

# More Methylene Chloride!

*The Most Common Solvent That is in Some of America's Favorite Decaffeinated Coffees*

## Introduction

*Over the past several years, Clean Label Project has investigated the coffee industry ranging from acrylamide contamination to methylene chloride. We decided to take a fresh look to see that after all the attention received on this "active ingredient in paint stripper" if this chemical continues to be used. Spoiler alert! It does. Read on for more details.*

## Background on Clean Label Project Coffee Investigations:

Over the past few years, Clean Label Project has conducted several investigations into coffee. The reason? According to YouGovAmerica<sup>1</sup>, we are a very caffeinated society. Three-quarters of American adult's drink coffee — and most (53%) drink at least one cup per day, according to a new YouGov poll conducted September 21 – 25, 2022. Coffee drinkers in the United States also are more likely to sip caffeinated coffee (79%) than decaf (10%), though some drink both (10%). Looking over the past five years, here is an overview of what Clean Label Project has researched when it comes to one of America's favorite beverages<sup>2</sup>.

## 2018-2019:

### Acrylamide in Coffee

Clean Label Project investigated<sup>3</sup> the levels of acrylamide in coffee given a lawsuit and pending State of California regulatory change. At the time, the State of California legislature was considering rulemaking related to the presence of acrylamide in coffee. Acrylamide, which remains classified by the International Agency for Research on Cancer (IARC)<sup>4</sup> as a "probable carcinogen," was the chemical at the center of an ongoing California Proposition 65 dispute. California Proposition 65<sup>5</sup> requires businesses to provide warnings to Californians about significant exposures to chemicals that cause cancer, birth defects or other reproductive harm. These chemicals can be in the products that Californians purchase, in their homes or workplaces, or that are released into the environment. By requiring that this information be provided, Proposition 65 (Prop. 65) enables Californians to make informed decisions about their exposures to these chemicals. While acrylamide is probable carcinogen, Clean Label Project tested top-selling brewed coffee and found it contained levels of acrylamide below the ability to quantify. Further, coffee does have its benefits<sup>6</sup>- it's an antioxidant and in moderation, a natural stimulant. In June of 2019<sup>7</sup>, the coffee industry was victorious and the agency that enforces Prop. 65

finally exempted coffee from the list of products requiring a cancer warning and Clean Label Project was supportive of that outcome.

2020-2021:

## Methylene Chloride in Coffee

The EPA banned methylene chloride in 2019<sup>8</sup> from being used as an active ingredient in consumer paint stripper. Meanwhile, to this day, methylene chloride is still permitted by the FDA<sup>9</sup> for use as a chemical to decaffeinate coffee. High-risk populations, including pregnant women and people with heart disease, are frequent consumers of decaffeinated coffee<sup>10</sup>. Most concerning is that brands with products that use the methylene chloride decaffeination process often fail to provide consumers with transparent information on the process, preventing customers from making informed choices. The State of California Office of Environmental Health Hazard Assessment website<sup>11</sup> even says that “[d]uring pregnancy, methylene chloride can pass from mother to baby.” If mothers-to-be were armed with information on the decaffeination process, chances are they might make different choices.

Clean Label Project commissioned Eurofins, an ISO 17025 scope-accredited analytical chemistry lab, to perform double-blind testing on various decaffeinated coffee products to determine whether methylene chloride persists as an industrial contaminant within decaffeinated coffee. These test reports<sup>12</sup> revealed levels of methylene chloride in products of top selling brands.

## Other Relevant Developments in the Coffee Industry

In January 2022, Peet’s Coffee<sup>13</sup>, one of the top five premium coffee brands and one of the brands selected as part of Clean Label Project’s original decaffeination coffee investigation, officially announced that the company fully transitioned to water processing across its entire line of decaffeinated roasted beans, pods, and handcrafted decaf coffee beverages available in Peet’s

coffee bars. Peet’s Coffee indicated that “the process is chemical-free and naturally removes caffeine while ensuring the integrity, taste, and quality of the coffee beans for an optimal sipping experience.”

This development was a huge win for public health, consumers, and Peet’s Coffee in terms of industry leadership and environmental stewardship.

## Rationale for This Year’s Testing

During the 2020-2021 Decaffeinated Coffee Methylene Chloride residue investigation, Clean Label Project received a lot of media and consumer attention. Given the increase in consumer commitment and accountability for their health in a post-COVID world, we wanted to see if the use of Methylene Chloride is still commonly used. Clean Label Project again commissioned Eurofins, an ISO 17025 scope-accredited analytical chemistry lab, to perform double-blind testing on various decaffeinated coffee products to determine whether methylene chloride persists as an industrial contaminant within decaffeinated coffee.

## Overview of Testing: Background on solvents:

When talking about residual solvents, it first makes sense to define what is meant by solvents. The term “solvents” refers to a class of chemical compounds described by their function. Solvents are generally in liquid form and are used to dissolve, suspend, or extract other materials. When solvents are used to extract compounds from plant matter (in this case caffeine from a coffee bean), residual amounts of those solvents can be transferred into the finished product.

