SPEX®

Characterization of the Elemental Composition of Botanical Products (Spices, Supplements, Teas, and Condiments) for Use as a Tool in Identifying Potential Adulteration and Heavy Metal Concentration Using ICP-OES and ICP-MS

INTRODUCTION

The consumption of botanical products has increased over the past two decades as consumers trend to what are perceived to be natural and high quality botanical products.

The primary regions of spice and tea production around the world have often been cited as having less stringent safety and quality standards in regards to consumer products. Products from these regions have been noted to contain a variety of adulterants and contaminants including wear metals and toxic elements.

The identification of adulteration, contamination and counterfeiting of food products can be a difficult task. The use of nutritional profiles and detection of adulteration compounds can be useful tools to screen groups of products for further analysis to combat contamination and adulteration.

This study looked at the elemental composition of spices to determine if it was possible to target samples as potentially contaminated or adulterated by the concentration of certain metals (heavy metals, wear metals and nutrient elements). Each metal or elemental group indicates possible sources of adulteration, contamination

Diversity of Element Use				
Element	Toxic	Wear	Nutrient	Additive
As	X			
Cd	X			
Hg	X			
Pb	X			
Sr	X			
Ni	X	X		
Cr	X	X	X	
Mn	X	X	X	
Zn	X	X	X	
Cu		X	X	
Fe		X	X	X
Mg		X	X	X
Al		X		X
Ca			X	X
Na			X	X
Si*				X

SPEX APPLICATION NOTE

or counterfeiting. Toxic elements can be found as either contaminants or adulterants. Wear metals can also be considered contaminants, but can cross over into nutrients or additives. In many cases, it is the concentration of a particular element which can move it from a nutrient to an additive.

In this study, common botanicals (red and black peppers, cinnamon, mustard, cumin, and turmeric) sold as spices, teas, condiments, and supplements were purchased at dollar stores, farmer's markets, chain stored, and online vitamin outlets. Products selected covered the range of preparations including ground spices, blends, supplements, teas, and sauces (retail and organic) products. Physical and chemical screening methods were used to detect gross adulteration and counterfeiting. ICP was used to determine the macro element components (Si, Ca, Mg, Fe, and K) that indicated possible adulteration or contamination. High levels of bulking agents, including silica and sodium, were often found in low cost spice and botanical samples indicating potential adulteration. ICP-MS was used to determine the presence and level of heavy metal contamination and adulteration. Most of the spice groups studied had many examples of high heavy metals content at the ppm level including very high lead levels which could be indicative of adulteration by lead chromate or lead oxides.

1. MATERIALS AND METHODS

Samples

- 7-spice groups and products (supplements, teas, sauces, and condiments)
    - Black pepper
    - Red Peppers: Spice, Hot Sauce, Chili Powder
    - Cinnamon: Spice, Supplement, Tea
    - Ginger: Spice, Supplement, Tea
    - Cumin: Spice, Curry Powder
    - Mustard Seed: Spice, Condiment
    - Turmeric: Spice, Supplement
- Whole and Ground Spices
- Types of Retailers
    - Dollar Store, Farmer's Markets, Grocery, Retail Chain, Name Brand, Organic
- Spex CertiPrep Standards:
    - CLMS-1: Multi-Element Solution Standard 1
    - CLMS-2: Multi-Element Solution Standard 2
    - CLMS-3: Multi-Element Solution Standard 3
    - CLMS-4: Multi-Element Solution Standard 4
- Reagents
    - High Purity Nitric Acid
    - Hydrofluoric Acid

Sample Preparation

- Sample Grinding: SPEX SamplePrep 6970 EFM Freezer/Mill®
    - General Program
        - 2.5 grams samples
        - Pieces cut to < 5 mm
        - Program
            - Precool = 20 minutes
            - Grind for 5 cycles (2 minutes per cycle)
        - Each cycle = 2 minutes of cooling
        - Impact rate = 16 minutes per second

- Sample Digestion: CEM Mars 5 Microwave with Easy Prep Vessels
    - 0.1 gram sample with 10 mL HNO3 and a few drops of HF
    - 15 minute ramp to 210 ºC
    - 15 minute hold

