Determination of Trace Metals in Seeds and Plant-Derived Feed by Microwave Assisted Digestion and Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Li Sheng

EPL BioAnalytical Services (www.eplbas.com), 9095 West Harristown Blvd., Niantic, IL 62551

Abstract

As, Cd, Co, Cr, Pb, Se and Hg are detrimental to plant growth if present in high levels in seeds. If introduced from plant-derived feeds they may be accumulated in livestock and marine animals, and eventually move to humans through the food chain to cause a variety of health problems. A method to determine these trace metals in seeds and feeds with high sensitivity and selectivity was developed and validated. Such a method is not currently available in the AOAC Official Methods of Analysis. In the reported method, trace metals in seed and feed samples are determined by ICP-MS after microwave assisted digestion with the reporting limits (in dry basis) of 0.04 ppm for Hg, 1.2 ppm for Cr, and 0.1 ppm for all the other metals. Maize grain, soy seed, canola seed, rodent diet, soy meal, canola meal and certified reference materials were evaluated. The coefficient of variation as a measurement of the assay precision was less than 10% for all sample matrices; and the spiking recoveries ranged from 80-120% for all metals except Se in soy seed which yielded a mean recovery of 124%.

Toxicological Information[1]

As Carcinogenic effects
LD50:145 mg/kg [Mouse]

Cd Carcinogenic effects
LD50: 229.9 mg/m^3 dust 4 hour(s) [Rat]

Co Toxic to lungs
LD50: 6170 mg/kg [Rat]

Cr Chronic exposure may cause liver and kidney damage.

Pb Carcinogenic effects
May cause damage to blood, kidneys, central nervous system.

Se LD50: 6700 mg/kg [Rat]

Hg May cause damage to blood, kidneys, liver, brain, nervous system.

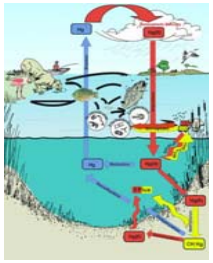

Figure 1. The mercury cycle[2].

Methods

Sample Preparation

- Frozen samples were ground to pass 0.75 mm sieve.
- After adding 6 mL nitric acid and 2 mL hydrogen peroxide samples were digested following the program in Table 1[3].
- Digested samples were diluted to 25 mL and filtered through a 0.45 µm syringe filter.
- Two 1:8 dilutions were performed for each sample: one with de-ionized water (Sample A for all except Hg), and another in 7% HCl (Sample B for Hg) [4, 5].

Stage	Power	Max %	Ramp	Temperature	Hold
1	1600	100	5	50	0
2	1600	100	10	180	0
3	1600	100	2	200	20

Table 1. Microwave digestion program. CEM MARS5 with 40 position carousel.

ICP-MS Analysis[6]

- ESI SC-4DX auto-sampler
- Bruker 820 ICP –MS
- Calibration Analytes:

A: Co59, Cdll4, Pb ... (Pb206+Pb207+Pb208)

B: Hg... (Hg199+Hg200+Hg201+Hg202)

A (CRI): Cr52, As75, Se78

- Internal Standards

Sc45, Y89, InII5, Tb159, Bi209

- Calibration Standards (ng/mL)

A: Co, Cd, As, Se, Pb - 0.25, 1, 10, 20

Cr - 3, 10, 20

B: Hg - 0.1, 1, 10

- Calibration Parameters

Linear, Correlation Coefficient > 0.99

Weighted fit, Error < 25%

	Parameters	Settings
Gas flow (L/min)	Plasma flow	17.5
	Auxiliary flow	1.8
	Nebulizer flow	1.0
	Sheath flow	0.19
CRI Gases (mL/min)	Skimmer (with He)	70
RF	RF Power (kW)	1.4
Sample Introduction	Sampling depth (mm)	6.5
	Pump rate (rpm)	5
	Stabilization time (s)	35
	Spray chamber (°C)	3
Ion Optics (volts)	1st Extraction lens	-1
	2nd Extraction lens	-189
	3rd Extraction lens	-242
	Corner lens	-179
	Mirror lens left	45
	Mirror lens right	38
	Mirror lens bottom	39
	Entrance lens	1
	Entrance plate	-41
	Fringe bias	-2.8
	Pole bias	0
Quadrupole scan	Scan mode	Peak hopping
	Dwell time (ms)	10
	Points per peak	1
	Scans/Replicate	30
	Replicates/Sample	5

Table 2. ICP MS condition.

