# CHEM 3170
# Instrumental Analysis
# Determination of Trace Metals in Bee Pollen by ICP-MS: Comparing Dilute and Shoot and Digestion Sample Preparation Methods

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## Abstract

Two different sample preparation methods were compared for inductively coupled plasma–mass spectrometry (ICP-MS) analysis of trace metal concentrations from six bee pollen samples. The ICP-MS used was the Agilent 7900 ICP-MS. The first preparation method was microwave digestion, the instrument used was an Anton Paar Multiwave Go Plus. Digestion samples used a 2% nitric acid and 0.5% hydrochloric acid solution with the five environmental calibration standards using the same solution mix. The second preparation method was the dilute & shoot method. The dilute & shoot samples were prepared using 10% acetic acid, 18 MΩ water and 1% Triton x-100. An environmental calibration standard was also used for the dilute method with 2% acetic acid and 1% Triton x-100. For every element tested within each bee pollen sample the microwave digestion method detected higher concentrations of every metal compared to the dilute & shoot method. Some elements, such as vanadium had 201 times higher concentration detection by the digestion method versus the dilute & shoot method. While others such as arsenic had 0.969 times higher concentration by digestion versus dilute & shoot.

## Introduction

In recent years there has been a lot of buzz about bee pollen as a new potential health supplement. Though critical supporting evidence is still lacking when it comes to human testing, consuming bee pollen may have many beneficial results. Some studies have suggested ingesting bee pollen may act as a natural medicine as it has demonstrated properties such as: antifungal, antimicrobial, antiviral, anti-inflammatory, and anticancer immunostimulating. There is also ongoing research regarding bee pollen's potential to alleviate allergy symptoms. By consuming small amounts of local pollen during the allergy season, it is thought to allow your body to build up a natural immunity to the pollen in your area and some human studies found results which support this claim. Some European countries such as Germany, have declared bee pollen as a medicine. Herbal medicine options are popular in Germany, and as such they are well regulated. That is not the case for supplements and herbal medicine in North America.

Bee pollen currently has a relatively small market as a supplement compared to commercial protein powders. However, even with the popularity of protein powders, food and health authorities in North America have yet to significantly regulate the production of any supplements, including bee pollen. This may lead to serious health issues as supplements such as protein powder and bee pollen may contain trace metals above safe daily limits of consumption.

To analyze the amount of trace metals in bee pollen an inductively coupled plasma – mass spectrometer was used (ICP-MS). The instrument is reliable and sensitive to ensure accurate quantification and identification of trace metals present in the pollen samples. The instrument works by adding the liquid sample into the high temperature plasma which ionizes the

elements within the sample. The ionized elements are detected, quantified, and identified by the MS based off their mass to charge ratios.

There are two ways of preparing samples for ICP-MS analysis. The first way of preparing a sample is by microwave digestion. This method uses a concentrated acid and a digestion instrument to dissolve the sample. Microwave digestion has the benefit of fully destroying the organic material within the sample which leads to a highly cleaned sample with the elements fully dissociated within the matrix. The dilution method (dilute & shoot) uses dilute acids, dilute alkali, or ultrapure water as the diluent depending on the sample requirements then the sample is injected directly into the instrument. The dilute & shoot technique uses significantly less energy than the microwave digestion, as well as less hazardous chemicals, which makes the dilute method more preferable from a green chemistry perspective.

In this experiment, the microwave digestion and dilute & shoot preparation methods will be employed to determine if there is a notable detectable difference between the two. Five bee pollen samples from regions across Canada (MVE, RMB, DBA, PBC and DGO) and one from Spain (PBS) will be prepared in triplicate using the two different methods and analyzed by ICP-MS. The results of this report will be used to determine which sample preparation method is more precise, as well as to notice any trends occurring between the two.

## Methods and Instrumental Parameters

**Table 1.** Instrument Parameters for Agilent 7900 ICP-MS.

| Parameter | Setting |
|---|---|
| **RF Power** | 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 |
| **$H_2$ Gas Flow** | 6.0 mL/min |
| **Energy Discrimination** | 5.0 V |
| **Nebulizer** | MicroMist Scott Double |
| **Spray Chamber** | Pass |

**Table 2.** Instrument Parameters for Anton Paar Multiwave Go Plus.

| **Steps** | | | |
|---|---|---|---|
| **No.** | **Ramp (mm:ss)** | **Temp (°C)** | **Hold (mm:ss)** |
| **1** | 10:00 | 180 | 15:00 |
| **Data** | | | |
| **Application Type** | **Vessel Mode** | **Temperature Control Mode** | **Temperature Limit (°C)** |
| **Digestion** | Multi vessel | Average | 200 |
| **Recipe** | | | |
| **$HNO_3$** | | | |

**Table 3.** Standards and their corresponding concentration of the 200.0 ppb intermediate environmental stock solutions diluted with 2% $HNO_3$ and 0.5% HCl in the microwave digestion standa for the dilute and shoot method standards were identical for the intermediate solution but were diluted with 2% acetic acid and 1% Triton X-100. These values will quantify the sample in the two different sample matrices on the ICP-MS.

| Standard | Volume (mL) of 200.0 ppb Intermediate | Total Volume (mL) | Concentration (ppb) of Standard |
|---|---|---|---|
| **0** | - | 50.0 | 0.0 |
| **1** | 0.025 | 50.0 | 0.10 |
| **2** | 0.250 | 50.0 | 1.00 |
| **3** | 2.500 | 50.0 | 10.0 |
| **4** | 12.500 | 50.0 | 50.0 |
| **5** | 25.000 | 50.0 | 100 |

*Microwave digestion sample preparation:*

Six different bee pollens were first ground into a fine powder by hand using a mortar and pestle. Approximately 0.5000 g of each sample was added to the microwave digestion tube. Next 15 mL of nitric acid was added to the digestion tube and the process was run according to **Table 2.** Once out of the microwave, the samples were vented and left to cool until they were at a safe temperature to handle. Each sample was gravity filtered and diluted to the 50 mL mark on the Falcon tube with 2% nitric acid and 0.5% hydrochloric acid solution. According to **Table 3.** Five environmental calibration standards were prepared with 2% nitric acid and 0.5% hydrochloric acid solution to the 50 mL mark on each Falcon tube. Next the samples were analyzed using the ICP-MS with the instrumental parameters shown in **Table 1.**

*Dilute & Shoot sample preparation:*

Six different bee pollens were first ground into a fine powder by hand using a mortar and pestle. To dissolve the bee pollen into solution approximately 0.2000 g of each pollen sample was added to a 50 mL Falcon tube. To each tube 10 mL of 10% acetic acid was and using a glass rod the pollen was mixed until the solution appeared homogeneous. The Falcon tubes were diluted to 50 mL with 18 MΩ water. The diluted stock samples were filtered to remove any remaining particulates. Next 2 mL of the stock sample solutions were combined with 5 mL of 1% Triton x-100 and diluted once more to the 50 mL mark using 18 MΩ water. The standards were prepared using an environmental calibration standard with 1 mL of 2% acetic acid and 5 mL of 1% Triton x-100 in a 50 mL Falcon tube. Next the samples were analyzed using the ICP-MS with the instrumental parameters shown in **Table 1.**

## Results

**Table 4.** Analysis of microwave digested MVE bee pollen sample by ICP-MS. The concentration is the average of the sample triplicates for each element.

| Element | Concentration (ppb) | Standard Deviation (ppb) | Mass of Element (ng) | Mass of element per gram of bee pollen (ng/g) |
|---|---|---|---|---|
| **Sodium ($^{23}$Na)** | 66148.6964 | 11656.6378 | 3.31 | 6.61 |
| **Magnesium ($^{24}$Mg)** | 543795.289 | 43206.3073 | 27.2 | 54.4 |
| **Aluminum ($^{27}$Al)** | 33732.1794 | 4696.14531 | 1.69 | 3.37 |
| **Potassium ($^{39}$K)** | 2844710.16 | 209501.521 | 142 | 284 |
| **Calcium ($^{44}$Ca)** | 728298.844 | 59471.8585 | 36.41 | 72.8 |
| **Vanadium ($^{51}$V)** | 74.9319833 | 10.5362314 | 0.00375 | 0.00749 |
| **Chromium ($^{52}$Cr)** | 44.6093067 | 5.55843974 | 0.00223 | 0.00446 |
| **Manganese ($^{55}$Mn)** | 6835.17235 | 488.043486 | 0.342 | 0.684 |
| **Iron ($^{56}$Fe)** | 50653.0492 | 5107.21224 | 2.53 | 5.07 |
| **Cobalt ($^{59}$Co)** | 30.67693 | 4.20658813 | 0.00153 | 0.00307 |
| **Nickel ($^{60}$Ni)** | 445.153837 | 52.5788249 | 0.0223 | 0.0445 |
| **Copper ($^{63}$Cu)** | 801.34005 | 58.9469231 | 0.0401 | 0.0801 |
| **Zinc ($^{64}$Zn)** | 4536.28729 | 294.886303 | 0.227 | 0.454 |
| **Zinc ($^{66}$Zn)** | 11.9817467 | 0.99206796 | 0.000599 | 0.00120 |
| **Arsenic ($^{75}$As)** | 118.34139 | 4.43465125 | 0.00592 | 0.0118 |
| **Selenium ($^{78}$Se)** | 583.203347 | 30.2619951 | 0.0292 | 0.0583 |
| **Molybdenum ($^{98}$Mo)** | 10.85834 | 1.709578 | 0.000543 | 0.00109 |
| **Cadmium ($^{111}$Cd)** | 2.47934333 | 1.04953403 | 0.000124 | 0.000248 |
| **Antimony ($^{123}$Sb)** | 951.841397 | 76.1349087 | 0.0476 | 0.0952 |
| **Barium ($^{135}$Ba)** | 8.06066 | 0.94646058 | 0.000403 | 0.000806 |
| **Thallium ($^{205}$Tl)** | 32.23933 | 2.32286866 | 0.00161 | 0.00322 |
| **Lead ($^{208}$Pb)** | 66148.6964 | 11656.6378 | 3.31 | 6.61 |

