

Elements in feed

New York State Department of Agriculture and Markets

Methods needs statement

- Detect as many elements as possible with high selectivity
 - 27 elements
 - Analyzed by ICP-MS and ICP-OES
- Quantify elements accurately at LOQ and 2x maximum tolerable limit (MTL)
 - Matrix samples analyzed 7 times at 2xLOQ and midrange
 - Samples generated using AAFCO feed samples, NIST material, or feed samples spiked

Method

To microwave vessel add:

1.0 gram feed
5 ml D-HNO₃
2 ml H₂O₂
1 ml RO/DI RO/DI water

Pre-digest overnight

Microwave:

<u>Ramp Time</u>	<u>Temp C</u>	<u>Hold Time(min)</u>
20	75	20
20	200	20

Transfer digest to a 100 ml volumetric flask

Dilute as needed

Analytical Instruments

- ICP-MS
 - Thermo ICAPQ
 - He mode for all but Be
- ICP-OES
 - Agilent 5100
 - Radial and axial view

Methods needs statement

- Detect as many elements as possible with high selectivity
 - 27 elements

Be	Pb	Mn
Al	Se	Zn
Tl	Cr	Cu
Hg	Co	Fe
U	Mo	Mg
Sb	Ni	Ca
Cd	V	P
Th	Na	S
As	B	K

Elements not included

F	Li
I	Rb
Cl	Si
Ba	Ag
Bi	Sr
Br	Sn
Ge	W

Method Performance Characteristics

Operational range (ppm)

target range		tested range	target range		tested range	target range		tested range
Be		0.1- 1000	Pb	0.5 – 200	0.5-200	Mn	1 – 4000	4.5 - 1000
Al	20-2000	20- 2000	Se	0.01-10	0.03-10	Zn	0.3 – 2000	6 - 2000
Tl		0.07- 30	Cr	0.02 -60 K	2 - 1000	Cu	0.4 – 1000	1 - 1000
Hg	0.01- 4	0.01- 4	Co	0.01 - 50	0.45 - 50	Fe	5 – 6000	7 - 6000
U	10-200	10-200	Mo	0.02 – 300	0.75 - 300	Mg	120 – 160K	200 – 160K
Sb	7-300	7-300	Ni	0.01 – 500	2.1 - 500	Ca	100 – 30K	95 – 30K
Cd	0.05-20	0.05-20	V	0.005 – 100	0.03 - 100	P	160 – 20K	600 – 20K
Th		1-8000	Na	100-120 K	100-120 K	S	50 – 10K	800 – 10K
As	0.2-60	0.2-60	B	15 – 300	15 - 300	K	150 – 20K	600 – 40K

Method Performance Characteristics (ppm)

2xLOQ midrange			2xLOQ midrange			2xLOQ midrange		
Be	0.2	500	Pb	1	100	Mn	9	2000
Al	40	1000	Se	0.06	5	Zn	11.6	1000
Tl	0.13	15	Cr	4.5	500	Cu	2.03	500
Hg	0.02	2	Co	0.9	25	Fe	14.11	3000
U	20	100	Mo	1.5	150	Mg	398	8000
Sb	14	150	Ni	4.2	250	Ca	191	150 K
Cd	0.1	10	V	0.06	50	P	1333	10K
Th	2	4019	Na	200	60 K	S	1645	5000
As	0.4	30	B	30	150	K	1325	20 K

Sample preparation

2xLOQ			2xLOQ			2xLOQ		
midrange			midrange			midrange		
Be	0.2	500	Pb	1	100	Mn	9	2000
Al	40	1000	Se	0.06	5	Zn	11.6	1000
Tl	0.13	15	Cr	4.5	500	Cu	2.03	500
Hg	0.02	2	Co	0.9	25	Fe	14.11	3000
U	20	100	Mo	1.5	150	Mg	398	8000
Sb	14	150	Ni	4.2	250	Ca	191	150 K
Cd	0.1	10	V	0.06	50	P	1333	10K
Th	2	4019	Na	200	60 K	S	1645	5000
As	0.4	30	B	30	150	K	1325	20 K

spiked feed

Incurred feed (NIST, AAFCO)

