Update-Validation of Nutritive & Non-nutritive Metals Method

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Method

- Weigh 1 g sample into microwave vessel
- Add 9 mL of TMG HNO_3
  - Add in increments: either 3x3 mL or 2x4.5 mL
  - Allow for exothermic reactions
- Cover, let predigest overnight in hood
- Add 3 mL of TMG HCl
- Cap vessels & put in turntable for microwave digestion
- 2 Stage Microwave Digestion:
  - 75 °C over 20 minutes, hold for 20 minutes
  - 200 °C over 20 minutes, hold for 20 minutes
- Let cool for 30 minutes, pour up to 100 mL w/DI H_2O

So Far

- 2008 Minicollaborative Study
  - 965.09 & 2006.03 compared to mixed acid microwave
  - Showed viability of interested metals in one method
  - Showed enhanced recovery
- SLV: 15 of 30 materials used in 2006 Study, NIST 695 & Magruder 2009-06
  - Supported results & trends in 2008 study
- Group A: As, Cd, Cr, Co, Mo, Ni, Pb, & Se
- Group B: Ca, Cu, Fe, Mg, Mn, & Zn

Why worry about metals method?

- AAPFCO
- SUIP 25: Statement of uniform interpretation and Policy No. 25 available from http://www.aapfco.org/rules.html

Metal	ppm per 1% P_2O_5	ppm per 1% Micronutrient[3]
Arsenic	13	112
Cadmium	10	82
Cobalt	136[6]	2228[6]
Lead	61	463
Mercury	1	6
Molybdenum	42	300[4]
Nickel	250	1900
Selenium	26	180
Zinc	420	2900[4]

Regulatory Information

- Requests for Method by Community
- Utilize equipment & instrumentation commonly found in state fertilizer laboratories
- Use ICP-OES as detection, not ICP-MS
- Have detection limits that encompass levels as in SUIP #25
- Not overly aggressive in undue time, acid quality, burdensome digestion equipment, & expensive clean room requirements
- Extend current method to include nutritive metals
- Use simple acid mixture of HNO_3 & HCl, not $HCLO_4$
- Include the largest scope of materials to include large number of matrices

Changes to manuscript

- Table 6 Comparison of results of certified & consensus values
- Add Bias Column to table
  - Bias = |(Found value) – (Reference Value)|

	NIST SRM 695				Magruder 2009-06		
	Certified	Mean	Recovery, %		Consensus, ICP	Mean	Recovery, %
As, mg/kg	200 ± 5	199.9	100.0		330.58 ± 20.55	358.4	108.4
Cd, mg/kg	16.9 ± 0.2	17.1	101.2		343.55 ± 19.70	348.1	101.3
Co, mg/kg	65.3 ± 2.4	61.7	94.5		945.97 ± 53.68	959.3	101.4
Cr, mg/kg	244 ± 6	226.4	92.8		111.68 ± 11.16	127.9	114.6
Mo, mg/kg	20.0 ± 0.3	19.5	97.5		17.80 ± 2.70	18.1	101.7
Ni, mg/kg	135 ± 2	127.6	94.5		1135.8 ± 81.32	1117.3	98.4
Pb, mg/kg	276 ± 17	284.9	103.2		3688.5 ± 1852.4	4869.6	132.0
Se, mg/kg	*2.1 ± 0.1**	1.6	74.6		116.46 ± 8.33	110.6	94.9
Ca, %	2.26 ± 0.04	2.28	102.5		1.78 ± 0.12	1.79	100.4
Cu, ppm	1225 ± 9	1214	99.1		334 ± 38	339.7	101.7
Fe, %	3.99 ± 0.08	3.98	99.7		2.03 ± 1.02	3.03	149.0
Mg, %	1.79 ± 0.05	1.76	98.2		0.18 ± .12	0.191	105.9
Mn, %	0.305 ± 0.005	0.311	101.9		0.153 ± 0.013	0.177	115.5
Zn, %	0.325 ± 0.005	0.317	97.7		0.165 ± 0.11	0.164	99.3
	[illegible]						

