

Investigation of Coffee Qualities through Electrostatic and Electrochemical Methods

by

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requirements for the degree of
Doctor of Philosophy
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DISSERTATION ABSTRACT

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Doctor of Philosophy in Chemistry

Title: Investigation of Coffee Qualities through Electrostatic and Electrochemical Methods

This thesis presents groundbreaking research on using electrochemical methods in conjunction with % Total Dissolved Solids (%TDS) as a marker for brewed coffee qualities. The study emphasizes the necessity of brewing reproducible coffee for accurate measurements. It highlights the impact of adding water to coffee beans before grinding, which reduces electrostatic charge and results in a more uniform particle size distribution, enhancing consistent extraction during brewing. The research further examines the relationship between roast degree, measured by Agtron value, and %TDS, utilizing cyclic voltammetry (CV) as a novel technique for analyzing brewed coffee. A strong correlation is found between the integrated area of the observed reduction wave and %TDS, linked to hydrogen underpotential deposition (HUPD) on a platinum electrode. It is also found that coffee matrix molecules adsorb to the electrode surface, block reaction sites, and suppress the HUPD signal with multiple CV cycles. The study further explores the effects of varying brew parameters (grind size, water temperature, water amount, bean amount, and brew time) on CV characteristics, demonstrating linear correlations between %TDS, HUPD reduction wave area, and peak height, with shifts in brew parameters impacting these metrics. Additional CV characteristics, peak center and peak full-width-half-maximum both of which are known to relate to solution composition, are observed to shift with brew parameters but do not correlate to

%TDS. The innovative use of CV for assessing coffee quality opens new avenues for electrochemistry techniques in food science, with potential applications in other acidic liquids such as wine and tea. Future research could leverage multifactor analysis for standard protocols in coffee scaling and flavor targeting, possibly incorporating electrochemical devices in brewing processes to allow consumers to adjust for individual flavor preferences. This dissertation includes previously published and unpublished co-authored material.

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CHAPTER I

INTRODUCTION

1.1 Making Measurements on Coffee

The coffee industry involves a complex supply chain that includes millions of smallholder farmers, international traders, roasters, and retailers. Global revenue for hot coffee drinks in 2023 alone totaled 445.5 billion USD.¹ The keystone of the coffee market is the consumers’ enjoyment of the end product – brewed coffee. Intense care is taken throughout the coffee bean’s life cycle to ensure the tastiest flavors reach the end brew. Many factors along the way influence the chemical composition which give rise to both desirable and undesirable flavors. To fully understand how these different chemical compositions affect the brew, we must have a way to measure the different chemicals present. The coffee industry relies on a measurement of total dissolved solids (%TDS), popularized as a quality metric by the Coffee Brewing Institute in the early 1960’s, to quickly determine if the brew is in the range that is considered “ideal” (see Figure 1^{2,3}). Despite the consumer enjoyment depending on the chemical composition of the brew, %TDS fails to capture these nuances that lead to different flavor profiles. Most coffee studies employ separation techniques to quantify the hundreds of compounds present with high fidelity. Others focus on only a few molecules that can be targeted by diluting the coffee far past what a consumer would classify as coffee. The work presented herein has been conducted on coffee under normal consumption conditions and is the first to relate compositional differences to the industry standard of %TDS.

There are many steps that impact flavor and composition of brewed coffee, starting with the bean species. The two main species of coffee that are cultivated and sold commercially are *Coffea arabica*, known as Arabica, and *Coffea canephora*,

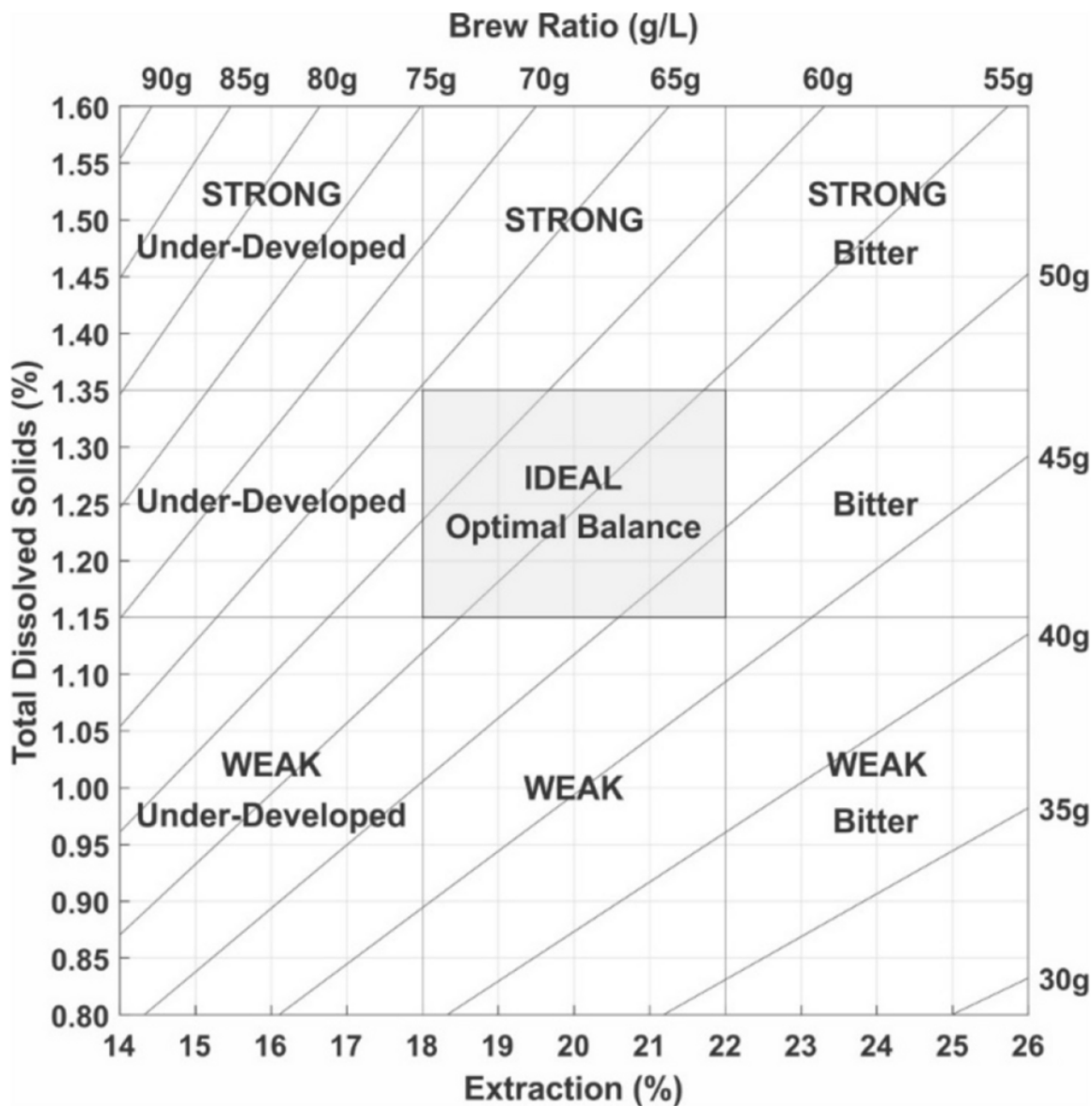


Figure 1. Coffee Brewing Control Chart originally designed by Lockhart in 1957. Reprinted with permission from *Sci Rep* **10**, 16450 (2020), doi.org/10.1038/s41598-020-73341-4.

known as Robusta⁴. Brazil has been the top coffee producing country since 1852 and specializes in Arabica varieties while most of the world's supply of Robusta coffee comes from Vietnam.⁵ The World Coffee Research website provides detailed profiles of 55 Arabica varieties and 47 Robusta varieties.^{6,7} Many of the varieties can be distinguished from one another based on physical characteristics such as plant size, bean size, optimal growing altitude, and susceptibility to diseases such as coffee leaf rust, coffee berry disease, and nematodes. Robusta varieties are generally more robust in terms of disease resistance and tolerance to differing climate conditions.^{8,9} However, Robusta coffee also has higher caffeine content in both green and roasted beans which contributes to the increased bitter flavor.¹⁰ In an attempt to combine the disease resistance of Robusta with the cup quality of Arabica, some producers graft Arabica plants into Robusta roots, though this information rarely reaches the consumer.

Due to its preferred flavor profile, the specialty coffee industry focuses almost exclusively on Arabica coffees. When the coffee plant cherries are ripe, they are harvested and processed (see Figure 2¹¹). This processing step is crucial in determining the end flavors that will reach the cup. Coffee beans considered “naturally” processed are laid out with the cherry mucilage still intact and allowed to ferment while drying, leading to distinct fruity flavors in the brewed coffee. Those that are “washed” have the cherry mucilage removed and are purposefully fermented without their natural fruit before drying. Washed coffees tend to taste strongly of chocolate, caramel, and tea. These are the flavors many American consumers expect to find in their morning brew. In the middle of washed and natural lies the “honey” process in which the cherries are pulped to remove the outer fruit skin, but some mucilage is allowed to remain coated on the beans during

fermentation. As one might expect, these coffees have more fruity flavors than washed coffees but are less fruit-forward than natural coffees. The processing step is in part controlled by the economy of the producing region. Washed coffees are more expensive in terms of energetic input and water usage.¹² As the specialty coffee industry has continued to expand, so too has innovation within the fermentation techniques which are applied to coffee. It is now common to find commercially available coffees that have undergone anaerobic fermentation, carbonic maceration, or co-fermentation in which a flavor addition, such as cinnamon sticks or coconut, has been incorporated into the fermentation step. All of these processing decisions impact the end flavor.

1.1.1 Separation Techniques Applied to Coffee Analysis.

A common chemistry technique for separating, identifying, and quantifying compounds from a complex mixture is chromatography. Chromatography is based on different components partitioning between a stationary phase and a mobile phase. The stationary phase is typically a column packed with fine particles, while the mobile phase is a liquid or gas that flows through the column.¹³ Chromatography alone is a separation technique and must be adequately coupled with a detector to be used as an identification technique. Common detectors used with liquid chromatography are mass spectrometry, UV-Vis, fluorescent, refractive index, or diode array detectors. Each of these detectors works by recognizing known properties of the compounds, such as their individual refractive indices or UV-Vis absorption wavelengths. In these cases, some prior knowledge about the compounds is useful so that the detector can be chosen with appropriate settings. Gas chromatography is often coupled with flame ionization or mass spectrometry detectors which ionize the compounds in predicted ways and are connected to large

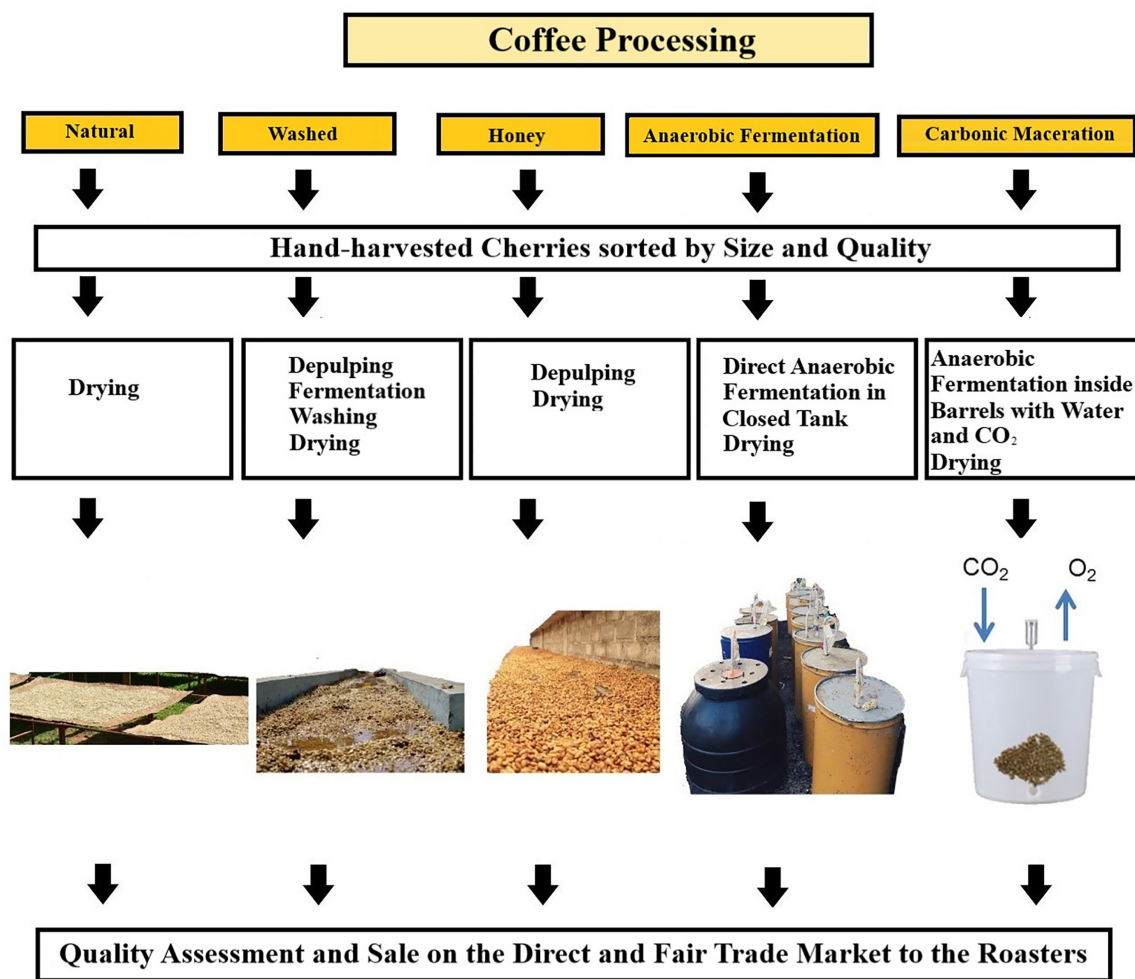


Figure 2. Flow chart of various specialty coffee processing methods. Reprinted with permission from *LWT* **172** (2022) 114245, doi.org/10.1016/j.lwt.2022.114245.

libraries of known compounds for identification.¹⁴ Gas chromatography is more often used for volatile compounds while liquid chromatography is best with soluble compounds.

