Sample Preparation Error in Fertilizer Analysis

Proposal

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Study Objective

Evaluate interlaboratory sample preparation variance in fertilizer analysis.

Justification

Definitions are extremely important in the subject matter that follows. Confusion easily arises if the word "sample" is used without an adjective or the words "sampling" or "sampled" are used without clear description of what is sampled. Appendix A contain a list of definitions used in this proposal.

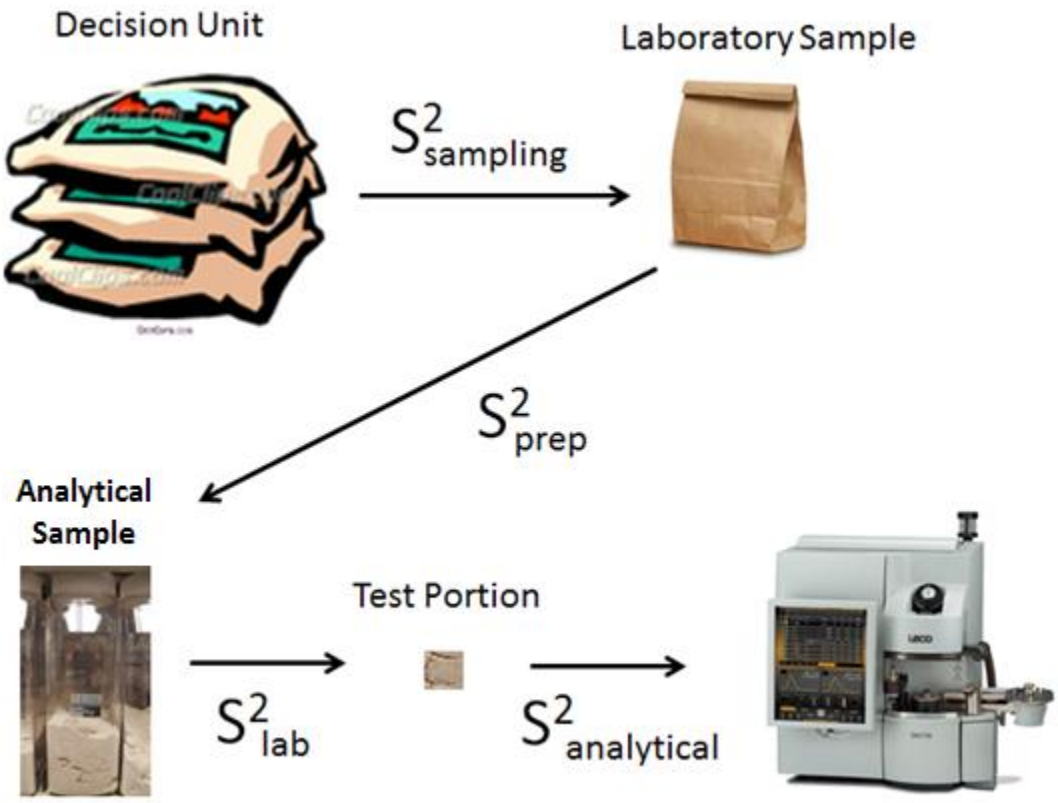
A laboratory analysis of fertilizer has an unavoidable error associated with it due to several processes from sampling to laboratory analysis. Investigational allowances published by the American Association of Plant Food Control Official (AAPFCO) are intended to include these errors (Rund, 1975). If a laboratory result is below a guaranteed analysis minus an investigational allowance, the nutrient is considered to be less than the guarantee for reasons other than this unavoidable error and action is taken on the manufacturer of the fertilizer.

Error is quantified by the variance of multiple determinations. The total error, or variance, of a laboratory result is a compilation of variances for each process that occurs from taking a sample of the decision unit to analyzing a test portion in the laboratory. If variances of each process are independent, variances can be summed to determine total variance. A summary of the processes and their associated variances are shown in the Table 1 and Fig. 1.

Table 1. Summary of variances in analysis of fertilizer from a Decision Unit.

Process	Variance	Descriptor	Location
Obtaining a Laboratory Sample from Decision Unit	$s^2_{sampling}$	Decision Unit variance	Field
Preparing an Analytical Sample from a Laboratory Sample	s^2_{prep}	Laboratory Prep variance	Lab
Obtaining a Test Portion from the Analytical Sample for analysis	s^2_{lab}	Test Portion variance	Lab
Chemical analysis of the Test Portion	$s^2_{analytical}$	Chemical Analysis variance	Lab

Figure 1. Diagram of variances in analysis of fertilizer from a Decision Unit.