	NIST SRM 695					Magruder 2009-06			
	Certified	Mean	Recovery, %	Bias		Consensus, ICP	Mean	Recovery, %	Bias
As, mg/kg	200 ± 5	199.9	100.0	0.1		330.58 ± 20.55	358.4	108.4	27.9
Cd, mg/kg	16.9 ± 0.2	17.1	101.2	0.2		343.55 ± 19.70	348.1	101.3	4.6
Co, mg/kg	65.3 ± 2.4	61.7	94.5	3.6		945.97 ± 53.68	959.3	101.4	13.4
Cr, mg/kg	244 ± 6	226.4	92.8	17.6		111.68 ± 11.16	127.9	114.6	16.2
Mo, mg/kg	20.0 ± 0.3	19.5	97.5	0.5		17.80 ± 2.70	18.1	101.7	0.3
Ni, mg/kg	135 ± 2	127.6	94.5	7.4		1135.8 ± 81.32	1117.3	98.4	180.5
Pb, mg/kg	276 ± 17	284.9	103.2	8.9		3688.5 ± 1852.4	4869.6	132.0	1180
Se, mg/kg	*2.1 ± 0.1**	1.6	74.6	0.5		116.46 ± 8.33	110.6	94.9	5.9
Ca, %	2.26 ± 0.04	2.28	102.5	0.0		1.78 ± 0.12	1.79	100.4	0.0
Cu, ppm	1225 ± 9	1214	99.1	10.6		334 ± 38	339.7	101.7	5.69
Fe, %	3.99 ± 0.08	3.98	99.7	0.0		2.03 ± 1.02	3.03	149.0	1.00
Mg, %	1.79 ± 0.05	1.76	98.2	0.0		0.18 ± .12	0.191	105.9	0.0
Mn, %	0.305 ± 0.005	0.311	101.9	0.0		0.153 ± 0.013	0.177	115.5	0.0
Zn, %	0.325 ± 0.005	0.317	97.7	0.0		0.165 ± 0.11	0.164	99.3	0.0
	*Reference Value								

Changes to manuscript

- Table 6 Comparison of results of certified & consensus values
- Add Bias Column to table
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- Table 7 Method precision & comparability to 2006.03
- Correct Horrat

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg Collaborative Study (2006.03)	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
A	41.49	1.86	22.15	42.93	187.32	0.58
B	478.89	1.39	263.2	47.96	181.95	0.62
C	6.89	3.05	4.87	63.12	141.42	0.72
D	5917.76	3.43	4945	6.09	119.67	2.24
E	2953.58	0.62	2432	10.56	121.45	0.36
F	10.36	2.1	9.75	41.73	106.26	0.54
G	22.32	0.35	22.43	9.36	99.49	0.10
H	2.92	3.32	2.36	17.6	123.63	0.70
I	11.95	1.77	13.04	13.27	91.63	0.46
J	189.46	2.23	185.45	4.27	102.16	0.86
K	168.49	2.23	175.28	7.84	96.13	0.86
L	bdl	NA	NA	NA	NA	NA
M	9.31	1.45	7.35	53.17	126.64	0.36
N	17.41	1.82	12.74	15.74	136.62	0.50
O	3.77	4.95	4.16	45.14	90.66	1.08
P	60.72	3.73	47.83	2.22	126.94	1.22

As
bdl: below instrument detection limit

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg Collaborative Study (2006.03)	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
A	2.4	3.92	2.25	39.14	106.78	0.80
B	5.29	7.83	7.56	19.65	69.97	1.78
C	22.07	1.79	21.28	0.61	103.72	0.50
D	44.91	4.04	36.64	3.2	122.56	1.28
E	27.86	6.51	22.58	4.25	123.4	1.90
F	235.39	0.76	214.6	3.06	109.69	0.30
G	28.73	1.61	26.69	5.79	107.65	0.48
H	63.58	0.9	55.29	1.25	115	0.30
I	bdl	NA	NA	NA	NA	NA
J	16.65	0.44	15.52	2.77	107.26	0.12
K	66.05	2.29	64.04	2.95	103.14	0.76
L	bdl	NA	NA	NA	NA	NA
M	4.32	9.64	4.19	3.18	103.17	2.14
N	bdl	NA	NA	NA	NA	NA
O	bdl	NA	NA	NA	NA	NA
P	0.52	20.46	0.57	66.74	92.02	1.88

Cd
bdl: below instrument detection limit

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg Collaborative Study (2006.03)	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
A	119.71	2.69	97.75	4.12	122.47	0.98
B	212.27	0.89	195.6	9.34	108.52	0.36
C	bdl	NA	NA	NA	NA	NA
D	19.8	0.39	17.33	4	114.25	0.10
E	26.5	1.28	23.01	3.53	115.15	0.38
F	9.05	1.14	8.91	2.94	101.57	0.28
G	bdl	NA	NA	NA	NA	NA
H	bdl	NA	NA	NA	NA	NA
I	bdl	NA	NA	NA	NA	NA
J	59.57	0.39	45.2	8.52	131.79	0.16
K	545.71	3.3	532.78	2.45	102.43	1.28
L	bdl	NA	NA	NA	NA	NA
M	22.54	4.39	21.25	4.98	106.08	1.52
N	bdl	NA	NA	NA	NA	NA
O	bdl	NA	NA	NA	NA	NA
P	13.65	2.12	10.67	9.14	127.93	0.56