Brewed coffee has its share of both soluble and volatile compounds, so it is unsurprising that both liquid and gas chromatography techniques have been used for its analysis. Traditional gas chromatography uses a liquid sample that is volatilized upon entry into the instrument. However, headspace gas chromatography coupled with mass spectrometry (headspace GCMS) is a variation that involves using gaseous sample. In Figure 3¹⁵, Jackels et al. used headspace GCMS to compare volatiles obtained from whole roasted bean samples. The whole beans were heated in a sealed container via a 60°C water bath for 60 minutes. After this equilibration time, gas was extracted from the sealed container (hence the name “headspace”) and underwent chromatographic separation. The two samples pictured show differences in the overall number of peaks present and especially in peak height of several of the labeled peaks. These two coffee samples, among others, were then brewed via cupping technique and tasted by professional coffee tasters. The top panel of Figure 3 shows a sample which was determined not to have a potato-taste defect while the bottom panel shows a sample that was found positive for potato-taste defect.¹⁵ Additional work has used GCMS for purposes such as determining metabolite composition of Indonesian coffees,¹⁶ aroma component comparison among coffee blends,¹⁷ and determination of polycyclic aromatic hydrocarbons present in coffee brew.¹⁸

Liquid chromatography is a natural choice for coffee analysis since most work is performed on brewed coffee. In fact, high-performance liquid chromatography (HPLC) systems have been used to analyze coffee samples for

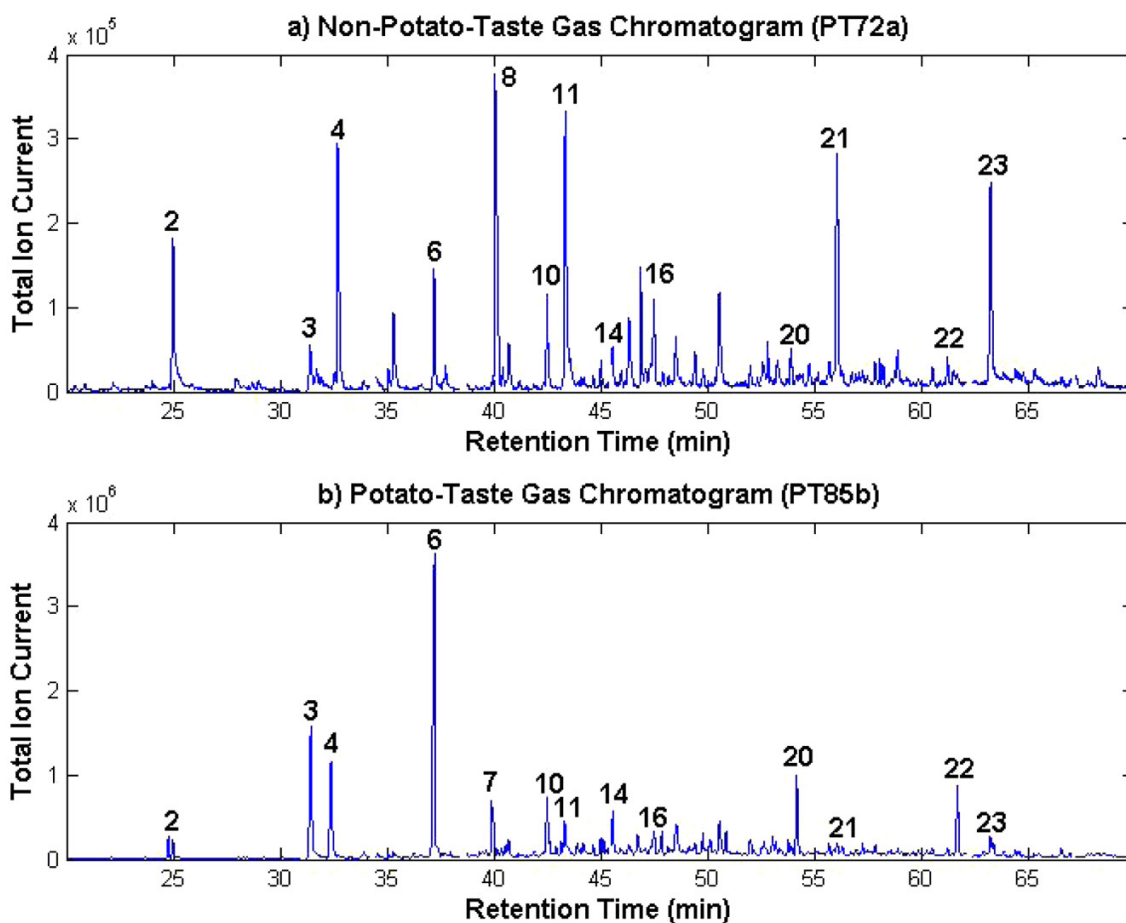


Figure 3. Headspace GCMS of volatile compounds from 70.0g of whole beans heated in 60°C water bath for 60 minutes. Comparison of two samples that were characterized as having or not having the potato-taste defect, common in Rwandan coffee, via cupping after GCMS data was collected. Reprinted with permission from *J. Agric. Food Chem.* 2014, 62, 42, 10222-10229. Copyright 2014 American Chemical Society.

such purposes as determining tocopherol and triglyceride content,¹⁹ chlorogenic acid content,²⁰ caffeine content,²¹ organic acid content,²² and bioactive compound content.²³ HPLC analysis of coffee samples is effective enough that Stathakis et al. proposed using it for an educational lab. The lab is reliable enough that HPLC alone is not the focus of the experience, but instead the authors encourage its use for teaching post-column derivatization and statistical analysis.²⁴ Figure 4²⁴ from Stathakis et al. and shows the HPLC chromatogram of two different commercially available coffee pods. The two samples are very similar in overall compounds present, as indicated by the largely overlapping peaks, but in different concentrations, as shown by the differing peak heights. HPLC, therefore, proves itself to be a highly sensitive technique which can inform on the minute differences from one brew to another. However, there is evidence that compounds within the complex matrix of brewed coffee interact with one another, such as the aggregate that forms between caffeine and chlorogenic acid,^{25,26} which are inherently missed in analysis performed involving separation techniques.

1.1.2 Electrochemistry Techniques for Coffee Analysis.

Electrochemistry is another approach used in the analysis of liquid brewed coffee but, unlike chromatography techniques, it does not involve compound separation. The field of electrochemistry studies chemical processes which involve the movement of electrons, particularly those transferring between the surface of an electrode (typically a metal) and a molecule present in the electrolyte solution.²⁷ These methods measure the electrical properties associated with oxidation, the loss of electrons, and reduction, the gain of electrons. For an electrochemical measurement to be viable, the system must allow for both the movement of electrons through the potentiostat (used to control the potential applied to the

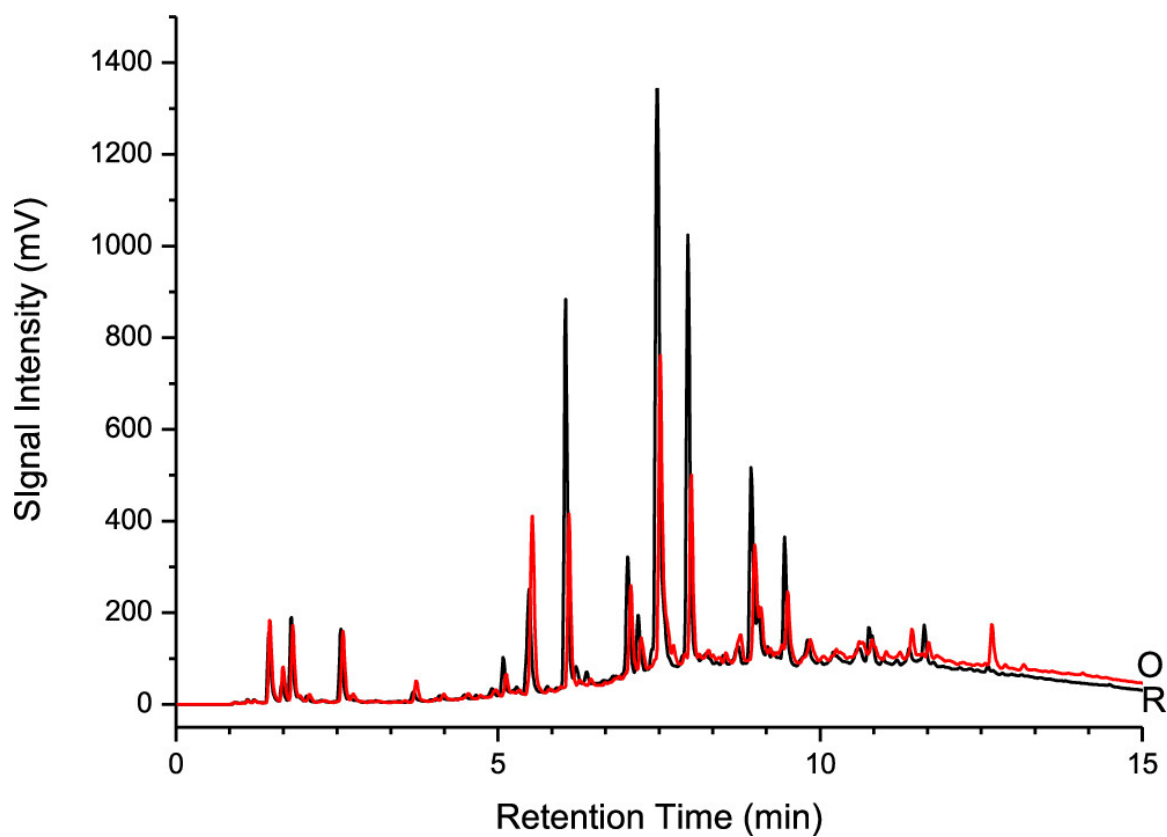


Figure 4. HPLC chromatogram performed on two samples of commercially available undiluted coffee brewed via coffee pods at a 1:6 ratio. (coffee pods 5g in, 30 mL out aka 1:6 ratio). Reprinted with permission from *J. Chem. Educ.* 2023, 100, 4, 1564–1570. Copyright 2023 American Chemical Society.

electrode surface) as well as the movement of charged species in the liquid sample. It is imperative that the liquid contains a supporting electrolyte to ensure that it is conductive and able to move charged species appropriately.²⁸ Resistance values observed in the coffee samples examined in the studies performed in chapters 3 and 4 of this work were between 500–2000 Ω , which was found to be sufficiently conductive for electrochemical measurements without an additional electrolyte. By analyzing the current response produced by the movement of electrons as the applied potential changes, one can determine the concentration of chemical species, gain insight into reaction mechanisms, and assess the composition of liquid samples.

Electrochemical techniques like square wave voltammetry (SWV) and differential pulse voltammetry (DPV) can provide highly sensitive and specific measurements of trace amounts of substances. SWV applies a series of potential pulses, via the potentiostat, in a staircase manner, with each pulse consisting of a forward and reverse potential step (see Figure 5²⁹). The current is measured at the end of each forward and reverse pulse, and the difference in current is plotted against the potential. Similarly, DPV superimposes a series of regular potential pulses on a linear potential sweep. The current is measured just before the pulse and at the end of the pulse, and the difference in current is plotted against the potential. It is through the application of these potential pulses that SWV and DPV techniques minimize background noise and achieve high sensitivity.²⁹ Figures 6³⁰ and 7³¹ show the application of SWV and DPV to green coffee extract by Šeruga and Tomac. In both publications, the green coffee extract was spiked with 10^{-5} M amounts of known isomers of chlorogenic acids and the resulting peak heights increased as expected. While these works highlight the use of both electrochemical techniques on specific compounds present in brewed coffee, no

proof that chlorogenic acid is the only compound contributing to these peaks is provided. SWV has also been used for the determination of caffeine³² and the presence of adulterants in coffee samples.³³ Along with determination of caffeine,³⁴ DPV has also been used to measure the total antioxidant capacity in coffee, juices, and wine.³⁵ SWV is commonly used in biological analysis for reversible or quasi-reversible reactions while DPV is better suited for irreversible reactions.^{29,36–38}

A common technique for examining the electrochemical reversibility of a redox active reaction is cyclic voltammetry (CV). CV involves sweeping the potential of the working electrode linearly back and forth between two set values at a given scan rate. The current is continuously measured and plotted against the potential, producing a cyclic voltammogram (see Figure 5). While less sensitive than SWV and DPV, CV provides detailed information on redox processes and reaction mechanisms, revealing both kinetic and thermodynamic information through careful interpretation of the voltammograms. Despite the broad applications of CV, it has been an underutilized technique for studying brewed coffee. Literature examples of its use for coffee include estimating phenolic content,³⁹ evidence of acrylamide contamination,⁴⁰ and preliminary electrode surface characterization followed by SWV for caffeine quantification.^{41,42}

These chromatographic and electrochemical techniques inform researchers about the compounds present in coffee samples, but they lack a connection to the consumers’ experience of brewed coffee. A typical cup of pour-over coffee is brewed with a ratio between 1:15 and 1:18, coffee to water. In the study performed by Kilmartin and Hsu, the coffee was extracted at a ratio of 1:100 by weight and then further diluted 50-fold into a phosphate buffer as the supporting electrolyte before CV analysis of phenolic content. Samples used for SWV and DPV by Šeruga and

