Contamination, Adulteration and Counterfeiting

An Examination of Sources and Concentrations of Heavy Metals Present in Food, Spices & Beverages

INTRODUCTION

Heavy metals, and in particular, lead, are some of the most documented and ubiquitous toxic substances in the world present in soil, plants, water, and air. Industrial activities and lead products transitioned heavy metal elements into highly dispersed toxic pollutants. In 2016, the US public was shocked over the high lead levels detected in Flint, Michigan's drinking water supply. The analytical testing community was concerned but not truly surprised. The bigger surprise for scientists was the public reaction to this one incident rather than the thousands of other cases of heavy metal and lead exposure the scientific community uncovers each year. Heavy metal exposure in the environment has led to toxic elements transitioning into our food and water supplies increasing human exposure. Agricultural and aquaculture products can be highly prone to heavy metal deposition and accumulation through repeated exposure to natural and contaminated environmental sources. This study will show examples of several types of products which may accumulate heavy metals through environmental exposure including chocolate and fish.

In some cases, heavy metals are intentionally introduced as products as adulterants or to counterfeit high value commodities. Some of these products include spices and hot sauces. The value of these commodities make them prone to adulteration and duplication. 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 be 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. A final route of accumulation and deposition of heavy metals is a quasi-intentional addition when heavy metals were historically used in industrial or agricultural processes and their persistence caused future products to become contamination which is the case with products such as apple juice and alcoholic ciders.

METHODS & MATERIALS

Samples were purchase at a variety of stores, markets and online outlets. Products included organic products. Cryogenic grinding and microwave digestion were employed in solid sample processing. Digestion and microwave digestion was used prior to ICP and ICP-MS analysis for the presence and level of heavy metal contamination and adulteration.

Sample Preparation

Solid samples such as whole spices, chocolate, etc. were ground using SPEX SamplePrep Freezer/Mill. Powdered spice samples and sauces were used as purchased. Cider samples were tested both as purchased and concentrated down prior to testing. Samples were purchased from several types of locations online, health food stores, grocery stores, retail chain stores, and discount or dollar stores. Some products were designated as 'organic'.

All samples were digested by nitric acid using a CRM Mars microwaves.

- Microwave conditions
  - Easy Prep vessels and XP vessels
  - 0.2 g sample to 1 g sample
  - 10 mL HNO_3
  - 1-2 drops HF in samples with high silica content
  - 15 minute ramp to 210 °C
  - 15 minute hold

Materials

- SPEX CertiPrep Standards
  - CLMS-1, CLMS-2, CLMS-3, CLMS-4: Multi-Element Solution Standards 1-4
  - Reagents:
    - High Purity Nitric Acid
    - High Purity HF

Instrumentation

- Instrumentation Agilent ICP-MS 7700 & Perkin Elmer Elan ICP-MS
  - Meinhard nebulizer
  - Cyclonic spray chamber
- Analysis performed
  - Normal mode: Air
  - Collision mode: Helium

RESULTS & DISCUSSION

Spices

Heavy metals found in spices could be contributed from a variety of sources. Some metals, such as lead oxides or lead chromates, can be intentional adulterations where as some other metals can be unintentional contamination from soil, pesticide applications, or processing issues.

Between all the dry spices and red pepper products, some of the highest lead levels, in terms of exposure, were in the commercially prepared red pepper sauces. Some sauces were packaged in individual services of about 10 grams per packet. The serving size of two packets or 20 grams were used to compare heavy metal concentrations. Two packets of the Chinese food fast food hot sauce contained 20.5 µg of lead and 63 µg of chromium which would contribute to almost 30% of an adult's allowable daily limit for each element. Lead and chromium were consistently found in all the hot sauces tested. Some of the samples also included measurable amounts of arsenic and cadmium (Figure 1).

