.97	41.35	41.05	0.38	0.08
	40.97	41.29	40.99	0.32	0.02
std(reproducibility)	0.00	0.04	0.04		
DAP 2006-07	45.66	45.69	45.30	0.03	-0.36
	45.66	45.67	45.31	0.01	-0.35
	45.66	45.61	45.24	-0.05	-0.42
std(reproducibility)	0.00	0.04	0.04		
Check 22 Rock Std.	33.06	33.26	33.01	0.20	-0.05
Check 22 Rock Std.	33.06	33.27	33.02	0.21	-0.04
	33.06	33.21	32.94	0.15	-0.12
std(reproducibility)	0.00	0.03	0.04		
Rock QA	28.88	28.74	28.46	-0.14	-0.42
	28.88	28.72	28.49	-0.16	-0.39
	28.88	28.79	28.60	-0.09	-0.28
std(reproducibility)	0.00	0.04	0.07		

Note from James Bartos*: "The potassium dihydrogen phosphate vs. MAP NIST standard data is interesting. We've found if we don't dry and desiccate the potassium dihydrogen phosphate first and if we don't let it sit in solution overnight before taking serial dilutions, we can get low results. It should be highly soluble, but we found it requires considerable shaking/stirring. I don't know if it's worth mentioning/studying, but I found a few labs make standards from commercial stock standards. Based upon the P source and/or matrix, this can impact the results."* ***Note from HF****: The solubility of KH_2PO_4 is 167 g/100 ml at 20°C and MAP solubility is 57.5 g/100 ml at 10°C and 106.0 g/100 ml at 70° C.*

Questions about using either MAP or KH_2PO_4 as standards?

a. Are you using 5 or 6 standards with an R^2 of 0.995?
b. In fertilizers there are other elements presents which may interfere with the results such as Ca, Fe, Al, Mg, K, Na and other elements. Standards prepared with MAP have concentrations of these elements added in the range expected called matric matching. This could be adding to the potential problem when analyzing fertilizer material if these elements are not added to the standards. This problem may not exist in gravimetric and colorimetric analysis, but could happen when using the ICP.
c. How often a standard curve is analyzed? Every day, every set of samples?
d. Analyze known samples with an unknown sample? Yes or No?
e. How often a known value sample is added in the sample run? Every set?

2. *How would these two standards compare on ICP analysis in Item 1?*

Using pure MAP for preparing standards on the ICP - how will samples containing potassium affect the results? DAP? Other samples? A set of standards prepared with KH_2PO_4 were compared to MAP standards (no K present.) The test was prepared with three conditions as follows:

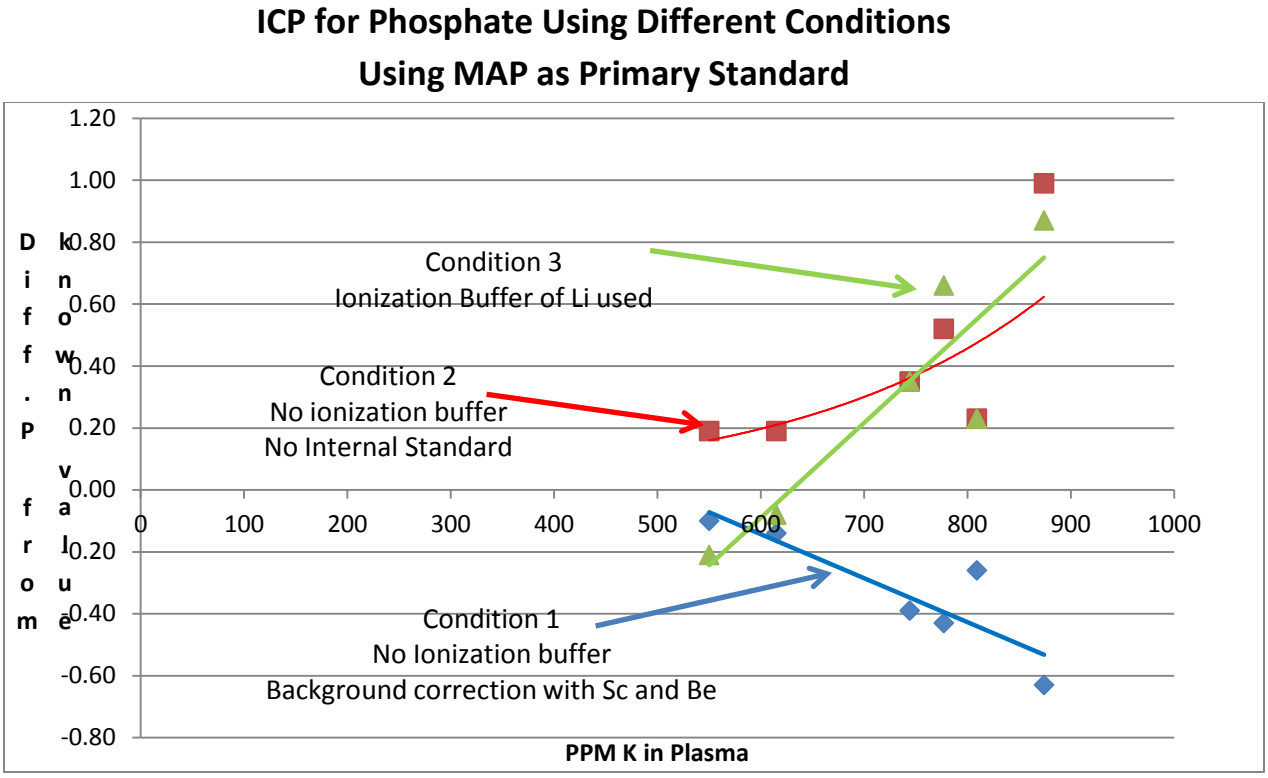
Condition 1: Using Sc and Be for background correction and no ionization buffer
Condition 2: No Background or Ionization buffer
Condition 3: Sc and Be used for background correction and Li used as ionization buffer

Results:

ppm K Level of K in Sample	ppm K Level of K in Plasma	Known Value	Axial View	Condition 1	Condition 2	Condition 3	
0	0	45.66	QA 1	46.71	46.00	45.63	DAP Std.
0	0	45.66	QA2	46.57	45.97	45.78	DAP Std
1100	550	17.00	17%	16.90	17.19	16.79	
1229	615	19.00	19%	18.86	19.19	18.92	
1488	744	23.00	23%	22.61	23.35	23.16	
1553	777	24.00	24%	23.57	24.52	24.66	
1618	809	25.00	25%	24.74	25.23	25.23	
1747	874	27.00	27%	26.37	27.99	27.87	

ppm K Level of K in Plasma	Difference Condition 1	Condition 2	Condition 3	
				Ideal Condition
550	-0.10	0.19	-0.21	
615	-0.14	0.19	-0.08	
744	-0.39	0.35	0.35	
777	-0.43	0.52	0.66	
809	-0.26	0.23	0.23	
874	-0.63	0.99	0.87	

Or in graph format:



DAP results gave the correct answer with Condition 3 whereas the other two conditions did not. What causes DAP to analyze 44.4% on a DAP of 46% by ICP*? Condition 4: Yttrium as background correction with no electron buffer – planned for near future as another possible reason for low phosphate results. Yttrium is found in fertilizer material and should not be used for Int. Std.*

The sample conditions above (1, 2 & 3) were used with KH_2PO_4 standards rather than MAP with no potassium to set up the ICP curve. Standards of 17, 19, 23, 24, 25 & 27% for the K-P standard were used to compare to DAP and standards of MAP (no K) of 20, 22, 24, 26 & 28%. The best results for the MAP and DAP samples were condition 2 with no internal standard and no electron buffer. Results were 19.83, 21.94, 24.19, 26.05, 28.15 for the MAP and 46.17 and 45.94 for the DAP samples. Know value for DAP was 45.66 or slightly high compared to the known value.