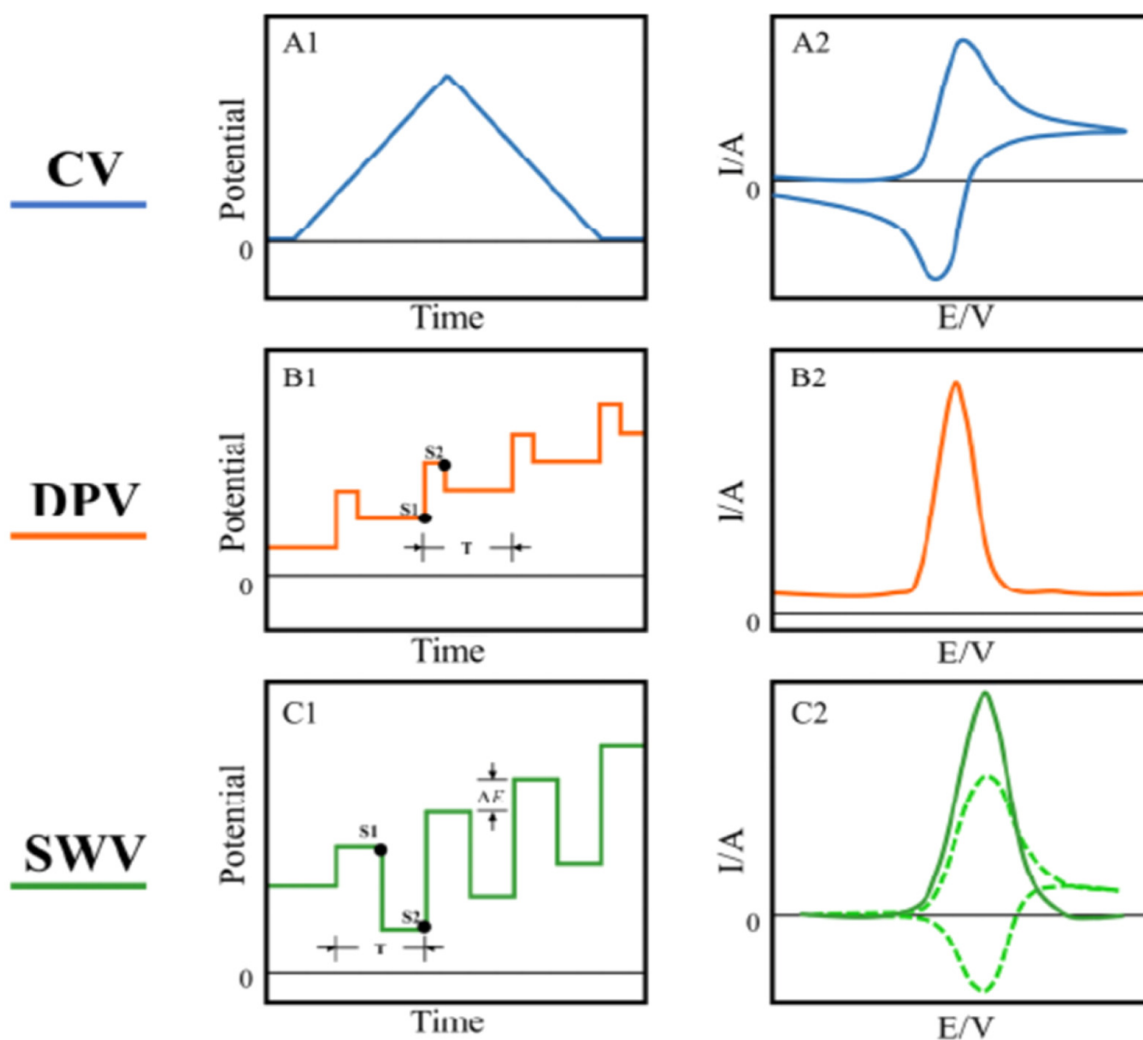


Figure 5. Visual description of applied potential versus time and associated current versus potential outputs for cyclic voltammetry (top, A), differential pulse voltammetry (middle, B), and square wave voltammetry (bottom, C). Reprinted with permission from *ECS Sensors Plus*, 2024 **3** 027001, doi.org/10.1149/2754-2726/ad3c4f, and Creative Commons <https://creativecommons.org/licenses/by-nc-nd/4.0/>

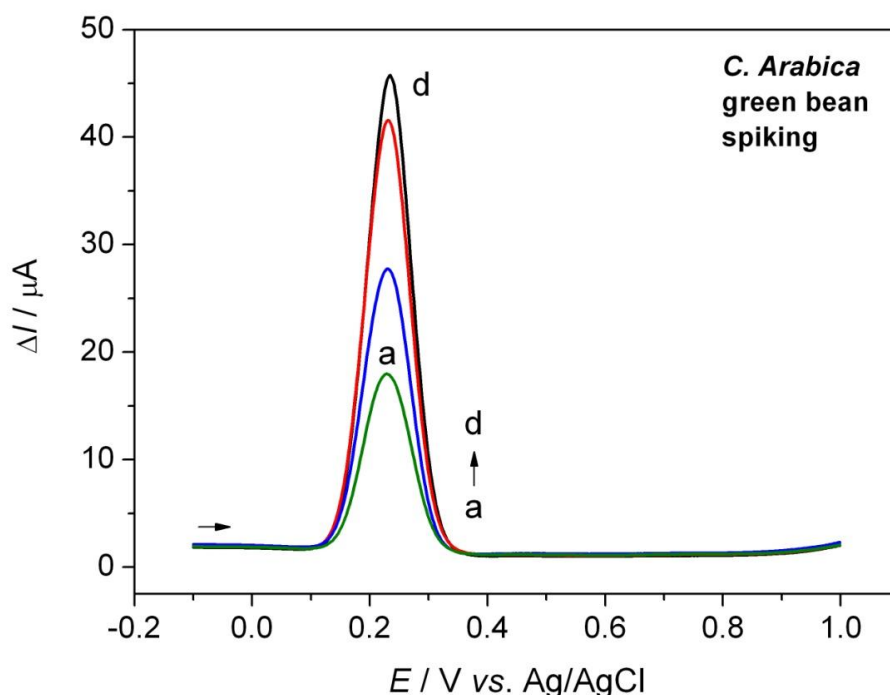


Figure 6. Square Wave Voltammetry of unroasted (aka green beans) coffee extracted at a 1:100 ratio and diluted 50-fold (green trace). Traces in blue, red, and black are each spiked with the same amount of a different chlorogenic acid isomer. Reprinted with permission from *Int. J. Electrochem. Sci.*, **9** (2014) 6134 – 6154, doi.org/10.1016/S1452-3981(23)10876-5, and Creative Commons <https://creativecommons.org/licenses/by-nc-nd/4.0/>.

Tomac in Figures 6 and 7 also used a 1:100 brew ratio with a 50-fold dilution.

Stathakis et al. samples had a brew volume more suitable for espresso coffee (30 mL) but used a 1:6 brew ratio as opposed to a more typical espresso ratio of 1:2.5.

Many researchers may choose to use more dilute brew ratios in part to ensure that data remains in the dynamic linear range for their instrumentation. While a comparison of brew ratios gives some insight into the apparent concentration or strength of the brew, the coffee industry standard is to use a refractometer to determine the %TDS. This measurement is notably lacking in the literature

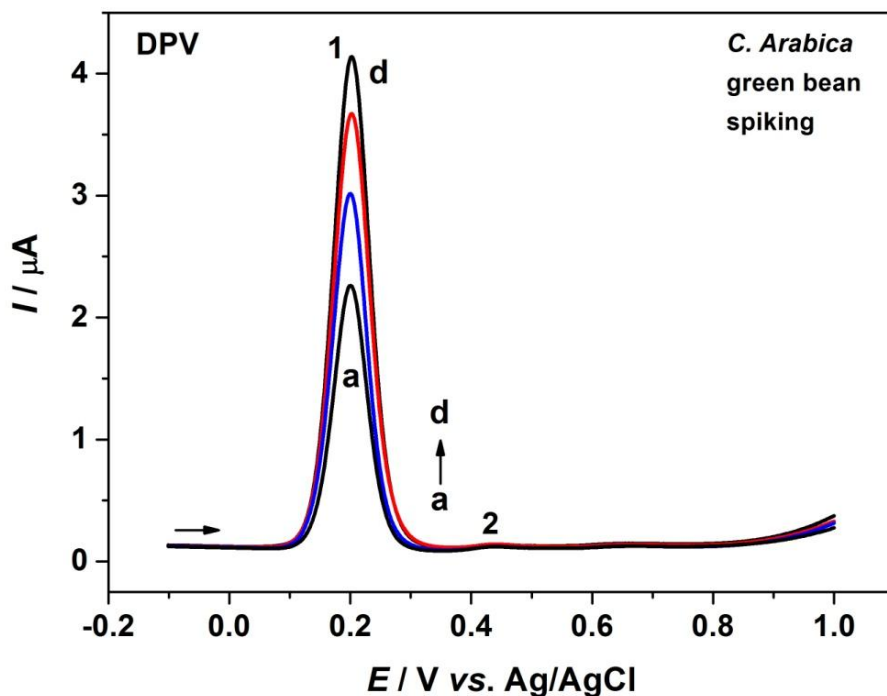


Figure 7. Differential Pulse Voltammetry of diluted green bean extract 1:100 ratio (opposed to 1:16.5 we use) (black trace, a). Traces b through d were each spiked with different chlorogenic acid isomers. Reprinted with permission from *Int. J. Electrochem. Sci.*, **11** (2016) 2854 - 2876, doi.org/10.1016/S1452-3981(23)16146-3, and Creative Commons <https://creativecommons.org/licenses/by-nc-nd/4.0/>.

on coffee studies. Even the plethora of coffee studies employing human sensory panels^{43–51} fail to include %TDS measurements.

To successfully analyze minute differences in brewed coffee composition, one must first ensure that reproducible samples can be prepared. This work begins with an examination of the electrostatics of coffee grinding and its impact on brewing. The following chapters detail work that is the first to report %TDS in conjunction with other chemical analysis, namely CV, on brewed coffee samples. It is also the first to use electrochemical analysis on as-brewed strength coffee, with no addition of a supporting electrolyte or dilution of the sample. Moreover, this

work demonstrates the use of multi-factor design of experiments to gain insight into brew factor interactions that cannot be captured through single factor experiments. These factor interactions are then leveraged for economical optimization of brew parameters and used to understand why a simple brewing scale-up does not result in the same composition and flavor profile.

1.2 Co-Authors and Publication Details

1.2.1 Chapter 2, Electrostatics of Coffee Grinding. The work presented in Chapter 2 of this dissertation has previously been published^{52,53} and is co-authored with Joshua Méndez Harper, Connor S. McDonald, Elias J. Rheingold, Lena C. Wehn, Elana J. Cope, Leif E. Lindberg, Justin Pham, Yong-Hyun Kim, Josef Dufek, and Christopher H. Hendon.

JMH acknowledges support from start-up funds at Portland State University. CHH acknowledges the support from the National Science Foundation under Grant No. 2237345 and support from the Camille and Henry Dreyfus Foundation. This work was supported by the Coffee Science Foundation, underwritten by Nuova Simonelli. The work was enabled by donations of green coffee from Farmers Union and Finca La Ilusión. We are grateful to Ikawa for providing the roaster, Pentair for providing the reverse osmosis water filtration system, and Tailored Coffee, Eugene, OR for the use of the EK43.

1.2.2 Chapter 3, Determining Roast Degree. The work presented in Chapter 3 of this dissertation will be published and is co-authored with Doran Pennington, Zachary S. Walbrun, Lena C. Wehn, Elias J. Rheingold, Joshua Williams, and Christopher H. Hendon.

CHH acknowledges the support from the National Science Foundation under Grant No. 2237345 and support from the Camille and Henry Dreyfus Foundation.

This work was supported by the Coffee Science Foundation, underwritten by Nuova Simonelli. We are grateful to Pentair for providing the reverse osmosis water filtration system, and Tailored Coffee, Eugene, OR for the use of the Ikawa Pro50 and for providing green coffee.

1.2.3 Chapter 4, Impact of Brewing Parameters. The work presented in Chapter 4 of this dissertation will be published and is co-authored with Benjamín Alemán and Christopher H. Hendon.

CHH acknowledges the support from the National Science Foundation under Grant No. 2237345 and support from the Camille and Henry Dreyfus Foundation. This work was supported by the Coffee Science Foundation, underwritten by Nuova Simonelli. We are grateful to Pentair for providing the reverse osmosis water filtration system.

CHAPTER II

ELECTROSTATICS OF COFFEE GRINDING

2.1 Moisture-controlled triboelectrification during coffee grinding

2.1.1 Author Contributions. The study was conceived by JMH, JP, REB, JD, and CHH. Coffee was roasted by LCW and JMH. Laser diffraction measurements were performed by EJH, CSM, REB, LEL, and JMH. Triboelectric measurements were performed by JMH, LEL, and REB. Espresso measurements were performed and interpreted by EJC and CHH. JMH and CHH wrote the manuscript and all authors contributed to the final version.

2.1.2 Experimental procedures. *Coffee roasting* was performed using an Ikawa Pro100. The roast profiles are available for download.⁵⁴ The *coffee color/roast degree* and *internal water content* of both commercially sourced and in-house roasted coffee were measured using The Dipper KN-201 and the Roastrite RM-800, respectively. The Roastrite compensates for variations in ambient temperature and humidity.

Coffee grinding was performed on a Mahlkönig EK 43 flat burr grinder using stock coffee burrs. The burrs were aligned using the Mahlkönig burr alignment tool. A grind setting of 0.0 was set to when the burrs were brought together to create a chirping sound. The axial, radial, and angular alignment was measured by applying a marker to the outermost edges of the burrs and then bringing the burrs to grind setting 0.0. The burrs were sufficiently aligned where all radial marker had been rubbed away, and there was homogeneity of the grind distribution from *laser diffraction particle size analysis*. Laser measurements were performed on a Malvern Mastersizer 2000 with the solid-particle feed system, Scirocco 2000. Vibration feed rate and air pressure were set to 60 % and 2 bar, respectively. The SOP parameters

were three measurements per aliquot, 2-second delay between measurements, an estimated refractive index and absorption of 1.59 and 0.1, respectively (similar to chocolate), measurement time of 10 seconds, 10,000 measurement snaps, background time of 5 seconds, and 5000 background snaps. Raw data for plots presented in **Figures 5** and **6** are available for download.⁵⁴ Twice ground coffee in **Figure 12** was obtained by first grinding at 2.0, then at 6.0. These settings were empirically determined by isolating when the particle size distribution was unchanged during the second grind (see Supplementary Information, **Figure S4** for further details). Grind settings less than 6.0 showed a minor increase in fines from random fracturing events of large particles. The raw triplicate data can be found in Ref.⁵⁴. *Photographic images* were collected using a Keyence VHZ-100UR microscope.

Charge-to-mass quantification was performed using a custom build Faraday cup, machined to fit the chute of the EK 43 grinder. The charge on particles entering the cup was then measured by a Keithley 614 electrometer operating in Coulomb mode with a range setting of ± 2 nC (see **Figure 8c**). The coffee collected in the Faraday cup was then weighed using a generic laboratory scale to obtain its mass. The mass and charge were then used to compute charge-to-mass ratio. The same Faraday cup setup was employed to measure the triboelectric response of whole coffee beans rolling down a coated vibrating ramp presented in **Figure 8a**.