The limits on the amount of solvent residue that can be present are established by the International Conference on Harmonization (ICH) and adopted by the FDA<sup>14</sup>. The ICH has determined three classes for solvents and requires processors to justify the presence

of any detected residue in final products. The three ICH classes are:

- **Class 1** — Solvents that are extremely hazardous. Class 1 solvents include known human carcinogens, strongly suspected human carcinogens, and environmental hazards. The ICH recommends that Class 1 solvents are avoided in production.
- **Class 2** — Solvents with degrees of toxicity that warrant solvent-specific exposure limits. The ICH recommends limiting the use of Class 2 solvents.
- **Class 3** — A broad group of solvents that have a set permissible exposure limit of 50 mg per day. In general, products that are produced with Class 3 solvents must not exceed 0.5 percent solvent residue volume by weight.

**Note:** When investigating what type of regulatory guidance is provided to industry about residual solvents, it is important to note that the above reference is provided by FDA but as written, is applicable to pharmaceuticals. We are uncertain if these FDA limits and recommendations are consistent for food.

## Residual Solvent Clean Label Project Tested for: Methylene Chloride (Class 2)

Methylene chloride<sup>15</sup>, or dichloromethane, is a colorless, nonflammable, and volatile liquid chlorinated hydrocarbon. It is commonly used as a solvent in paint removers, a solvent in the manufacture of pharmaceuticals, and as a degreasing and blowing agent for industrial use.

Recently, the California Environmental Health Hazard Assessment<sup>11</sup> added it to its Prop. 65 list. The State of California evaluation concluded that during pregnancy, methylene chloride can pass from mother to baby. In March of 2019, Methylene Chloride was banned for consumer use by the U.S. Environmental Protection

Agency<sup>16</sup> following controversial deaths linked to its use. Consumers and workers can be exposed to methylene chloride through inhalation and absorption by the skin. Inhalation of this chemical can cause instant dizziness, loss of consciousness, and irritation of the nose and throat. According to the World Health Organization<sup>17</sup>, an inhalation study in mice provided conclusive evidence of methylene chloride's carcinogenicity. Similarly, a drinking-water study provided suggestive evidence of carcinogenicity.

Methylene Chloride is used extensively for decaffeinating green coffee and tea. During the decaffeination process, the coffee beans come into direct contact with the solvent, which is then removed through vaporization.

## Selecting the Samples

Clean Label Project wanted to select the decaffeinated coffees that were the most representative of the decaffeinated coffees in pantries across America. Clean Label Project used best-seller lists found on Amazon, Walmart, and Target's websites, in addition to retesting products previously tested during Clean Label Project's original decaffeinated coffee investigation. The samples were procured using Clean Label Project's Consumer Chain of Custody Sampling & Testing Process. Clean Label Project visited local co-ops, national retailers, and marketplace websites and purchased the products just as any consumer would to replicate the consumer shopping experience.

## Evaluating the Samples: (February 2022)

Clean Label Project had the products tested by an accredited analytical chemistry laboratory for methylene. Clean Label Project utilized blind testing to fully protect impartiality. All decaffeinated coffee samples were sampled out into conical tubes and numbered. Where possible, the product name and corresponding number was maintained exclusively by Clean Label Project to protect independence and confidentiality. The numbered samples were submitted to an accredited analytical chemistry lab for testing.

## Overview of testing: Sample Preparation

The standards and samples were prepared for analysis using the following approach:

- An internal standard (IS) solution containing deuterated chloroform (CAS No.: 865-49-6) was used.
- A stock standard solution of methylene chloride (DCM) and/or other applicable solvents was also prepared at a working concentration.
- The standard stock solution was spiked into 5 mL of water at various levels with the internal standard being added at the same level throughout the calibration range.
- The calibration curve was analyzed by Purge and Trap Gas Chromatography Mass Spectrometry (P&T-GC/MS).
- The samples were prepared by adding ca. 1 gram ground coffee to a vial, along with 5 mL of water, stir bar, and internal standard.

## Overview of testing: Purge And Trap Gas Chromatography With Mass Spectrometry (P&T-Gc/Ms)

- Calibration curves were generated for each analyte and observed to have a correlation coefficient of 0.999 or greater for methylene chloride.
- For quantitation, Extracted Ion Chromatograms (EICs) were used. In an EIC, specific mass to charge ratio (m/z) unique to the target analytes are extracted from the TIC, allowing for more precise quantitation. In this case EICs were necessary, as significant matrix interferences were observed in the chromatograms and were unresolved from the target analytes. (See Appendix 1 for an example of the chromatograms)

## February 2022 Results: (See Appendix 2 to see the Brand/Product Results)

**Table 1. Sample Analysis Results for S1 - S17**

SAMPLE DESCRIPTION	CONCENTRATION OF ANALYTE (µg/kg) <sup>1</sup>
	METHYLENE CHLORIDE
S1	< 30
S2	<b>3928</b>
S3	<b>3579</b>
S4	< 30
S5	<b>1419</b>
S6	<b>20</b>
S7	< 30
S8	< 30
S9	<b>8931</b>
S10	<b>42</b>
S11	< 30
S12	< 30
S13	< 30
S14	<b>1556</b>
S15	< 30
S16	< 30
S17	< 30

While the use of methylene chloride is routine, Clean Label Project was surprised at the quantity of residual methylene chloride observed compared to the 2020-2021 testing cycle.

## Possible Rationale for the Elevated Methylene Chloride Test Results Compared to 2020-2021

While methylene chloride is a commonly used decaffeination solvent, the test results were 10x-100x higher than observed levels several years ago. Consistent with 2020-2021 data, all test results were all below regulatory limits<sup>9</sup>. According<sup>18</sup> to ChemAnalyst which tracks the real-time price movements of over 300 chemical and petrochemical products, in the last quarter of 2022, the methylene chloride market showed a downward price trajectory due to sufficient availability and limited trading activities. It identified “muted demand” as the major factor affecting this price trend. Perhaps since the cost of methylene chloride is low, the same quality assurance/quality control diligence wasn’t put into the solvent recovery process.