Co
bdl: below instrument detection limit

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
			Collaborative Study (2006.03)			
A	892.48	2.46	731.5	10.09	122.01	2.34
B	461.2	1.26	396.99	14.2	116.17	1.10
C	172.14	0.47	159.5	1.31	107.93	0.36
D	45.39	0.66	38.25	3.66	118.67	0.40
E	122.57	1.23	101.15	2.29	121.18	0.88
F	586.13	0.83	566.16	8	103.53	0.76
G	302.41	1.00	281.91	2.88	107.27	0.84
H	380.12	0.32	341.28	3.05	111.38	0.28
I	18.31	0.71	18.11	1.26	101.09	0.38
J	219.62	0.14	164.4	10.38	133.59	0.10
K	189.16	1.89	169.49	2.76	111.6	1.44
L	6.41	1.97	5.84	5.52	109.78	0.46
M	129.29	2.29	115.55	2.69	111.89	1.66
N	6305.07	2.55	5980.93	0.99	105.42	3.34
O	120.89	1.36	108.85	6.75	111.88	0.98
P	146.07	2.83	134.77	7.08	108.38	2.10

Cr
bdl: below instrument detection limit

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
			Collaborative Study (2006.03)			
A	109.17	0.9	69.16	7.35	157.85	060
B	156.58	2.47	116.69	18.28	134.18	1.78
C	4.84	2.5	3.89	10.04	124.4	1.08
D	3.72	3.19	2.73	21.89	136.22	1.32
E	6.88	6.27	4.39	22.27	156.79	1.40
F	20.48	1.26	18.47	1.68	110.91	0.68
G	4.41	1.47	4	12.49	110.31	0.64
H	13.69	0.79	11.74	4.75	116.61	0.40
I	bdl	NA	NA	NA	NA	NA
J	19.39	0.36	13.21	7.94	146.76	0.18
K	44.68	2.1	42.88	5.23	104.19	1.30
L	bdl	NA	NA	NA	NA	NA
M	14.7	1.93	11.53	15.03	127.53	0.98
N	9.31	1.92	7.83	7.22	118.88	0.46
O	bdl	NA	NA	NA	NA	NA
P	15.53	0.76	12.44	14.46	124.83	0.40

Mo
bdl: below instrument detection limit

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
			Collaborative Study (2006.03)			
A	384.29	0.57	331.92	3.94	115.78	0.70
B	330.3	3.66	295.83	18.02	111.65	1.10
C	30.1	3.63	26.6	3.55	113.14	0.74
D	bdl	NA	NA	NA	NA	NA
E	39.14	3.35	36.39	5.75	107.57	0.74
F	296.16	0.38	279.34	0.93	106.02	0.46
G	44.33	1.9	42.45	3.05	104.42	0.42
H	60.14	1.83	52.76	3.73	113.98	1.70
I	bdl	NA	NA	NA	NA	NA
J	122.1	0.67	101.89	7.03	119.84	0.70
K	1683.6	3.08	1683.27	4.63	100.02	1.18
L	bdl	NA	NA	NA	NA	NA
M	85.14	4	86.22	21.3	98.75	0.98
N	20.96	3.12	18.55	12.64	112.97	0.52
O	bdl	NA	NA	NA	NA	NA
P	38.9	3.89	33.39	13.42	116.5	0.84

Ni
bdl: below instrument detection limit

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
			Collaborative Study (2006.03)			
A	136.03	8.63	119.6	64.13	113.74	3.20
B	3729	8.23	3070.11	30.44	121.47	1.20
C	1072	1.22	996.25	1.64	107.64	0.62
D	3790	0.47	3292.06	4.55	115.12	0.40
E	4121	4.04	4075.75	16.36	101.11	2.50
F	4.08	6.44	3.08	4.54	132.53	2.00
G	4.35	3.56	3.81	15.89	114.16	0.78
H	bdl	NA	NA	-NA	NA	NA
I	bdl	NA	NA	-NA	NA	NA
J	275.84	0.49	245.35	3.9	112.43	0.22
K	514.92	1.66	509.54	3.47	101.06	0.76
L	bdl	NA	NA	NA	NA	NA
M	70.73	0.24	66.29	17.21	106.69	0.08
N	62.25	7.02	58.53	6.55	106.36	2.32
O	3.25	13.07	3.34	61.88	97.38	2.78
P	383.07	3.83	343.08	10.13	111.66	1.66