**Table 5.** Analysis of dilute & shoot MVE bee pollen sample by ICP-MS. The concentration is the average of the sample triplicates for each element, and have been adjusted to match the mass used for the digestion samples.

| Element | Concentration (ppb) | Standard Deviation (ppb) | Mass of Element (ng) | Mass of element per gram of bee pollen (ng/g) |
|---|---|---|---|---|
| **Sodium ($^{23}$Na)** | 3215.37573 | 16.3306364 | 0.161 | 0.804 |
| **Magnesium ($^{24}$Mg)** | 26877.3817 | 145.063784 | 1.34 | 6.719 |
| **Aluminum ($^{27}$Al)** | 130.088658 | 22.1066576 | 0.00650 | 0.0325 |
| **Potassium ($^{39}$K)** | 36551.1386 | 249.639799 | 1.83 | 9.14 |
| **Calcium ($^{44}$Ca)** | 46015.0125 | 237.498941 | 2.30 | 11.5 |
| **Vanadium ($^{51}$V)** | 0.37411667 | 0.20095375 | 0.0000187 | 9.35E-05 |
| **Chromium ($^{52}$Cr)** | 8.46060833 | 0.57960256 | 0.000423 | 0.00212 |
| **Manganese ($^{55}$Mn)** | 618.942525 | 8.54718092 | 0.0309 | 0.155 |
| **Iron ($^{56}$Fe)** | 745.620383 | 52.1461897 | 0.0373 | 0.186 |
| **Cobalt ($^{59}$Co)** | 3.03318333 | 0.09241476 | 0.000152 | 0.000758 |
| **Nickel ($^{60}$Ni)** | 147.015033 | 1.42599609 | 0.00735 | 0.0368 |
| **Copper ($^{63}$Cu)** | 83.2769 | 3.44368806 | 0.00416 | 0.0208 |
| **Zinc ($^{64}$Zn)** | 1506.19402 | 14.9549093 | 0.0753 | 0.377 |
| **Zinc ($^{66}$Zn)** | 12.37055 | 0.30387087 | 0.000619 | 0.00309 |
| **Arsenic ($^{75}$As)** | 2.26623333 | 0.79945156 | 0.000113 | 0.000567 |
| **Selenium ($^{78}$Se)** | 0 | 0 | 0 | 0 |
| **Molybdenum ($^{98}$Mo)** | 9.41185 | 0.27076973 | 0.000471 | 0.00235 |
| **Cadmium ($^{111}$Cd)** | 0.36586667 | 0.08486382 | 0.0000183 | 9.15E-05 |
| **Antimony ($^{123}$Sb)** | 80.703675 | 0.82065773 | 0.00404 | 0.0202 |
| **Barium ($^{135}$Ba)** | 0.51924167 | 0.01579813 | 0.0000260 | 0.000130 |
| **Thallium ($^{205}$Tl)** | 20.3849 | 0.85513888 | 0.00102 | 0.00510 |
| **Lead ($^{208}$Pb)** | 3215.37573 | 16.3306364 | 0.161 | 0.804 |

