## Methods

Five standards of varying concentrations were prepared by diluting a 200-ppb stock solution with a solution containing 2%HNO<sub>3</sub> + 0.5% HCl in 50-mL centrifuge tubes [1]. The concentration of each of the standards is as shown in table 1 below. The blank was created using just the 200ppb stock solution as shown in table 1 below.

The four samples used were Hershey's natural unsweetened cocoa powder, PC Organics organic cocoa powder, Cocoa Camino organic cocoa powder, and Fry's cocoa premium cocoa. Each of the cocoa powder samples was prepared by weighing out approximately 0.50g of the cocoa powder directly into a microwave digestion cell, the actual masses of each cocoa powder are shown in Table 2 below. Next, 5 mL of concentrated nitric acid was added to each cocoa powder sample in the fume hood [2]. The cells were placed in the Anton Paar Multiwave GO Digestor for about 35 mins for the sample to digest [3]. When the digestion was complete, the cells were removed from the GO Digester and placed in the fume hood to cool for about 10 mins. Next, the cell lids were opened and vented in the fume hood, while ensuring that the cells were directed away. Next, a filter was set up and water was used to wet the filter paper. Afterwards, about 15 mL of the stock solution was added to the cell and then each solution was filtered into the 50-mL centrifuge tube. Next, the 50-mL centrifuge tube was filled to the mark using the 200-ppb stock solution. Next, all ten centrifuge tubes were taken to the ICP-MS instrument for analysis.

**Table 1.** Volumes of stock intermediate solution (200.0 ppb) used and the concentrations of each standard.

Standard	Volume (mL) of 200 ppb stock solution	Total Volume (mL)	Concentration of the standard (ppb)
S0	-	50.00	0.0000
S1	0.0250	50.00	0.1000
S2	0.2500	50.00	1.000
\$3	2.500	50.00	10.00
S4	12.50	50.00	50.00
85	25.00	50.00	100.0

**Table 2.** Masses of the four different commercial cocoa powders used for the heavy metal analysis.

Cocoa Powders	Samples	Mass (g)
Hershey's cocoa	Sample 1	0.5092
PC Organics	Sample 2	0.5245
Cocoa Camino	Sample 3	0.5012
Fry's Cocoa	Sample 4	0.5009

Table 3. Optimized experimental conditions for ICP-MS analysis of heavy metals

Instrument parameter	Setting
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RF Powder	1550 W	
RF Matching	1.80 W	
Carrier Gas	1.00 L/min	
Makeup Gas	0.10 L/min	
He Gas Flow	5.0 mL/min	
H2 Gas Flow	6.0 mL/min	
Energy Discrimination	5.0 V	
Nebulizer	MicroMist Scott Double	
Spray Chamber	Pass	

Table 4. Optimized experimental conditions for Anton Paar Multiwave Go Plus digestion system

Steps				
No.	Ramp (mm:ss)	Temp ()	Hold (mm:ss)	
1	2:00	100	1:00	
2	5:00	180	5:00	
Data				
Application Type	Vessel Mode	Temperature Control Mode	Temperature limit ()	
Digestion	Multi vessel	Maximum	200	

Ι	Recipe
	HNO3

References

- New Study of Protein Powders from Clean Label Project Finds Elevated Levels of Heavy Metals and BPA in 53 Leading Brands. Clean Label Project.
   <u>https://cleanlabelproject.org/blog-post/new-study-of-protein-powders-from-clean-label-project-finds-elevated-levels-of-heavy-metals-and-bpa-in-53-leading-brands/.</u>
- Kutscher, D. Six Key Errors to Avoid for Routine Analysis Using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). www.spectroscopyonline.com 2019, 34 (8), 28– 3028–30.
- 3. Donkor, K. Chemistry 3170 Instrumental Analysis Laboratory Manual, Fall 2024;