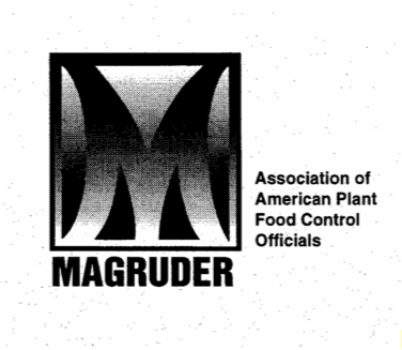

Magruder Newsletter for May 2015

This will be the sixth Magruder Newsletter since its inception in September 2012. The hope of this newsletter was to share laboratory procedures techniques and information where the results generated by the Magruder Check Sample Program indicated a need for improvement, thereby resulting in an enhancement in the overall performance of each laboratory participating in the program. Most fertilizer products analyzing below 30% NPK and other elements have been below the investigational allowance (IA) of AAPFCO. Products analyzing higher than 30% have been steadily increasing since in one standard deviation over the past 14 years (2000 - 2014) and has surpassed the IA of AAPFCO. The IA was increased in 2012 for 46% P_2O_5, 52% P_2O_5, and 60 - 62% K_2O from 0.7, 0.7, 1.44 to 1.0, 1.1 and 1.8, respectively. The overall average IA for DAP and MAP before year 2000 was 0.7, which translates into 0.35% one standard deviation. Currently 2015 data shows the one standard deviation results for 46% P_2O_5, 52% P_2O_5, and 60 - 62% K_2O are 1.02, 0.84 and 1.18, respectively. This translates to 2.04, 1.68 and 2.36 IA's which closely matches Horowitz theoretical calculated standard deviation of 2.1, 2.2 and 2.7.

This Newsletter shared information about the AOAC official methods and a new method (ICP) for direct available P and soluble K who all would like to work as well as the official methods of the past. James Bartos of State of IN (Bartos, James M jbartos@purdue.edu) has been working for the past year on how to correct the problems found during a trial run by several labs with the direct procedure for P and K. There are still many issues related to this direct method by ICP and some changes will have to be made to have AOAC approve this method as official. If you are experimenting with using the ICP for P and K it would be of value to go back and read the previous Newsletters or contact James Bartos. This ICP method is still evolving but the method is not ready for AOAC official status. The ICP is a great tool to speed up analysis but what analyses are you finding and how does it compare with the official AOAC gravimetric and colorimetric analyses? This method is not as simple as making up a few standards and running your sample with them.

Failing results on high concentrates such as DAP, MAP and Potash should be analyzing by the AOAC official methods as a cross check until the ICP method has been approved by AOAC.

Articles in the Sixth Edition of the Newsletter

1. Discussion of evaluating lab proficiency in the new Magruder Check Sample Program. Lab accuracy, lab precision, and AAPFCO investigational allowance are discussed.
   See article at Magruder web site at the web link entitled "Analyte Report Cards"
2. A review summary of previous data (standard deviations) from the Magruder Check Sample Program for the past fourteen (14) years for DAP, MAP, potash (60-62), including GTSP, Fe, Zn and minor trace metals for high concentrate fertilizer materials. IA's for high concentrates like DAP, MAP and Potash (60-62) are 0.7, 1.0-1.1, and 1.8, respectively. IA's for elements like Zn, Cu, Ca, Mg, Fe, S and Mn are lower. IA's for Ca, Mg and S are 0.2% unit + 5% of guarantee. Example a 10% S sample IA is 0.2 + 5% of guarantee or 0.2 + 0.5 = 0.7 units and 1.0% Fe sample IA is 0.005 unit + 10% of guarantee or 0.005 + 0.1 = 0.105 units. *The maximum IA for any of these metals shall be no more than 1%.* A Zinc concentrate of 35% the IA would be 0.005 unit + 10% of guarantee or 0.005 + 3.5% = 3.5005. The IA for 35% Zn sample from AAFPCO Manual states that it will be no more than 1%. The standard deviation below in table is 2.29% or equivalent to 4.58% as the IA. Most likely a Zn product of this concentration will be penalized with this high standard deviation. (This is a problem area and need changes above 1% for high concentrates.)