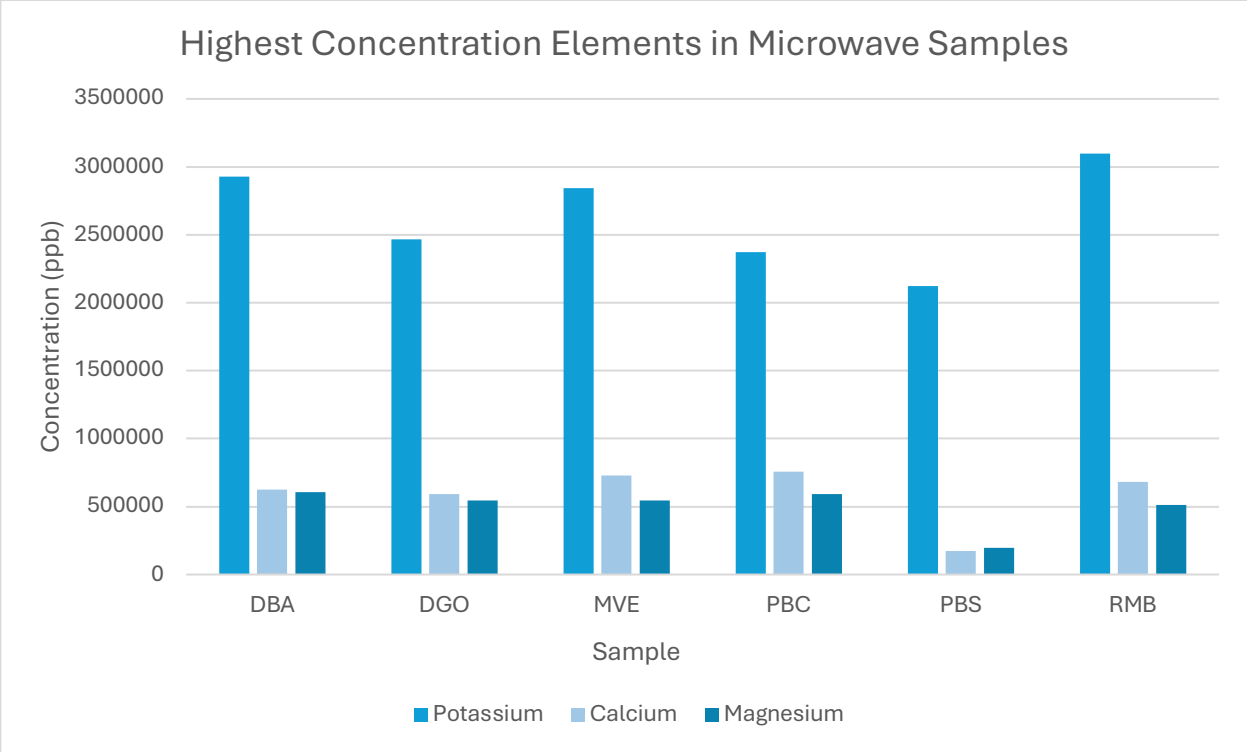


**Figure 1.** ICP-MS analysis of microwave-digested samples at the highest concentration of the elements.

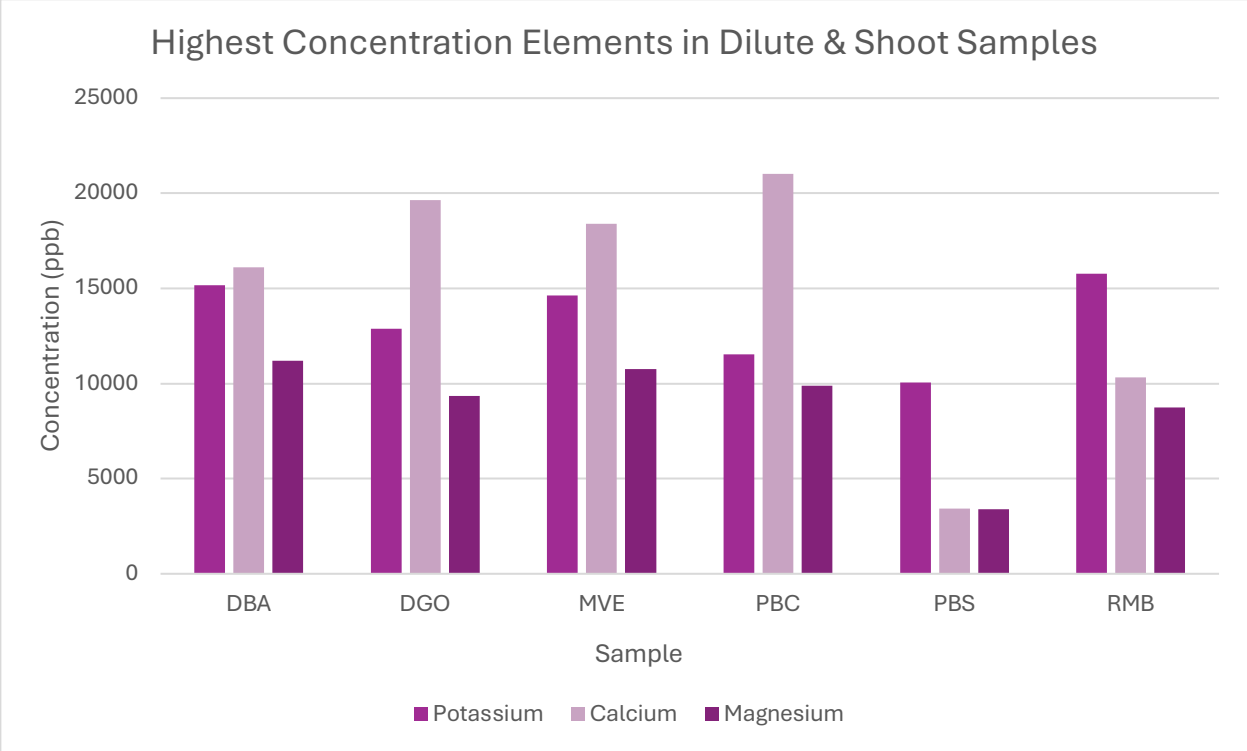


**Figure 2.** ICP-MS analysis of dilute & shoot samples at the highest concentration of the elements.

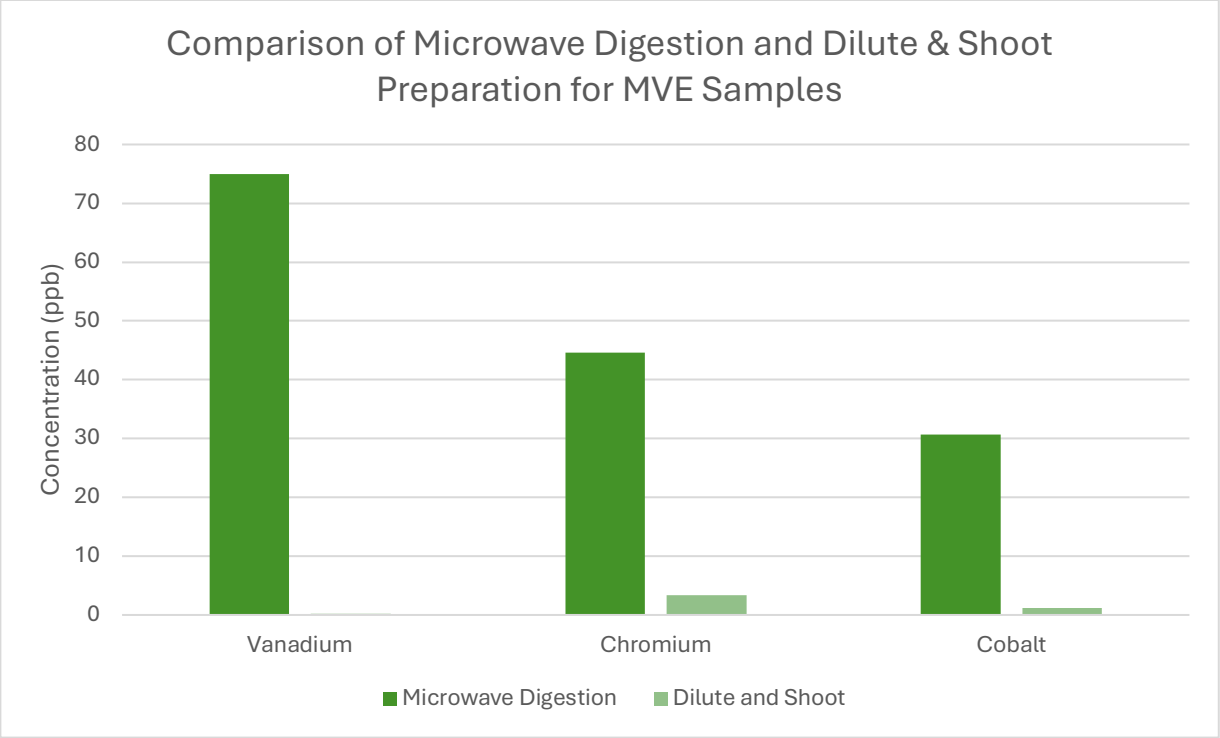


**Figure 3.** Comparison of a few trace elements present in the MVE sample for the two sample preparation methods. Vanadium in the dilute & shoot method was detected in extremely low concentration ($^{51}V$ = 0.374116667 ppb) and is invisible in this figure.