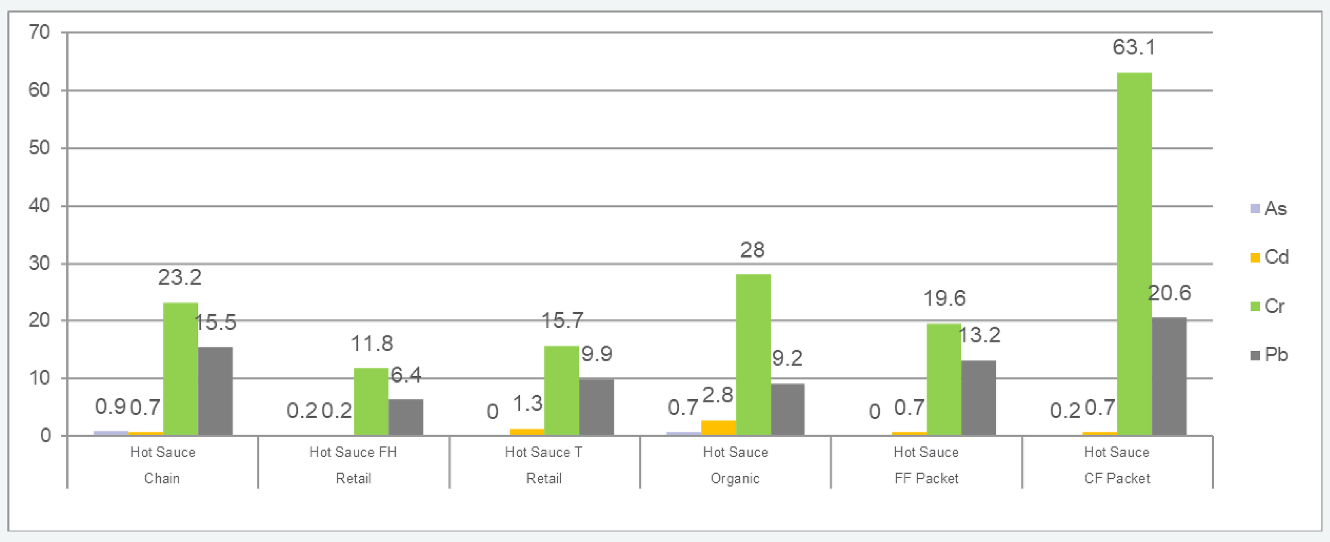

Figure 1. Heavy Metal Concentrations in Hot Sauce (µg/20 g serving = 2 fast food packets.

The red pepper spice and product samples we tested all contained some notable amounts of heavy metals. The most prevalent heavy metals found were lead and chromium. The dry spices had the highest concentrations of both lead and chromium but the exposure to these concentrations was minimized by the typical serving of these dry spices. However, the hot sauces which did have lower overall concentrations of heavy metals in comparison with the dry spices had high exposure levels when looked at within the context of serving size. In the case of some of the hot sauce packets, two packets would contain over a quarter of an adult's exposure to chromium and lead for the day.

Red pepper, when compared to our other study spices, contained some of the highest overall concentrations of heavy metals only exceeded by some cinnamon and turmeric samples for the highest levels of lead. Red pepper and chili powder blend samples did contain the highest amounts of arsenic and cadmium found in all of the spices. The only heavy metal not found in significant concentrations in red pepper spices was mercury (Figure 2).