It’s important to note that just because a methylene chloride test result was non-detect (or below the level of detection) in previous studies, it doesn’t mean that methylene chloride isn’t used. It could mean that the manufacturer did a better job at recovering the solvent from the product after it underwent the decaffeination process.

Since Clean Label Project conducted finished product testing, there is no way to know for certain the rationale for the elevated results.

Clean Label Project would need to do additional testing to see if these results are confirmed over time.

## XI. Conclusion

Whatever the case for the elevated levels of methylene chloride in some of the decaffeinated coffee samples, the issue is the use of harsh solvents to decaffeinate. Consider reaching out to your favorite decaffeinated coffee brands and demand to know how they decaffeinate their coffee. If you are concerned about you or your family’s exposure to chemicals, consider reaching for organic, water, or carbon dioxide decaffeinated products.

## What’s A Concerned Consumer to Do?

**1. Recognize that decaffeinated coffee has many important qualities.** In fact, coffee is the biggest source of antioxidants in the American diet.<sup>9</sup> Drinking two or more cups of decaf coffee per day has also been linked with up to a 48% lower risk of developing rectal cancer<sup>11</sup>. Remember, there are many great tasting decaffeinated coffees across all price points that use organic or non-chemical decaffeination methods. Find a decaffeinated coffee that best represents your health and environmental priorities.

**2. Look for claims on product packaging such as solvent-free, chemical-free, Swiss-water, or certified organic.** These decaffeination approaches do not use harsh chemicals.

**3. Listen, we know that you have your personal favorites when it comes to your morning coffee** Did your favorite decaf product test positive for methylene chloride? Call, email, or message them on social media and demand better.

**4. Didn’t see your favorite decaf coffee on the list of products tested?** Go to the brand’s website and call, email, or message them on social media and demand to know more

about their decaffeination process. You deserve to know what's in the food and consumer products you purchase and provide for your family. CheckYourDecaf.org is another great Clean Label Project resource.

**5. Concerned?** If you are concerned about your exposure to methylene chloride or have questions about your caffeine exposure, always speak with your doctor.

Clean Label Project conducted a survey on decaffeinated coffee consumer sentiments and their opinions on harsh solvent extraction. The findings are in Appendix 3.

*Clean Label Project is a 501c3 funded through grants, donations, and its certification activities.*

## References

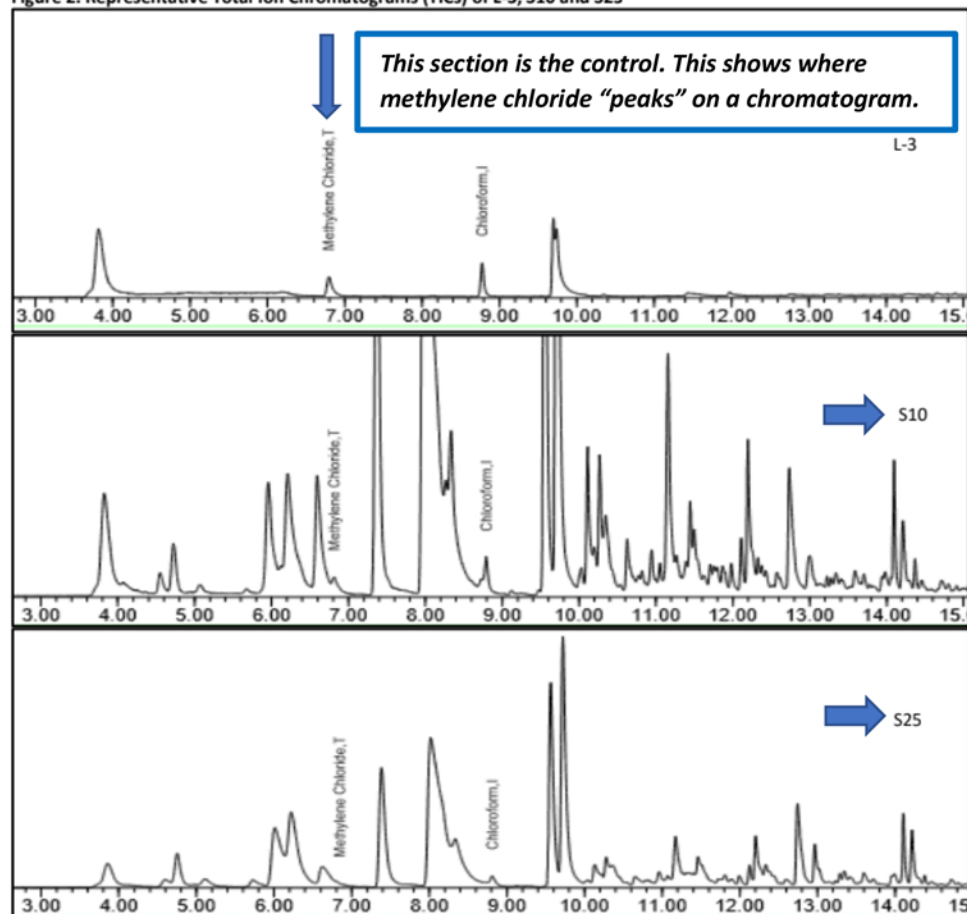
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- <sup>4</sup> American Cancer Society. (2019). Acrylamide and cancer risk. American Cancer Society. Retrieved from <https://www.cancer.org/healthy/cancer-causes/chemicals/acrylamide.html>
- <sup>5</sup> Coffee infographic. (n.d.). Retrieved from <https://cleanlabelproject.org/coffee-infographic/>
- <sup>6</sup> Bjarnadottir, A. (2019, February 20). Coffee and antioxidants: Everything you need to know. Healthline. Retrieved from <https://www.healthline.com/nutrition/coffee-worlds-biggest-source-of-antioxidants>
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- <sup>8</sup> United States Environmental Protection Agency. (2022). Final Rule on Regulation of Methylene Chloride in Paint and Coating Removal for Consumer Use. EPA. Retrieved from <https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/final-rule-regulation-methylene-chloride-paint-and#:~:text=In%20March%202019%2C%20EPA%20issued%20a%20final%20rule,that%20have%20resulted%20from%20exposure%20to%20the%20chemical.>
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- <sup>10</sup> Shlonsky, A. K., Klatsky, A. L., & Armstrong, M. A. (2003). Traits of persons who drink decaffeinated coffee. *Ann Epidemiol*, 13 (4), 273-9.
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- <sup>12</sup> Clean Label Project. (2020). Decaf coffee: Our point of view [White paper]. Retrieved from <https://cleanlabelproject.org/wp-content/uploads/CLP-Decaf-Coffee-White-Paper-updated.pdf>
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- <sup>18</sup>ChemAnalyst. (2022). Methylene dichloride price trend and forecast. ChemAnalyst. Retrieved from <https://www.chemanalyst.com/Pricing-data/methylene-dichloride-1092>