Decision Unit variance quantifies the error in obtaining a sample from a Decision Unit. Laboratory Prep variance quantifies the error in preparing a Laboratory Sample to a finely ground Analytical samples that is sent to the lab. This process normally involves mass reduction via splitting then particle size reduction via grinding. Test Portion variance is the error in obtaining a Test Portion from the Analytical Sample for chemical analysis which is normally 0.5 to 2 g. Chemical Analysis variance includes error in the processes of determining an analyte concentration in the Test Portion. This includes both preparing a Test Portion for analysis (eg. extraction or digestion) and analysis via an instrument (eg. ICP). When just one lab is considered, each variance is a within-lab variance. When considering multiple labs analyzing a fertilizer, additional variances of each process are involved which are between-lab variances.

In proficiency test programs like Magruder, a unit of material is ground and split into several Analytical Samples. The Analytical Samples are sent to several laboratories for analysis. The process of grinding and splitting is done with much attention to ensure all the samples sent to laboratories are homogenous in order to eliminate occurrence of Decision Unit and Laboratory Prep variances in the data. Each laboratory determines an analyte concentration in the sample in duplicate. A reproducibility variance (S_R^2) is determined as the sum of between-lab (S_L^2) and within-lab (S_r^2) variances:

$$S_R^2 = S_L^2 + S_r^2$$

Square root of the variances are the standard deviations for reproducibility, between-lab error, and within-lab error.

Results from proficiency test programs with ground material sent to laboratories can only determine between-lab and within-lab error associated with the latter two processes in Table 1 which are Test Portion and Chemical Analysis variances. To determine total error associated with estimating an analyte concentration present in a Decision Unit, data is required on variance associated with obtaining a Laboratory Sample from the Decision Unit and preparing an Analytical Sample from the Laboratory Sample in the processes of mass and size reductions.

With regards to preparing an Analytical Sample from a Laboratory Sample, several sources of error can occur as listed below.

a. mass reduction
b. variable temperature and humidity
c. samples too large for the splitting equipment
d. sample storage conditions prior to splitting
e. differing hardness of materials resulting in different sizes in the Analytical Sample affecting test portion variance
f. humidity and loss of N via grinding
g. cross contamination in splitting and grinding processes

Determination of total error is important for validating or updating Investigational Allowances. Work on defining field sampling and preparation error was conducted in 1966 (Quackenbush et al., 1966) and used in developing AAPFCO Investigational Allowances (Rund, 1975). The Investigational Allowances only included N, P_2O_5, and K_2O guarantees up to 32%. Magruder proficiency test data were analyzed to update Investigational Allowances for higher guarantees (Bartos, 2010). However, the analysis of Magruder proficiency test data did not include errors associated with Decision Unit sampling and Laboratory preparation.

A current assessment of both Decision Unit and Laboratory Preparation variances are needed. An interlaboratory study is proposed here to evaluate Laboratory Preparation variance to help assess the appropriateness of current Investigational Allowances.

Experimental Design

Participating Labs

A survey was developed with www.surveymonkey.com asking labs to participate in the program. Results from the survey are shown in Table 2. A total of 17 labs responded with 12 of them being regulatory labs. Most of the labs perform mass reduction of the Laboratory Sample. Eight of the labs use riffle splitting and 5 use rotary splitting. Retsch grinders were the most common equipment used for size reduction. The median weight of Laboratory Sample was 1750 g. The median weight of Analytical Sample was 112 g.

Table 2. Participating laboratories with their protocols for mass reduction, size reduction, Laboratory Sample mass, and Analytical Sample mass.

Lab ID	Wt of Laboratory Sample (grams)	Mass reduction	Equipment for size reduction	Screen size for size reduction (mm)	Wt of Analytical Sample (grams)
Public Labs					
	2200 to 3300	Rotary splitting; Retsch PT 100	Retsch ZM 200	2 followed by 0.5	225
113	900	Does not occur	Retsch ZM 200		900
105	450 to 900	Rotary splitting	Retsch PT 100	1 followed by 0.5	90
114	2000	Riffle splitting; Gilson Versa-Splitter, SP-2.5	Retsch ZM 100	1	200
		Riffle splitting; Open pab riffler, humboldt divider	Retsch grinder	0.5	50
	4400	Does not occur			4400
107	2000 to 2500	Rotary splitting; Fritsch Laborette 27	Fritsch Pulverisette 14	0.75	100
106	2000	Rotary splitting; Retsch PT 100 with the DR 100	Retsch ZM 200	0.75	85
104	1000	Riffle splitting; Humbolt H-3985 riffler	Pulva-sizer model A		450
102	2000	Riffle splitting; carpco 16-25X sample splitter (gated riffler)	Retsch ZM 200	0.75 (1 for some P products)	125
103	1500	Does not occur	Retsch ZM 200	1.5	1500
111	3000 to 4000	Riffle splitting; gated riffler	Retsch		100
Private Labs					
110	200	rotary splitting; Retsch Sample Divider PT 100	Retsch Centrifugal Mill ZM 200	0.5	50
109	500	Riffle splitting; sample divider with chutes	grinder	<2 mm	20