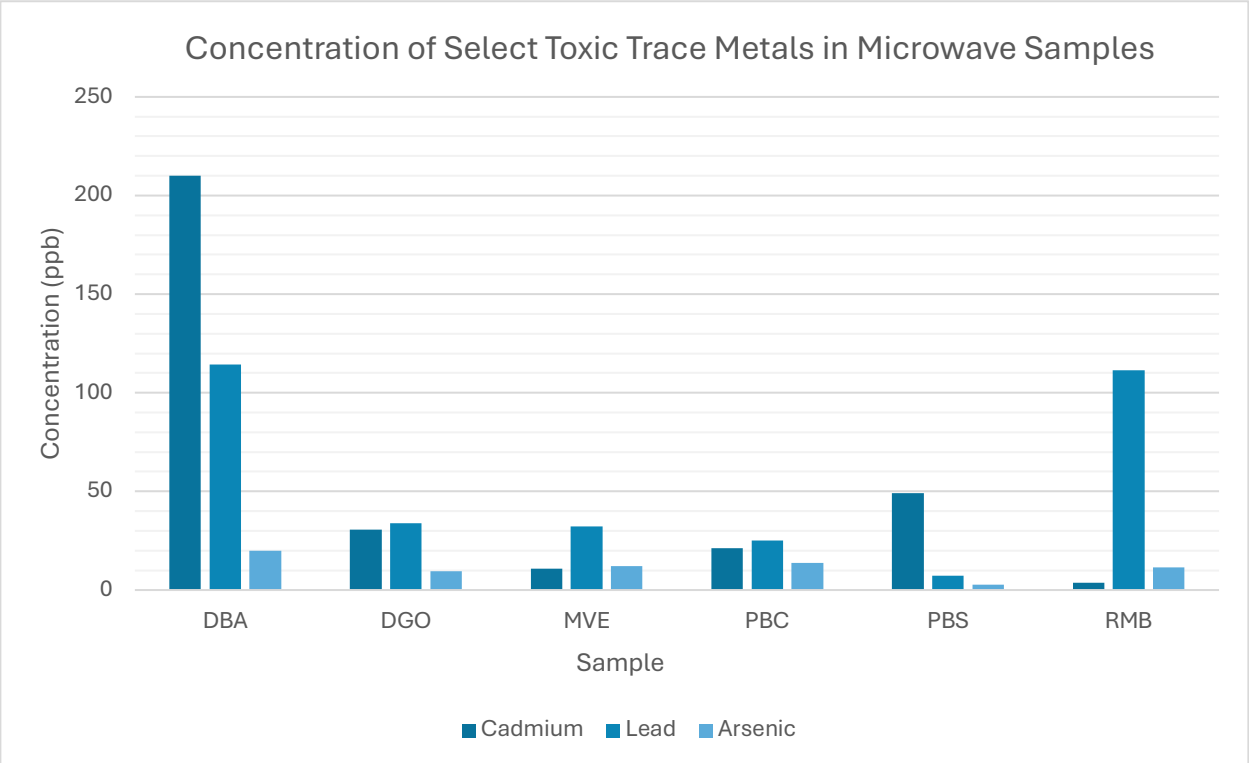


**Figure 4.** ICP-MS analysis of microwave-digested samples for select toxic trace metals.

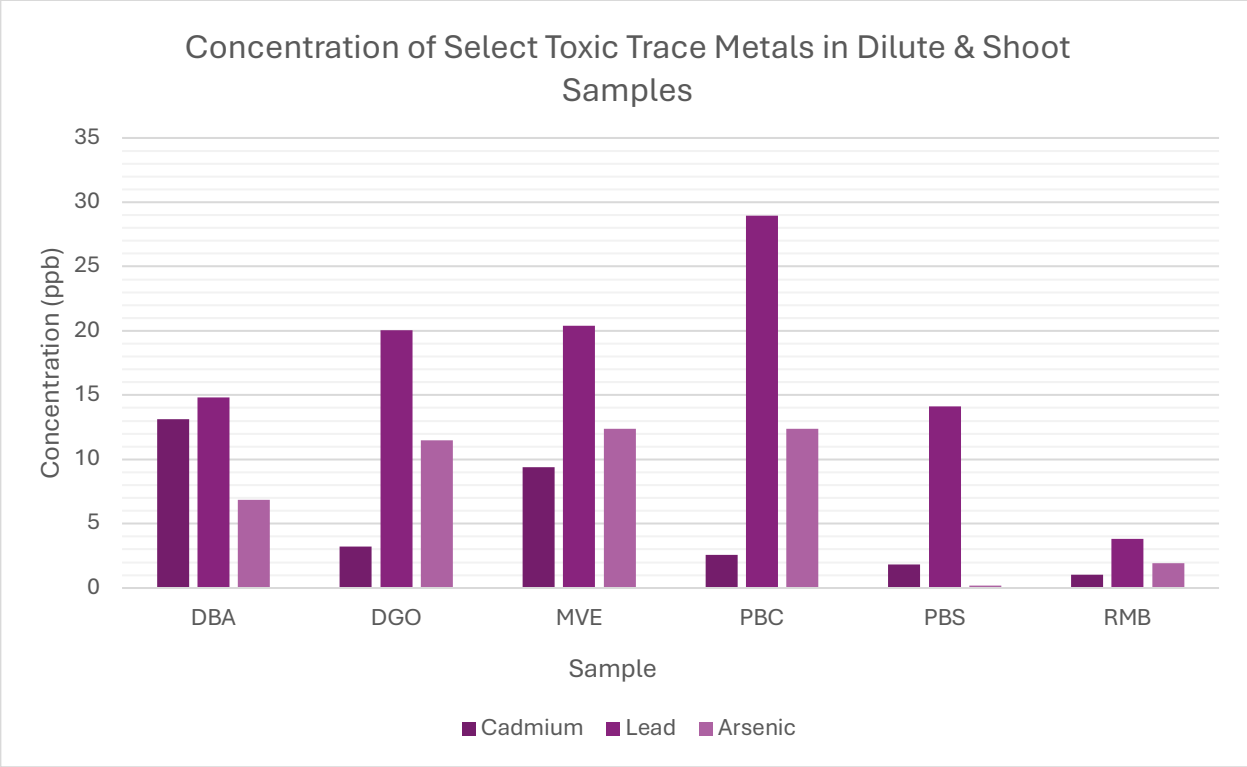


**Figure 5.** ICP-MS analysis of dilute & shoot samples for select toxic trace metals.

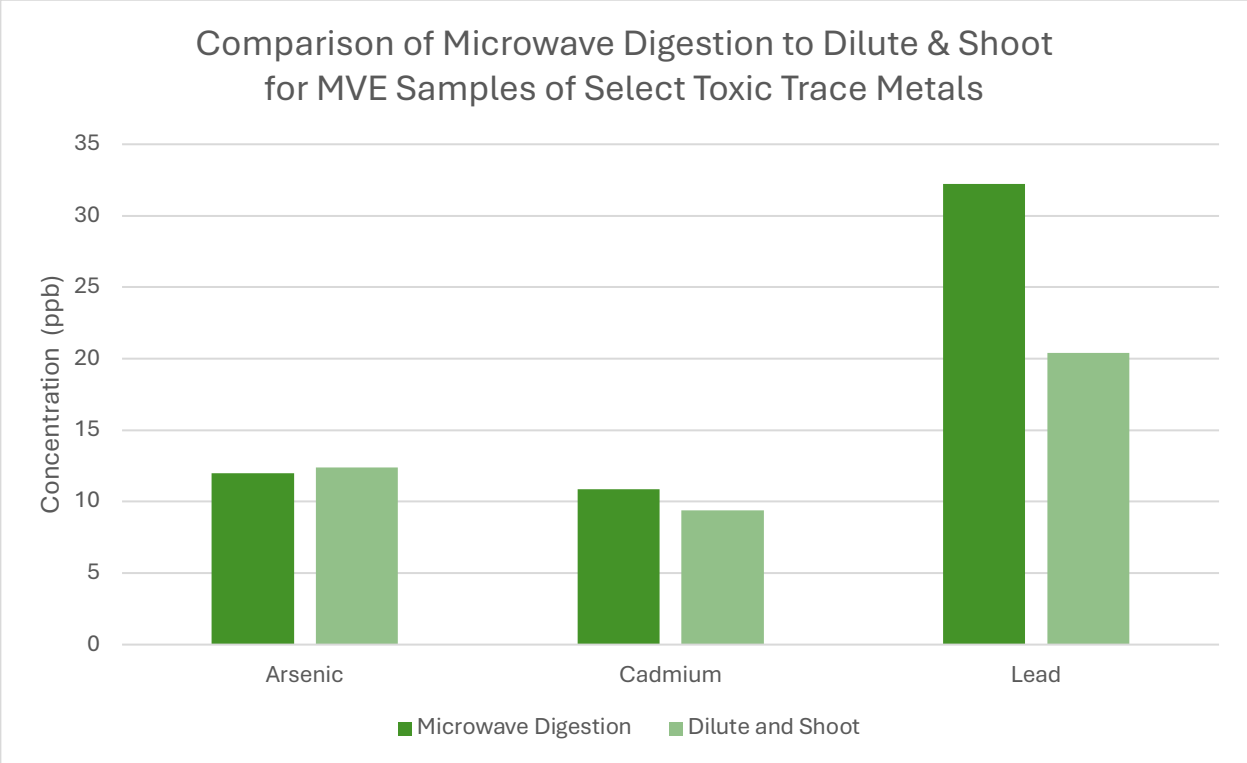


**Figure 6.** Comparison of select toxic trace metals present in the MVE sample for the two sample preparation methods.

## Calculations

Concentration (ppb) in standard 1:

$C_1$ = 200.0 ppb
$V_1$ = 0.025 mL
$V_2$ = 50.0 mL

$$\text{Concentration (ppb)} = \frac{(200.0 \text{ ppb})(0.025 \text{ mL})}{50.0 \text{ mL}} = 0.10 \text{ ppb}$$

**Microwave Digestion Samples:**

MVE sample averaging of vanadium for digestion samples:

MVE1 = 64.80593 ppb
MVE2 = 85.83534 ppb
MVE3 = 74.15468 ppb

MVE Average = (64.80593 + 85.83534 + 74.15468) / 3 = 74.93198 ppb

Amount of vanadium (ng) in MVE 50.0 mL digestion sample:

Vanadium = 74.93198 ug/L
Volume of sample = 50.0 mL = 0.0500 L

$$\text{vanadium (ng)} = 74.93198\frac{\text{ug}}{\text{L}} \text{ x } 0.0500\text{L x}\frac{1 \text{ ng}}{1000 \text{ ug}} = 0.00375 \text{ ng}$$

Sample calculation of an element in the sample: Vanadium concentration in each gram of bee pollen for microwave digestion (ng/g):

vanadium = 0.0110 ng
mass of bee pollen in MVE1 sample = 0.4973 g

$$\text{vanadium (ng/g)} = \frac{0.00375 \text{ ng}}{0.4973 \text{ g}} = 0.00753\frac{\text{ng}}{\text{g}}$$

**Dilute & Shoot Samples:**

To match the digestion sample values, the concentrations need to be multiplied to have matching sample masses:

$$\frac{Digestion\ mass}{Dilute\ mass}\ ratio = \frac{5.000\ g}{2.000\ g} = 2.5$$

All subsequent values will be multiplied by 2.5 to ensure the concentrations are comparable to 0.5 g of sample.

MVE sample averaging of vanadium for digestion samples:

MVE1 = 0.37805 ppb
MVE2 = 0 ppb
MVE3 = 0.07089 ppb

MVE Average = (0.37805 + 0 + 0.07089) / 3 = 0.14965 ppb

Amount of vanadium (ng) in MVE 50.0 mL Dilute & Shoot sample:

Vanadium = 0.14965 ug/L x 2.5 = 0.37413 ug/L
Volume of sample = 50.0 mL = 0.0500 L

$$\text{vanadium (ng)} = 0.37413\ \frac{\text{ug}}{\text{L}}\ \text{x}\ 0.0500\text{L}\ \text{x}\frac{1\ \text{ng}}{1000\ \text{ug}} = 1.87\ x10^{-5}\ \text{ng}$$

Sample calculation of an element in the sample: Vanadium concentration in each gram of bee pollen for microwave digestion (ng/g):

vanadium = 1.87 x$10^{-5}$ ng
mass of bee pollen in MVE1 sample = 0.2022 g

$$\text{vanadium (ng/g)} = \frac{1.87\ x10^{-5}\ \text{ng}}{0.2022\ \text{g}} = 9.25\ x10^{-5}\frac{\text{ng}}{\text{g}}$$

**Difference between the two methods:**

Vanadium:

Digestion mass: 0.00375 ng

Dilute & Shoot: 1.87 x$10^{-5}$ ng

$$\text{Difference} = \frac{0.00375 \text{ ng}}{1.87\ x10^{-5} \text{ ng}} = 201\ x$$

Digestion has a 201x higher concentration than dilute and shoot.