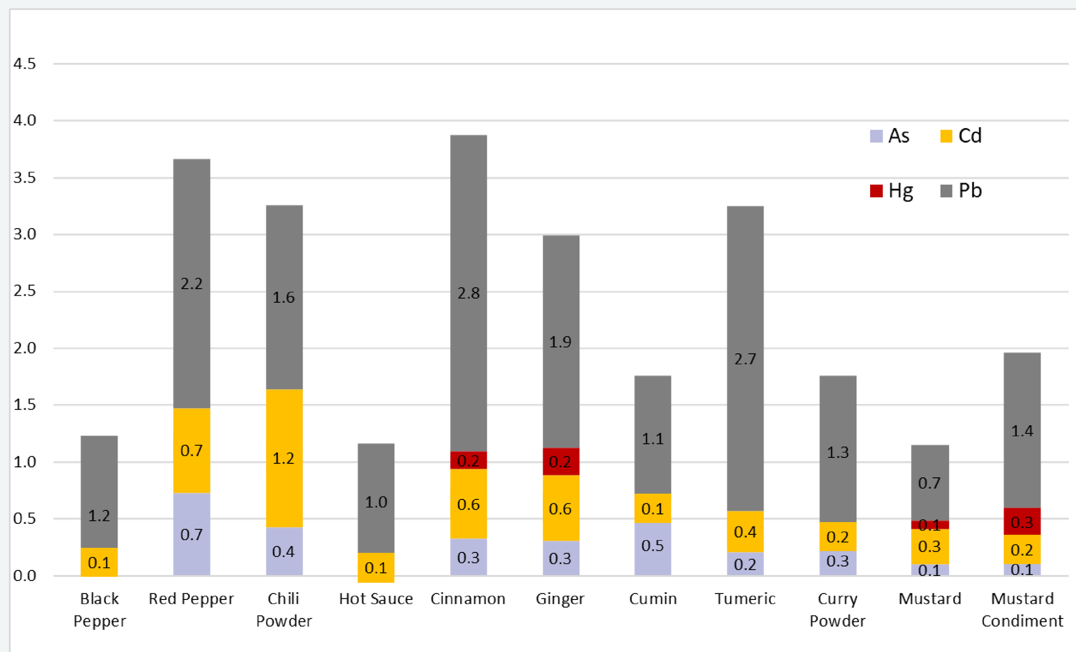

Figure 2. Comparison of Overall Concentration of Heavy Metals in Spice Sample Groups (µg/g).

Fish

For years, the American Heart Association (AHA) has recommended eating an average of two to three fish meals each week to help reduce cholesterol, high blood pressure, and hardening of arteries. Unfortunately, due to industrial pollution, many fish have high levels of contaminants including mercury, methyl mercury, and PCBs (polychlorinated biphenyls), which are absorbed by surrounding waters and from foods they eat. Currently, the EPA limit for mercury in fish is 1 ppm. About 22% of all PCBs are in estuarine and coastal sediments, which accounts for 95% of the fish production(2). The EPA estimates up to 15% of mercury emissions from these utilities fall within 30 miles of a plant, and up to 50% falls within six hundred miles. The mercury bio-accumulates through the food chain and reaches the predator species. Inorganic mercury and methyl mercury are found in small concentrations in fresh and saltwater, however, these compounds are easily absorbed as methyl mercury by algae, plankton and zoo plankton which are then consumed higher up the food chain. Fish tissue is an excellent absorption matrix for methyl mercury which is then slow to excrete through the organism. The methyl mercury is not soluble and accumulates in the visera and muscle tissues which causes the bioaccumulation of methyl mercury. The higher up the food chain a species of fish is found, the more methyl mercury is retained in its tissues.

RESULTS & DISCUSSION

The fish samples ranged from farm raised salmon to wild catch Marlin steaks. The samples were examined for total mercury content. The lowest concentrations of mercury were found in the salmon and tuna products. The highest amounts of mercury were in the swordfish and marlin steaks. The amount of mercury in even the lowest samples accounted for almost half the average adult's US daily exposure limit for methyl mercury. Frozen tuna, swordfish and marlin steaks would exceed the allowable US daily limit for adults up to 4000% (See Table 1).

Table 1. Mercury Content (Total) in Various FIsh Samples Compared to Allowable US Adult Daily and Weekly Limits for Methyl Mercury (µg in 4 oz. service) (as of 2018).