Summary for Major Elements in the Magruder Program from 2001 to 2014

Product	%TN 1 STD	% Total P_2O_5 1 STD	%AP 1 STD	%S 1 STD	%K_2O 1 STD	%Zn 1 STD	%Cu 1 STD	%Ca 1 STD
10-34-0-18	0.19	0.46	0.51	0.53				
Potash					1.18			
DAP	0.26	0.66	0.56	0.11				
MAP	0.22	0.87	0.74	0.12				
UAN	0.44							
AS	0.23			0.60				*Two diff
Zn/S/Cu				1.14*		2.29	0.77*	Samples
GTSP		1.24	1.39					0.95
Urea	0.46			0.42				

Micros	%Ca 1 STD	%Mg 1 STD	%Fe 1 STD	%S 1 STD	%Mn 1 STD	%Zn 1 STD	ppm Cr 1 STD	ppm Cd 1 STD	ppm Ni 1 STD
GTSP							66.6	8.7	19.3
Micros	0.39	0.19	1.46	0.32	0.35	0.43	65.0		

3. Element of the Month – Zinc (Zn)

   The element Zinc (Zn) is a transition metal and is one of the seventeen essential nutrients for plants. It plays an important role in plant growth with the correct combinations of other nutrients. The main role of zinc in the world market is galvanization of nails, US pennies after 1982 and making brass. When applying zinc in fertilizer mixtures usually requires ounces of zinc compared to pounds of other nutrients per acre. An example of plant growth shows yields of corn increase from a fertilizer on corn yields up to 180 bu. /acre with about 0.5 lb. Zn/acre and wheat of sixty bushels per acre only needs approximately 0.28 lbs. Zn/ acre.

   Chemist analyzing at low levels may find in a fertilizer at 0.20% Zn, which usually does not give the analyst difficulty, but the Chemist analyzing the concentrates Zn sulfate or oxysultate at 36% it becomes a problem with the one standard deviation at 2.29% for these products. (For advice on how to analyze zinc at these high levels go back and read the previous Magruder Newsletters)

   When zinc is used in a small way (ounces) will seem insignicant in growing the food we eat yet it plays a significant large role in feeding the growing world by 2050 by increasing the yields of the food we eat.

4. Testimonials about experiences using ICP's:

   "When the Yttrium internal standard problem was raised, we changed over to using Scandium. Having heard about the Scandium and ammonium polyphosphate problem, we saw direct evidence of this problem this month. Ammonium polyphosphates came in low by ICP, but sample guarantees were confirmed using the AOAC phosphorus gravimetric method. The onus is really on the Lab Services Committee to evolve ICP methods that are robust enough to work over a broad range of samples. We are now having to start using Be as our internal standard for ICP. "

5. A survey for a second Magruder Check Sample Program is being proposed, which will run along aside the current program. The new program will feature high concentrates in this program. Please fill in the questionnaire below and send to Bill Hall (bill.hall@mosaicco.com) concerning the new proposed program. The program would include DAP, MAP, Potash 60-62%, High Zn, Fe, S and micronutrients. Hopefully you will consider joining this program in addition to the regular program.

(Answer questions below)

a. Cost of the program would be approximately $300 per year? The format would be similar to the current new program. Would you support this amount? (Yes or No)
b. What amount would you support? _____
c. If you do not want to analyze all samples/year you can pick and choose which ones you prefer at $75 per sample. Yes or No
d. How many samples would you support at $75/ sample? 1, 2, 3
e. What type of high concentrates would you prefer?

   List samples: _____

f. Magruder checks a sample for homogeneity once per year. There have been no samples found not mixed correctly over the past 14 years. An independent laboratory prepares and ships all samples. How many samples/ year should be tested to be homogeneous? 1, 2, 3 or _____
g. The testing of Magruder samples for homogeneity will increase the cost of the program. How much would you be willing to pay for testing homogeneous on all samples? $500, $1000, $1500 or _____
h. Will you participate in the new program? Yes or No
i. Will you participate in both programs? Yes or No

6. Next meeting of AAFPCO's Analytical Services and Magruder Committee along with the Method Forum discussing fertilizer analytical methods and related problems with the ICP would be a meeting worth attending in February 2016. Stay tuned for the location by going to the AAPFCO website for information and making plans to attend. A half day course on operating techniques for ICP will be included in the forum. (http://www.aapfco.org)

7. Special Offer from Magruder Check Sample Program.

Magruder Check Samples for Sale – **Fire Sale** – any date beyond five years reduced to ½ prices for a limited time. Place order with Jamey Johnson of AAPFCO.