112	5000	Riffle splitting; Gilson Universal mini splitter	Tungsten Carbide Ring and Puck		30
105	1000	Riffle splitting; riffle with cut-off gate – ½" chute width w/ two pans			100 to 125
108	150	Does not occur	Retsch ZM 200	0.75	150

Fertilizer Material

Two-thousand grams of fertilizer will be prepared and sent to each participating lab. The study will include two fertilizer samples as shown below.

Sample A: 2000 g MAP
Sample B: 1000 g MAP and 1000 g of DAP

Sample A is included as a control where error due to mass reduction should be minimal since it is one material. Sample B is a mixture of a material with different N concentrations. Since N will be the analyte measured, a mixture of two materials with different N concentration will evaluate errors associated with mass and particle size reduction.

Care will be taken to prepare 17 samples with as little intersample heterogeneity as possible so that error associated with obtaining a Laboratory Sample from a Decision Unit is minimal. Each sample will be prepared in a sample bag labelled with Lab ID (see Table 2) and Sample ID (Sample A or Sample B). Description of preparing each sample is shown below.

Sample A: Weigh 1000 g MAP into each sample bag.
Sample B: Weigh 500 g MAP and 500 g of DAP into each sample bag. Pass the mixture through a riffle splitter twice to blend the materials together.

The two samples will be sent to each participating laboratory. Detailed instructions will be provided to each laboratory (Appendix B) on what to do with the samples. Generally, the laboratory processes involve:

a) Preparing the samples following their routine protocols
b) Analyze N for each sample in duplicate reporting the method used according to the Magruder Method Codes
c) For each sample, weigh two Test Portions in vials and send to Nutrien Lab (attn: Tim Fau) for N analysis via Kjeldahl (Magruder Method Code 001.10, AOAC 920.03) and combustion (Magruder Method Code 10.60, AOAC 993.13).

Laboratory Analysis

Laboratories will be asked to analyze N via a method they normally use in their laboratory. They will submit duplicate results for each sample and report the method they used using the Magruder Method Codes.

Test portion samples in the sample vials will be weighed and analyzed in Nutrient lab for ammoniacal N via Kjehdahl (Magruder Method Code 001.10, AOAC 920.0) and total N via combustion (Magruder Method Code 10.60, AOAC 993.13). The measurement of uncertainty for Kjeldahl N is 0.124%. Measurement of uncertainty for N via combustion in Tim's lab is 0.144%. Analysis of N in all the samples will occur in the same sample set in one lab to eliminate interlab Chemical Analysis variance.

Data Analysis

A summary of the variances that can exist in the N data analyzed by the individual labs and central lab are presented in Table 3.

Laboratories will be asked to analyze N via combustion during their routine procedure. The data collected from the laboratories will be analagous to routine Magruder data except the data will be obtained from unground samples rather than ground material. Between-lab, within-lab, and reproducibility errors from this data can be compared to the errors obtained from similar materials in the Magruder program (Table 4). Higher error is hypothesized to occur with the unground material due to Laboratory Preparation of unground material (Table 3).

Data obtained from the laboratories submitting test portions to a central lab for N analysis will not include error associated with interlab Chemical Analysis but will include interlab Laboratory Prep, inter- and intralab Test Portion, and intralab Chemical Analysis variances (Table 3). Thus, errors calculated from this set of data are hypothesized to be less than the set of data with each lab analyzing N but greater than Magruder data with ground material (Table 4). An assessment of intralab Chemical Analysis error can be made in the central lab to be able to assess error associated with interlab Sample Preparation and inter- and intralab Test Portion sampling.

The data will be useful to estimate interlaboratory error occurring with sample preparation of unground fertilizer in regulatory laboratories. This information cannot be gleaned from ground fertilizer results in the Magruder proficiency test program. The estimate of errors that include interlaboratory sample preparation error will be useful to compare to the current AAPFCO Investigational Allowances.

Table 3. Summary of sources of variances in data collected in routine samples from the Magruder program and proposed N data from the unground samples.