Fish	Hg (total) in 4 oz. serving (µg)	% of ADL (MgHg) In serving	% of Week Limit (MeHg) In serving
Wild Alaskan Salmon	5.1	63.70%	10.41%
Farm Raised Salmon	4.9	61.20%	10.00%
Black Peal Salmon	3.5	43.70%	7.14%
Fresh Tuna	6.1	76.20%	12.45%
Frozen Tuna	21.8	272.00%	44.49%
Swordfish Steaks	110.8	1385.00%	226.12%
Marlin Steaks	329.1	4113.00%	671.63%

Chocolate

Chocolate has been harvested for human consumption for thousands of years. Present day consumption of chocolate is measured on a global scale. In the US, Americans consume over 11 pounds of chocolate per person per year. Cocoa plants are native to tropical climates with high levels of humidity and rainfall. This climate increases the need for pesticide application to protect the cocoa bean crops. Heavy metals from pesticide and fertilizer applications can accumulate in the soil and add to the possible accumulation of those metals in the cocoa beans. Seven chocolate samples both light and dark were examined for heavy metals. The highest amounts of cadmium, lead and arsenic were found in the dark chocolate bars (Table 2). The exposure to heavy metals from the chocolate bars ranged 1-50% of allowable daily limits for adults (Table 3).

Table 2. Heavy Metal Concentrations µg in 40 g Chocolate Bars (1 Average Bar) Serving.

Element	Brand 1 (dark choc)	Brand 2 (dark choc)	Brand 3 (dark choc)	Brand 4 (milk choc)	Brand 5 (milk choc)	Brand 6 (milk choc)	Brand 7 (liquor)
Cd	3	3.8	5.3	0.9	1.5	1	< 0.2
Pb	2.95	2.75	0.87	1	2.21	1.5	0.4
Hg	2	0.1	< 0.04	4	0.22	<0.06	0.4
As	0.39	0.98	2	0.4	0.37	0.3	0.045
Ti	0.25	0.2	0.09	0.1	0.11	0.07	0.005
U	0.14	0.04	0.02	0.04	0.04	0.04	0.008

Table 3. Exposure of Heavy Metals (µg) from Chocolate Compared to US Allowable Daily Limits (ADL).

Element	ADL (total µg)	Result	% Of ADL
Cd	55	1 - 5 µg	2 - 9%
Pb	50	0.8 - 3 µg	2 - 6%
As	130	0.3 - 1 µg	0.2 - 0.8%
Hg	8	0 - 4 µg	0 - 50%

Cider

Alcoholic hard ciders have a long history around the world but only have become readily available in the United States over the past decades. Recent studies have been conducted showing the presence of arsenic in apple juices and wine. Arsenic based pesticides, particularly lead arsenate, were in widespread and use in the United States and Europe up until the final ban in the 1980's and 1990's. Despite arsenic residue being recognized as a potential problem from the turn of the century, lead arsenate was one of the most widely used pesticides in the nation and was applied to millions of acres of crops through the 1940's. Lead arsenate was the most commonly applied pesticide in apple orchards, many still in use, so potential for arsenic contamination remains. Heavy metal pesticides were designed to be persistent and can cause environmental and health problems decades after being banned.

In this study, samples were obtained of popular American and European hard ciders. Modern hard ciders are produced from either fresh apples or apple concentrates. American ciders are required to be at least 50% apples or concentrate, while UK ciders are required to be at least 35% apples (Table 4).

Table 4. Alcoholic Cider Samples.

Code	Country of Origin	% Alcohol	Carbs (g)	Approx. % Apples
WDR	US	6.90%	NR	> 50%
EAP	US	5.20%	6	> 50%
SSO	England	5.00%	8	> 35%
OSR	US	6.00%	10	> 50%
AOD	US	5.50%	11	> 50%
MIO	Ireland	4.50%	14	> 35%
RAA	US	5.00%	17	> 50%
DEU	US	5.10%	17	> 50%
SBA	England	6.00%	17	> 35%
SBG	England	5.00%	19	> 35%
SAC	Belgium	4.50%	22	Unknown
LPL	Belgium	3.50%	37	Unknown
IBC	US	5.20%	42	> 50%