Results

accuracy

ICP-MS

2x LOQ

n=7

	ave. % rec	preferred accuracy		ave. % rec	preferred accuracy		ave. % rec	preferred accuracy
Be	101	80-110	Pb	107	80-110	Mn	98	80-110
Al	99	80-110	Se	101	60-115	Zn	102	80-110
Tl	98	80-110	Cr	97	80-110	Cu	101	80-110
Hg	98	60-115	Co	99	80-110	Fe	94	80-110
U	101	80-110	Mo	101	80-110	Mg	95	90-107
Sb	105	80-110	Ni	102	80-110	Ca	99	90-107
Cd	104	80-110	V	103	60-115	P	103	95-105
Th	102	80-110	Na	103	90-107	S	92	95-105
As	104	80-110	B	104	80-110	K	96	95-105

Results

repeatability

ICP-MS

2x LOQ

n=7

	CVr	preferred CVr		CVr	preferred CVr		CVr	preferred CVr
Be	7.24	<22	Pb	3.37	<16	Mn	2.92	<11
Al	2.38	<9	Se	3.70	<22	Zn	1.73	<11
Tl	3.55	<22	Cr	5.93	<13	Cu	1.48	<16
Hg	7.78	<22	Co	5.20	<16	Fe	6.55	<11
U	4.25	<11	Mo	3.08	<16	Mg	2.27	<8
Sb	2.70	<11	Ni	6.98	<13	Ca	1.82	<8
Cd	7.86	<22	V	8.03	<22	P	3.71	<6
Th	4.97	<15	Na	4.78	<15	S	3.59	<6
As	2.25	<18	B	4.44	<22	K	3.06	<6

Results

accuracy

ICP-MS

Midrange

n=7

	ave. % rec	preferred accuracy		ave. % rec	preferred accuracy		ave. % rec	preferred accuracy
Be	105	95-105	Pb	108	85-110	Mn	101	95-105
Al	102	95-105	Se	103	80-115	Zn	103	95-105
Tl	101	80-110	Cr	104	92-106	Cu	102	90-107
Hg	102	75-120	Co	100	80-110	Fe	107	90-108
U	103	85-110	Mo	108	85-110	Mg	105	92-105
Sb	107	85-110	Ni	109	85-110	Ca	105	92-105
Cd	107	80-115	V	102	85-108	P	102	97-103
Th	107	96-104	Na	107	95-102	S	104	95-105
As	103	80-115	B	100	90-107	K	95	97-103

Results

repeatability

ICP-MS

Midrange

n=7

	CVr	preferred CVr		CVr	preferred CVr		CVr	preferred CVr
Be	11.3	<6	Pb	7.83	<8	Mn	8.69	<6
Al	3.02	<6	Se	4.56	<8	Zn	3.50	<6
Tl	5.63	<11	Cr	8.02	<6	Cu	3.88	<8
Hg	6.57	<16	Co	4.61	<11	Fe	2.89	<6
U	4.75	<8	Mo	6.59	<8	Mg	2.27	<8
Sb	3.46	<8	Ni	8.43	<8	Ca	3.15	<4
Cd	6.02	<11	V	3.81	<9	P	2.68	<4
Th	3.61	<6	Na	6.20	<3	S	5.81	<5
As	4.43	<11	B	1.31	<8	K	2.51	<4

ICP-OES

- All toxic metals suffered from interference due to so many elements being present in a complex matrix.
- Possibly could be investigated by spiking each element individually
- Some elements (Al, B, Be, Co, Na, Fe, Cu, Mg, Ca) ok but a new LOQ would have to be determined and spiked at that level to validate

AAFCO check samples

Repeatability

CVr (n=7)

201422

	MS	OES	preferred
Ca	1.68	1.75	<4
Cu	2.43	7.33	<8
Fe	2.73	3.9	<7
Mg	3.13	1.3	<6
Mn	5.03	2.91	<9
P	2.3	1.73	<5
K	1.81	4.87	<4
Na	4.01	1.96	<6
Zn	3.87	2.02	<8

201321

	MS	OES	preferred
Ca	1.68	1.82	<4
Cu	2.32	25.8	<12
Fe	1.68	2.25	<8
Mg	1.22	1.03	<6
Mn	2.18	2.35	<9
P	1.72	1.48	<4
K	1.59	4.22	<4
Na	3.2	0.94	<6
Zn	4.71	2.35	<8