Data collected	Variance	Between-lab (inter)	Within-lab (intra)
Routine N data collected with ground samples in the Magruder program	s^2_{lab}	X	X
	$s^2_{analytical}$	X	X
Labs analyze N in duplicate in Analytical Sample in proposed study	s^2_{prep}	X	
	s^2_{lab}	X	X
	$s^2_{analytical}$	X	X
Lab sends duplicate test portions to central lab for N analysis	s^2_{prep}	X	
	s^2_{lab}	X	X
	$s^2_{analytical}$		X

Table 4. Precision data for total N via combustion for sample 170111 (18-46-0 DAP) and 170411 (15-15-15-micros) in the Magruder program from US laboratories.

Labs	Sample	Mean	n	S_L (between lab)	S_r (within lab)	S_R (reproducibility)	S_L Between Labs % RSD	S_r Within Labs % RSD	S_R Reproducibility % RSD
Regulatory	170111 (18-46-0)	18.26	22	0.3059	0.1569	0.3438	1.68	0.86	1.88
Private	170111 (18-46-0)	18.33	20	0.2584	0.0875	0.2728	1.41	0.48	1.49
Regulatory	170411 (15-15-15)	20.13	26	0.2427	0.1128	0.2676	1.21	0.56	1.33
Private	170411 (15-15-15)	20.1	23	0.3508	0.1146	0.3691	1.75	0.57	1.84

References

Bartos, J. 2010. Clarification: High P and K IAs: Proposed New Table for AAPFCO OP.

Rund, R.C. 1975. "The Background and Rational for AAPFCO Recommended Investigational Allowance", AAPFCO OP, No 28, pp 67 - 75.

Quackenbush et al. 1966. "Variations in Analysis of Fertilizers", J.AOAC, Vol 49, No 5, pp 915 - 943.

APPENDIX A

Instructions for Preparing Samples for Fertilizer Sample Preparation Study

Important Definitions

Please read the definitions below which explain the various types of samples prepared in this study.

Decision Unit: The material from which a sample is collected and to which an inference is made.

Laboratory Sample: The material received by the laboratory.

Analytical Sample: subsample or sample prepared from the laboratory sample and from which test portions will be taken

Reserve sample: material left over from the laboratory sample when divided or subsamples have been taken and on which no further particle size reduction is done.

Test Portion: The quantity of material taken for measurement.

Mass Reduction: part of the sample preparation procedure to reduce the mass of a sample by dividing or subsampling it using (stationary or rotary) dividers or fractional (alternate) shoveling, without changing the consistency of the sample. (not to be confused with particle size reduction/comminution)

Particle Size Reduction (also Comminution): Reduction of particle size of a sample by chopping, crushing, cutting, blending (homogenizing), macerating, milling (grinding), pressing, pulverizing, among others.

The shipment sent to you contains:

a. Two laboratory samples each with a mass of 2000 g. Laboratory samples are labeled as A and B. Sample A is MAP and Sample B is a combination of MAP and DAP.

b. Eight glass vials to place test portions. Vials are labeled as:

A 1	B 1
A 2	B 2
A 3	B 3
A 4	B 4

c. Plastic funnels for delivering test portions into glass vials.

d. Mailing envelope for vials and bubble wrap to protect vials for return shipment.

Laboratory Directions:

1. Sample A and Sample B shall be prepared separately.

2. Do not open laboratory samples until you are ready to mix, grind, analyze, and prepare for shipment back to Nutrien-Aurora in Aurora, NC (see step 8).

3. Prepare the laboratory samples with mass and particle size reduction as you normally would treat other samples in your lab. The ground sample prepared for laboratory analysis is the analytical sample. Any remaining unground laboratory sample from splitting the laboratory sample is the reserve sample.

4. Weigh and record the mass of the analytical sample and reserve sample.

5. Analyze N in test portions from the analytical sample following your routine laboratory procedures.

6. An excel file will be sent to you to enter the data from steps 4 and 5. Email the excel file with data to fsikora@uky.edu by **June 7th, 2019**.

7. Prepare test portions by weighing approximately 1 g of the analytical sample and transferring it to the appropriate vial provided. Prepare 4 test portions for sample A and 4 test portions for sample B. Wrap the vials in bubble wrap and place in envelope provided.

8. Send the 8 vials of test portions to the following address **by June 7th, 2019**:

Timothy Fau
Nutrien
1530 NC Hwy 306 S – Drop 2
Aurora, NC 27806

6. Identification of your laboratory will be kept anonymous on all report summaries. Only the individuals performing data and chemical analysis will be aware of laboratory identification in this program.