Arsenic:

Digestion mass: 0.000599 ng

Dilute & Shoot: 0.000619 ng

$$\text{Difference} = \frac{0.000599 \text{ ng}}{0.000619 \text{ ng}} = 0.969\ x$$

Digestion has a 0.969 x higher concentration than dilute and shoot.

## Discussion

In this experiment, six bee pollen samples were prepared through two different sample preparation methods: microwave digestion, and dilute & shoot. ICP-MS then analyzed the samples to detect the trace metals present within the bee pollen to see the difference between the two methods. Moving forward, only the data from the MVE bee pollen sample will be discussed to simplify the amount of data talked about as the key point is the differences between the two. Based on **Table 4**, some of the highest concentrations of trace elements in the microwave digestion method were found to be potassium (2844710.16 ppb), calcium (728298.844 ppb), and magnesium (543795.289 ppb). Following this, as per **Table 5**, some of the highest concentrations of trace elements in the dilute & shoot method were found to be calcium (46015.01253 ppb), potassium (36551.13863 ppb), and magnesium (26877.3817 ppb). The reason for these to be highest in concentration can be attributed to the soil that the plants are sourced from having high concentrations of these metals.

When comparing these three elements across the two sample preparation methods, the microwave-digestion method far exceeds the dilute & shoot data. Specifically for these three elements, microwave-digesting was detected up to 78 times more than the dilute & shoot method. When looking at lesser detected metals, this difference can be seen as large as 201 times when it comes to vanadium. However, it should be stated that this trend isn't seen for all of the elements, as arsenic is lower in concentration in the digestion sample when compared to the dilute & shoot samples (12.4 ppm and 12.0 ppm, respectively). Across the board, the digestion method far surpasses the concentrations of the dilute & shoot samples, with a few outliers existing among the elements.

Along with the trend seen with the arsenic in the dilute & shoot samples, molybdenum was completely undetectable within the dilute & shoot sample. Interestingly, molybdenum was in abundance in the digestion sample (583.2033467 ppb). One suggestion is that lower concentrations of elements could remain undetected with the ICP-MS, however, all the other elements present in the microwave-digestion samples were appearing in the dilute & shoot samples. This could suggest that some matrix effects were occurring within the dilute & shoot samples, where the acetic acid may not have effectively solubilized or stabilized the molybdenum, leading to molybdenum precipitating or adsorbing to the sides of the falcon tube, preventing detection. The Triton X-100 could also have interfered with the molybdenum by interfering with the ionization in the plasma or forming a complex with molybdenum in solution. In future experiments, trying to find a different combination of acetic acid and Triton X-100 should prevent the lack of molybdenum from being detected.

When it comes to the toxic trace metals of interest, arsenic, cadmium, and lead are highlighted to show the detection difference between them. According to **Figure 6**, arsenic is shown to have a marginally higher detection within the dilute & shoot sample (12.4 ppb vs 12.0 ppb), however, slightly lower cadmium levels (9.41 ppb vs 10.9 ppb) and greatly lower lead levels (20.4 ppb vs 32.2 ppb) when compared to the microwave-digestion method. While arsenic and cadmium are relatively close to each other in concentration, the difference in lead is problematic. The bee pollen used in this experiment is marketed and sold as a health supplement, so any trace metals detected should be accurate due to regular human consumption. With respect to lead, the difference between the two is greater than the 5 ppb acceptable concentration from HealthLink BC (2023). This notable difference in a toxic metal between the two samples can be the difference between the safe consumption of a food product or lead poisoning, so more work

should be done to improve on the dilute & shoot method, or microwave digestion should only be used instead.

In future experiments, some aspects of the preparation techniques could be significantly improved, such as the pulverization of the bee pollen samples. Grinding the pollens by hand led to inconsistencies in granule size and overall powder consistency varied greatly. This could have affected the ability of the pollen to create a homogeneous mixture to be analyzed by the ICP-MS, this was particularly an issue for the dilute & shoot preparation technique. In the future, a coffee grinder should be used to fully grind down the pollen. It is likely when preparing the dilute & shoot stock solutions that not all the elements within the pollen homogenized, as granules were viewed in the filter after gravity filtration. To increase the sample fully dissolving work may be done to find a different acid to use for sample preparation that is also compatible with the ICP-MS.

In addition to this, some work should be done to assess the ICP-MS as some of the values in comparison seem extremely high. In the MVE sample, the potassium was in extremely high concentration (2844710.158 ppb). In addition to this, all of the toxic trace metals are above the daily allowable intake, which when previously analyzed were within the allowable levels of consumption. It is safe to say that the quantification of trace metals within the bee pollen samples is not accurate, and details should not be inferred from this report. This report just shows the difference in the concentration of trace metals between the two sample preparation methods, and the relationship can be determined from the results given.

## Conclusion

When comparing the dilute & shoot method to the microwave digestion method of sample preparation for analysis with ICP-MS it was found that for every element tested within the six bee pollen samples the microwave digestion method resulted it significantly higher concentrations of detection. There was variation between each element concentration and sample with some values for the digestion detecting 0.969 to 201 times more of that element compared to the dilute & shoot results. In future comparisons between these methods, a coffee grinder should be used to process the bee pollen into a fine consistent powder, as well as the dilute & shoot method may be significantly improved if higher concentrations of both acetic acid and Triton x-100 was used.

## Literature Cited


Donkor, K. CHEM 3100 Lecture notes. Fall 2024.

Komosinska -Vassev, K., Olczyk, P., Kazmierczak, J., Mencer, L., Olczyk, K. (2015) Bee Pollen: Chemical Composition and Therapeutic Application. *Evidence-Based complementary and Alternative Medicine.* 2015 (1), 297425. https://doi.org/10.1155/2015/297425

Saarinen, K., Jantunen, J., Haahtela, T. (2010) Birch Pollen Honey for Birch Pollen Allergy – A Randomized Controlled Pilot Study. *Int Arch Allergy Immunol.* 155(2), 160-166. https://doi.org/10.1159/000319821

Saper, R. (2024). Bee Pollen: What it is and Why You Really Don't Need it. *Cleveland Clinic.* https://health.clevelandclinic.org/bee-pollen-benefits (Accessed: November 25th, 2024).

HealthLink BC. *Lead in Drinking Water*; HealthLink BC, 2023. https://www.healthlinkbc.ca/healthlinkbc-files/lead-drinking-water (accessed Nov 26, 2024).

Microwave Data w/ microwave standards (2% nitric acid, 0.5% hydrochloric acid)

