SPEX
by ZeptoMetrix

App Note

# Elemental Content of Black Pepper to Determine Adulteration and Heavy Metal Contamination


## Abstract

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 most traded spice in the world is black pepper and accounts for 20% of the world spice market. It is also one of the most commonly adulterated spices on the marketplace with up to 70% of commercial black pepper samples showing some form of adulteration or counterfeiting.

Black pepper samples were purchased at dollar stores, farmers markets, chain stores, and online vitamin outlets. Products selected included both whole black peppercorns and ground black pepper sold as both retail and organic products. Physical and chemical screening methods were used to detect gross adulteration and counterfeiting. ICP was used to determine the macroelement components (Si, Na, 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 spices indicating potential adulteration. ICP-MS was used to determine the presence and level of heavy metal contamination and adulteration. The black pepper samples had many examples of high heavy metals content at the ppm level, including high lead and chromium levels, which could be indicative of adulteration by lead chromate or lead oxides.

The United States Department of Agriculture (USDA) maintains an extensive database of chemical and physical data for food products. These databases show the normal distribution of values of nutritional components for spices. The black pepper samples were compared to the USDA values to determine if their composition was within the normal distribution for a black pepper spice. Many samples were identified with a high probability of adulteration or counterfeiting since they did not fit the spice profile.


## Methods & Materials

### Samples

- 8 Black Pepper Samples: 2 Whole and 6 Ground (1 Organic Ground)
- Range of Prices: \$2 - \$15 per 100 g
  - Dollar Store, Farmers Market, 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

## Solid Sample Preparation

- Sample Grinding: SPEX SamplePrep 6970 EFM Freezer/Mill
  - General Program
  - 2.5 g of spice
  - Program
    - Precool for 20 minutes
    - Grind for 5 cycles (2 minutes per cycle)
    - Each cycle = 2 minute cooling
    - Impact Rate: 16 impacts/second
- Sample Digestion: CEM Mars 5 Microwave with Easy Prep Vessels
  - 0.1 g sample with 10 mL $HNO_3$
  - 15 minute ramp to 210 °C
  - 15 minute hold
- Instrumentation:
  - Perkin Elmer ICP-OES - Wear Metals and Macroelemental Composition
  - Agilent ICP-MS 7700
    - Cyclonic spray chamber
    - Analysis performed
    - Normal mode: air
    - Collision mode: helium

## Results & Conclusion

## Physical Inspection

The initial inspection of the black pepper samples showed a great variation in the color and consistency of the samples. The ground samples ranged from a light gray or brown to a dark black color. Some samples were a mixture of black and white particles, while others were a uniform black or gray color.

Figure 1. Black pepper physical appearance.

## Macroelements and USDA Distribution

The USDA database was used to compare the macroelements found in the samples to the database distribution. The normal distribution was calculated from three standard deviations from the database mean to create the upper boundaries and upper limits for the normal pepper distribution. The comparison of the pepper samples showed that the cheaper pepper (Farmer Ground) and the dollar store ground pepper (Dollar Ground E) did not fall within normal distribution for black pepper for many elements, suggesting possible adulteration and counterfeiting. In particular, very high levels of silica were found in the suspect samples suggesting the addition of bulking agents.

Table 1. Comparison of Black Pepper Samples to USDA Normal Distribution for Black Pepper (µg/g).

| | USDA National Nutrient Database for Standard Reference for Black Pepper | | | | Farmer Ground | Chain Ground GV | Dollar Ground SI | Dollar Ground E | Dollar Whole | Retail Ground | Organic Ground | Retail Whole |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Mean (µg/g) | Max | UB | 3s UL | $2.35 | $2.65 | $3.51 | $3.64 | $4.00 | $4.03 | $7.69 | $14.29 |
| Mn | 128 | 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 Teas | 800 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 Seeds | 100 Dried Fruit | 100* | 20* | 783 | 362 | 608 | 1016 | 496 | 845 | 825 | 328 |

* No USDA cited reference for this product. Similar product references used to create a reference range.

## Heavy Metals

The black pepper samples contained up to 1.2 ppm levels of lead. The highest lead levels were found in the ground samples which were purchased at the dollar stores. In addition to the lead, chromium was found in levels up to 3 ppm (total Cr).