201426

	MS	OES	preferred
Ca	4.62	1.47	<3
Cu	2.31	28.9	<12
Fe	2.33	1.44	<8
Mg	3.68	0.705	<5
Mn	5.14	1.84	<8
P	2.19	1.16	<4
K	0.713	3.84	<4
Na	4.55	1.65	<4
Zn	3.41	2.47	<7

201432

	MS	OES	preferred
Ca	3.90	2.75	<3
Cu	5.56	13.8	<12
Fe	1.95	3.96	<8
Mg	3.56	1.45	<6
Mn	2.38	3.46	<8
P	2.49	2.37	<5
K	3.19	4.45	<4
Na	2.44	2.45	<6
Zn	4.86	6.00	<8

201428

	MS	OES	preferred
Ca	3.06	3.38	<4
Cu	3.44	14.3	<12
Fe	2.36	2.77	<7
Mg	2.98	1.39	<6
Mn	2.15	2.17	<9
P	2.62	1.49	<4
K	1.61	4.52	<4
Na	1.96	1.09	<5
Zn	3.37	1.42	<8

201430

	MS	OES	preferred
Ca	1.31	2.59	<4
Cu	1.40	3.67	<8
Fe	1.78	2.77	<7
Mg	2.68	1.98	<6
Mn	3.46	2.05	<9
P	2.71	1.57	<5
K	1.20	4.17	<4
Na	3.93	1.47	<6
Zn	3.45	2.58	<6

201424

	MS	OES	preferred
Ca	2.60	1.79	<4
Cu	3.60	20.2	<12
Fe	7.63	9.61	<8
Mg	2.62	0.991	<5
Mn	2.84	2.28	<8
P	2.08	0.827	<4
K	0.881	4.50	<4
Na	1.67	1.00	<6
Zn	3.07	0.726	<8

OES Cu result for many of the samples were near or below LOQ

AAFCO check samples z scores (n=7)

201422

	<u>MS</u>	<u>OES</u>
Ca	-0.030	0.238
Cu	0.072	0.226
Fe	-0.0596	-0.0272
Mg	0.136	-0.587
Mn	-0.348	0.178
P	0.425	-0.558
K	-0.347	-0.282
Na	-0.344	-0.266
Zn	0.839	0.022

201321

	<u>MS</u>	<u>OES</u>
Ca	-0.487	-0.255
Cu	0.0867	1.37
Fe	0.482	0.877
Mg	-0.252	-0.208
Mn	-0.222	0.441
P	0.460	0.136
K	-0.380	-0.134
Na	-0.270	-0.436
Zn	0.954	-0.0261

201426

	<u>MS</u>	<u>OES</u>
Ca	0.427	-0.254
Cu	-0.493	0.846
Fe	0.441	0.504
Mg	0.272	-0.126
Mn	-0.310	0.589
P	1.21	0.117
K	-0.490	-0.321
Na	0.0343	-0.209
Zn	0.838	0.608

201432

	<u>MS</u>	<u>OES</u>
Ca	0.519	-0.367
Cu	-0.298	0.264
Fe	0.128	-0.0653
Mg	-0.485	-0.255
Mn	0.102	0.657
P	0.499	-0.150
K	-0.272	-4.25
Na	-0.162	-0.182
Zn	0.415	0.281

201428

	<u>MS</u>	<u>OES</u>
Ca	-0.363	-0.343
Cu	-0.0991	1.12
Fe	0.146	0.565
Mg	0.0411	-0.120
Mn	-0.495	0.276
P	0.395	-0.0358
K	-0.485	0.563
Na	-0.241	-0.429
Zn	0.827	0.0769

201430

	<u>MS</u>	<u>OES</u>
Ca	-0.595	-0.572
Cu	-0.0857	0.235
Fe	0.391	0.513
Mg	0.231	-0.139
Mn	-0.385	0.493
P	0.482	-0.294
K	-0.230	-0.185
Na	-0.281	-0.407
Zn	0.438	-0.304

201424

	<u>MS</u>	<u>OES</u>
Ca	0.357	-0.363
Cu	0.350	1.05
Fe	0.0322	0.186
Mg	0.463	-0.268
Mn	-0.124	0.770
P	0.684	0.0120
K	0.0833	0.154
Na	-0.237	-0.302
Zn	0.750	0.283

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- Thanks to Thomas King and Kristen Gilbert

Questions?