## Appendix 1: Example Chromatogram “Peaks” Observed During the 2020-2021 Methylene Chloride Residual Solvent Investigation

Figure 2. Representative Total Ion Chromatograms (TICs) of L-3, S10 and S25



S10 and S25 are actual samples from the 2020-2021 methylene chloride investigation. Here you can see how the analytical chemistry instrumentation is able to identify the presence of methylene chloride in samples.

The top frame of Figure 2 shows a 10 ppb standard, the second frame shows the TIC for one preparation of S10, and the last frame shows a TIC for S25. The methylene chloride peak can be seen in the L-3 standard at approximately 6.80 minutes. S10 shows the methylene chloride peak protruding from the shoulder of a matrix peak. S25 does not show the methylene chloride peak on the shoulder of the matrix peak due to its absence in this sample.



## Appendix 2: Specific Product Test Results

### A. February 2022 Results:

Table 1. Sample Analysis Results for S1 - S17	
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S11	< 30
S12	< 30
S13	< 30
S14	<b>1556</b>
S15	< 30
S16	< 30
S17	< 30

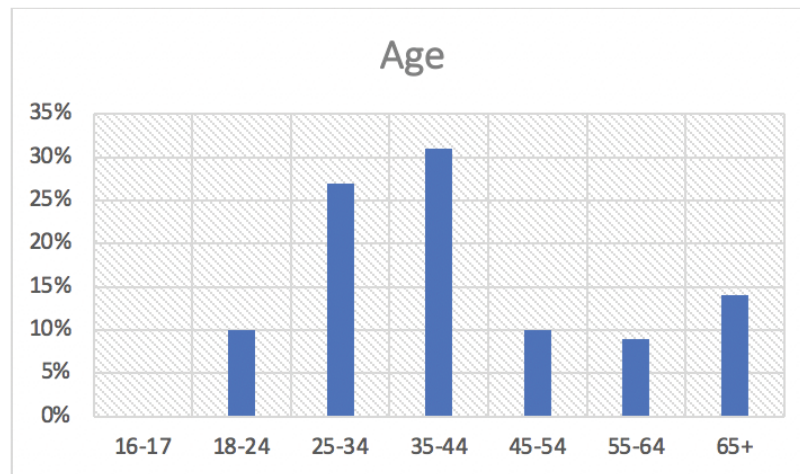
Sample Description	ID	Brand	Product	Lot
S1	40238	McCafé	Decaf Premium Roast Medium Tin	28 Jul 2022 P21209 06:12
S2	40239	Dunkin'	Decaf Arabica Coffee Medium Roast	Use by Aug 6, 2022
S3	40240	Dunkin'	Decaf Medium Roast k-cups	<i>Not listed</i>
S4	40241	The Coffee Bean & Tea Leaf	Decaf French Roast Dark Roast	Mfg: Sept 16, 2021 Exp: 16 Mar 2023
S5	40242	Wegmans	100% Arabica Ground Coffee Decaffeinated tin	Roasted on: May 13, 2021 Enjoy by May 13, 2022
S6	40243	The Coffee Bean & Tea Leaf	The Coffee Bean House Blend Decaf Light Roast Coffee k-cups	Exp: 2/19/2023 LC107 021821 1113
S7	40244	Sprouts Farmers Market	Freshly Roasted Bulk Coffee Breakfast Blend Auto-drip	17753
S8	40245	Starbucks	Via Instant Dark Roast Coffee Decaf Italian Roast	Best Before 8 Feb 2022 10102 1039 23:18 1
S9	40246	Publix Arabica Ground Coffee	House Blend Decaf Medium Roast	Best By: 06 21 2021 04:35
S10	40247	Sprouts Farmers Market	Freshly Roasted Bulk Coffee French Roast Auto-Drip	17719
S11	40248	Wegmans	Decaffeinated Chocolate Cherry	Roasted on: 9/8/21 Enjoy by: 9/8/22
S12	40259	Wegmans	Decaffeinated Hazelnut	Roasted On: 11/29/21 Enjoy by: 11/29/22
S13	40260	Starbucks	Decaf House Blend Medium Roast k-cups	Best By: 30 Mar 2022 PL095 1104
S14	40261	Wegmans	Decaf Medium Roast Single Serve	Roasted On: July 28, 2021 Enjoy by: Oct 27, 2022
S15	40262	Starbucks	Decaffeinated Espresso Roast	1091098312
S16	40263	McCafé	Decaf Premium Roast Medium - Ground Coffee	Best before: June 5, 2022 AD BP 21 156 18:29
S17	40264	McCafé	Decaf Premium Roast Medium - K-Cups	<i>Not captured</i>