Particle charge polarity measurements were performed using the electrostatic separator following a configuration presented in a previous study.⁵⁵ The system shown in **Figure 8c** consists of two sub-parallel 1 meter long electrodes with a potential difference of 16.4 kV. The electric field separates particles by charge

polarity, and particles are collected in negative, neutral, and positive bins at the base of the separator.

Water solutions used for fractoelectric charge reduction were constructed from reverse osmosis water from a Pentair Conserv 75E, and mineralized using sodium chloride obtained from Sigma Aldrich. A pipette was used to introduce water onto whole bean coffee, and the coffee was shaken in a sealed container to ensure homogeneous distribution. Samples were prepared in triplicate.

Whole bean coffee was stored in H₂O impermeable vacuum bags, and kept at -20°C. The coffee was allowed to equilibrate to room temperature in the vacuum bag before grinding. *Humidity measurements* were performed in a glove box, and the grinder was allowed to reach equilibrium with the atmospheric water. Coffee was not allowed to equilibrate, to isolate the role of internal versus external water. Otherwise, all experiments were conducted in air at 25±2°C, 20-45%RH, and 101±1 kPa.

Espresso was prepared using a Nuova Simonelli Black Eagle prepared at 7 bar of static water pressure, with 94°C water, and a fixed brew ratio of 18 g of coffee to produce 45.0 g of espresso. The grounds were tamped using PUQpress Q1, set to apply 196 N, and a normcore 58.5 mm diffusing screen was added to the top of the compacted bed. Flow rate data was computed from the gravimetric change measured at the scale.

2.1.3 Progress and Potential. Coffee grinding produces large quantities of static charge due to both fracturing and rubbing. Charge causes particle aggregation and discharge, a familiar problem in industrial coffee production. This study demonstrates that the magnitude of charge depends on the roast profile, and more importantly, the internal moisture content of whole

bean coffee. In an effort to control the charge, we demonstrate that the addition of external water mitigates its accumulation during grinding and promotes particle declumping. Notable differences in brew parameters are achieved. Implementation of our findings directly addresses a key issue of static accumulation and particle clumping, and highlights the challenges of making physical property predictions based on bean color.

2.1.4 Introduction. Triboelectrification is the physical process where materials acquire surface charge from frictional interactions at their interfaces.⁵⁶ The magnitude of charge depends on the interfacial material composition⁵⁷ and can be harnessed in emergent technologies for energy generation.^{58–62} The mechanism of electrostatic accumulation is complex, and is further obscured in granular materials where collisions are sufficiently energetic to cause fracturing. In this "fractoelectric" regime, crack initiation and propagation is thought to charge particles through transfer of electrons and/or ions at the hot crack interface.^{63,64} Whether a material's charging is dominated by tribo- or fractoelectrification, fracture-generated granular flows often comprise of particles whose surface charge density may exceed the theoretical maximum value of $27 \mu\text{C m}^{-2}$ ^{65–68}, or charge-to-mass ratios in the range of 0.1 to 100 nC g⁻¹.^{69,70} There remains fundamental interest in studying the mechanism and magnitude of charging, and methods to control the process, in particular to mitigate spurious effects such as electrostatic discharges and agglomeration within industrial settings.^{71–75}

The electrification of chemically complex materials (*e.g.* foodstuffs, wood)⁷⁶ present unique and complex problems in materials science. While most food is not subject to fracturing resulting in appreciable electrical charge formation, coffee is a paragon of material complexity, as all coffee is ground, and the chemical

composition of whole-bean coffee depends on numerous factors (*e.g.* roast, origin).^{77–79} The effects are particularly emphasized in espresso preparation, where the coffee must be ground fine, imparting large amounts of static charge. Here, we use coffee to provide fundamental insights into the electrification processes in organic materials composed of a variety of molecules. We demonstrate that i) conventional coffee parameters – roast, internal water content, grind setting – dictate the charging of roasted coffee and offer an explanation why; ii) both triboelectric and fractoelectric processes occur during grinding, with the majority of charging coming from fracturing events, and iii) charging depends on the coffee bean’s internal and external water content, with higher water content suppressing charge accumulation. For industrial-scale operations, uncontrolled coffee charging can cause clumping, leading to product heterogeneities and clogged conduits. At the brewing level, aggregation may also affect liquid-solid accessibility,⁸⁰ leading to inhomogeneous extraction, and unpredictably unpleasant espresso.⁸¹ In the context of both understanding the fundamentals of triboelectrification, and bolstering our efforts towards brewing more reproducible and sustainable coffee, this paper offers strategies to control the charging of coffee particles and posits opportunities therefrom.

2.1.5 Electrifying Coffee. We first sourced numerous commercially roasted coffees, canvassing many major producing countries and coffee processing paradigms. These coffees are further categorized by their processing method – natural (N), washed (W), decaffeinated (D) – and are all single origin unless designated as a blend (B). Full details of the commercial coffees are presented in **Table S1**. The color of roasted coffee can be quantified using a spectrophotometric method that places coffee on the "Agtron Gourment Scale".⁸² The scale ranges

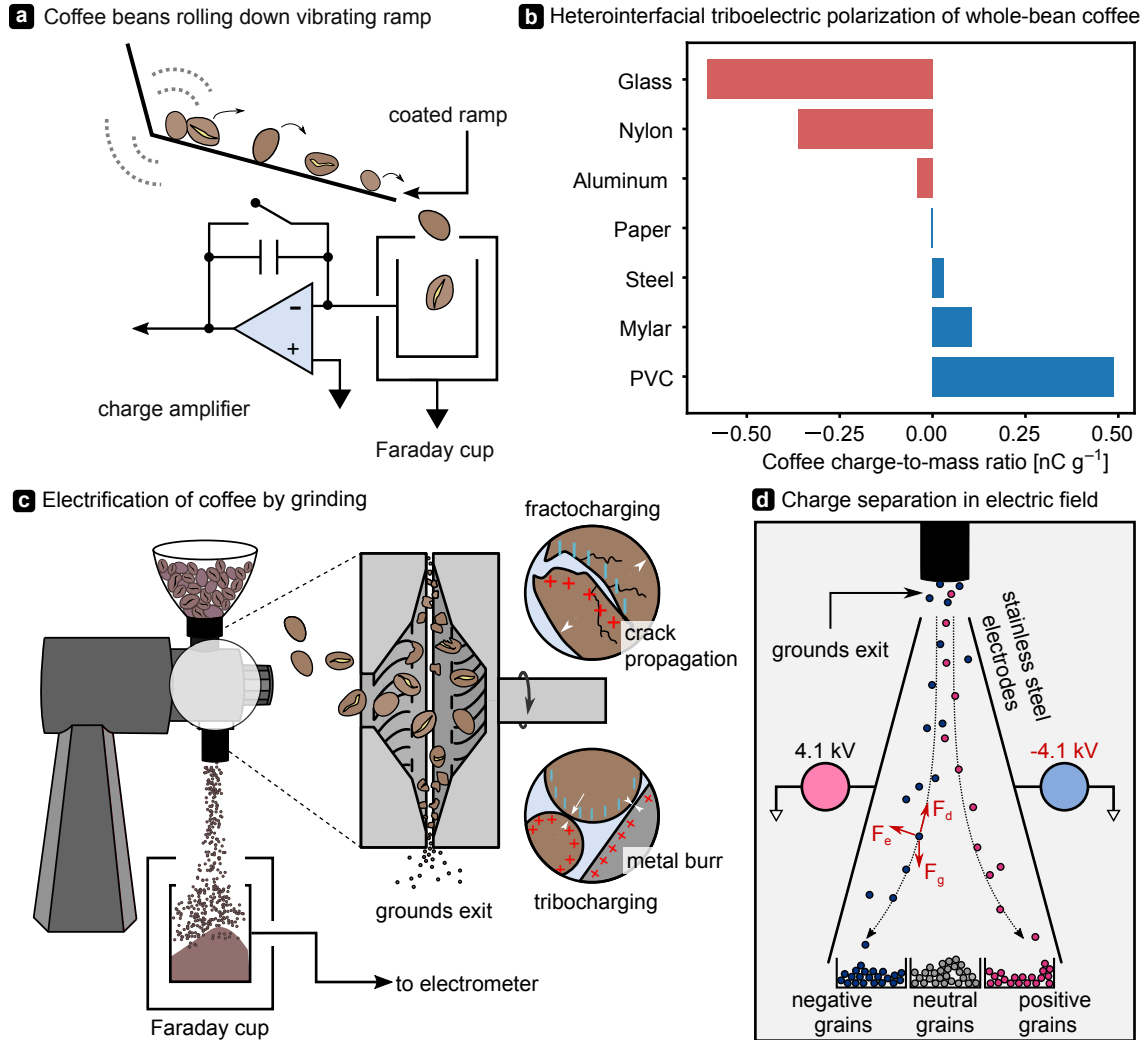


Figure 8. Electrification of coffee beans and particles. **a)** Whole coffee beans accumulate charge when rolled down a vibrating ramp coated in a variety of materials. **b)** These surfaces materials can be arranged according to their capacity to charge whole beans. Here, Starbucks Blonde Espresso Roast weakly charges against steel, while glass and nylon result in positive charging, and plastics like PVC and Mylar lead to negative charging. **c)** During fracture, coffee particles accumulate charges from the burr-coffee interface and coffee-coffee rubbing (tribocharging), as well as fracture points (fractocharging). **d)** After grinding, the charge is quantified by allowing the particles to fall between two sub-parallel electrodes with a potential difference of 8.2 kV. The electric field separates particles by charge polarity, and particles are collected in negative, neutral, and positive bins at the base of the separator.

from 0 (black/carbonized) to 150 (green/unroasted), with most specialty coffees falling within the range of 40-90 as measured on our spectrophotometer. Examples are presented in **Figure 9**.

To assess surface charging of whole beans, we first selected Starbucks Blonde Espresso Roast (a dark roast coffee: Agtron 65.2, water content 1.3%) and rolled it down a vibrating ramp coated in various materials. At the end of the ramp, beans were collected in a Faraday cup where the charge and weight are recorded, **Figure 8a**. Coffee generally charges poorly against metallic surfaces but may acquire relatively large charge when contacting dielectrics. To assess the charging of coffee against other materials, we created a series of heterointerfaces between whole bean coffee and other common materials found in coffee grinding environments. From **Figure 8b**, it is found that coffee charges positively against plastics such as polyvinyl chloride (PVC) and biaxially-oriented polyethylene terephthalate (Mylar, a material widely used in coffee grinder technologies), but acquires negative charge when rubbed against glass and nylon, **Figure 8b**. Coffee gains almost no charge against office paper. These data indicate that coffee is similar to wood, cellulose, and grain in the triboelectric series.⁵⁷

Coffee beans must be ground — a process that results in significant electrification. The process typically produces particles with sizes ranging from 100 nm to 2 mm. The distribution is controlled by grind setting and bean temperature.⁸³ In flat-burr grinder architectures such as the configuration housed within the Mahlkönig EK 43 (a grinder with steel 98 mm burrs, **Figure 8c**), the grind setting is determined by the separation between rotating metal plates. Finer grind settings result in more fracturing events, longer coffee-burr contact time, the production of more fines (sub 100 μm particulates), and smaller boulders (post 100

μm particulates). While grinding can lead to minute spark discharges, especially if the grinder is not grounded, the primary consequence of electrification is the formation of particle aggregates held together by electrostatic forces.

The net charge acquired by a coffee sample is measured by placing a Faraday cup under the grinder chute, **Figure 8c**. An electrometer then reports a voltage proportional to the particle charge, with a sensitivity of 10 nC V^{-1} . Although we used 1 g (5-10 beans) of coffee across all experiments, the amount of ground coffee that enters the Faraday cup varies between experiments (some material is retained in the space between the burrs). To account for this variation, we normalized the measured charge by the mass collected in the cup, allowing us to calculate a cumulative charge-to-mass (Q/m) ratio (*i.e.* the total charge of the coffee in the cup). Furthermore, we performed a different experiment to separate the positive, negative, and neutral particles. By replacing the Faraday cup with an electrostatic separator consisting of two sub-parallel plates held at a potential difference of $\sim 8.2 \text{ kV}$ and grinding 10 g of coffee, the negatively-charged grains drift towards the positive plate, the positive grains towards the negative plate, and net neutral particles fall straight down, **Figure 8d**. Imaging and laser diffraction particle size analysis can then be used to determine whether polarity impacts size distributions, in addition to determining a Q/m for each bin.