Pb
bdl: below instrument detection limit

ID	Average, mg/kg by Proposed Method (n=3)	RSD, %	Average, mg/kg Collaborative Study (2006.03)	RSDr, % Collaborative Study (2006.03)	Recovery, %	Horrat(r)
A	3.09	9.06	6.96	12.43	44.34	1.90
B	30.31	1.47	31.03	14.15	97.68	0.44
C	bdl	NA	NA	NA	NA	NA
D	34.7	4.01	28.4	4.77	122.17	1.22
E	26.73	1.37	25.9	11.05	103.2	0.40
F	7.1	6.93	1.4	83.34	507.16	1.66
G	5.54	14	1.73	47.46	320.11	3.22
H	bdl	NA	NA	-NA	NA	NA
I	bdl	NA	NA	NA	NA	NA
J	5.14	8.53	3.2	42.1	160.53	1.94
K	245.39	3.15	257.17	2.89	95.42	1.26
L	bdl	NA	NA	NA	NA	NA
M	9.16	10.35	9.47	8.57	96.7	2.56
N	bdl	NA	NA	NA	NA	NA
O	bdl	NA	NA	NA	NA	NA
P	bdl	NA	NA	NA	NA	NA

Se
bdl: below instrument detection limit

Changes to manuscript

- Table 6 Comparison of results of certified & consensus values
- Add Bias Column to table
  - Bias = |(Found value) – (Reference Value)|
- Table 7 Method Precision & Comparability to 2006.03
- Correct Horowitz
- Table 8 Method Precision & Comparability for Group B

	Calcium			Copper			Iron		
ID	Mean, % (n=3)	RSD, %	Horrat(r)	Mean, mg/kg (n=3)	RSD, %	Horrat(r)	Mean, % (n=3)	RSD, %	Horrat(r)
A	0.869	1.07	0.52	6636.7	0.58	0.76	53.76	4.49	0.48
B	2.497	0.93	0.54	9123.2	1.33	1.98	24.95	2.58	2.10
C	0.51	1.94	0.88	11547	1.75	1.64	4.458	0.28	0.46
D	3.411	1.42	0.86	14284	1.88	1.60	13.96	3.67	2.74
E	2.797	1.57	0.92	9767.8	0.95	0.58	16.59	2.88	2.20
F	0.913	0.96	0.48	5421.2	1.06	0.24	1.074	0.74	0.38
G	1.418	0.57	0.30	684.31	0.52	0.16	0.241	0.45	0.36
H	0.378	0.42	0.18	589.86	8.32	1.56	1.417	0.56	0.30
I	0.149	2.81	1.06	498.88	1.98	0.38	0.62	0.33	0.32
J	2.169	1.36	0.76	368.99	1.85	1.88	3.805	1.52	0.94
K	4.58	2.35	1.48	370.35	0.70	0.66	2.268	1.13	0.64
L	0.109	4.13	1.48	1800	1.86	0.40	2.103	0.63	0.36
M	1.724	0.52	0.28	3192.9	1.04	0.84	4.045	0.89	0.56
N	3.976	1.29	0.80	4651.4	2.39	1.86	8.927	1.15	0.80
O	2.493	1.88	1.08	3214.1	3.12	0.88	0.23	2.00	1.60
P	6.511	0.39	0.26	1757.3	1.80	0.60	23.82	3.95	3.18

	Mg			Mn			Zinc		
ID	Mean, % (n=3)	RSD, %	Horrat(r)	Mean, mg/kg (n=3)	RSD, %	Horrat(r)	Mean, % (n=3)	RSD, %	Horrat(r)
A	0.24	0.81	0.32	15065	1.22	2.60	1.506	2.51	2.66
B	1.102	0.74	0.38	63109	1.07	2.82	5.371	0.79	1.02
C	0.343	0.92	0.40	6251.7	0.58	1.08	36.57	0.91	1.56
D	1.964	1.23	0.68	780.77	1.36	1.86	1.265	0.96	1.00
E	1.728	0.84	0.46	10646	1.17	2.36	4.115	1.00	1.24
F	0.652	0.9	0.42	227.94	0.81	0.92	0.287	1.18	0.98
G	0.377	0.51	0.22	25.76	1.14	0.92	0.0424	0.74	0.46
H	1.379	0.58	0.30	146.61	0.36	0.38	0.098	0.78	0.56
I	1.044	0.65	0.32	217.12	0.28	0.32	0.0176	1.01	0.56
J	1.657	1.34	0.72	2835	2.09	3.46	0.302	1.36	1.14
K	1.35	1.91	1.00	2084.3	2.36	3.72	0.356	4.18	3.58
L	0.168	0.65	0.24	167.15	1.26	1.36	0.0046	2.87	1.28
M	0.568	1.11	0.52	269.41	2.61	3.04	0.0568	1.08	0.70
N	0.387	0.55	0.24	1618.5	0.11	0.16	0.0353	1.95	1.18
O	0.208	0.79	0.32	114.46	3.49	3.56	0.0085	1.70	0.84
P	0.412	1.10	0.48	9625	1.00	1.98	0.0065	2.22	1.04