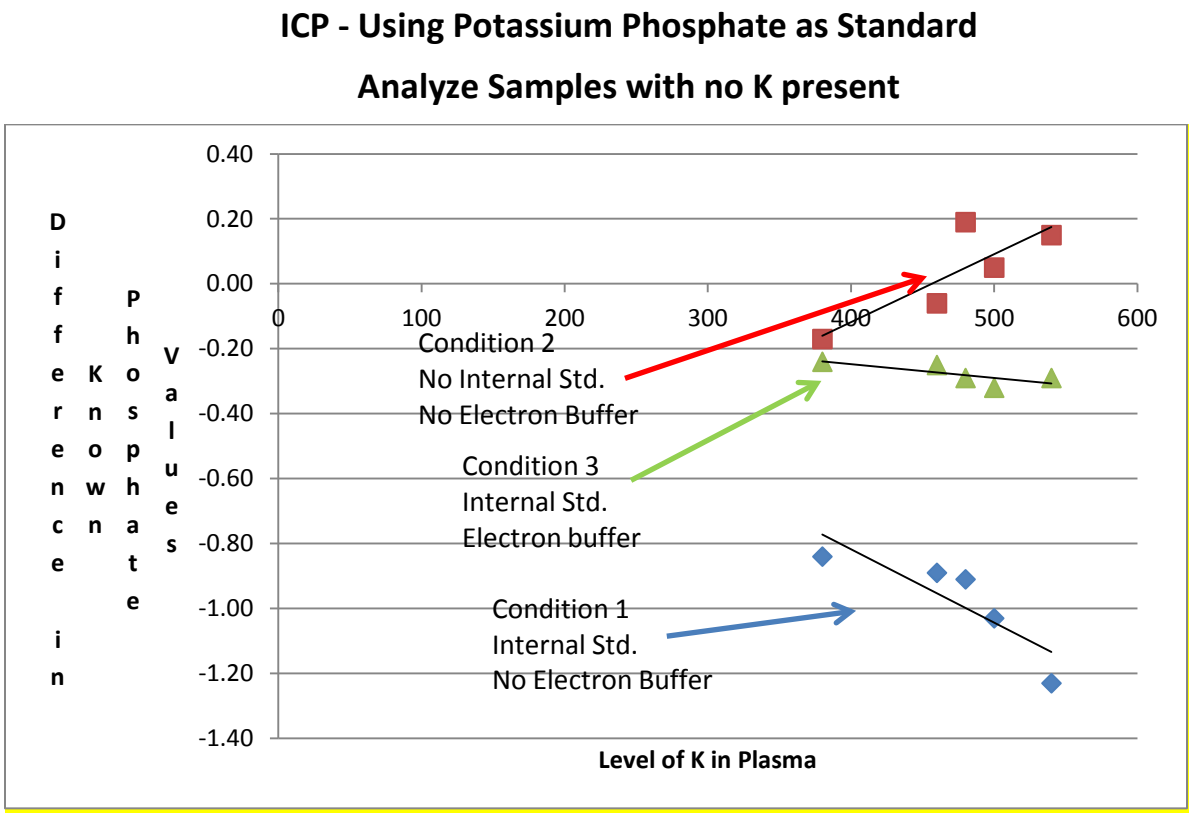
Condition 1 with internal standard and no electron buffer gave results for the MAP standards of 19.19, 21.05, 23.06, 24.93 & 26.88% with the DAP analyzing 43.79 and 43.87. What does this tell us about this condition **– it cannot be used for analyzing DAP.** If we add the internal standard an electron buffer it may improve the results. Results from **Condition 3** with internal standard and electron buffer gave results for MAP at 19.76, 21.75, 23.71, 25.68 and 27.71 with DAP analyzing at 45.08 and 45.13. This condition improves slightly but **should not use with these standards of K-P for DAP.**

What has been causing DAP and MAP to analyze low in the Magruder Check Sample Program when using ICP?