Results

CRM

Values (µg/g)	As	Cd	Co	Cr	Hg	Pb	Se
Tomato Leaves Certified	0.112± 0.004	1.52± 0.04	0.57 ± 0.02	1.99± 0.06	0.031± 0.007*	NA	0.054± 0.003*
Tomato Leaves Measured	0.113	1.53	0.568	2.05	0.0362*		0.062*
Peach Leaves Certified	0.060± 0.018*	0.026± 0.003*	(0.07)*	(1)	0.034± 0.004*	0.87± 0.03	0.120± 0.009
Peach Leaves Measured	0.079*	0.023*	0.08*	0.968	0.0335*	0.849	0.119

*Table 3. Test results of NIST CRM 1573a-tomato leaves and 1547-peach leaves. ( ) Noncertified values. * Values lower than EPL reporting limit.*

Seeds

Seed	Result	As	Cd	Co	Cr	Hg	Pb	Se
Maize Grain	Content (ppm DB)	<0.1	<0.1	<0.1	<1.2	<0.04	<0.1	<0.1
	CV (%)	1.75*	2.39*	3.05*	2.66*	2.68*	2.68*	4.58*
	Recovery (%)	104	106	102	93.7	104	105	112
Canola Seed	Content (ppm DB)	<0.1	<0.1	<0.1	<1.2	<0.04	<0.1	0.475
	CV (%)	0.59*	1.06*	1.09*	0.68*	6.87*	1.10*	4.64
	Recovery (%)	112	111	106	107	111	107	112
Soy Seed	Content (ppm DB)	<0.1	<0.1	<0.1	<1.2	<0.04	<0.1	<0.1
	CV (%)	1.66*	3.32*	3.33*	1.62*	1.85*	3.41*	2.27*
	Recovery (%)	115	109	109	114	106	108	124

Table 4. Test results of commercial available seeds. ppm DB = µg/g Dry Base. Moisture values were tested according to AOAC 925.09. The calculations were based on eight samples and four spikes. Spike:10 (lowest standard). *Calculated using the spiked samples.*

Meals and Diet

Seed	Result	As	Cd	Co	Cr	Hg	Pb	Se
Canola Meal	Content (ppm DB)	<0.1	<0.1	<0.1	<1.2	<0.04	0.143	1.12
	CV (%)	1.59*	2.42*	2.82*	2.08*	2.06*	4.47	4.02
	Recovery (%)	111	111	108	107	94.2	105	109
Soy Meal	Content (ppm DB)	<0.1	<0.1	<0.1	<1.2	<0.04	<0.1	<0.1
	CV (%)	1.66*	1.63*	1.92*	3.04*	2.28*	2.55*	1.88*
	Recovery (%)	118	114	105	110	100	110	106
Rodent Diet	Content (ppm DB)	0.292	<0.1	0.309	<1.2	<0.04	0.223	0.408
	CV (%)	5.24	2.06*	1.74	0.89*	1.26*	7.13	7.26
	Recovery (%)	92.8	84.4	91.4	107	107	100	108

Table 5. Test results of commercial available meals and diet. ppm DB = µg/g Dry Base. Moisture values were tested according to AOAC 925.09. The calculations were based on eight samples and four spikes. Spike:10 (lowest standard). *Calculated using the spiked samples.*

Discussion & Conclusion

Sample Preparation

- Low leachable metal content and acid washed (following EPL SOP) containers were utilized throughout the analysis.
- Test CV% seemed to be consistent with the homogeneity of samples.
- Minor Cr contamination (<15 ppb in sample A) might result from stainless steel tools (e.g. grinding machines).

ICP MS Analysis

- CRI (collision/reaction interface) successfully removed the polyatomic interferences (Table 7)[6].
- Signal enhancement[7] appeared to be the major reason of the high spike recovery of Se in soy seed.

Elements	Isotope	Interfering Ion
Chromium	^{52}Cr	$^{40}Ar^{12}C^+$
Arsenic	^{75}As	$^{40}Ar^{35}Cl^+$
Selenium	^{78}Se	$^{40}Ar^{38}Ar^+$
	^{80}Se	$^{40}Ar^{40}Ar^+$

Table 7. Spectral interferences in ICP MS[6].

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