| Sample Name | 23 Na [He] Conc. [ppb] | 24 Mg [He] Conc. [ppb] | 27 Al [He] Conc. [ppb] | 39 K [He] Conc. [ppb] | 44 Ca [He] Conc. [ppb] | 51 V [He] Conc. [ppb] | 52 Cr [He] Conc. [ppb] | 55 Mn [He] Conc. [ppb] | 56 Fe [He] Conc. [ppb] | 59 Co [He] Conc. [ppb] | 60 Ni [He] Conc. [ppb] | 63 Cu [He] Conc. [ppb] | 66 Zn [He] Conc. [ppb] | 75 As [He] Conc. [ppb] | 78 Se [He] Conc. [ppb] | 95 Mo [He] Conc. [ppb] | 111 Cd [He Conc. [ppb] | 123 Sb [He] Conc. [ppb] | 135 Ba [He] Conc. [ppb] | 205 Tl [He] Conc. [ppb] | 208 Pb [He] Conc. [ppb] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1DBA1 | 78937.628 | 553790.4179 | 27097.5312 | 2737382.58 | 597358.091 | 54.34638 | 223.28196 | 27220.141 | 60328.6489 | 51.94518 | 554.1682 | 865.78877 | 6447.1456 | 11.79143 | 18.9209 | 485.16656 | 201.79056 | 7.38903 | 2987.08795 | 2.02777 | 84.42405 |
| 1DBA2 | 87494.731 | 656942.8702 | 64209.7793 | 3145975.56 | 674862.7274 | 188.19813 | 136.72239 | 29277.1682 | 113820.807 | 82.61018 | 673.38938 | 908.68278 | 7964.6551 | 32.66472 | 25.73242 | 497.08699 | 222.12472 | 8.42009 | 3242.46386 | 4.82325 | 132.38939 |
| 1DBA3 | 97443.714 | 607963.8515 | 51373.8265 | 2893850.05 | 609536.2784 | 109.73978 | 241.5067 | 27419.358 | 83054.393 | 88.31564 | 599.63414 | 829.03941 | 7500.51 | 15.14373 | 27.24609 | 457.74052 | 205.79604 | 12.80209 | 2876.43791 | 4.54097 | 125.99563 |
| Average | 87958.691 | 606232.3799 | 47560.379 | 2925736.07 | 627252.3656 | 117.428097 | 200.50368 | 27972.2224 | 85734.6164 | 74.2903333 | 609.06391 | 867.836987 | 7304.1036 | 19.8666267 | 23.96647 | 479.998023 | 209.90377 | 9.53707 | 3035.329907 | 3.79733 | 114.26969 |
| STDev | 9261.7625 | 51598.01935 | 18847.7194 | 206154.297 | 41678.97518 | 67.2562667 | 55.982813 | 1134.49745 | 26846.6098 | 19.5606103 | 60.167373 | 39.8611715 | 777.58626 | 11.2094993 | 4.4346512 | 20.1760131 | 10.771473 | 2.87420213 | 187.7211064 | 1.538969605 | 26.0440341 |
| 1DGO1 | 72141.03 | 517324.9555 | 30819.268 | 2361094.94 | 556663.8121 | 47.23391 | 81.88103 | 9028.98774 | 42729.8606 | 28.93708 | 219.53982 | 555.5995 | 3936.3444 | 9.5808 | 103.70166 | 278.27051 | 30.44412 | 1.35011 | 521.81376 | 1.57221 | 27.57426 |
| 1DGO2 | 119807.77 | 565036.0921 | 37465.277 | 2579649.45 | 626267.5537 | 59.04783 | 91.86878 | 9015.789 | 52887.513 | 30.31472 | 215.42097 | 630.47672 | 4181.7484 | 10.00867 | 75.68359 | 315.18726 | 30.45953 | 1.68156 | 575.8972 | 1.94175 | 36.56968 |
| 1DGO3 | 96967.507 | 555561.4944 | 36366.6241 | 2463722.84 | 589106.629 | 57.3281 | 87.23281 | 9370.13816 | 45825.3892 | 28.53024 | 192.45491 | 583.47314 | 4035.1447 | 9.3431 | 86.29443 | 304.98399 | 31.18041 | 2.04976 | 591.20676 | 1.95385 | 37.30855 |
| Average | 96305.434 | 545974.1806 | 34883.723 | 2468155.75 | 590679.3316 | 54.5366133 | 86.994207 | 9138.30497 | 47147.5876 | 29.26068 | 209.13857 | 589.849787 | 4051.0792 | 9.64419 | 88.559893 | 299.480587 | 30.694687 | 1.69381 | 562.9725733 | 1.822603333 | 33.81749667 |
| STDev | 23840.263 | 25259.16817 | 3562.52799 | 109344.665 | 34828.51213 | 6.3825132 | 4.9981483 | 200.881865 | 5206.30699 | 0.93521652 | 14.594503 | 37.8437014 | 123.47554 | 0.33728263 | 14.145752 | 19.0637665 | 0.4207193 | 0.34998582 | 36.45725707 | 0.216931368 | 5.419408204 |
| 1MVE1 | 78083.361 | 511478.417 | 29633.517 | 2729066.35 | 709137.7343 | 64.80593 | 38.84263 | 6712.05846 | 47139.6685 | 30.32385 | 455.58605 | 794.38247 | 4458.9165 | 11.86274 | 115.06177 | 557.01112 | 12.2003 | 2.82301 | 892.19984 | 7.49153 | 29.62312 |
| 1MVE2 | 65571.172 | 592870.2834 | 38856.3286 | 3086545.02 | 794989.3005 | 85.83534 | 49.933 | 7372.98413 | 56511.6579 | 35.04893 | 491.73454 | 863.457 | 4862.1455 | 13.02795 | 123.38696 | 616.33103 | 11.44116 | 3.31396 | 1037.59685 | 9.15322 | 33.03528 |
| 1MVE3 | 54791.555 | 527037.1659 | 32706.6928 | 2718519.1 | 680769.4973 | 74.15468 | 45.05229 | 6420.47445 | 48307.8213 | 26.65801 | 388.14092 | 746.18068 | 4287.7998 | 11.05455 | 116.57544 | 576.26789 | 8.93356 | 1.30106 | 925.7275 | 7.53723 | 34.05959 |
| Average | 66148.696 | 543795.2888 | 33732.1794 | 2844710.16 | 728298.8441 | 74.9319833 | 44.609307 | 6835.17235 | 50653.0492 | 30.67693 | 445.15384 | 801.34005 | 4536.2873 | 11.9817467 | 118.34139 | 583.203347 | 10.85834 | 2.47934333 | 951.8413967 | 8.06066 | 32.23933 |
| STDev | 11656.638 | 43206.30727 | 4696.14531 | 209501.521 | 59471.85853 | 10.5362314 | 5.5584397 | 488.043486 | 5107.21224 | 4.20658813 | 52.578825 | 58.9469231 | 294.8863 | 0.99206796 | 4.4346512 | 30.2619951 | 1.709578 | 1.04953403 | 76.13490874 | 0.946460584 | 2.322868661 |
| 1PBC1 | 78255.145 | 607992.6531 | 26478.7613 | 2431229.57 | 767678.6413 | 71.24187 | 41.20699 | 7282.22524 | 39733.7799 | 25.61334 | 203.20405 | 608.07299 | 3830.5658 | 13.33673 | 136.25317 | 720.49611 | 24.8765 | 1.22757 | 611.00955 | 8.75931 | 24.47951 |
| 1PBC2 | 63649.44 | 554010.753 | 28803.5939 | 2283592.39 | 717871.8148 | 77.97609 | 47.25015 | 6947.81559 | 40635.9854 | 25.9229 | 200.52767 | 562.35876 | 3567.1414 | 12.62362 | 120.35962 | 731.17717 | 19.98384 | 0.81007 | 609.90548 | 8.16103 | 22.28298 |
| 1PBC3 | 66761.844 | 608503.5802 | 35927.5192 | 2408258.35 | 787551.9173 | 104.2649 | 50.1398 | 7965.86421 | 47297.3043 | 28.35466 | 193.78128 | 581.70235 | 3795.54 | 15.26258 | 114.29736 | 723.92842 | 19.10969 | 1.33785 | 708.19349 | 9.15725 | 28.73685 |
| Average | 69555.477 | 590168.9954 | 30403.2915 | 2374360.1 | 757700.7911 | 84.4942867 | 46.19898 | 7398.63501 | 42555.6899 | 26.6303 | 199.171 | 584.0447 | 3731.0824 | 13.7409767 | 123.63672 | 725.200567 | 21.323343 | 1.12516333 | 643.0361733 | 8.69253 | 25.16644667 |
| STDev | 7693.1749 | 31314.99855 | 4923.31501 | 79441.818 | 35895.64447 | 17.4497935 | 4.5582335 | 518.911529 | 4131.06212 | 1.50133937 | 4.8556734 | 22.9469531 | 143.05312 | 1.36513333 | 11.338824 | 5.45298345 | 3.10801 | 0.2783941 | 56.43059169 | 0.501456128 | 3.281313911 |
| 1PBS1 | 72760.715 | 192255.786 | 6803.6698 | 2069744.39 | 170702.3882 | 7.44927 | 36.70883 | 5882.7563 | 17724.4417 | 97.27532 | 349.09671 | 405.38874 | 2202.5648 | 2.44904 | 22.70508 | 12.99381 | 48.78861 | 0.2823 | 634.56604 | 0.48911 | 6.96768 |
| 1PBS2 | 63160.682 | 197030.6345 | 7889.99651 | 2103051.84 | 167645.2133 | 9.86025 | 38.85855 | 6117.44257 | 15086.807 | 96.40047 | 380.8239 | 409.55746 | 2236.5608 | 3.68509 | 26.48926 | 14.70523 | 48.75794 | 0.63823 | 585.20178 | 0.53345 | 7.86797 |
| 1PBS3 | 49556.943 | 207058.6268 | 6895.00964 | 2201481.77 | 177739.5747 | 10.87615 | 44.55057 | 6398.14341 | 15388.5701 | 100.19573 | 406.52446 | 430.99558 | 2328.6592 | 2.25888 | 21.19141 | 13.22703 | 50.0005 | 0.74869 | 558.66272 | 0.58586 | 6.6777 |
| Average | 61826.113 | 198781.6824 | 7196.22532 | 2124759.33 | 172029.0587 | 9.39522333 | 40.039317 | 6132.78076 | 16066.6062 | 97.9571733 | 378.81502 | 415.313927 | 2255.9283 | 2.79767 | 23.461917 | 13.6420233 | 49.18235 | 0.55640667 | 592.81018 | 0.53614 | 7.171116667 |
| STDev | 11659.312 | 7555.173789 | 602.556714 | 68498.8775 | 5176.299219 | 1.76013181 | 4.0520216 | 258.035682 | 1443.63395 | 1.98738335 | 28.766531 | 13.7397324 | 65.240089 | 0.77438743 | 2.7288102 | 0.92811864 | 0.7087046 | 0.24372362 | 38.51940173 | 0.048431061 | 0.62066539 |
| 1RMB1 | 94450.964 | 510185.0317 | 19426.5718 | 3104578.42 | 675455.7093 | 39.26805 | 28.78818 | 6724.69287 | 51839.6597 | 25.30813 | 350.75527 | 694.62344 | 4506.0433 | 9.03409 | 161.22876 | 1131.54918 | 3.63476 | 0.77325 | 2133.2366 | 4.86223 | 31.56881 |
| 1RMB2 | 78313.002 | 483654.9139 | 27054.3789 | 2904995.23 | 654663.2786 | 59.07501 | 32.34646 | 6596.53917 | 60082.9604 | 26.62096 | 360.14172 | 636.27813 | 4191.2706 | 11.91052 | 110.52075 | 1103.51527 | 3.36641 | 0.92053 | 1976.20598 | 5.12568 | 24.36246 |
| 1RMB3 | 132358.61 | 545124.4339 | 25751.1565 | 3283572.48 | 720782.8583 | 59.33227 | 36.07207 | 7461.83573 | 61767.7224 | 29.63969 | 397.34385 | 708.26365 | 4723.7716 | 13.43181 | 151.38989 | 1263.92217 | 3.74977 | 1.06785 | 2261.39487 | 5.56522 | 277.84634 |
| Average | 101707.53 | 512988.1265 | 24077.3691 | 3097715.37 | 683633.9487 | 52.5584433 | 32.402237 | 6927.68926 | 57896.7808 | 27.1895933 | 369.41361 | 679.72174 | 4473.6952 | 11.4588067 | 141.04647 | 1166.32887 | 3.5836467 | 0.92054333 | 2123.612483 | 5.184376667 | 111.2592033 |
| STDev | 27743.923 | 30830.47969 | 4080.07767 | 189381.913 | 33809.94537 | 11.510537 | 3.6422653 | 467.001268 | 5312.82816 | 2.22106076 | 24.639398 | 38.236426 | 267.72025 | 2.23338734 | 26.889875 | 85.6727127 | 0.1967248 | 0.1473 | 142.8378222 | 0.35515167 | 144.3136807 |