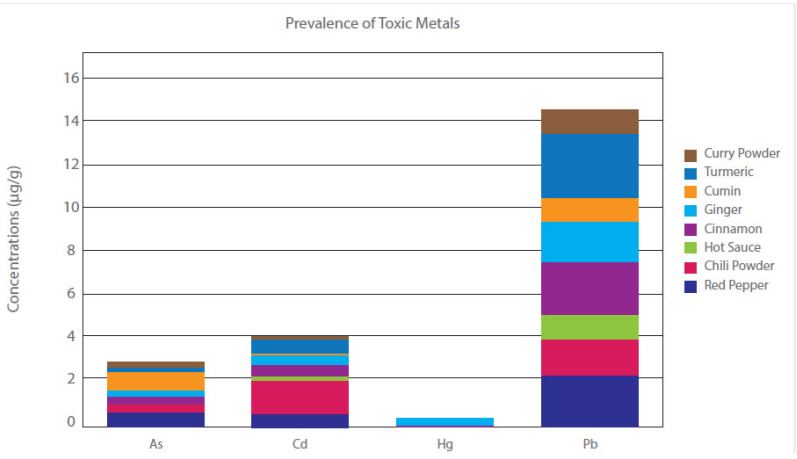
- Instrumentation
  - PerkinElmer ICP-OES - Wear Metals
  - Agilent ICP-MS 7700
    - Cyclonic spray chamber
    - Analysis performed
        - Normal mode: Air
        - Collision mode: Helium

ICP-MS Instrument Conditions		
Element	**m/z**	**GAS Mode**
As	75	Air & He
Cd	111-113	He
Cr	52 & 52	Air & He
Hg	201	Air
Pb	206-208	Air

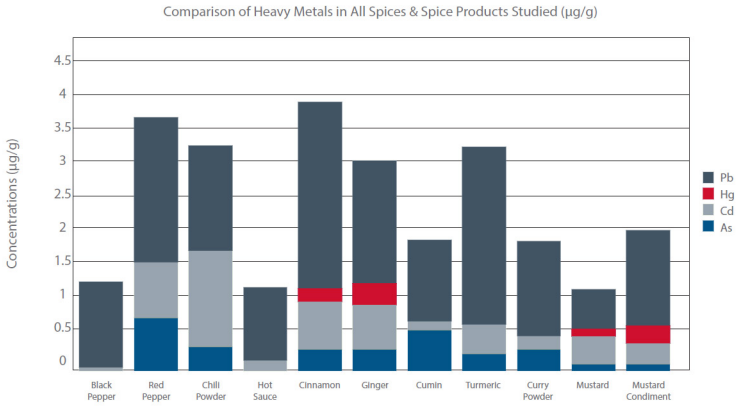
2. RESULTS

Heavy Metals

Heavy metal adulterations or contamination was found in all spice groups and spice products. The most common heavy metals found were chromium (total up to 15 ppm), lead (up to 2.8 ppm) followed by cadmium (1,2 ppm), and arsenic (0.7 ppm).



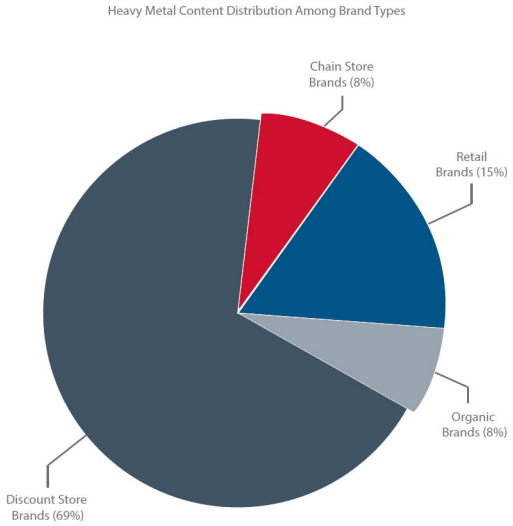
Lead concentrations were highest in spices such as cinnamon, turmeric and red pepper. Cadmium concentrations were the highest in chili powder and red pepper. Arsenic levels were highest in red pepper and cumin spices. Mercury was found in small amounts only in cinnamon, ginger, mustard seed, and mustard condiment up to 0.3 ppm.



The most traded spice in the world is black pepper and accounts for 20% of the world spice market. Only Cr (total) and Pb were found to any significant level in black pepper samples.

Red pepper is also highly and widely used around the world. The spectrum of red pepper and red pepper products range from ubiquitous 'Ground Chili Peppers' and 'Red Pepper Flakes' to 'Smoked Paprika', 'Cayenne Peppers' and all the world's hot pepper sauces and blends. The examination of heavy metals in the red pepper spices showed a trend where the more highly processed the spice, the more heavy metal content was found. Red pepper flakes, which are generally minimally processed or ground before packaging, had the lowest levels of heavy metals including possible wear metal constituents such as Cr (total) and Pb. The more highly ground and processed red peppers (i.e. chili, cayenne and paprika) had much higher heavy metal content especially for Cr (12 µg/g) and Pb (> 2 µg/g) for Dollar Store paprika.

The heavy metal content of the red pepper showed some small amounts of As and Cd but not Hg. The most abundant heavy metals were Cr (total) and Pb. Retail brands had overall the lowest amount of heavy metals.