2.1.6 General trends in electrification of grinding commercially roasted coffee. Using this experimental setup, we first examined three Mexican coffees, **Figure 9a**. Those samples showed net positive, net negative, and both positive and negative charging. But those coffees were roasted by different roasters, to different colors and the data suggests, perhaps unsurprisingly, that origin alone does not dictate the polarity of charge. **Figure 9b** summarizes the charging

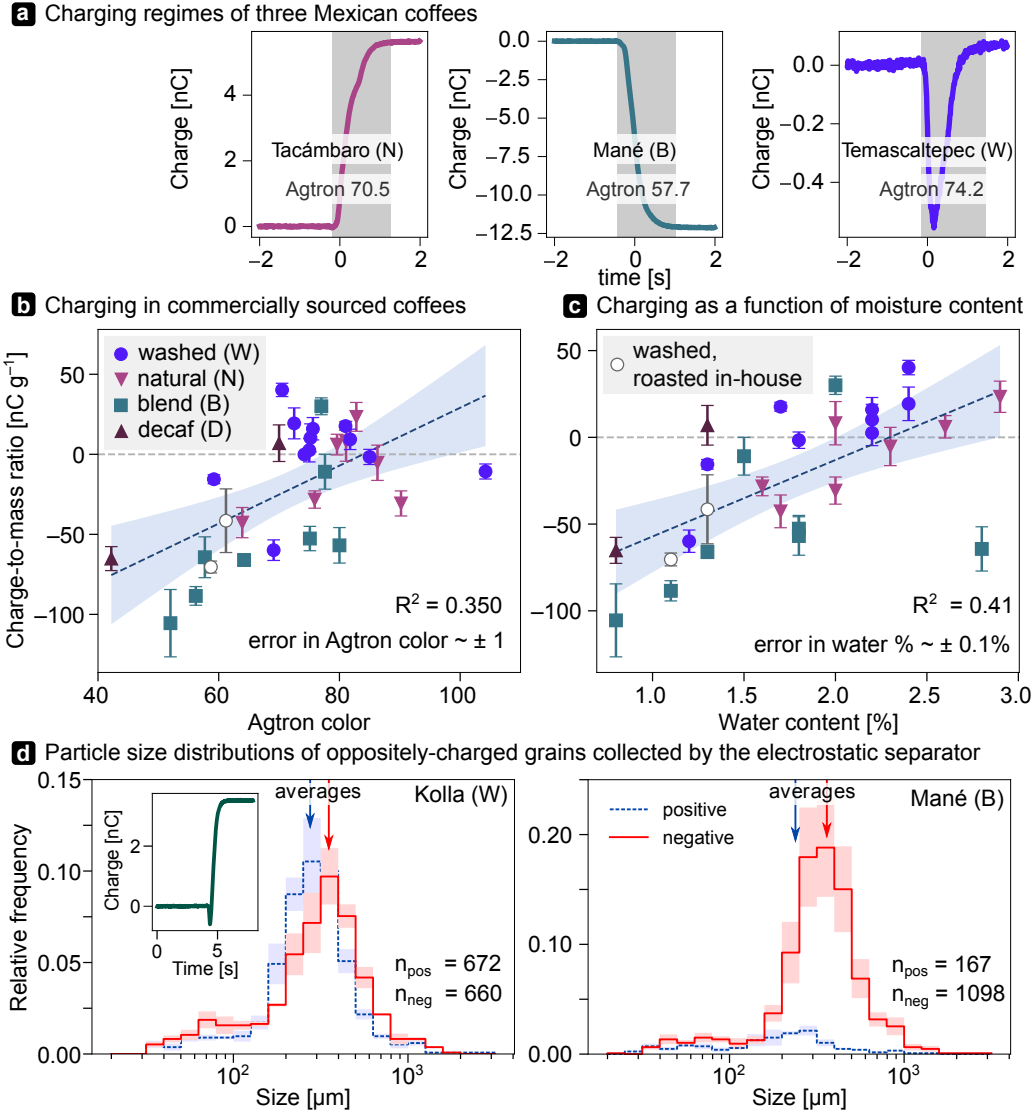


Figure 9. Charging regimes of commercially sourced coffees **a)** Three Mexican coffees – Tacámbaro (N), Mané (B), and Temascaltepec (W), show three possible charging regimes. **b)** Charge-to-mass ratio as a function Agtron color for a variety of coffees ground at setting 2.0. There is no strong relationship between charge magnitude and polarity, and coffee processing method. Confidence bands are plotted at 90%). A polarity switch is observed for darker coffees (Agtron = ≤ 70). The magnitude of negative charge continues to increase with darkness. **c)** Internal moisture - a property proportional to roast color - results in more positive charging. Moisture content is a slightly better predictor of charge-to-mass ratio than color. **d)** Examination of the particles collected for two representative coffees, Kolla (W, a positive charging, coffee) and Mané (a negative charging coffee), reveals that positively charged particles are generally smaller than the boulders, as denoted by the average arrows in blue.

behavior of ~ 30 coffees as a function of Agtron color. Although we observed both positive and negative charging, the charge-to-mass ratio magnitudes of positive samples are generally smaller ($< 50 \text{ nC g}^{-1}$) than that of negative coffees (up to 120 nC g^{-1}). We observed a weak relationship between roast color and charging, with positive charging occurring only at Agtron values exceeding 70. Post-roast internal moisture content showed a slightly better relation to the sign and magnitude of charge, **Figure 9c**. Here, the transition from negative to positive charging occurs when the water content increases above $\sim 2 \%$ by mass. The substantial scatter in **Figure 9b** and **c** likely reflect the fact that there are infinite ways to roast to an arbitrary Agtron color and resultant chemical composition. For example, one could obtain a dark coffee by roasting at low temperature for prolonged time, or roasting hot and fast. Additionally, the internal water content of pre-roast green coffee varies with time, and depends on storage environment.⁸⁴ Both variables have significant impact on roast chemical composition,⁸⁵ and are also known to affect the resultant beverage properties.⁸⁶

However, the relationship between water content in roasted coffee and charging transition from negative to positive is somewhat surprising, given other reports of decreasing charge-to-mass ratios with increasing moisture.⁸⁷ One possibility is that the polarity flip reflects degrees of strain at fracture.⁸⁸ In that work, lower degrees of strain were associated with negative charging. Since dark coffee is more brittle, they may support less strain before failure than their more ductile, light roast counterparts.⁸⁹ Another possibility is that the water is affecting the physical properties of the coffee, which we will discuss later in the paper.

Beyond performing net charge-to-mass measurements, we also separated particles by polarity and then sized them photographically. An example particle

size distribution of positive and negative coffees is presented in **Figure 9d**. These data suggest that the boulders carry negative charge independent of roast, process, and origin. High-speed videography reveals that these boulders exit the grinder first, explaining why we occasionally observe negative charge entering the Faraday cup at the onset of grinding, even if the net charge is ultimately positive (see inset in **Figure 9d** and the third panel in **Figure 9a**). Fine particles ($<100\ \mu\text{m}$) tend to be biased slightly toward negative charging, or have comparable positive and negative abundances. The distribution of charge on mid-size particles is more complicated. We observed a peak in the abundance of positively-charged particles at diameters of $100\text{-}300\ \mu\text{m}$, regardless of net charge polarity. For light roasts, the abundance of particles in this size range exceeds that of negative grains. For coffees with lower Agtron values, the positive maximum is still present, but the quantity of negatively-charged particles outnumbers positive particles at all sizes. In other words, the polarity of the particles in this intermediate range appears to dictate the overall polarity of a coffee’s net charge-to-mass ratio. This size range also corresponds to the sizes of particles typically produced for espresso format brewing, adding to the ever-increasing challenge of brewing reproducible espresso.⁸¹

Regardless of relative abundances, positive particles generally have smaller mean diameters than negative ones across all coffees (noted in **Figure 9d** by the average arrows). This size-dependent bipolar-charging provides insight into the basic electrification mechanisms operating during grinding. The observation that the larger particles charge negatively is consistent with the charge separation described by James and coworkers⁶⁵ in the context of volcanic pumice fracture. Although an equal number of positive and negative surfaces are likely created during any given fracture event, those authors hypothesize that subsequent ion

scavenging processes lead to particles of different sizes concentrating opposite polarity charges. This bias – larger, negative particles and smaller, positive particles – is opposite to that often reported in purely triboelectric systems (*i.e.* processes with little to no fracture).⁵⁵ In those contexts, charge segregation has been attributed to the exchange of trapped electrons, polarization,⁹⁰ and hydrated ions.⁹¹ For now, we can summarize that dark roast coffees appear to charge more negatively than light roasts, large particles carry negative charge, and that commercially roasted coffees charge in an a seemingly unpredictable way.

2.1.7 Isolating the impact of roast profile. The data presented in **Figure 9** points to a general challenge in the coffee industry: the words "light," "medium," and "dark" describe the end color and to some extent provide a touch point for flavor profile.⁹² But roast color does not yield sufficient information about the chemical composition and resultant tribocharging. The large amount of scatter in the data likely reflects the compounded effects of origin and processing⁹³ in addition to the temperature profile used to take it from green to brown.^{94,95} Many commercial coffee roasters treat their roast profiles as proprietary, and it is impossible to back-calculate the precise profile from examination of only the roasted whole beans. There is academic value in standardizing roast profiles across the industry, thereby allowing for direct comparisons between coffees. But we are not advocating for this on the industrial scale, as that would sterilize an artisanal aspect of the industry. Instead, we developed our own profiles with the aim of isolating roast through the development of systematically "darker" coffees.

Noting that pre-roast internal moisture content is known to dictate roast induced swelling and other properties,⁹⁶ we sourced coffees with moisture content representative of conventional specialty coffees. We obtained a green Ethiopian

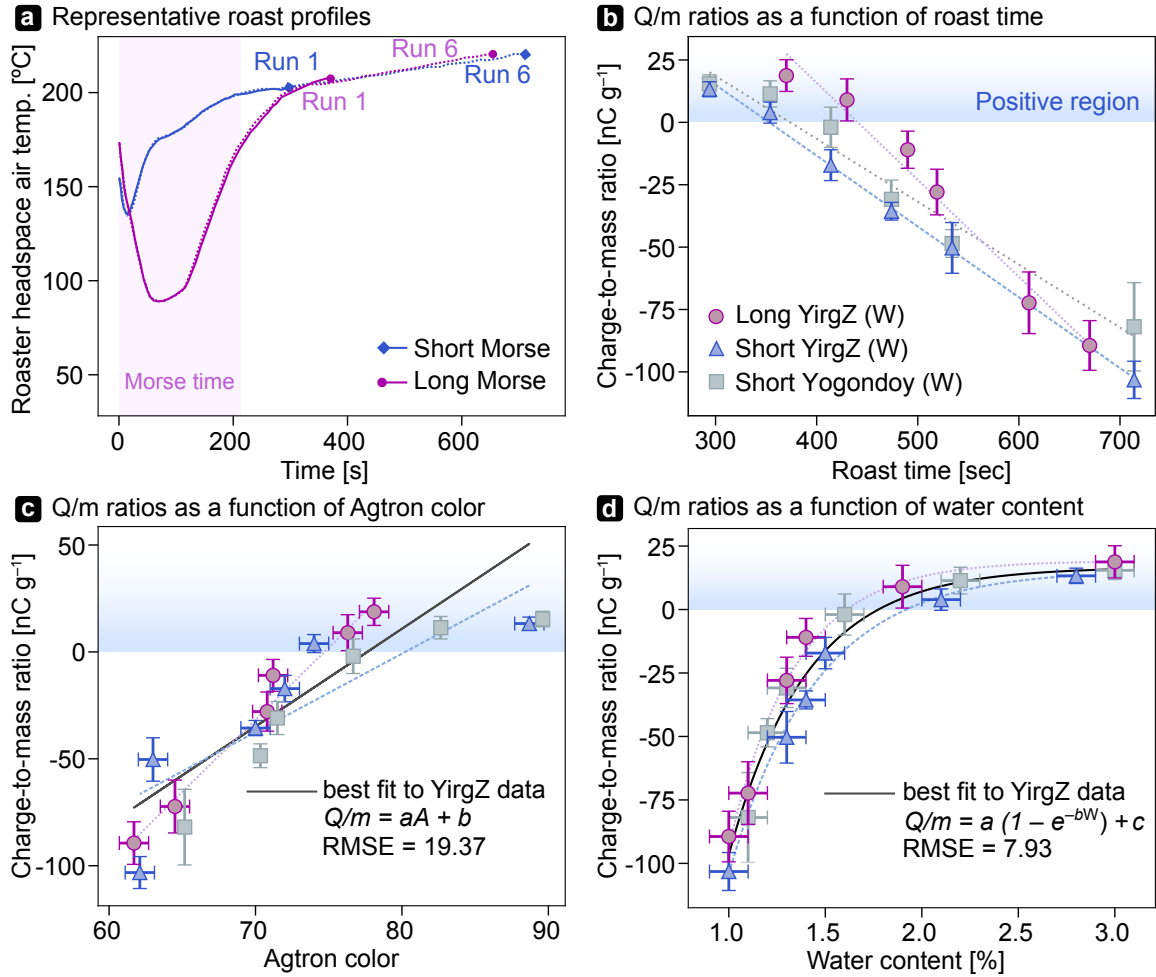


Figure 10. The effect of roast profile on charging **a)** Two sets of roast profiles were explored: Short Morse (blue) and Long Morse (purple). **b)** Charge-to-mass ratios as a function of roast time for a representative Ethiopian coffee (YirgZ) shows that charging increases with darker roasts. Prolonged Morse transitions to the negative charging regime at a slower rate than the shorter Morse. An additional Mexican coffee (Yogondoy) was roasted using the short Morse profile, yielding a similar electrification behavior to the Ethiopian coffee. **c)** Charge-to-mass ratios for Ethiopian and Mexican coffees as functions of Agtron color. **d)** Charge-to-mass ratios for Ethiopian and Mexican coffees as functions of residual water content.

coffee from the Yirgacheffe region, "YirgZ", featuring 12% internal moisture at the time of roasting. This coffee was roasted using an Ikawa Pro100 to achieve five different roasts by systematically increasing the terminal headspace air temperature and time by 2 °C and 60 s, respectively (**Figure 10a** in blue). A sixth coffee was generated by adding 8 °C and 180 seconds to the fifth profile. Additionally, a second roast profile was employed, differing by a parameter we call the "Morse time" (the empirical time taken for the headspace thermocouple to read a temperature equal to the initial temperature in an Ikawa roaster). The long Morse profiles were constructed in increments of 3 °C and 60 s, **Figure 10a**, purple. **Figure 10a** shows the profiles for the shortest (solid) and longest (dotted) roasts. In summary, 12 dissimilar roasts were achieved; their details are presented in **Table S2**.

After degassing for 24 h, the coffees were ground at a setting of 2.0. **Figure 10b** shows the charge-to-mass ratio of the YirgZ as a function of roast time for the two profiles. In both cases, the resultant charging is positive for short roasts (*i.e.*, lighter coffees) with a transition to negative charging as the roast time increases. However, we observe an earlier transition to negative charging for the short Morse roast. To test whether these behaviors are specific to the YirgZ, we repeated the short roast experiment with a washed Mexican coffee, Yogondoy (9% internal moisture at time of roasting). The result of this ancillary experiment is presented in **Figure 10b** (grey squares). Within error, the charge-to-mass ratios of the Ethiopian and Mexican coffees roasted using the same roast profile are comparable. Such congruence hints that the product of the roast, more than the characteristics of the green coffee, ultimately determines the charging behavior of coffee when ground.

We can further test the hypothesis that roast is a primary control on charging by casting our data in terms of roast color and residual water content, **Figure 10c** and **10d**, respectively. In agreement with the data presented in **Figure 9**, we observed weak linear relationship between color and electrification, with a transition from positive to negative charging at Agtron colors in the vicinity of 70-80. Lightly roasted coffee also retained more internal moisture than the darker roasted analogues, **Figure 10d**. In line with our findings in **Figure 9c**, we observe an abrupt transition to negative charging at water contents $<2\%$. Notably, the internal moisture content appears to be an very good predictor for charging (RMSE = 7.93 for charge versus moisture content, compared to RMSE = 19.37 for charge versus Agtron). Also, dehydration follows an exponential relationship between moisture and charge, in line with the dehydration profile of bananas,⁹⁷ seeds,⁹⁸ and other foodstuffs. Together, these data suggest that internal water content is a primary factor in the electrification behavior of roasted coffee.