Free or reduced rate for Magruder Check Sample Program - Your laboratory invites another lab to join the check sample program and when they join your fee will be reduced to ½ price. If you sign up two new members to the check program your lab will have one free year of service.

8. Final Thoughts from Harold Falls -

My career of 48 years in the quality control laboratory of manufactured facilities for fertilizer products has come to the end. I will be retiring on June 1st, 2015. It has been a very interesting and pleasurable journey working for CF Holdings and Mosaic and I am thankful for the opportunities to work in an industry which primary purpose is to feed the world. Experiences include working in (one) nitrogen and (two) phosphate manufacturing facilities from North Carolina to Florida. My job has been fun and rewarding working with the AFPC in methods developed, publishing the AFPC Method Manual, maintaining the website, while traveling to the AAPFCO/TFI/Method Forums serving on the Magruder, Analytical Services, Labels and Definitions & Slow Release committees in AAPFCO, in quality control of products maintaining a high degree of accuracy & precision while watching over the environmental work including gas emissions and water at the chemical plants. A lot of excitement was generated with EPA finding perchlorate in all fertilizers including the pure MAP sample of NIST. It gave me a chance to meet excellent personnel in the fertilizer business and regulators who are making sure the manufactures' product meet the specification as advertized.

Some of you will remember the lab equipment in the 60's using a swing balance, & nessler tubes for color analysis? What was the equipment like when Madam Curie discovered Radium and Polonium in 1898? Mettler balances were introduced around this period (1960's) with hanging weights and was subject to vibrations which a marble table and rubber pads were used to stabilize the balance. Distillations, titrations and wet chemistry methods were the norm. Slide rules were the calculators of years past, which teach how scientific notation helps in understanding math. Today we have been witness to the new technology – Computers, ICP, XRF, and NIR – *almost* as simple as dropping a sample in a cell area and within 1 minute or less have your answer *and not thinking about how you got the answer.*

Final Thoughts

1. Improving your analytical methods and results can be done by using known standards along with several check samples for each analytical run. Never say I ran it three times and repeated the same results each time, so it has to be right. This could be great precision but not very accurate. In manufacturing it is always obvious when the analytical results are wrong and not so obvious in other labs. In some cases the sampling and grinding of the sample may be the error or a bad sample. Start with a fresh well representative sample if you suspect something wrong.
2. Enjoy your work and continue to learn new skills related to your work. In other words "be the best you can in your work field" and you will be recognized for your

work throughout your career. Be cautious about changing a method for expediency from the Official Method of AOAC or non-official method. It takes time for study of a new method such as analyzing total phosphate on fertilizers by ICP. *Note: In AOAC it takes volunteers from Laboratories to set up a new method and prepare all the statistics by analyzing many samples.* In year 2000 it took over 2 years of work to understand this method by ICP for total P on high concentrates but with sheer determination it was completed and I am thankful for the employees working on this project. Now this ICP method is trying to obtain results on high concentrates for direct P and K. The protocol developed for this ICP direct method was tested many times over a year or more with the final test with other laboratories. The procedure to be tested needs to be followed at every detail – this is no time to experiment during the study by changing other details. Official AOAC methods have gone through single lab testing and finally collaboration with other laboratories to determine if the method is robust. The ruggedness testing usually uses 7-8 small parameter changes such as chemical addition in extraction from 100 ml's vs 95 ml's vs 105 ml's. Once all the protocols are tested a committee of peers will review the data and procedures for finally approval. Major changes in this method should not be made by a single lab until thoroughly tested and the change is submitted for review and approved. The process seems slow and it is slow but necessary for accurate AOAC referee method results.

3. What is sheer determination? It's a bit like 'will power' or strength of character. It is normally used to describe a situation where someone is struggling to achieve something (normally some sort of task or personal goal) and does so by drawing on their desire to win/ achieve rather than outside assistance.
4. Analytical Chemists are important in determining the values needed for accurate analysis of products in every aspect of life. Be proud of your work but be cautious until you are absolutely sure of your answer.
5. Last but not least I am thankful for Campbell University where I obtained my degree in Chemistry. It changed my life.

Harold Falls