### **Appendix 3: Results of Decaffeinated Coffee Consumer Survey**

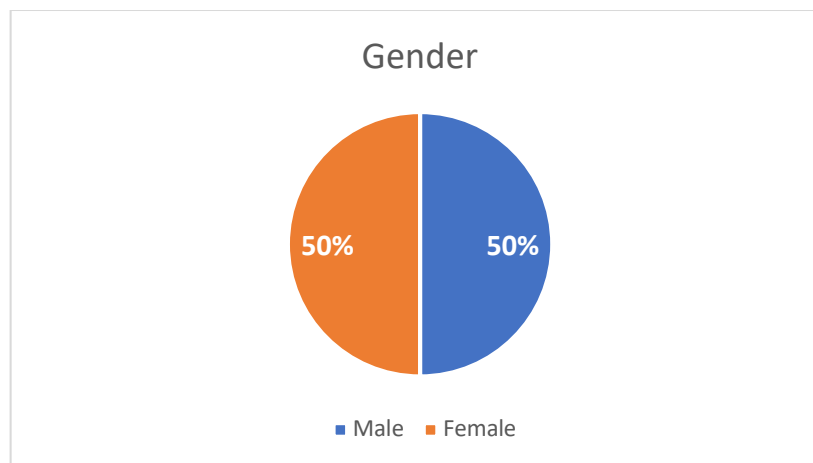
Date of survey: December 2022

Number of respondents: 750 decaffeinated coffee drinkers

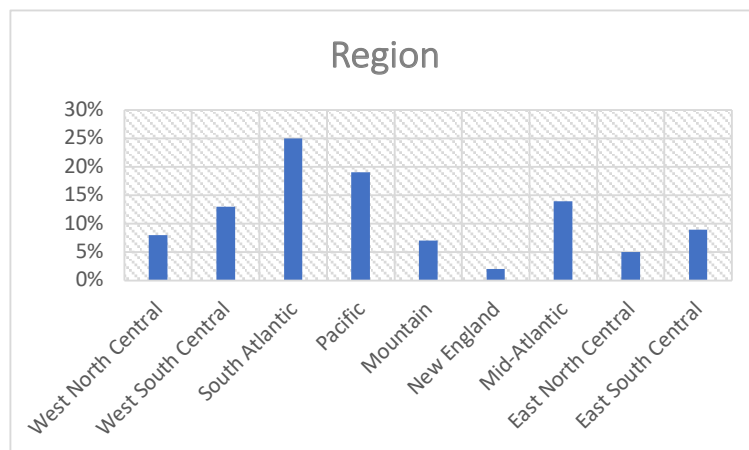
#### **Question 1 - What is your age?**



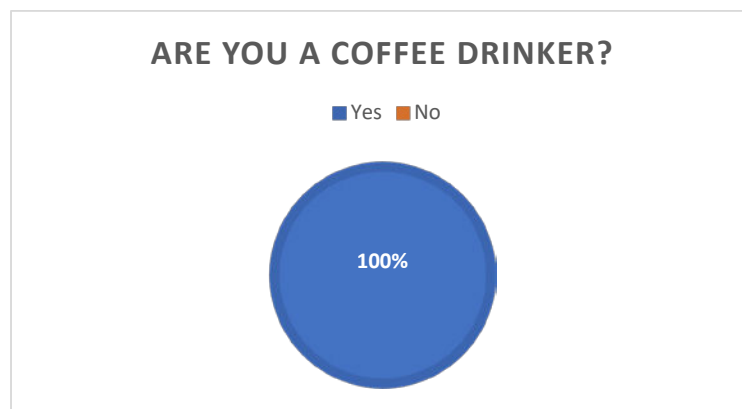
#### **Question 2 - What is your gender?**



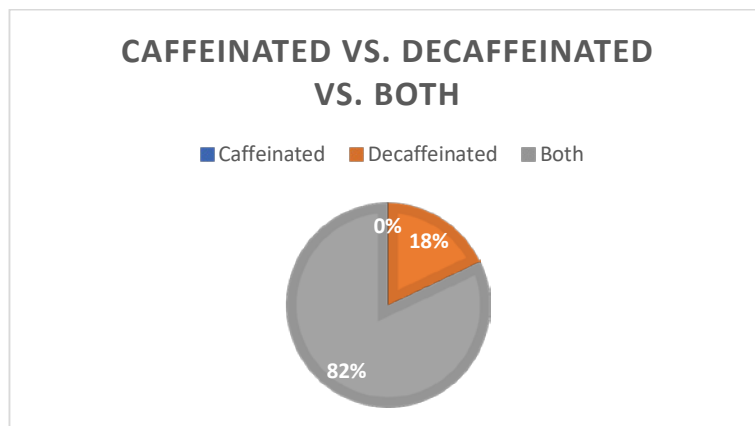
**Question 3 - Where do you live? For each region, please read the list of states carefully and select the one that applies to you.**



