

## Magruder Newsletter September 2012



The purpose of the Check Sample Program is to help participating laboratories identify and improve their individual performance in analyzing N, P<sub>2</sub>O<sub>5</sub>, K<sub>2</sub>O, S, Zn and other nutrients on a diverse range of fertilizer samples. The purpose of this newsletter is to review information about the results from the Magruder Check Sample Program. In recent years, a variety of new methods, some approved by AOAC and some not, have been used by different laboratories, for example ICP. A review of the past 12 years of data indicates the standard deviations for the major elements have increased over time and the standard deviations are now exceeding the investigation allowance (IA) issued by AAPFCO. This could result in a fertilizer manufacturer or distributor receiving unwarranted deficiency notices due to the increase in laboratory analytical variation. There are many reasons why this is happening and, where needed, this newsletter will hopefully help each laboratory improve their performance. Laboratory information from participating labs in the Magruder Programs is confidential.

**Request:** Magruder sample 2011-03A a MAP (10-50-0) reported a grand average of 50.08% available phosphate with one standard deviation of 1.22%, for 35 labs reporting. This would suggest an Investigational Allowance of approximately 2.44% (or two times STD Dev). Ten labs reported results below 49.08% which would be outside the current IA of 1.09%, and would result in a penalty. Four labs reported values above 51.17%. A total of 14 of the 35 participating labs, or 40%, reported values outside of +/- 1.09%. We are trying to determine what standard deviation is acceptable when reporting values for your lab? **Magruder Committee would like to hear what deviations are acceptable to your laboratory and your comments.** Report your comments to Dr. Mel Bryant, Vice-Chair of Magruder at [mbryant@uky.edu](mailto:mbryant@uky.edu). Examples of other samples having apparently high deviations would be: 2012-05B and 2010-09.

- I. [Attached is a graph with the trend of P<sub>2</sub>O<sub>5</sub> and K<sub>2</sub>O standard deviations.](#) In most of the high fertilizer concentrates such as DAP, MAP, and Potash, the IA's are increasing beyond the AAPFCO IA's. From 1995 to 2000, the trend appeared to be stable for phosphate products. Most current fertilizer blends, such as 10-10-10, have deviations below the IA's, as expected, with the exception of potash (K<sub>2</sub>O).

On a related issue, sample 2011-02B a Zn Oxy Sulfate averaged 35.28% Zn with a Standard Deviation of 2.63%. This would translate into an IA of approximately 5.26% for this sample. AAPFCO's IA is capped at 1.00% for secondary and trace elements. Currently, there are limited

fertilizer certified Zn reference materials in the market place. In a recent survey of digestion methods and acids used, the microwave digestion produced the highest values, which were approximately 1% higher than the hot plate or hot block digestions. The only approved method by AOAC is hydrochloric digestion using Atomic Absorption analysis for Zinc. No other methods are approved by AOAC.

### Tips for Thought

1. When a monthly check sample, such as a 0-0-60 potash sample, is received, go back and pull a similar check material, with reported values from the Magruder Report and compare the two results before reporting. Magruder sells past check samples for \$28 each and they can be ordered through [Jamey.Johnson@aspb.ar.gov](mailto:Jamey.Johnson@aspb.ar.gov)
2. Many industrial laboratories analyze samples for available phosphate by the indirect method. Most other labs use the direct method for available phosphate. Typically, the average standard deviation for industrial labs is 0.16% for total nitrogen and 0.25% for available phosphate on high P<sub>2</sub>O<sub>5</sub> fertilizers. The samples are rechecked when their result exceeds two standard deviations of 0.32% for nitrogen and 0.50% for available phosphate. Currently the IA's for nitrogen and phosphate are 0.70% and 1.0%, respectively for an 18-46-0 (DAP) sample.
3. Preparations of a low-cost MAP (11-52-0) Reference Standard for all labs is being developed by SGS. This reference material is currently being processed, will be certified and available by the end of year. SGS will also develop a 10-40-0-10-1 sample with 10%S and 1%Zn, which will be ready in 2013. *Both samples will be ISO Certified.* NIST standards – 120c, 193, 194a, 200b, 694 and 695 can be used, but are expensive. Note: [NIST](#) 194a will be available in November 2012. You can purchase a similar sample from [Aldrich](#) for lower cost and will be certified secondary standard by comparing to NIST 194a. Your initial investment in 194a will last a long time.
4. ICP is currently being used for a variety of nutritive metal, phosphate and potash analyses, but no official method has been adopted by AOAC. It has been found to be fast, but results from the Magruder Check Sample Program show a higher standard deviation when used, especially with higher phosphate and potash samples. Below are some tips for improved ICP operation:
  - a. Keep the room and gas temperature constant – temperature change will affect the ICP. (Within 2°C)
  - b. Five evenly distributed standards per calibration on ICP will improve your results. Two point calibrations, or a blank and high standard, can produce a high or low slope resulting in a high or low value. Serial dilutions (i.e. 100, 10, 1, 0.1) are only marginally better because of the gap between the high and low standards.

- c. Consideration for matrix effects – whenever possible, a similar matrix for the calibration standards and the sample unknowns will improve results.
  - d. Use an internal standard, such as Sc or Be, and an ionization buffer, such as Li or Cs, for all samples, which will help compensate for minor matrix differences and improve consistency of results.
  - e. Use multiple wavelengths for each element. Example: Use wavelengths of 177.434, 178.284, 213.618 and 214.914 for P. Lines 213 and 214 are the strongest, but have a Cu interference, if significant Cu levels are present. If necessary, use the instrument’s spectral deconvolution software and/or check background correction points to ensure the exclusion of neighboring peaks.
  - f. Use a similar known sample as a reference, such as a previous Magruder sample of DAP, MAP, Urea, Potash or Zn in the analytical determination.
  - g. Use an appropriate certified standard in a sample batch during each analysis. Use NIST 194a or similar material from Aldrich.
  - h. The ammonium citrate with or without EDTA needs to be removed by digesting with nitric acid before ICP analysis. [Note: Ammonium Citrate interferes in colorimetric analysis and is recommended to be destroyed before analysis.](#)
5. The Magruder Committee is compiling a list of contacts with expertise in the various methods. If you are experiencing a problem with accuracy by ICP analyses, or another method, please contact [“James Bartos or Dr. Mel Bryant”](#) and we will try to provide contact information for someone who can help you.

The Magruder Committee is reviewing the [method codes](#) for the check sample program. **If there is not a method code for any of the methods used in your lab to analyze the Magruder Check Samples, please send the reference (AOAC, JAOACI, AFPC, etc) for your method to Rhonda Boles (email preferred - [BolesR@Missouri.edu](mailto:BolesR@Missouri.edu)).** If there is not a reference available, please include enough information about your method so that it can be assigned a method code. The information from the data for the check sample program will be improved if the method codes accurately reflect the methods performed to analyze the samples.

*In general terms, better (more specific) data to investigate poor performing methods  
 “Other” in some/many cases is a large pool of data that cannot help identify trends or method issues  
 Bring attention to labs incorrectly reporting data under the wrong code  
 Used to identify additional methods being used with potential to perform better than current methods  
 Sulfur forms are identified and separated in the calculations*

Note: University of Missouri – Columbia is manually analyzing nitrogen by kjeldahl determination of fertilizers – if you have any questions about the lab procedure – the contact person is Paul Eggeman, email [EggemanPK@Missouri.edu](mailto:EggemanPK@Missouri.edu).