Magruder Number	Grade of Fertilizer	No. of Labs Low in Results
2013-07	MAP (11-52-0)	6
2013-03	MAP (10-50-0)	5
2013-01	MAP-S/Zn (12-40-0-10-1)	4
2012-06	DAP (18-46-0)	4
2012-03	DAP (18-46-0)	4

Certainly the conditions used above could be and may be the contributing factor. Other causes may contribute to this result for DAP. (See note in 1b.) Once everyone has tried these conditions when using MAP or KH_2PO_4 Standard and the problem still exist future work will be required.

See graph below with the data using KH_2PO_4 standards:



Let me know how it works out for your results on ICP with changing conditions.

3. Magruder Sample 201306 (18-24-6). The total phosphate and direct available were found to be 24.65 +/- 0.40 and 24.58 +/- 0.44, respectively. The investigational allowance for available phosphate at the 24% level as found in the AAPFCO's handbook is 0.73%. Using a multiplier of 2 times one standard deviation for total and available phosphate calculated IA's would be 0.80% and 0.88%, respectively, which is over the investigation limit. *Note: The total phosphate and available are essential the same, but in most cases the direct available takes four to five hours longer than analyzing a total. In using a screening method for phosphate the total would be a great time saver.*

Breakdown of Direct Available Methods for 2013-06

Method	AOAC Ref.	Method Code	No. of Labs	Average	1 STD
Dir. AP, Spectro.	960.03E	041.10	9	24.65	0.19
Dir. AP, Automated	978.01	041.20	4	24.50	0.50
Dir. AP, ICP		041.50	8	24.41	0.48
Dir. AP, EDTA	993.01	041.60	11	24.78	0.36
Dir. AP, Other		041.99	2	23.96	0.66
Method Group		Average	34	24.58	0.44

4. Join the Debate: AAFPCO meets to discuss methods, check samples and other areas of interest in the fertilizer world. The next meeting is in San Diego, CA at the Hotel Marriott Downtown – February 17-19, 2014. Two committees of interest are the Magruder Check Sample and Analytical Services Committees. The agenda and meeting times are found on the AAPFCO website: http://www.aapfco.org/. The Method Forum will be at the end of the AAPFCO meeting on February 19-21, 2014. Fertilizer methods will be discussed – old, new and proposed methods. If you have a method of interest this is the time and place to bring it to the Method Forum to discuss and see if there is enough interest in carrying your method to completion and official status with AOACI or ISO. Look for details on the AAPFCO website.

5. Magruder 2013-07 MAP and Potash Samples. – *Good News and Bad News.* Results are mixed with the MAP and Potash samples submitted in July 2013. The total phosphate improved for one standard deviation from a previous sample of MAP (2013-03) from 0.75 to 0.46%. Direct Available standard deviation improved from 1.01 to 0.72%. The IA for 52% is 1.1%, which 0.72 (2 x 0.72 = 1.44%) is still over the IA. The Magruder sample 2011-03 total phosphate and direct available standard deviations were 2.07 and 1.22%, respectively.

   The potash standard deviation was found at 1.43% for the 2013-07 compared to 2012-03 at 1.35% and 2011-03 at 0.93%. Four labs were still reporting values over theoretical of 63.15%. (three (3) State Labs and one (1) commercial Lab). This is an improvement over samples 2012-09 and 2011-03 with 10 Labs and 8 Labs reporting over theoretical, respectively. The IA for 60% potash is 1.78%. Taking one standard deviation of 1.43% and multiplying by 2 = 2.86% IA.

   The total nitrogen value was 11.07 +/- 0.17% by combustion and overall average standard deviation by all methods. Forty out of fifty-seven labs reported combustion or 81% of the lab uses this method. A previous sample of pure MAP was analyzed at 12.07 +/- 0.18%, which is an improvement over sample 2012-05 (UAN 32) at 0.53%. The IA's for 11% and 32% nitrogen were 0.60 and 0.88, respectively.