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- Correct Horowitz
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  - Table 8 Method Precision & Comparability for Group B
- Fertilizer Subgroup of the Agricultural Materials Community Statement of Method Need & Support Trace Metals in Fertilizer

Fertilizer Subgroup of the Agricultural Materials Community Statement of Method Need & Support Trace Metals in Fertilizer

- In 2002 the fertilizer community began holding annual meetings (Fertilizer Metals Forum) to discuss their needs pertaining to methods of analysis of trace metals in fertilizers. This need rose primarily from a regulatory impetus to establish limits for certain metals. Results of this work included guidance for setting metals limits in fertilizers that formed the basis for the current proposed guidance published in the AAPFCO annual publication (publication #69) as Statement of Uniform Interpretation and Policy No. 25 (SUIP #25) available from http://www.aapfco.org/rules.html.
- The second result was a fully collaborated method (AOAC 2006.03). This method came about as the result of input from the community between 2002 and 2006. While the method was successfully collaborated, it was done quickly in response to an urgent nation-wide need.. Several states had regulations in place but no “official” method. Any existing methods for the metals (primarily environmental methods) were not validated for fertilizers as a matrix. Fertilizers present a very unique matrix; it was determined that existing methods did not give reliable results due to high concentrations of salts, spectral interferences and ionization effects not properly controlled. The 2006 method was an improvement on the methodology used in the environmental sector, but still needed additional refinement as it was not optimized for all elements and interference posed by high levels of Iron.

Support Letter Continued:

- With the success of the model, the Metals Forum evolved into the Methods Forum in 2008 to address a wide array of methods needs of the fertilizer community. Over the years hundreds of hours have been spent by dozens of volunteers discussing and forming proposals to establish science/risk based limits as well as develop and validate methods of analysis to monitor those limits.
- The community continued to work on the improving the metals method and eventually requested that a revised method be collaborated that addressed the concerns of the community. Guidance to the study director was prepared to address the concerns and meet the needs of the community. Below are the primary charges to the study director and method champion.
- The method must –
- Use equipment and instruments commonly available in state fertilizer laboratories –
- Utilize ICP-OES for detection, not ICP-MS as it is rarely available to state fertilizer labs
- Have detection limits that encompass the levels established in SUIP #25, but not overly aggressive avoiding undue time, acid quality and expensive clean room procedures
- Not be burdensome as it relates to digestion equipment or cross contamination

Support Letter Continued:

- Extend the current method to also encompass nutritive metals for greater efficiency
- Include a simple acid mixture of nitric and hydrochloric acids, avoid perchloric acid
- Ensure the greatest possible scope of materials be incorporated to include as many fertilizer matrices as possible, realizing that some sacrifices in performance would be worth the expanded scope.
- The community has kept in close contact with the study director during method development and validation through face-to-face annual meetings and by the use of email and conference calls. The community has consensus that all of the above expectations are met in the currently proposed method as documented in *JAOAC* 97, pp 700-711 and as submitted to the Fertilizer ERP.

Summary of Method:

- Scope: Group A & Group B
- Materials/Matrices: micronutrient mixes, concentrated phospahte products, NPK blends, organic materials, & phosphate ores, Magruder & NIST
- Group A:

Metal	High Concentration	Medium Concentration	Low Concentration
As, ppm	5900	190	2.03
Cd, ppm	235	66	0.39
Co, ppm	546	26	0.97
Cr, ppm	6300	220	2.13
Mo, ppm	157	45	0.53
Ni, ppm	1684	296	1.74
Pb, ppm	4121	136	2.09
Se, ppm	245	30	1.60

Summary of Method:

Group B:

Metal	High Concentration	Medium Concentration	Low Concentration
Ca, %	6	0.9	0.0045
Cu, ppm	14000	1.33	0.49
Fe, %	54	0.241	0.0018
Mg, %	2	0.4	0.0015
Mn, %	15000	0.0147	0.00003
Zn, %	36	0.3	0.0009

- Proposed method is both 2006.03 & mixed acid
- Meets community requirements
- Reviewers concerns adequately met
- Communication is maintained with community

Conclusions & Next Steps

- Collaborative Study ?
- Assign number ?

Questions/Comments?

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