**Appendix 1.** Concentrations of elements in the bee pollen samples from the microwave-digestion method.

Dilute & Shoot Data w/ D&S Standards (2% acetic acid sample solution w/ 5 mL 1% Triton X-100)

| Sample Name | 23 Na [He] Conc. [ppb] | 24 Mg [He] Conc. [ppb] | 27 Al [He] Conc. [ppb] | 39 K [He] Conc. [ppb] | 44 Ca [He] Conc. [ppb] | 51 V [He] Conc. [ppb] | 52 Cr [He] Conc. [ppb] | 55 Mn [He] Conc. [ppb] | 56 Fe [He] Conc. [ppb] | 59 Co [He] Conc. [ppb] | 60 Ni [He] Conc. [ppb] | 63 Cu [He] Conc. [ppb] | 66 Zn [He] Conc. [ppb] | 75 As [He] Conc. [ppb] | 78 Se [He] Conc. [ppb] | 95 Mo [He] Conc. [ppb] | 111 Cd [He Conc. [ppb] | 123 Sb [He] Conc. [ppb] | 135 Ba [He] Conc. [ppb] | 205 Tl [He] Conc. [ppb] | 208 Pb [He] Conc. [ppb] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| DBA1 | 841.1298 | 11369.89938 | 37.51057 | 15494.8594 | 16290.85955 | 0.4018 | 2.20786 | 989.8249 | 186.36655 | 1.69662 | 28.43627 | 47.62323 | 533.19107 | 2.82974 | 2.11515 | 0 | 5.47778 | 0 | 58.09689 | 0.18627 | 6.023 |
| DBA2 | 807.4036 | 11090.84835 | 34.36863 | 14848.5173 | 16098.9141 | 0.59086 | 2.9287 | 949.74951 | 53.22495 | 1.61769 | 27.42505 | 35.14246 | 515.75828 | 2.33045 | 0.90649 | 0 | 5.18416 | 0 | 55.92935 | 0.1939 | 4.69164 |
| DBA3 | 820.23398 | 11127.4448 | 51.06513 | 15164.3921 | 15926.50099 | 0.35444 | 3.36427 | 979.05586 | 166.75106 | 1.60292 | 29.21405 | 36.74963 | 528.84396 | 3.04156 | 3.32381 | 0 | 5.1164 | 0 | 59.34364 | 0.18301 | 7.04637 |
| Average | 822.92246 | 11196.06418 | 40.9814433 | 15169.2562 | 16105.42488 | 0.44903333 | 2.83361 | 972.876757 | 135.44752 | 1.63907667 | 28.358457 | 39.83844 | 525.9311 | 2.73391667 | 2.11515 | 0 | 5.2594467 | 0 | 57.78996 | 0.187726667 | 5.920336667 |
| STDev | 17.023075 | 151.6536629 | 8.87290817 | 323.198473 | 182.2665157 | 0.12508735 | 0.5840399 | 20.7399424 | 71.8791008 | 0.05037822 | 0.8970348 | 6.78954824 | 9.0740891 | 0.36511086 | 1.20866 | 0 | 0.1920936 | 0 | 1.72771484 | 0.005589225 | 1.180717224 |
| Corrected average | 2057.3062 | 27990.16044 | 102.453608 | 37923.1406 | 40263.5622 | 1.12258333 | 7.084025 | 2432.19189 | 338.6188 | 4.09769167 | 70.896142 | 99.5961 | 1314.8278 | 6.83479167 | 5.287875 | 0 | 13.148617 | 0 | 144.4749 | 0.469316667 | 14.80084167 |
| DGO1 | 1165.5214 | 9535.40676 | 66.13381 | 13136.1692 | 20030.72682 | 0.66175 | 3.52952 | 339.09196 | 248.86657 | 1.0801 | 15.38431 | 49.81499 | 880.19511 | 4.82718 | 2.11515 | 0 | 1.32162 | 0 | 22.54452 | 0.1939 | 8.7868 |
| DGO2 | 1120.2536 | 9159.91233 | 40.85753 | 12639.9354 | 19325.02122 | 0.30723 | 2.68843 | 333.24669 | 73.98714 | 0.88282 | 15.80435 | 41.96818 | 863.60956 | 4.61506 | 2.11515 | 0 | 1.38926 | 0 | 21.5148 | 0.20043 | 6.457 |
| DGO3 | 1134.7966 | 9376.31256 | 41.4402 | 12817.4668 | 19580.92894 | 0.02368 | 2.89874 | 337.69253 | 157.05958 | 1.01105 | 15.60208 | 65.94153 | 894.87051 | 4.31247 | 2.41732 | 0 | 1.1407 | 0 | 22.38195 | 0.2146 | 8.80053 |
| Average | 1140.1905 | 9357.21055 | 49.47718 | 12864.5238 | 19645.55899 | 0.33088667 | 3.0388967 | 336.67706 | 159.971097 | 0.99132333 | 15.596913 | 52.5749 | 879.55839 | 4.58490333 | 2.2158733 | 0 | 1.28386 | 0 | 22.14709 | 0.202976667 | 8.014776667 |
| STDev | 23.110895 | 188.4746185 | 14.4280064 | 251.441352 | 357.2644417 | 0.31969213 | 0.4377111 | 3.05207795 | 87.4760622 | 0.10010847 | 0.2100677 | 12.2226513 | 15.640198 | 0.25867676 | 0.1744579 | 0 | 0.1285102 | 0 | 0.553579474 | 0.010582374 | 1.349091634 |
| Corrected average | 2850.4763 | 23393.02638 | 123.69295 | 32161.3095 | 49113.89748 | 0.82721667 | 7.5972417 | 841.69265 | 399.927742 | 2.47830833 | 38.992283 | 131.43725 | 2198.896 | 11.4622583 | 5.5396833 | 0 | 3.20965 | 0 | 55.367725 | 0.507441667 | 20.03694167 |
| MVE1 | 1304.8224 | 10916.54536 | 46.54577 | 14889.12 | 18581.97187 | 0.37805 | 3.57444 | 253.11969 | 318.07713 | 1.31686 | 59.80168 | 34.30389 | 600.23014 | 5.29636 | 1.20866 | 0 | 4.07733 | 0.20954 | 31.92008 | 0.22331 | 8.87545 |
| MVE2 | 1279.0957 | 10690.01497 | 33.19092 | 14395.6546 | 18500.18221 | 0 | 3.84485 | 237.73366 | 239.09614 | 1.13928 | 57.17242 | 29.47964 | 588.77363 | 4.73625 | 0 | 0 | 3.6028 | 0.17961 | 33.2208 | 0.19172 | 7.20939 |
| MVE3 | 1274.5328 | 10646.29771 | 76.3697 | 14576.5918 | 18135.86095 | 0.07089 | 2.73344 | 251.87768 | 337.57119 | 1.18368 | 59.44394 | 36.14875 | 618.42905 | 4.81205 | 1.51082 | 0 | 3.61409 | 0.04989 | 31.70353 | 0.20806 | 8.37704 |
| Average | 1286.1503 | 10750.95268 | 52.0354633 | 14620.4555 | 18406.00501 | 0.14964667 | 3.3842433 | 247.57701 | 298.248153 | 1.21327333 | 58.806013 | 33.31076 | 602.47761 | 4.94822 | 0.9064933 | 0 | 3.76474 | 0.14634667 | 32.28147 | 0.207696667 | 8.15396 |
| STDev | 16.330636 | 145.0637841 | 22.1066576 | 249.639799 | 237.498941 | 0.20095375 | 0.5796026 | 8.54718092 | 52.1461897 | 0.09241476 | 1.4259961 | 3.44368806 | 14.954909 | 0.30387087 | 0.7994516 | 0 | 0.2707697 | 0.08486382 | 0.820657732 | 0.015798134 | 0.855138875 |