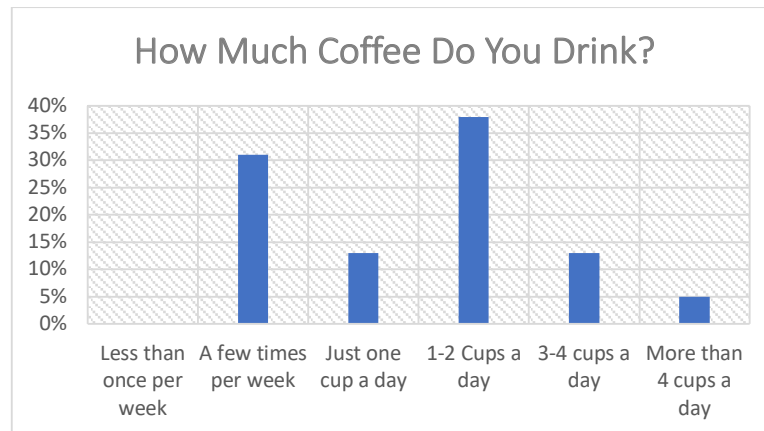
**Question 4 - Are you a coffee drinker?**



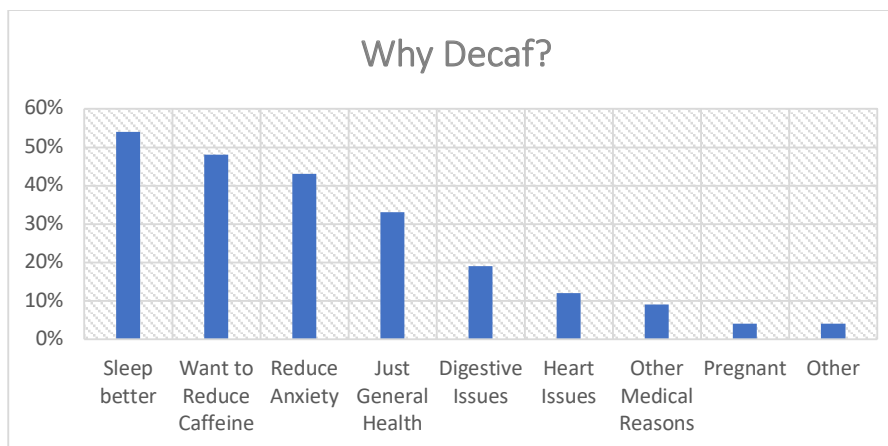
**Question 5 - Do you drink caffeinated or decaffeinated coffee?**



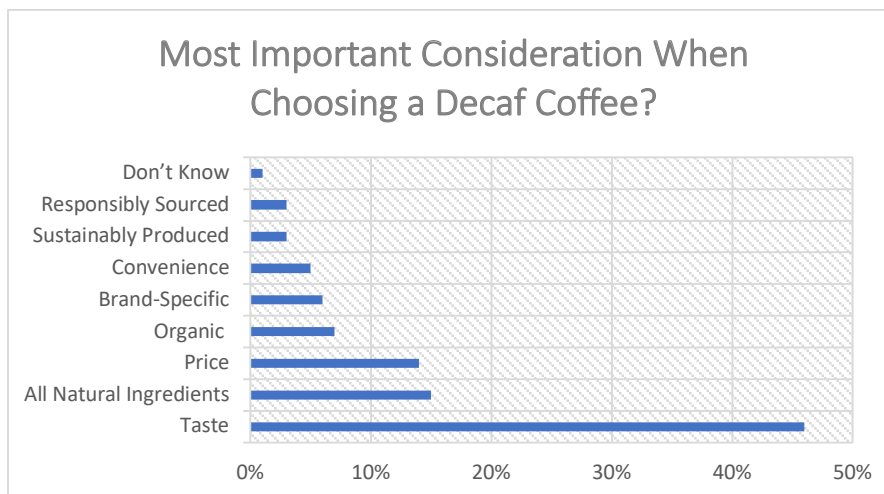
**Question 6 - How frequently do you drink decaf coffee?**



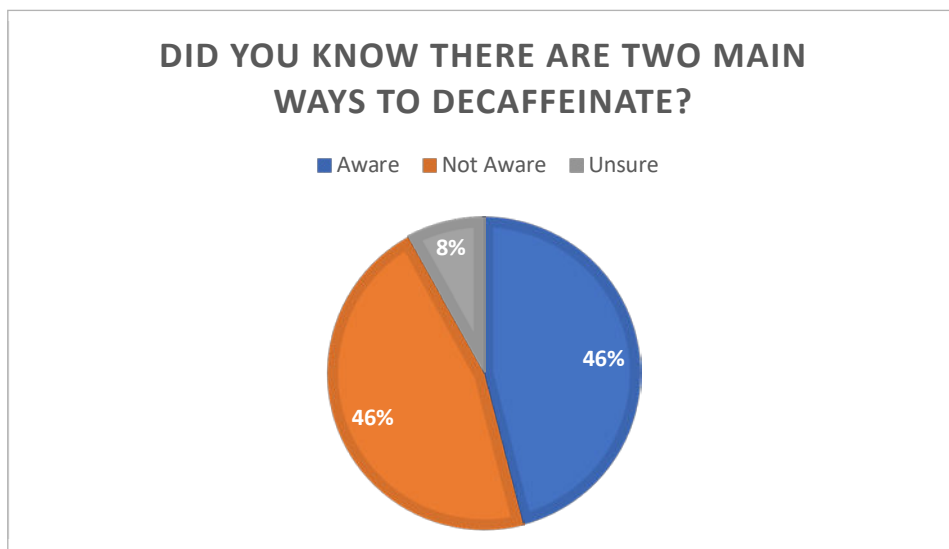
**Question 7 - Why do you choose to drink decaf coffee?**