2.1.8 Grind setting-dependent charging. Finer grind settings necessitate more fractures for the coffee to exit the grind chamber. Additionally, kinetic theory predicts that finer particle flows have higher granular temperatures (provided that particles have significant inertia to overcome fluid modification of granular temperature⁹⁹), with individual grains undergoing large numbers of collisions.¹⁰⁰ Thus, grinding finer should generate more charging through both fracto- and triboelectrification, regardless of polarity. To probe this hypothesis, we performed the same experiments presented in **Figure 9**, but at varied the grind setting. Two examples are displayed in **Figure 11a**, revealing that coarser settings yield lower charge, independent of whether the coffee is positive charging (Amatepec, W) or negative charging (Kicking Horse, D).

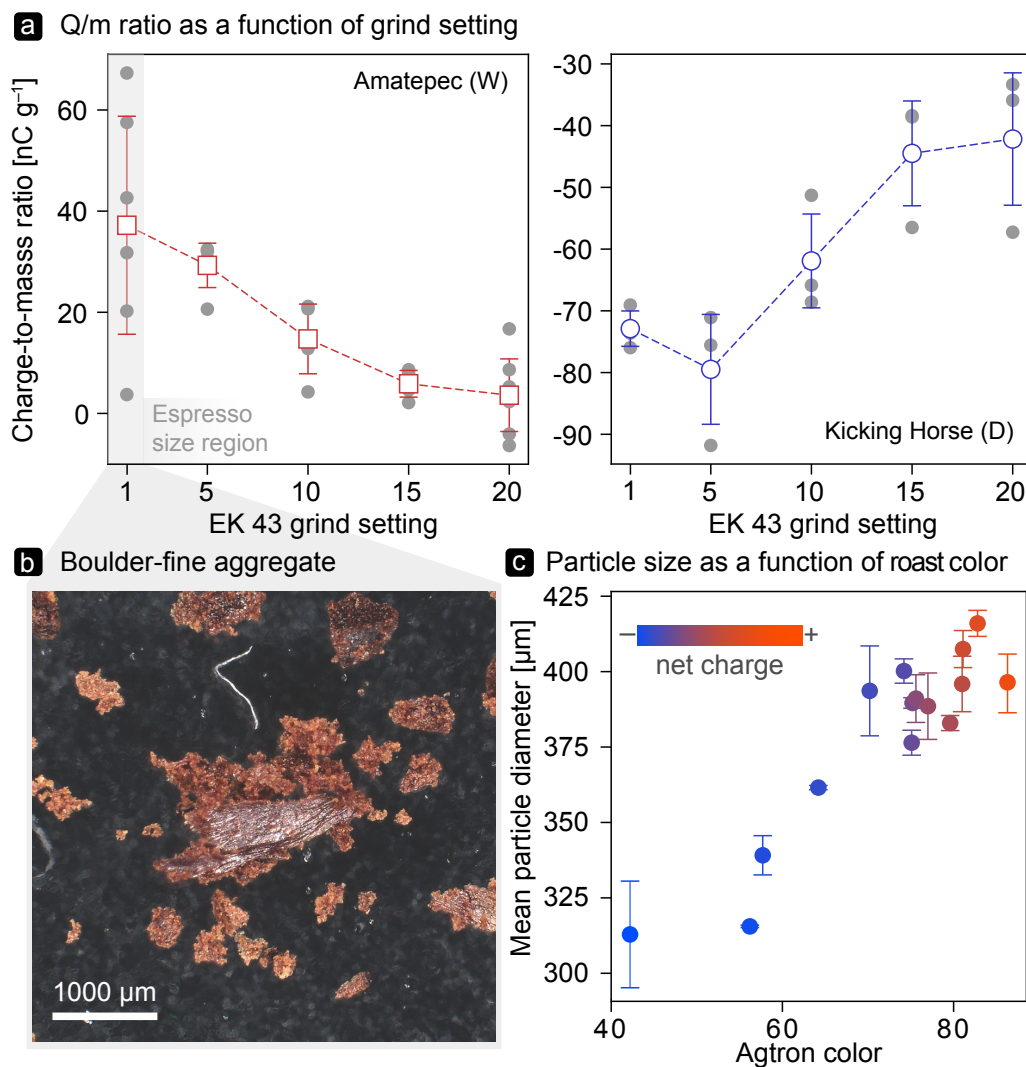


Figure 11. Charging as a function of grind setting and roast a) Charge-to-mass ratios of two representative coffees ground at settings spanning espresso (fine) to French press (coarse). In general, grinding finer increases charging, and at settings around 1.0 (the espresso region), positively charging coffees a large spread due to the formation of **b)** aggregates as the coffee exists the grind chamber. For negatively charging coffees, grinding at 1.0 yields a slightly more positive average charge, with relatively small spread. We attribute this to the higher charging resulting in the very rapid formation of aggregates. **c)** At a constant grind setting, dark coffees have approximately 100 μm finer mean particle size than light coffees.

The general trend is that the Q/m magnitude increases as coffee is ground finer. Yet some unexpected behavior is observed at the finest grind settings. For instance, Amatepec shows a large spread in the charge-to-mass ratio values and microscopic examination reveals that the variance is attributed to the formation of aggregates, *i.e.*, particles sticking to each other and other grinder surfaces, **Figure 11b**. The effect is exemplified in the Kicking Horse samples, where the finer particles have even higher surface charge and result in a minor reduction in observed electrification at the finest grind setting. We attribute this reduction to expeditious formation of the aggregates, analogous to those shown in **Figure 11b**. Additionally, our measurements reveal that dark roast coffees do produce much finer particles when ground at the same setting, **Figure 11c**. The darkest coffee in our dataset exhibits a $-100\mu\text{m}$ shift in particle size relative to the lightest coffee. These data build upon a previous study that showed that four light roast coffees produced similar particle sizes⁸³ because they were similar in roast color. **Figure 11c** offers one explanation as to why darker coffees may yield slower espresso shots for the same brew parameters. It may not only be the increased volatile content⁹⁴, but also the reduced bed permeability.

Since finer grinding generates more charge, a direct relationship between roast and charge must include an empirical correction for the difference in particle sizes shown in **Figure 11c**. To do this, we can manually change the grind setting and monitor the particle size data until the dark and light roast coffees produce the same size distribution. In practice, this meant grinding dark roasts at a slightly coarser setting, 2.3, to achieve the same particle size distribution as our lightest coffee ground at 2.0. **Figure S2** reveals that variations in particle size alone cannot account for the trends we observed in **Figure 9**. That is, dark roast

coffees accumulate more negative surface charge during grinding than their lighter relatives, independent of the size differences.

2.1.9 How granular mechanics influence electrification. With the impact of roast and grind isolated (where dark roasts and fine grinding yields the most charge), we next sought to investigate the impact of granular mechanics on electrification during coffee grinding. Much effort has been devoted to ascertain the roles of fragmentation and triboelectric charging in granular flows,^{55,101,102} and some authors invoke a common physio-chemical origin for charging,^{103,104}. Although this matter remains unsettled, it seems as though flows that do include material fracture behave differently from those that do not. For example, Lim and colleagues showed that pre-ground coffee particulates accumulated approximately -2 to -5 nC g⁻¹ by simply rubbing upon a stainless steel mixing auger and against themselves.¹⁰⁵ In contrast, coffees ground in our experiments gained absolute Q/m ratios exceeding 100 nC g⁻¹. This lays the foundation for the hypothesis that fragmentation processes are, to a large degree, responsible for electrostatic charging in coffee.

To isolate the impact of fracturing, we allowed ground coffee to pass through the grinder a second time at a coarser setting, preventing additional comminution. Without additional fracturing events, most charge should arise from coffee-coffee and coffee-burr interactions. The inset in **Figure 12** shows the particle size distribution before and after the coffee traversed the grinder a second time, first at setting 2.0 and second at a much larger burr aperture (setting 6.0). The latter setting was selected because it was empirically shown to not alter the particle size distribution upon re-grinding (see **Figure S4** for further details). The minimal differences between the particle distributions indicates that pre-ground coffee

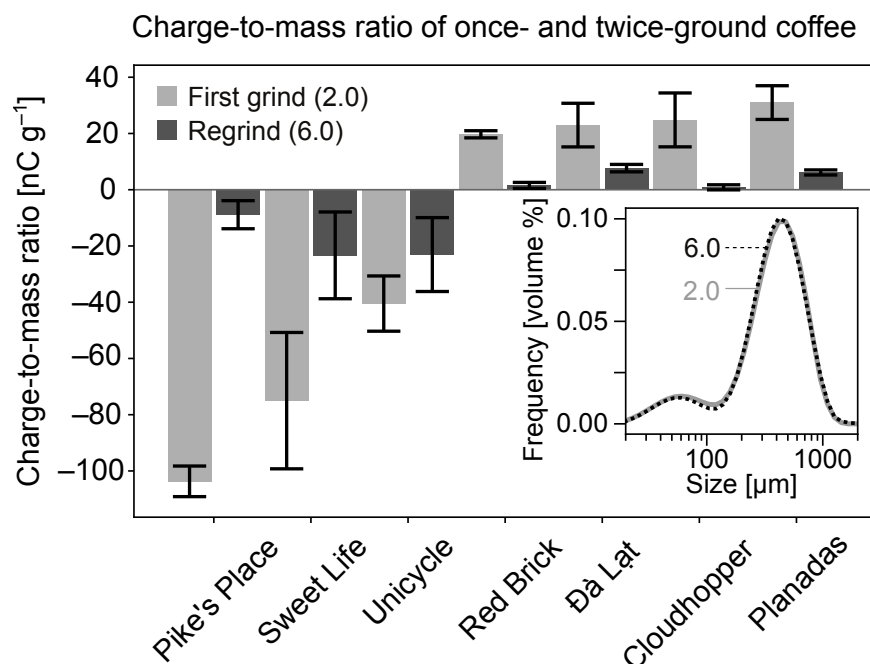


Figure 12. Twice-grinding coffee to assess the role of fracture in electrification. The first grinding of whole bean coffee at setting 2.0 results in charging from both triboelectric and fractoelectric processes, with a corresponding particle size distribution presented inset in grey. Regrinding the same particles at setting 6.0 results in a reduction in surface charge, with essentially no change in volumetric particle size distribution. First grinding is presented in grey, and second grinding in black.

particles are sufficiently small to exit the grind chamber without further fracture, but still accumulating some charge. To assess the generality of this observation, we performed these experiments on seven coffees, **Figure 12**. Twice-ground coffees (black) acquired significantly less charge than their primary ground counterparts (grey). Indeed, we observe a reduction of charge by up to 90%, with most pre-ground coffees acquiring Q/m ratios in the range of 5-10 nC g⁻¹. Such values are comparable to the findings made by Lim and others¹⁰⁵ during the fluidization of powdered coffee. While we cannot isolate coffee-coffee and coffee-burr rubbing interactions, this experiment points to a general observation that reduced fracturing greatly reduces charging.

2.1.10 Grinding with supplemental external water and its impact on brewing. Recalling the progression towards zero/positive charging with increasing internal moisture, **Figure 10d**, we next sought to understand the impact of adding external moisture. This process - known in the coffee industry as the "Ross Droplet Technique" - was posited to have been originally presented in an online message board.¹⁰⁶⁻¹⁰⁸ Anecdotally, baristas have observed that the incorporation of small amounts of liquid water onto the whole-bean coffee prior to grinding results in seemingly reduced charging. In our hands it also resulted in near-zero grounds being retained by the grinder, an observation that has implications for reducing waste and increasing quality of beverages. Perhaps we will revisit this in a future study, but for now we are more interested in whether the addition of water neutralizes the effects of fracto- and triboelectrification or modulates particle aggregation via capillary forces. Indeed, while abundant water does seem to preclude charge buildup¹⁰⁹, recent work suggests that small amounts of free water during granular electrification can produce unexpected behaviors. For

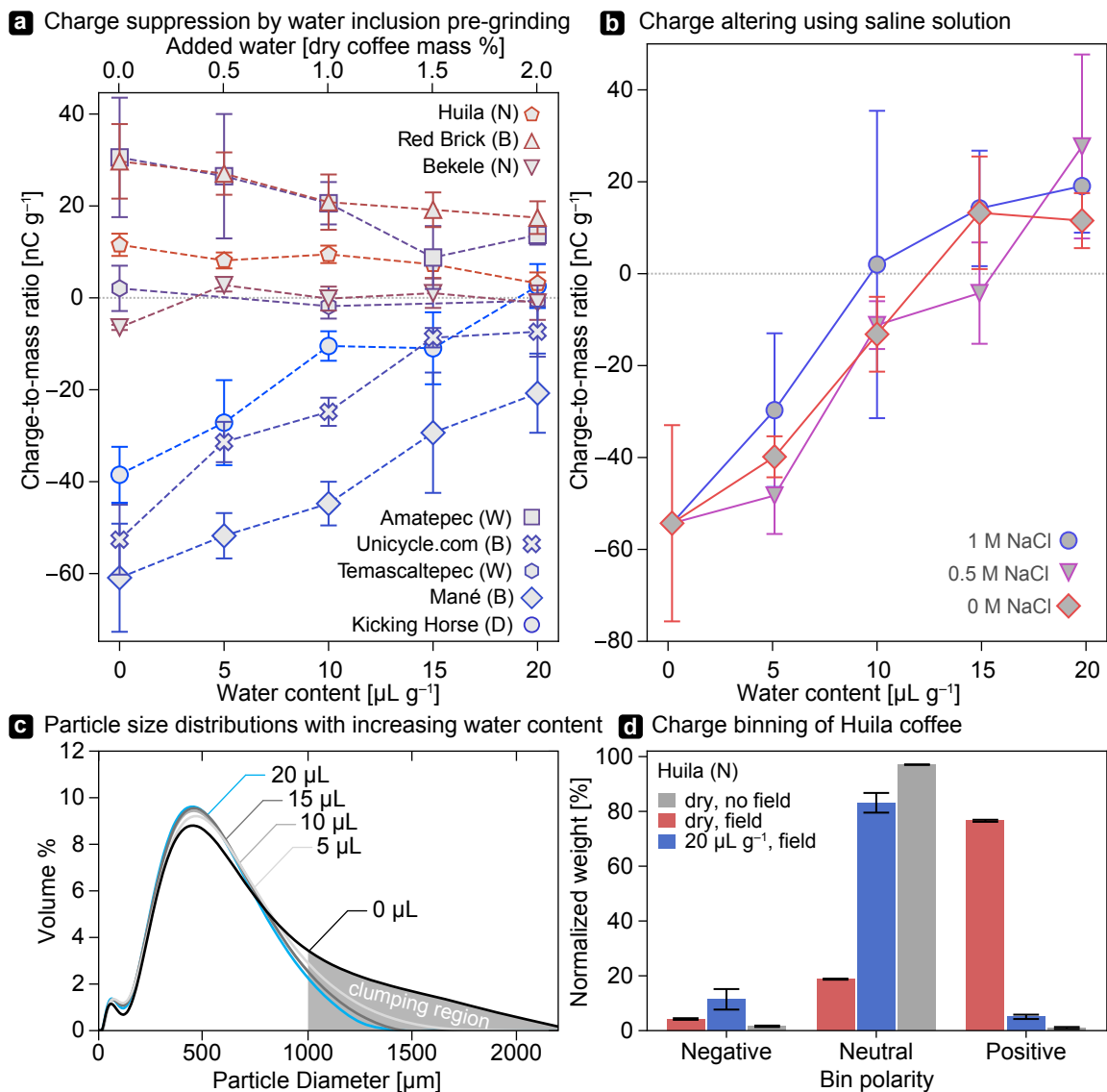


Figure 13. External moisture controls surface charging and causes particle deaggregation **a)** Charge-to-mass ratios for several coffees that span positive, neutral, and negative charging, with increasing amounts of water introduced to the whole beans prior to grinding. The red-to-blue coloring is indicative of the roast color, where blue are darker roasts. The upper x-axis provides an estimate for the effective change in total moisture content contained within, and coated on the surface, of the whole beans. **b)** The inclusion of minerals in the water solution has no effect on the magnitude of charge suppression achieved by the water itself. **c)** The inclusion of water during grinding causes deaggregation of fines from boulders. **d)** The redistribution of particle polarity upon the addition of 20 $\mu\text{L g}^{-1}$ water added to the whole beans.

