

Update--Validation for Nutritive and Nonnutritive Metals Method

Dr. Sharon F. Webb

University of Kentucky

Division of Regulatory Services

Background

- ❑ 2008 James led interlaboratory study
- ❑ Comparing Official AOAC methods with proposed method
- ❑ AOAC 965.09 for nutritive metals as basis
- ❑ AOAC 2006.03 for nonnutritive metals as basis
- ❑ 9 Magruder samples
 - Dynamic range in metals concentration
- ❑ Reagent Grade KCl
- ❑ 5 samples with more dynamic Fe range

Goals Inter-Laboratory Study

- ❑ Determine if universal method is viable for both nutrients and non-nutrients in fertilizer
- ❑ Evaluate if using mixed acids rather than one acid enhances recoveries

Conclusions of Study

- ❑ Study shows universal method for both nutritive and nonnutritive metals in fertilizer is viable
- ❑ Mixed acid digestions can enhance recovery of nutritive and nonnutritive metals in fertilizer, *versus Nitric alone*

Validation Materials

| ID | 2006.03 | Description |
|----|-----------|-------------------------------------|
| A | 4321/2025 | Metal Fe oxysulfate |
| B | 4031/5938 | Magruder 2002-09B |
| C | 5488/5890 | Zinc Oxysulfate |
| D | 2818/7669 | Granulated mine waste |
| E | 1615/2056 | Metal oxysulfate |
| F | 3313/6267 | Western MAP |
| G | 7999/3375 | DAP from North African rock |
| H | 6501/4812 | NC MAP |
| I | 7738/7418 | China DAP |
| J | 3917/8165 | Magruder 2003-11 |
| K | 4459/8931 | Magruder 2004-07 |
| L | 8873/9469 | N-P-K lawn product blend |
| M | 9886/9774 | Organic biosolid |
| N | 4626/8088 | Organic mixed fertilizer + biosolid |
| O | 6411/3401 | Composted manure |
| P | 3716/4606 | Fe humate |
| Q | NA | NIST SRM 695 |
| R | NA | Magruder 2009-06 |

Term Changes

❑ Nonnutritive Metals

❑ Nutritive Metals

❑ Group A

❑ Group B

❑ As, Cd, Cr, Co, Mo, Ni,
Pb, Se

❑ Ca, Cu, Fe, Mg, Mn, Zn

LOD and LOQ

Group A

| | As, mg/L | Cd, mg/L | Cr, mg/L | Co, mg/L | Mo, mg/L | Ni, mg/L | Pb, mg/L | Se, mg/L |
|-----|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| LOD | 0.61 | 0.12 | 2.26 | 1.03 | 0.16 | 0.52 | 0.63 | 0.48 |
| LOQ | 2.03 | 0.39 | 7.55 | 3.43 | 0.53 | 1.74 | 2.09 | 1.60 |

Group B

| | Ca, % | Cu, mg/L | Fe, % | Mg, % | Mn, % | Zn, % |
|-----|--------|----------|--------|--------|---------|--------|
| LOQ | 0.0045 | 0.49 | 0.0018 | 0.0015 | 0.00003 | 0.0009 |

Completed to Date

- ❑ Method has been published in Journal of AOAC Intl. May/June 2014
- ❑ Open Access is available
- ❑ FREE access
- ❑ Collaborative Study Packet has been submitted
- ❑ External Review Panel (ERP) Reviewed September 2015
- ❑ Received comments from reviewers and ERP

Comments Received

- ❑ Expansion of method for inclusion of “heavy” metals
 - ❑ Hg & Al not included
- ❑ Total versus plant available nutrients/nonnutrients
 - ❑ Acidic vs alkali digestion to mimic metals’ reactions acids vs. bases
 - ❑ Adjust pH of digestion to mimic pH of soils that most crops are grown (pH ~5.5-6.5)
 - ❑ Use “leachable metals test” to mimic metal plant availability
 - ❑ Inclusion of macro- and micronutrients is misleading for label guarantees and not user-friendly to the end user

Comments, cont'd

□ Statistician:

- Incorrect calculations
- Conclusions not reflect statistical parameter estimates
- Poor precision for As, Se, Pb ($H_{orRat} > 2$)
 - Results of 2006.03 not correct either
 - AOAC 2006.03 not best choice for As, Se, & Pb
- Units different for different elements (% vs ppm)
- No assessment of values (?) presented in paper
 - No assessment of values presented in 2006.03 paper
- J AOAC Int. 2007; 90: 844-56
 - ICP/MS of As, Cd, Hg, & Pb of foods by Nordic Committee on Food Analysis

Although I felt like this...



**SCIENCE
CAN DO IT!**



...we will move on

Next Steps

- Address ERP comments
- Address statistician comments
- Address reviewer's comments
- Proceed forward like planned

Questions or comments?