Cider samples tested in this study contained between 0.16 and 4.8 ppb of total arsenic and between 0.6 to 6.6 ppb of lead. (Figure 3) Four of the six samples containing the highest concentration of arsenic and lead were manufactured in Europe. The FDA has current arsenic limits for bottled water set at 10 ppb of inorganic arsenic and is proposing an action limit in juice for the same. While the alcohol cider samples all had total arsenic concentrations less than half the suggested limits, there is a question of exposure through serving size. Typical juice servings are limited to 8 ounces per day. Most beer and cider servings are a minimum of 12 to 16 ounces per bottle with most adults consuming more than one serving in a day when the beverages are consumed. In the case of multiple servings, the potential exposure can become up to five times more than the potential amount of exposure from a small eight ounces of juice. The question of the impact of that exposure comes down to the type of arsenic in the cider. Follow-up studies are being conducted on these cider samples to determine the arsenic species of these cider samples using LC-ICP-MS. The characterization of the arsenic species will help in understanding the potential impact and exposure to potentially toxic arsenic in alcoholic cider.

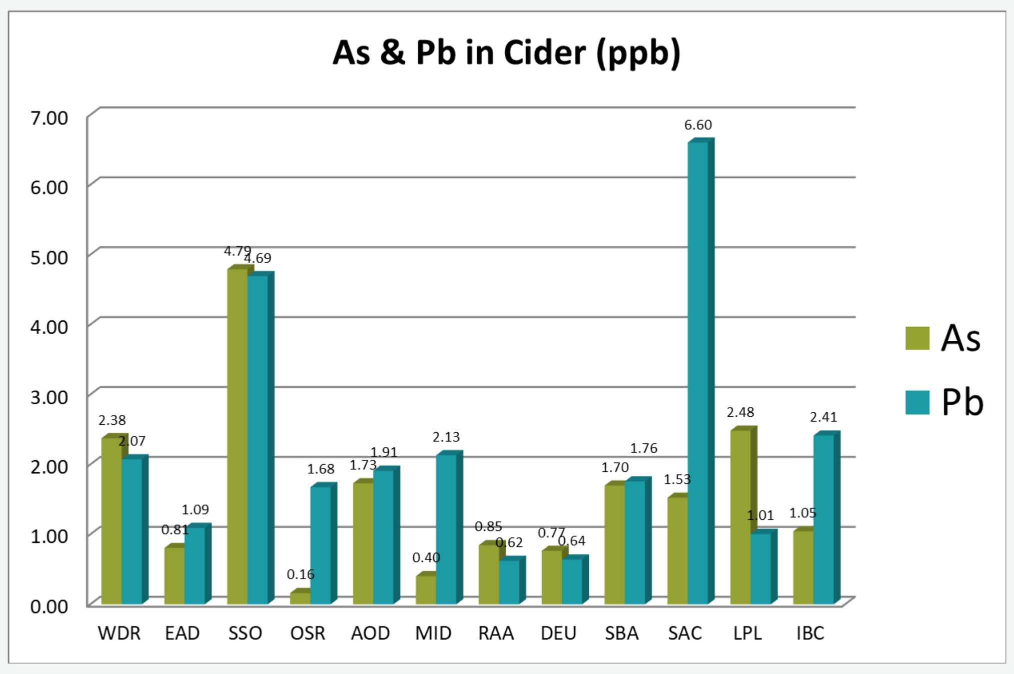

Figure 3. Lead and Arsenic Concentrations in Alcoholic Ciders (ppb).

CONCLUSION

Lead was the most prevalent heavy metal found in all the products studied. The concern for these heavy metal concentrations comes from the serving size of these common products. The serving sizes suggested are fairly large and instructions are absent on impact of heavy metals for children. In cases of spices, fish and chocolate the heavy metal concentrations are potentially exceedingly high for adults and in the case of children could bee very detrimental to their health and growth.

The limits imposed by organizations such as the AHPA, WHO, EPA, FDA who are attempting to create limits for heavy metal exposure, do not necessarily provide limits which are applicable for a child's exposure to these natural products. By using adult limits and calculating them against the body weight of a child, the exposure to heavy metals from these products can be potentially very high. Products that at first did not exceed the heavy metal limits for adults could then be seen as potentially hazardous to a child, especially a child with health concerns.

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