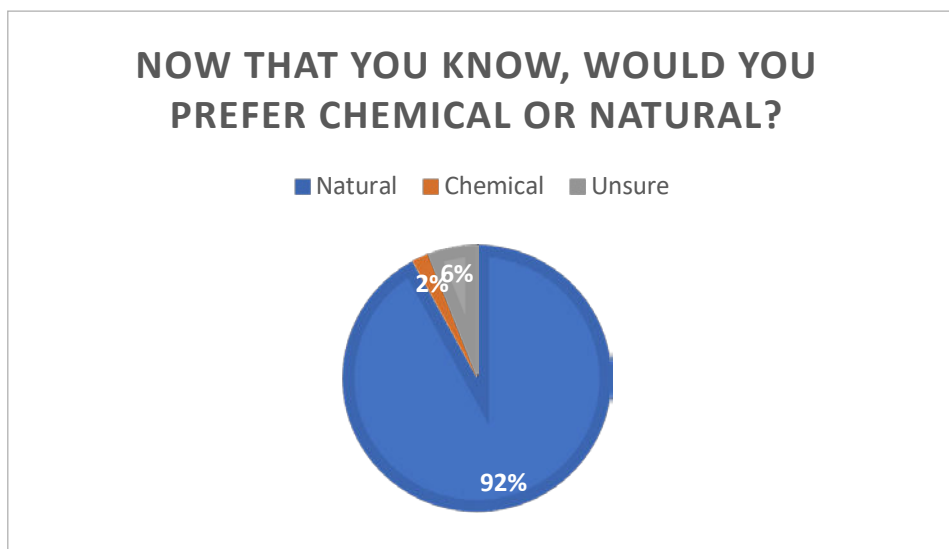
**Question 8 - What is the most important factor in determining which decaf coffee you purchase?**



**Question 9 - Are you aware that there are two basic processes to decaffeinate coffee, one using chemicals and the other natural (using water or air)?**

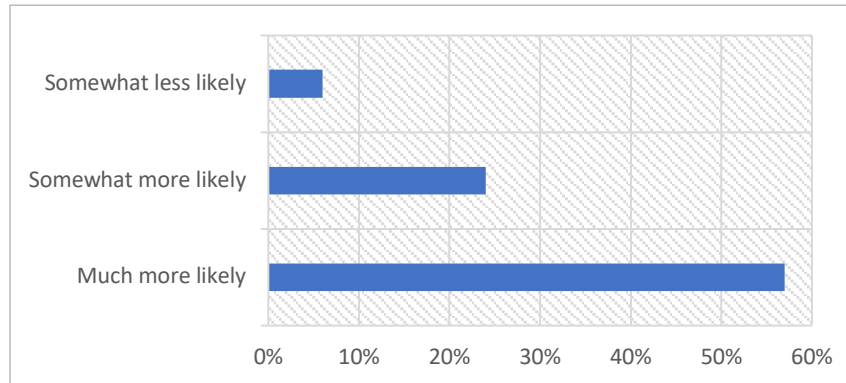


**Question 10 - Knowing there are two basic processes to decaffeinate coffee, would you prefer your coffee be decaffeinated by a chemical or natural decaffeination process?**