instance, Grosjean and Waitukaitis¹¹⁰ showed that water can change the charging behavior randomly and irreversibly. Hu and colleagues found that the open-circuit voltage of a triboelectric nanogenerator increases with relative humidity up until values of 50%.¹¹¹ We also performed humidity experiments, **Figure S4**, and found that humidity only affected charging above approximately 60 %RH, in line with Ref.¹¹¹.

To assess the the impact of water addition, we systematically introduced water to whole bean coffee and ground at setting 2.0. Charge-to-mass ratios as a function of added water are presented in **Figure 13a**. All commercially sourced coffees of varying darkness, moisture content, and origin/processing methods (see Supplementary **Table S1**) show a systematic reduction in charging with increasing external water content. As water content approaches $20\mu\text{L g}^{-1}$, the charging approaches towards 0 nC g^{-1} . We performed further experiments to isolate the impact of ambient humidity, and found while humidity can begin to reduce charging above 60 %RH (see **Figure S4**), all of our measurements were performed between 25-45 %RH, and were largely unaffected by atmospheric water. This result is somewhat surprising, given the majority of charging comes from fractoelectrifying events, and the water is only introduced to the surface of the whole beans near instantaneously prior to grinding (preventing uptake and homogeneous wetting of the insides of the coffee). Here, water may be acting to reduce interfacial temperatures during fracturing (the coffee does exit the chamber cooler in the presence of water, see **Figure S5**), or perhaps it is facilitating some other physical process, *e.g.* enabling rapid solvated ion transfer.

Since both tribo- and fractocharging may originate from electronic ionization, nuclear ion transfer, or a combination of the two,¹¹² we further

developed an experiment to suppress ion transfer through the inclusion of ions directly into the wetting solution. If ion transfer is an operative mechanism, the inclusion of salt water should produce markedly reduced charging, dissimilar to that of pure water. **Figure 13b** reveals that the inclusion of NaCl, at either 0.5 M or 1.0 M, shows the same fractoelectric charge reduction as that of pure water. These data lead us to conclude that ionic electrification is likely not the mechanism of charging in coffee, but rather electron transfer.

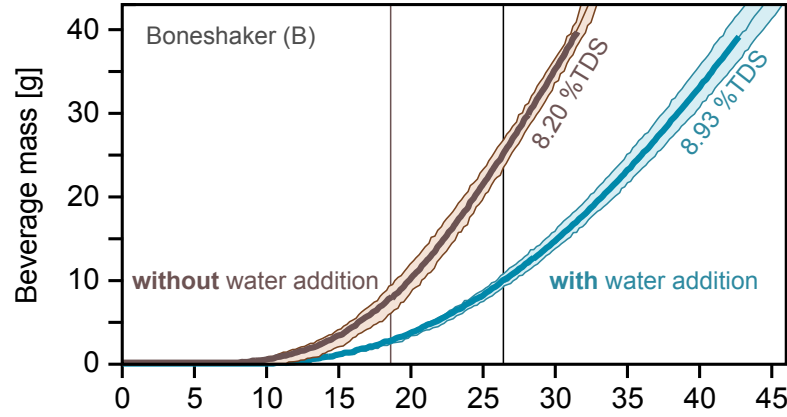
To deduce whether the coffee particles were forming neutral aggregates we examined both the laser diffraction particle size distributions as well as the electrostatic binning, **Figure 13c** and **d**. From the particle size distribution it is clear that the inclusion of even small quantities of water (as low as 5 $\mu\text{L g}^{-1}$) results in an immediate reduction in electrostatic aggregates of boulders and fines (the clumping region in **Figure 13c**). From **Figure 13d**, the data reveals that a positive charging coffee transitions from to neutral with a corresponding slight increase in negative particle formation. Taken together, we surmise that water directly passivates the fractoelectric and triboelectric charge formation in coffee, and causes particle deaggregation. Thus, the water addition approach does appear to achieve two key goals in coffee grinding by reducing both positive and negative electronic charging, and reducing clumping, and should result in notable differences in flow dynamics when brewing.

The impact of the water addition during grinding was demonstrated by brewing some espresso. There, all espresso parameters were kept constant (18.0 g of dry mass coffee was used to produce 45.0 g of liquid coffee extract, ground at setting 1.0, tamped at 196 N, and brewed using 94 °C water, kept at 7 bar of static water pressure with a 2 second pre-infusion), and shot time and flow rate were

hence dependent on the particle size and permeability of the espresso bed. From the data presented in **Figure 14**, several physical differences are noted. First, the shot time is nearly 50% longer for coffee produced using the addition of water. We understand this to be due to increased bed density, since the fines and boulders are not electrostatically attracted to one and other, the average particle size is smaller. Second, despite this, the first drops of coffee make their way to the cup at approximately the same time (10 seconds). At the end of the shot, the espresso prepared without water added to the whole beans produces a cup concentration of 8.2 % total dissolved solids (%TDS) while the addition of water yields a cup with 8.9 %TDS. Perhaps the increase in concentration could simply be attributed to elongated contact time, but as we highlighted in an earlier paper⁸¹, shots with the same degree of extraction, but different time parameters should have markedly different flavors.

Finally, we also examined flow rate throughout the shot. Since the coffee bed simultaneously swells while also being eroded from, we hypothesized that the process should be described by a sigmoidal/logistic function where the flow rate will approach a constant as the espresso bed approaches a constant resistance (before the bed is either destroyed or channels are created). By fitting sigmoids to an average of three espresso shots for the wet and unwet samples, we can calculate that the rate in which the bed progresses to equilibrium flow. For the dry-ground samples, the rate is nearly $2\times$ greater than the wet-ground analogues. This, paired with the midpoint of the sigmoidal fits, *i.e.* the time taken to reach the inflection point in flow rate, reveals that shots prepared without the addition of water during grinding are reaching equilibrium flow rates around the same time it takes the shot prepared with the addition of water to reach their inflection point. In other words,

a Beverage mass and total dissolved solids as a function of time



b Flow rate through an espresso puck as a function of time

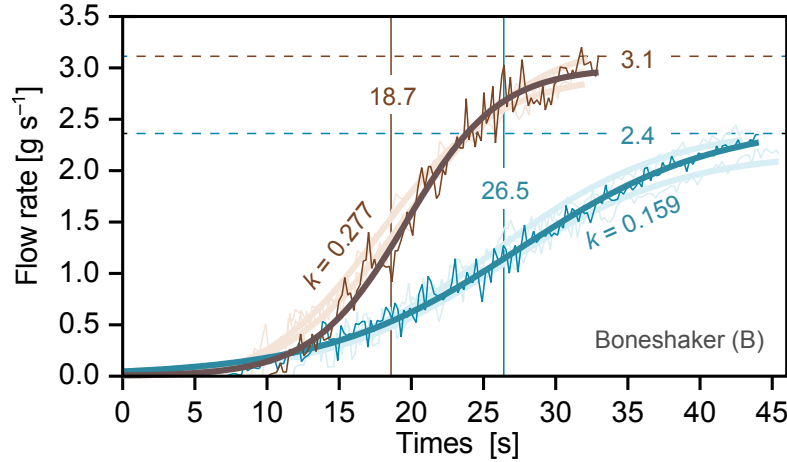


Figure 14. Shot time and flow rate dependence with and without water added to whole bean coffee **a)** Without changing any other parameter, coffee prepared using the addition of water to whole beans during grinding produces consistently slower shots with increased beverage strength. **b)** The change in flow rate can be fit using a logistic function such that the permeability of the bed approaches a constant within conventional espresso brewing times. The time in which the sigmoid takes to reach its inflection is nearly half that of the shots prepared with water indicating that the bed is more permeable, and progresses towards equilibrium permeability more rapidly.

this is conclusive evidence to suggest that dry-ground coffee is producing a bed with markedly more porous pathways. By comparison to the exact same coffee but wet-ground, we can conclude that wet-grinding results in less space within the compacted bed, and likely more homogeneous contact with water over the duration of the shot. Recalling that our previous study⁸¹ highlighted that finer grind settings yielded uneven and variable extraction, here we now offer one remedy to this variation. The addition of water during grinding should produce markedly different flavor profiles and we expect that if one were to then alter both coffee mass and grind setting, the process should result in highly reproducible espresso.

2.1.11 A theoretical explanation for the role of water in charge passivisation. While the precise role of water remains enigmatic, the observation that it controls charging is clear. Here we posit an explanation for water’s role in controlling the sign and magnitude of charging in coffee. In a recent study by Shin and colleagues,¹¹³ the authors present a comprehensive theory for predicting the magnitude and polarity of electrification based on interfacial thermoelectric effect. In short, material charging can be predicted from their ”triboelectric factor”, a descriptor that relates a material’s Seebeck coefficient (S) and the square root of the material’s density (ρ), specific heat (c), and thermal conductivity (k); $S/\sqrt{\rho ck}$. The sign of S is determined by the charge carrier type if they were to conduct electricity, *i.e.*, positive for hole and negative for electron, and the magnitude of S depends on the electronic band gap (*i.e.*, S of metals are nearly zero). The Fermi level of most metals used in grinder burrs (*e.g.*, steel with coatings of titanium nitride, diamond-like carbon,) sit *ca.* -5.0 eV relative to vacuum.^{114–116} Because ρ and k of metals are very high, the triboelectric factor of the burrs would be very small and positive. We note that other burr compositions will produce markedly

different charging effects. For now, assuming the tribofactor of the burrs is treated as constant, we can then estimate how coffee parameters (roast, water content, grind setting) may affect the tribofactor of coffee particles by altering S , ρ , c , and k ,^{117,118} and deduce qualitative trends in electrification.

Agtron number is proportional to the electronic band gap, both of which are reduced with darker roasts. This should yield the coffee Seebeck coefficient decreasing with roast, and likely so would the tribofactor. This hypothesis generally aligns with the observation that oxidized organic molecules have low lying unoccupied orbitals and explains the similarity in charging between coffee and other organic media.⁵⁷ Furthermore, since grinding causes heat (see **Figure S5**) and assuming that the specific heat and thermal conductivity are near-unchanged for most coffees, but dark coffees generally result in smaller particles, darker coffees should heat up more and should produce increasingly negative charge. This concentration of negative charge on “warm”, small particles has been previously invoked by Gu and coworkers to account for the fact that smaller, windblow sand particles are often observed to carry negative charge.¹¹⁹ The complicating factor then remains the role of residual internal water. One possibility is that water is affecting the internal pH, which in turn shifts the internal chemical potential by 60 mV per pH unit.¹²⁰ At lower pH, the Seebeck coefficient should increase. Since light roast coffees generally contain more acid than dark roast analogues,¹²¹ higher internal water may prove to be affecting local chemical potentials, and offers one explanation for how coffee charges positively with increased water content. Then, the addition of external water may serve many purposes, including reducing thermal gradients during grinding, affecting the surface chemistry of the metal

burrs, or facilitating recombination of nominally trapped charge carriers. Future studies will isolate the dominant effects.

2.1.12 Outlook and conclusion. From studying both commercially sourced and in-house roasted coffee, it is clear that many factors play a role in determining the magnitude of charging during grinding. Residual internal moisture content has a first order effect, with lighter roasts ($>2\%$ internal moisture) showing positive charging. Drier coffees result in a transition to largely negative charging. The magnitude of polarity may then be modulated by the grind setting, with coarser grinds yielding less charging than finer grinds. There did not appear to be a dependence on origin or processing method. Instead, we can speculate that it is the interplay between color and moisture content that governs charging, and we highlight that after roasting the color may not change much but internal moisture will depend on age, environment, and so forth. Perhaps this is why commercially sourced coffees behave less predictably than our sample roasts?

Furthermore, light, medium, and dark coffees, and their roast profiles can feature markedly different charging regimes, even for coffees with the same Agtron values. This highlights that modern roasting paradigms are artisanal and poses fundamental challenges for using commercially sourced coffee in academic settings. This is important at both the small and large scale, potentially elevating quality control in roasting facilities. Similarly, one could imagine using the charging of whole bean and ground coffee as a marker for a number of chemical and physical quality metrics. Could chemical defects be detected by monitoring the electrification of whole beans using the rolling technique presented in **Figure 8**?