| Corrected average | 3215.3757 | 26877.3817 | 130.088658 | 36551.1386 | 46015.01253 | 0.37411667 | 8.4606083 | 618.942525 | 745.620383 | 3.03318333 | 147.01503 | 83.2769 | 1506.194 | 12.37055 | 2.2662333 | 0 | 9.41185 | 0.36586667 | 80.703675 | 0.519241667 | 20.3849 |
| PBC1 | 1346.6425 | 10040.26193 | 50.08067 | 11773.0894 | 21248.37575 | 0.11817 | 3.28926 | 241.9517 | 306.12725 | 0.72009 | 14.04652 | 46.616 | 785.67581 | 5.40212 | 6.04329 | 0 | 1.06165 | 0 | 31.26996 | 0.24619 | 16.49463 |
| PBC2 | 1311.7042 | 9839.03156 | 48.11998 | 11402.4015 | 21074.20974 | 0.23634 | 2.44808 | 238.43182 | 220.33814 | 0.8039 | 14.18664 | 52.47496 | 780.24081 | 4.7364 | 0 | 0 | 1.03907 | 0 | 30.40281 | 0.22331 | 8.80299 |
| PBC3 | 1316.1915 | 9804.02131 | 49.09855 | 11386.8041 | 20779.13078 | 0 | 3.30417 | 238.11605 | 241.17738 | 0.78417 | 13.9999 | 55.53014 | 791.64386 | 4.73625 | 1.81299 | 0 | 0.98249 | 0 | 31.81408 | 0.24183 | 9.43081 |
| Average | 1324.8461 | 9894.438267 | 49.0997333 | 11520.765 | 21033.90542 | 0.11817 | 3.0138367 | 239.499857 | 255.880923 | 0.76938667 | 14.077687 | 51.5403667 | 785.85349 | 4.95825667 | 2.61876 | 0 | 1.0277367 | 0 | 31.16228333 | 0.23711 | 11.57614333 |
| STDev | 19.009147 | 127.4944508 | 0.98034554 | 218.658431 | 237.2046351 | 0.11817 | 0.4900164 | 2.12922039 | 44.7447035 | 0.04381711 | 0.097193 | 4.52996374 | 5.7036011 | 0.38439693 | 3.1011752 | 0 | 0.0407788 | 0 | 0.711769943 | 0.01214835 | 4.271085671 |
| Corrected average | 3312.1152 | 24736.09567 | 122.749333 | 28801.9125 | 52584.76356 | 0.295425 | 7.5345917 | 598.749642 | 639.702308 | 1.92346667 | 35.194217 | 128.850917 | 1964.6337 | 12.3956417 | 6.5469 | 0 | 2.5693417 | 0 | 77.90570833 | 0.592775 | 28.94035833 |
| PBS1 | 395.54343 | 3438.43591 | 23.76217 | 10243.4241 | 3342.87491 | 0 | 2.14776 | 151.20489 | 19.66024 | 1.94322 | 12.69318 | 17.719 | 9.02962 | 0.19669 | 0 | 0 | 0.73404 | 0 | 15.1741 | 0.09695 | 5.66602 |
| PBS3 | 384.81644 | 3363.99633 | 25.92258 | 9970.68329 | 3504.51486 | 0 | 1.33667 | 156.95611 | 0 | 1.97282 | 14.46646 | 16.73035 | 10.00893 | 0 | 0.60433 | 0 | 0.72275 | 0 | 14.14438 | 0.05556 | 6.90509 |
| PBS2 | 374.86626 | 3379.03313 | 20.22845 | 9920.39146 | 3445.90186 | 0 | 1.68214 | 149.40111 | 0 | 1.9679 | 14.12439 | 17.08266 | 9.44692 | 0 | 0.30216 | 0 | 0.74534 | 0 | 15.6618 | 0.07734 | 4.37908 |
| Average | 385.07538 | 3393.82179 | 23.3044 | 10044.833 | 3431.09721 | 0 | 1.72219 | 152.520703 | 6.55341333 | 1.96131333 | 13.761343 | 17.1773367 | 9.4951567 | 0.06556333 | 0.3021633 | 0 | 0.7340433 | 0 | 14.99342667 | 0.076616667 | 5.650063333 |
| STDev | 10.341017 | 39.36167065 | 2.87453373 | 173.813563 | 81.83062755 | 0 | 0.4070255 | 3.94563427 | 11.3508449 | 0.01586121 | 0.9407352 | 0.5010788 | 0.4914337 | 0.11355902 | 0.302165 | 0 | 0.011295 | 0 | 0.774676064 | 0.020704479 | 1.263080596 |
| Corrected average | 962.68844 | 8484.554475 | 58.261 | 25112.0824 | 8577.743025 | 0 | 4.305475 | 381.301758 | 16.3835333 | 4.90328333 | 34.403358 | 42.9433417 | 23.737892 | 0.16390833 | 0.7554083 | 0 | 1.8351083 | 0 | 37.48356667 | 0.191541667 | 14.12515833 |
| RMB1 | 323.24137 | 8828.38214 | 40.65368 | 16062.1044 | 10566.6751 | 1.13472 | 2.16573 | 205.56394 | 266.13841 | 0.725 | 34.41032 | 14.22373 | 19.28273 | 0.80203 | 0.60433 | 0 | 0.40655 | 0.11972 | 55.27874 | 0.48584 | 2.2517 |
| RMB2 | 313.72764 | 8691.13796 | 51.45633 | 15655.2958 | 10269.95513 | 0 | 4.46604 | 207.45881 | 228.76028 | 0.72993 | 35.20378 | 13.24175 | 19.5216 | 0.75664 | 0 | 0 | 0.36138 | 0.03993 | 54.84517 | 0.50436 | 2.25763 |
| RMB3 | 317.97818 | 8755.79679 | 39.67157 | 15581.3805 | 10131.28405 | 0 | 1.15646 | 198.9775 | 137.12958 | 0.60664 | 34.33263 | 12.05373 | 20.01638 | 0.75664 | 0 | 0 | 0.45172 | 0.04989 | 54.95377 | 0.5109 | 0.06989 |
| Average | 318.31573 | 8758.438963 | 43.9271933 | 15766.2602 | 10322.63809 | 0.37824 | 2.5960767 | 204.000083 | 210.67609 | 0.68719 | 34.64891 | 13.17307 | 19.606903 | 0.77177 | 0.2014433 | 0 | 0.40655 | 0.06984667 | 55.02589333 | 0.500366667 | 1.526406667 |
| STDev | 4.7658388 | 68.660229 | 6.53888823 | 258.860398 | 222.4251842 | 0.6551309 | 1.6962396 | 4.45167278 | 66.3784453 | 0.06980188 | 0.482099 | 1.08662906 | 0.3741899 | 0.02620593 | 0.3489101 | 0 | 0.04517 | 0.04347772 | 0.225603785 | 0.012998497 | 1.261383919 |
| Corrected average | 795.78933 | 21896.09741 | 109.817983 | 39415.6505 | 25806.59523 | 0.9456 | 6.4901917 | 510.000208 | 526.690225 | 1.717975 | 86.622275 | 32.932675 | 49.017258 | 1.929425 | 0.5036083 | 0 | 1.016375 | 0.17461667 | 137.5647333 | 1.250916667 | 3.816016667 |

**Appendix 2.** Concentrations of elements in the bee pollen samples from the dilute & shoot method. The adjusted average is what is compared to the digestion samples due to the samples including 2.5x less bee pollen.