MN Dept of Agriculture Sample Preparation Experiment of Dry Feed Materials

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Background

- MN Dept. of Agriculture (MDA) requests for analysis of feed material include
  - Proximates (e.g. crude fat, crude protein, moisture, and ash)
  - Metals (e.g. arsenic, calcium, phosphorus, lead, and zinc, etc.)
  - Drugs (e.g. monensin, lasalocid, etc.)
- Analysis is performed to verify product label claims as well as determining presence of contaminants. Analytes may be present at high concentrations or trace residue levels.
- Matrices include dry materials (e.g. finished feed, single ingredients, dry pet foods) and range in heterogeneity from single ingredient powders (e.g. milk replacers) to complex finished feeds (e.g. texturized medicated feeds).

Background

- The lab's current practice is to split a representative portion from the original lab sample using a motorized seed splitter followed by reduction to a 0.75 mm particle size using a centrifugal mill.
- In GOOD Test Portions it recommends that "a laboratory sample should be comminuted in its entirety before splitting to control FSE (Fundamental Sampling Error) of the splits" which represents a significant departure from MDA lab's current procedure for dry feed materials which consists of splitting followed by comminution.

Goals

- Implement recommendations of GOOD Test Portions for dry feed materials by comminuting the entire Lab Sample followed by mass reduction into representative analytical sample portions.
- Evaluate sample preparation equipment.
- Estimate error contributions from sample preparation procedure.

Definition of Samples

- Lab Sample (LS) – the material submitted by FFSD/Feed program to MDA lab for analysis. The entirety of the lab sample will be comminuted.
- Analytical Sample (AS) – the material split from the comminuted lab sample using a rotary splitter.
- Test Portion (TP) - the material removed from an analytical sample during performance of a test method.

Sample Selection

- MDA lab chose a textured feed because it is highly heterogeneous and represents a worst-case scenario for achieving representative analytical samples. Textured feeds typically contain whole or partial grains along with pelleted materials.
- Removed five random 2-lbs portions from a 50-lbs bag of textured feed.
- Dedicate each portion to an analyte or group of analytes. Label each sub as *LS-test* (i.e.: (1) LS-Proximates, (2) LS-Metals, (3) LS-Drug, (4) LS-Mycotoxin, and (5) LS-Vitamin A).

Comminution and Mass Reduction Process

- Comminute each sub using centrifugal mill with a 0.75 mm screen.
  - Weigh material before and after to calculate loss during grinding.
- Split each sub into 6 representative portions using a 6 port rotary splitter.
  - Determine the net weight of each portion to verify that the rotary splitter is splitting material into equivalent analytical samples.
  - Label each portion as *AS-test-increment* (e.g. AS-Proximate-1, AS-Proximate-2, … AS-Proximate-6).
- Acceptance Criteria:
  - Lab sample can be comminuted in its entirety to the desired fineness.
  - Lab sample can be split into equivalent portions.
  - Minimal loss of material.
  - Minimal potential for cross-contamination.
  - Minimal safety concerns.

Comminution Results

- Comminution of the lab sample into analytical samples using this equipment resulted in an average loss of approximately 2% of the material.
- Added a cyclone attachment to the cutting mill, allowing the entirety of a typical lab sample of dry feed material to be comminuted to the desired fineness with minimal loss of sample material.

Loss of Material for Lab Sample following Comminution & Splitting

LS-Proximates	LS-Metals	LS-Drugs	LS-Mycotoxin	LS-Vitamin A	
Loss of Material (%)					Average
1.95	1.99	2.15	2.20	2.09	2.08%

Mass Reduction (Splitting) Results

- Rotary splitter unit outfitted with a vibratory feeder divided material into 6 representative sub-samples
- The average RSD of net weights of analytical samples using rotary splitter is 0.919%.

Evaluation of Net Weight of Analytical Sample Splits

Split #	LS-Proximates	LS-Metals	LS-Drugs	LS-Mycotoxin	LS-Vitamin A
	Net Weights (g)				
AS-1	160.9	162.7	147.3	150.4	150.1
AS-2	162.4	160.5	148.5	148.5	151.7
AS-3	158.5	161.4	149.0	151.7	150.3
AS-4	157.8	159.8	148.8	148.3	151.4
AS-5	156.6	160.4	149.1	153.5	149.7
AS-6	159.6	163.1	148.3	148.9	149.4
s	2.12	1.33	0.66	2.07	0.92
mean	159.3	161.3	148.5	150.2	150.4
RSD (%)	1.330	0.827	0.445	1.376	0.615

Analytes to be Analyzed

Tests assigned to Analytical Samples

Analytical Sample Desription	Tests
AS-Proximates	Crude Fat, Crude Protein, Moisture, Ash
AS-Metals	ICP-OES: Ca, Cu, Fe, K, Mg, Mn, Na, Zn ICP-MS: As, Cd, Co, Cr, Hg, Mo, Pb, Se
AS-Drug	Lasalocid
AS-Mycotoxin	DON
AS-Vitamin A	Vitamin A

Analysis Activity Plan

- For each Analytical Sample, perform a single analysis for each assigned test.
  - Perform analysis in a single batch.
  - Use results to calculate the error contribution from selection of the analytical sample (as).
- Select a single Analytical Sample from each category and analyze 7-10 replicates for each test assigned.
  - Perform analysis in a single batch.
  - Use results to calculate the error contribution from selection of test portion (tp).
- For all tests, except proximates, randomly select one prepare extract and inject/analyze 7-10 times.
  - Use results to calculate total analytical error (TAE).

Analysis Calculations

- RSD_n (%) = Error contribution from selection of the analytical sample (as)
  - $RSD_n\ (\%) = 100 * \sqrt{RSD_{as}^2 - RSD_{tp}^2}$
- RSD_p (%) Error contribution from selection of test portion (tp)
  - $RSD_p\ (\%) = 100 * \sqrt{RSD_{tp}^2 - TAE^2}$
- Total Analytical Error (TAE) = RSD of replicate injections/analysis of single extract

Analysis Results

Proximates, Lasalocid and Vit A	Ash	Fat	Moisture	Protein	Lasalocid	Vitamin A
RSD_n (%):	0.526	1.31	0.284	1.016	0.326	N/A
RSD_p (%):	--	--	--	--	0.984	22.731

Metals on OES	Calcium	Copper	Iron	Magnesium	Manganese	Phosphorus	Potassium	Sodium	Zinc
RSD_n (%):	N/A	N/A	N/A	0.552	N/A	N/A	N/A	N/A	1.622
RSD_p (%):	4.783	8.974	3.694	1.081	7.515	1.288	0.421	1.324	2.862

Metals on ICP-MS	Arsenic	Cadmium	Chromium	Cobalt	Lead	Mercury	Molybdenum	Selenium
RSD_n (%):	< MRL	2.843	1.61	2.09	< MRL	< MRL	0.664	5.069
RSD_p (%):	< MRL	2.463	1.767	3.295	< MRL	< MRL	1.855	2.920

Note for Proximates: Analysis consumes the test portion in entirety. Only the selection of the analytical sample can be evaluated for error.

Note: N/A for RSD_n (%) indicates that the $\%RSD_P > \%RSP_n$

Thank you!

Collaborators:

- Kristy Broten, Analytical Lab Specialist
- Katlyn Hook, Chemist 1
- Jerry Karschnik, Analytical Lab Specialist
- Michele Swarbrick, Research Scientist 2
- Treeske Ehresmann, Chemistry Toxicology Unit Supervisor
- Brian Miller PhD, Quality Assurance Officer