The distribution of heavy metals within the spice groups showed that, overall, the highest heavy metal concentrations were found in the discount and less expensive brands. Almost 70% of the highest heavy metal content was found in these dollar store and budget spice products. This trend can indicate an intentional adulteration of spices for economic gain as opposed to just random environmental exposure.

Wear Metals, Nutritional Elements & Spice Profiles

The USDA curates a database of nutritional data for thousands of food products and additives. Common spices, such as black pepper, red pepper, chili powder, etc., have documented elemental distributions. Using some of these documented elemental/nutritional profiles a normal distribution was calculated to compare to the various corresponding spice samples.

Contamination of Black Pepper Spice Samples to USDA Nutrient Database Normal Distribution

	USDA National Nutritional Database Standard Reference for Black Pepper				Farmer Ground	Chain Ground CV	Dollar Ground SI	Dollar Ground E	Dollar Whole	Retail Ground	Organic Ground	Retail Whole
	Mean µg/g	Max µg/g	UB	35 UL	$2.35	$2.65	$3.51	$3.64	$4.00	$4.03	$7.69	$14.29
Mn	125	186	164	153	252	75	147	155	180	218	72	146
Zn	12	18	21	18	12	14	13	22	14	15	16	11
Cu	13	19	25	21	15	10	15	28	20	19	19	14
Fe	97	229	676	239	297	166	123	305	209	150	115	143
Mg	1710	2380	2471	2243	2294	1664	1932	4147	2463	1992	2141	1498
Al*	100 µg/g Teas	800 µg/g Bake Mix	800*	100*	254	202	149	382	191	203	137	142
Ca	4430	6520	7575	6625	5179	3883	4733	9697	4763	6162	5916	4402
Na	200	290	323	282	274	82	203	288	220	125	155	110
Si*	20 µg/g Seeds	100 µg/g Dried Fruit	100*	20*	783	362	608	1016	496	845	825	328

The comparison of the black pepper spice samples showed that several of the samples fell outside 3 standard deviations within the normal distributions, especially the lower cost dollar store and farmer's market samples (Dollar Ground E & Farmer Ground). These ground samples showed high amount of adulterant metals, such as Na, Ca and Si as well as high amounts of potential wear metals such as Al, Mg and Fe.

Another group of spice samples that showed intentional adulteration were the spice blends, such as the curry powders and chili powders. These blends all percentage levels of sodium that was not documented on their labels. The lowest cost samples, such as Dollar E, Dollar SI and Dollar SS, all had greater than 10% sodium added to the product whereas retail brands, hat documented the sodium levels had, on average, less than 2% sodium.

Comparison of Chili Powder Spice Samples to USDA Nutrient Database Normal Distribution

	USDA National Nutritional Database Standard Reference for Black Pepper		Dollar E Chili Power	Dollar SI Chili Powder	Dollar SS Chili Powder	Chain Chili Powder	Chain B Chili Powder	Retail Chili Powder	Organic Chili Powder
	Mean µg/g	Max µg/g							
Mn	17	34	41	29	22	26	25	26	24
Zn	43	86	16	20	19	32	38	31	26
Cu	10	20	8	7	10	17	14	14	10
Fe	173	346	254	495	361	258	234	229	500
Mg	1490	2980	1294	1385	2560	2510	2824	2964	2249
Al*	100 µg/g Teas	800 µg/g Bake	430	827	698	634	331	403	984
Ca	3300	6600	3230	2160	4274	2916	3657	3200	3350
Na	0.3%	< 1%	11%	13%	12%	1.2%	1.4%	1.4%	3.8%
Si*	20 µg/g Seeds	100 µg/g Dried Fruit	10006	2957	6537	6493	5970	5863	1645

3. CONCLUSION

The presence of heavy metals found in many of the spice groups may indicate contamination since heavy metals can be a common agricultural contaminant for products grown in areas with historical heave metal pesticide applications. The geographic locations where many spices are produced often fall within these historically contaminated areas.

In addition to contamination, some heavy metal compounds are documented adulterants in food products. The cost of spices often make these products a target of adulteration. The presence of heavy metals in spices can indicate contamination or intentional adulteration of these values economic products. Other groups, such as nutrient elements and potential wear metals, can also be adulterants when additives, such as Mg or Na compounds are added to bulk the weight or volume of the spice without being reported on the label.

Finally, some products are counterfeit either in part of in the entirety. The use of nutritional elemental profiles can be used in some cases to find the normal distribution for the constituent nutrient elements. These profiles can then be compared to the sample distribution to determine if the samples fit within the normal distribution for that product. Samples that fall outside the distribution can be considered suspect.