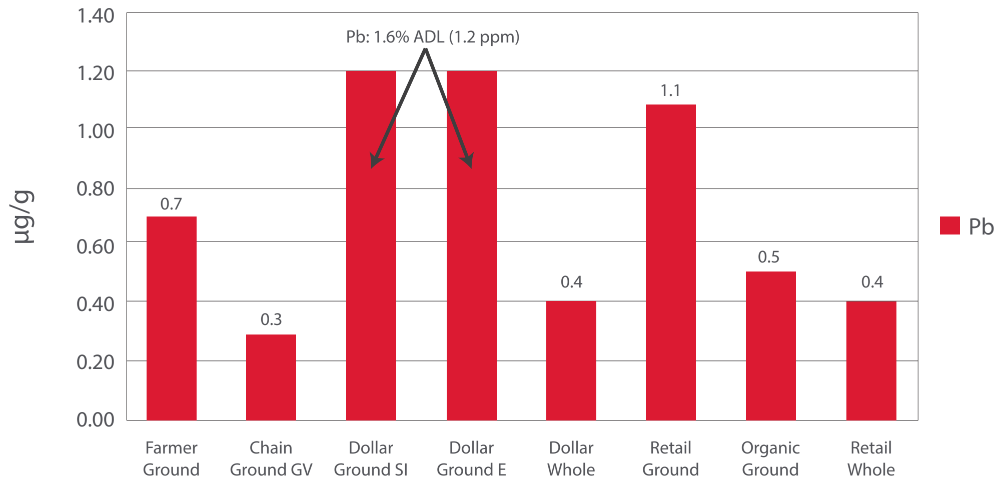


Figure 2. Lead Content Found in Black Pepper Samples (µg/g)

The distribution of heavy metals and macroelements within the spices showed that, overall, the highest heavy metal, wear metal and divergent macroelement concentrations were found in the discount and less expensive brands. Almost 70% of the highest heavy metal content was found in the 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.

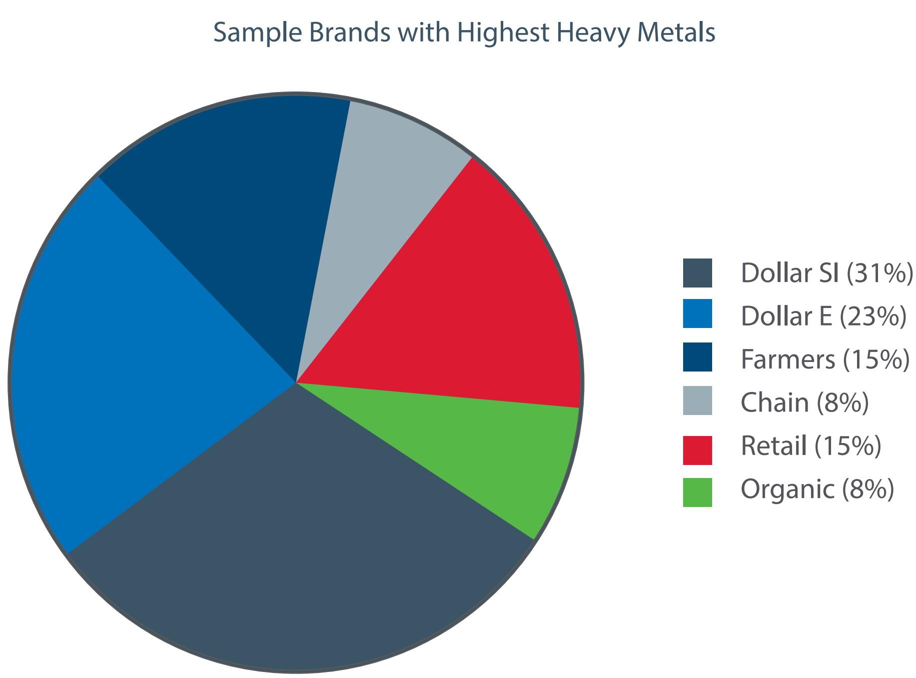


Figure 3. Heavy Metal Distribution Within Spice Retailer Groups