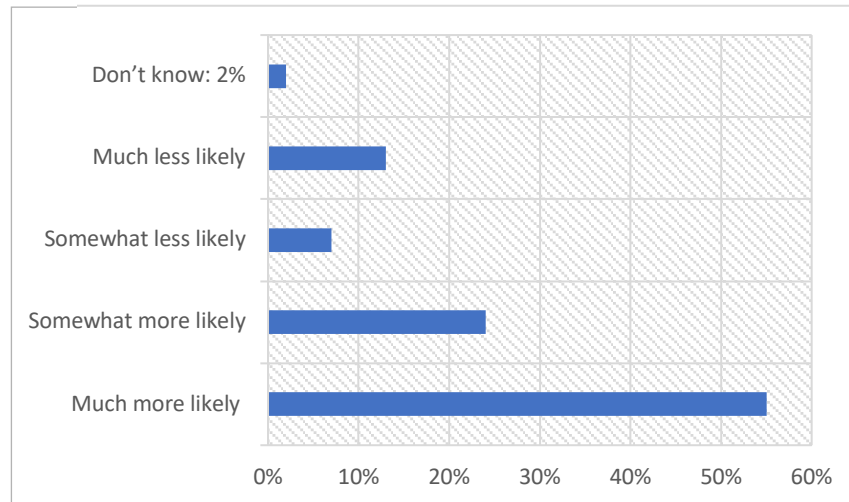




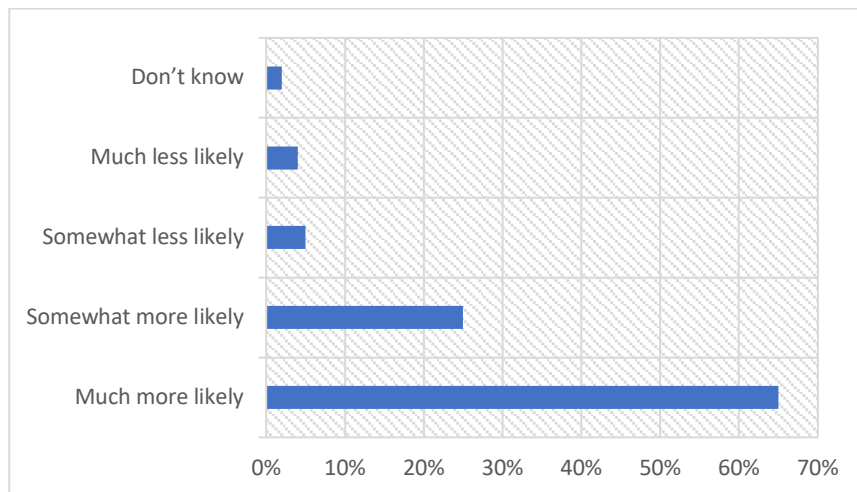
**Question 11 - If you knew that the most common chemical to decaffeinate coffee leaves trace elements of Methylene Chloride (which is an active ingredient in paint stripper and has been linked to cancer and reproductive harm) would you be more likely or less likely to only drink naturally decaffeinated coffee?**



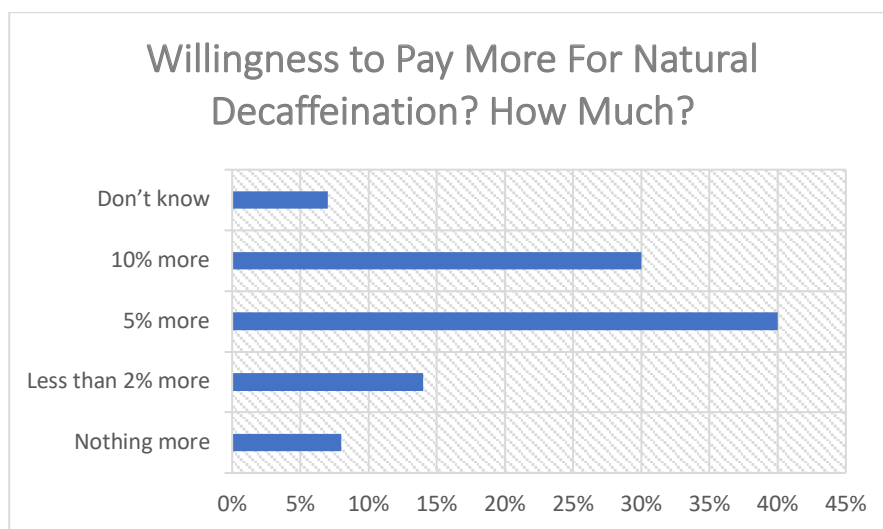
**Question 12 - If you knew that the chemical process that utilizes Methylene Chloride to decaffeinate your coffee can also impact workers and the local environment of the facility, would you be more likely or less likely to only drink naturally decaffeinated coffee?**



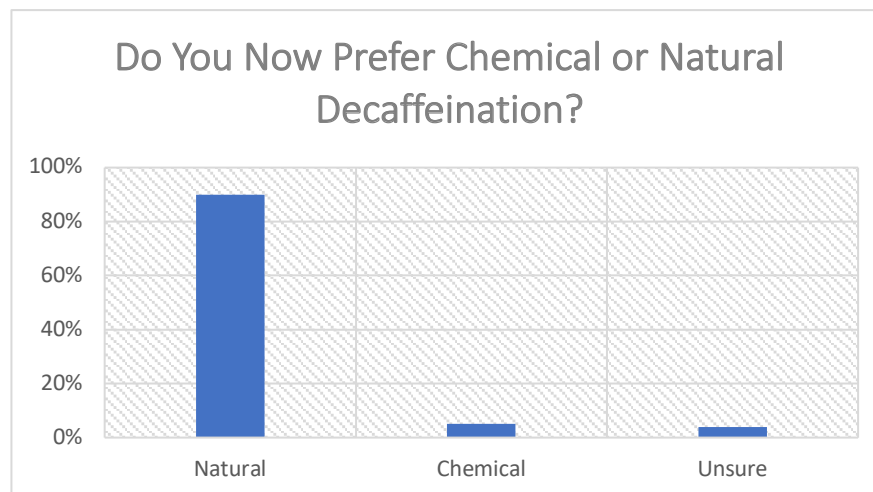
**Question 13 - If you knew common natural processes to decaffeinate your coffee uses water or air and avoided chemicals, would you be more likely or less likely to drink only naturally decaffeinated coffee?**



**Question 14 - Knowing that the natural decaffeinating process can be more expensive than the chemical process, how much more would you be willing to pay for naturally decaffeinated coffee?**



**Question 15 - Now that you know more about the different processes to decaffeinate coffee, do you prefer your decaf coffee be decaffeinated by a natural or by a chemical decaffeination process?**



**Question 16 - Do you agree or disagree that decaf coffee products should be labeled by the type of decaffeination process they use - a natural or chemical process?**