We demonstrated that charging of coffee depends less on the initial water content of the green coffee, and more so on the terminal water content (both

internal and external) of the roasted beans. Through the inclusion of small amounts of external water, the coffee effectively declumps and suppresses charging during grinding. The same process provides tantalizing opportunities to introduce ions into the coffee grounds using salted water. One could imagine the development of in-ground mineralization to make designer brewing water¹²² *in situ* without the risk of damaging boilers in espresso settings. To that end, we also demonstrated that the inclusion of water on whole bean coffee results in markedly different flow dynamics in espresso brewing, which will undoubtedly yield differences in cup quality. The inspired reader is encouraged to experiment using the water addition technique, but to further include both coffee mass (controlling the brew ratio and resultant strength) and grind setting (controlling flow restriction and resultant contact time) as variables. Wide implementation may reveal that simple squirt of water has solved the problems of clumping, channeling, and poor extractions, and aids in the pursuit of attaining the tastiest espresso.

2.1.13 Supplemental Information. Supplemental Information can be found online at <https://doi.org/10.1016/j.matt.2023.11.005> and in Appendix A.

2.2 Strategies to mitigate electrostatic charging during coffee grinding

2.2.1 Author Contributions. J.M.H. and R.E.B. and C.H.H. all partook in conceptualization, data collection and interpretation, and drafting of the manuscript. J.M.H. and C.H.H. acquired the funding and supervised the research.

2.2.2 Method Details. We electrified coffee by grinding whole beans using a Mahlkönig EK43 grinder with stock 98mm burrs. Here we conducted experiments using three coffees (two Mexican coffees and one Ethiopian) roasted in-house on an Ikawa Pro100 roaster following two temperature profiles (see **Figure**

S1), yielding dark and light colors. Salient characteristics of both green and roasted coffee are noted in **Table 1**. The coffee color/roast degree and internal water content were measured using The Dipper KN-201 and a RoastRite RM-800, respectively. The RoastRite uses capacitance to report moisture content, and is potentially susceptible to environmental convolution. To ensure quantitative moisture reporting, the device was calibrated to an Ohaus MB23. In our hands (at 35 %RH), the RoastRite factory software provided readings that were identical to the Ohaus device.

We assessed the performance of four techniques to reduce static generated during grinding: time-resolved discharge, the addition of external water, unipolar corona discharge, and balanced corona discharge. With the exception of the grind-and-wait technique, all experiments consisted in applying an electrostatic reduction technique during grinding and measuring the residual charges on particles exiting the grinder using a Faraday cup. Charge-to-mass (Q/m) ratios were then calculated, allowing comparative analysis between the various techniques. The particulars of each method are described in the sections that follow.

Roasted coffee was stored in sealed, evacuated bags and kept at -20 °C. Prior to grinding the coffee was allowed to reach equilibrium temperature before unsealing. For all experiments, we used a grind setting of 2.0 (arbitrary units) on the EK43, producing particle size distributions comparable to those shown in **Figure 15b**. Particle size measurements were performed on a Malvern Mastersizer 2000 with the solid-particle feed system, Scirocco 2000. Experiments were conducted at $20 \pm 3^\circ\text{C}$ and $35 \pm 7\%$ RH. Each Faraday cup experiment was conducted a minimum of 3 times. Surface charges were measured using a Keithley 614 electrometer.

Espresso was prepared using 18.0 g of dry mass coffee, with shots stopped at 45.0 g of liquid coffee extract. The coffee was ground to an arbitrary setting of 1.0 on our EK43, tamped at 196 N, and brewed using 94 °C water, kept at 7 bar of static water pressure with a 2 second pre-infusion on a Victoria Arduino Black Eagle.

2.2.3 Introduction. Grinding roasted coffee reduces whole beans into flows of highly electrified powders.^{105,123} Charged granular materials can lead to electrostatic discharges,¹²⁴ jamming and sheeting (*i.e.* coating the interior walls of conduits),^{71,125} spontaneous segregation,¹²⁶ and product non-uniformity.¹²⁷ Specific to coffee preparation, charging can produce erratic dispersal of grounds, making whole bean grinders somewhat messy. More importantly, however, static charging during grinding results in particle-particle clumping.^{105,123} These electrostatic agglomerates affect extraction quality when brewing by changing the packing of coffee particles and influencing solid surface area available to percolating water.^{80,81} The elimination of these clumps should increase soluble availability, posing substantial financial and sustainability motivations to eliminate their formation.

Recently, we demonstrated parameters that control charging by grinding commercially-sourced coffees and measuring the charge-to-mass ratio of the grounds using the process presented in **Figure 15a**.¹²³ As whole beans are fractured into small grains with broad size distributions (**Figure 15b**),⁸³ particles may acquire charge densities comparable to those of volcanic ash and thundercloud ice, through both fracto- and triboelectrification.^{55,70} Generally, the polarity and magnitude of charge loosely depends on the roast level or color of a coffee, and we observed that dark roasts charge largely negative, and lighter roasts charge positively, **Figure 15c**. Residual moisture levels, a property typically inversely proportional to color,

was found to be the primary determiner of charge polarity, where positive-to-negative charging transition occurs at moisture contents less than $\sim 2\%$. Some coffees, especially dark coffees, can charge sufficiently to cause gaseous breakdown in the form of millimeter-long spark discharges, **Figure 15d**.

The coffee industry has long maintained an intuitive understanding that water can significantly modulate grinding-associated electrostatics. A small amount of water added to whole beans before grinding—the so-called Ross droplet technique (RDT)—is known to prevent static accumulation, and causes the grinder to retain less grounds within its chamber.^{106,123} However, the inclusion of too much water may result in caking or corrosion in the grinder, the limit of which will depend on the coffee and grinder. Concurrently, there is interest in the industry in developing water-free charge mitigation strategies, but their utility and impact on achieving high extraction yields remains unknown. In this paper, we examine the effectiveness of various electrochemical techniques to suppress electrostatic build up – grinding and waiting, adding external water, and alternate ionization methods. We show that de-electrification techniques that introduce charges after the agglomerates have formed (*i.e.* simply waiting or ionization methods) do not improve the particle availability in espresso brewing, resulting in variable extractions and no improvement in total dissolved solids (%TDS). The addition of water mitigates charging during the grinding process, and results in extraction increase of beyond 15%.

2.2.4 Canvassing charge passivation strategies. *Time-resolved discharge*

Perhaps the simplest discharge method is to let the ground coffee sit for a period of time after grinding. This respite permits discharge through

volumetric or surface conduction or, in the case of exceedingly high charges, gaseous breakdown.^{128–130} To a zeroth order, Jones and Tang¹³¹ have described the relaxation of the volumetric charge density $\rho(t)$ in a powder by;

$$\rho(t) = \rho_0 e^{[-t/(\kappa\epsilon_0\gamma)]} \quad (2.1)$$

where ρ_0 is the initial charge density, t is time, κ is the dielectric constant of the material, ϵ_0 is the permittivity of free space, and γ is the effective resistivity. The denominator in the exponent defines a time constant, τ . This exponential behavior of charge decay can be readily observed using a non-contact electrostatic voltmeter probe (Trek 541A-2) placed 5 mm over 10 g of freshly ground coffee (collected in a metal cup, resting on an insulating surface), **Figure 16a**. Charge relaxation curves for both light and dark roasts of the same Ethiopian coffee (a washed Yirgacheffe) are rendered in **Figure 16b**. There, the light roast (2.8 % residual water) loses its charge faster ($\tau \sim 15$ s) than its darker, drier counterpart (1.0 % residual water, $\tau \sim 65$ s). Overall, however, charge appears to dissipate on timescales of minutes, but exceed the average time between preparing shots in a busy cafe. Also, grinding and waiting poses problems for volatile loss and quality degradation, which occurs over similar time frames.¹³²

2.2.4.1 De-electrification through external water inclusion.

While time-resolved de-electrification is both cost-effective and predictable, it does not prevent the formation of aggregates during grinding and also provides the particles with prolonged off-gassing time, resulting in a significant loss of volatiles.¹³³ Thus, a number of active strategies have been devised to address charging during the act of grinding. We recently demonstrated that the addition of extrinsic water mitigated fractocharging in both positive and negative charging

coffees.¹²³ By incorporating up to 30 μL of water per g of whole coffee beans, our in-house roasts behave similarly to other literature coffee samples, with the charge-to-mass ratio decreasing with increasing water content, **Figure 16c**. Although, in many cases, charging was not completely eradicated, we find that 20-30 $\mu\text{L g}^{-1}$ reduced the charge by a minimum of 50-60 %. In practice, this reduction appears to sufficiently mute electrostatic forces, precluding dispersal of grains, clumping, and other effects. A video of the behaviour is presented in the Supplementary Information (**Video S2**). We also note that it is difficult to ensure that all of the added water ends up on the beans in the grinder, and this likely contributes to the variability in each data point in Figure 16c.

Although we have not observed it in our hands, the addition of water could lead to residual water accumulation within the grinder. This could pose problems for bacterial growth within the chamber, corrosion of the burrs, or other effects. By placing a small humidity sensor (Honeywell HIH-4030) within the grinding volume of the EK43, we measured the buildup of moisture associated with the RDT. For additive water in the range of 0-50 $\mu\text{l g}^{-1}$ and a base RH of 40%, we find that the relative humidity (%RH) within the grinder may increase up to 75% for a few tens of seconds (see **Figure S2**), but returns back to ambient within minutes. The water is presumably consumed in electrochemical reactions, or boiled off. We did not detect condensation. Grinding 10-20 dry beans after grinding the wetted ones returns the grinder to equilibrium %RH instantaneously.

2.2.4.2 Static reduction using ion beams. To move away from adding water, charge may also be neutralized by recombination with extrinsically generated negative and positive ions. Such techniques draw from an extensive heritage in other settings,^{134–136} and generally employ one of two methods; 1)

corona discharge, which uses high-voltages at sharp, conducting tips to accelerate naturally-occurring free ions and also cause collisions with neutrals;^{135,137,138} and 2) ionizing radiation, involving a radioactive or X-ray source to generate similar numbers of positive and negative ions.¹³⁹ Towards the former, high-voltage ionizers may be unipolar, involving net negative or positive ions, or balanced, where the production of negative and positive charges are equal. Some manufacturers have begun to include these devices in grinders or sell them as accessories to reduce charging.^{140,141} Towards the latter, we note that in an earlier version of the manuscript examined de-electrification using a helium nuclei source, Figure S4. However, given the results are largely similar to the effects produced by the balanced ionizer, but balanced ionizer present significantly less risk than using radioactive sources,¹³⁹ we have elected to not present those data in the manuscript and do not recommend the reader attempt that experiment.

Unipolar ionization – The efficacy of unipolar ionization on charge reduction can be tested using a high-voltage ionizer. The device consists of a bundle of fine carbon needles fed by a high-voltage source that can generate either 12 or -12 kV. The tip of the ionizer was placed at a controlled distance (30–120 mm) from the coffee grinder chute (see schematic in **Figure 17a**). Using a Gerdien condenser (AIC, AlphaLabs Inc.), we estimate the negative and positive ion densities to be 1.5 and $1.2 \times 10^6 \text{ cm}^{-3}$ at a distance of 0.3 m, respectively. These densities can be augmented by moving the bundle closer to the chute. To shield the Faraday cup from direct influence of generated ions, we placed a coarse, grounded copper mesh over the cup’s aperture.

The plots in **Figure 17a** show the Q/m ratios gained by dark and light roasts of the YirgZ and Yogondoy during grinding as a function of ion density,

as measured by the Faraday cup. With the ionizer off, the dark roasts nominally charge negatively, whereas the light roasts gain positive charge. Systematically increasing the positive ion density reduces the negative Q/m of the dark roasts toward 0 nC g^{-1} (middle panel of **Figure 17b**). However, bringing the positive ion source too close to the chute causes a polarity flip and the dark roasts end up depositing positive charge into the Faraday cup. A similar effect is true for light roasts (rightmost panel of **Figure 17b**); low degrees of negative ionization reduce positive charge, but moderate-to-high ion densities result in negative charging.

These experiments demonstrate that corona discharge is highly effective at neutralizing charge and minimizing dispersal effects, (*i.e.* mess, see **Video S3**), but only if the characteristics of the ion source are tuned to the charging behavior of a particular coffee. Despite originating from the same green coffee, the light and dark Yogondoy samples require vastly different ion densities and polarity to achieve a reduction in Q/m ratio comparable to that produced by the water addition technique. The dark roast necessitates ion densities around $6 - 7.5 \times 10^6 \text{ cm}^{-3}$, whereas charge on the light roast is minimized between -5 and $-2.5 \times 10^6 \text{ cm}^{-3}$. While these ranges can be achieved by adjusting the distance between coffee and ion source, ion densities outside of these ranges compound existing problems (*increase* charge) and create new problems (such as scattering fine particles via an ionic wind). Because the behavior will depend on environmental variables such as humidity, coffee moisture, roast color, and other parameters, implementing unipolar ionization discharge necessitates trial and error.

Balanced ionization – If the charge behavior of a granular material is not known beforehand, implementing electrostatic reduction using ionizing devices that produce an equal number of positive and negative charge carriers may be effective.

In general, these bipolar static eliminators concurrently produce positive and negative ions as well as electrons at atmospheric pressure in air. Here, we test a commercially-available bipolar static eliminator (Shopcorp 12M). Like the unipolar setup, the bipolar systems generate ions from bundles of fine carbon needles. The positive and negative outputs were placed facing each other just below the chute of the EK43 grinder with a separation of 10 cm, **Figure 17c**. In the space between the outputs, we measured positive and negative ion densities in the range of $\pm 9.8 \times 10^6 \text{ cm}^{-3}$ (for a net density of $\sim 0 \text{ cm}^{-3}$).

During an experiment, ground coffee was allowed to fall through the volume of ionized air generated by the balanced ionizer. The bar graphs in **Figure 17d** show the Q/m ratios measured on dark and light roasts of all three coffees in the absence (grey bars) and presence (purple bars) of the balanced ionizer. For dark roasts (left panel), we observe a minimum reduction in charge-to-mass ratio of $\sim 50\%$, comparable to that imparted by the Ross droplet technique (at the highest water contents of $20\text{-}30 \mu\text{L g}^{-1}$). For light roasts, we also see up to 90% reduction in electrification. Interestingly, light-roasted samples that nominally charge positively (YirgZ and Yogondoy) may occasionally acquire small negative charges in the presence of the balanced ionization. We suspect that this polarity flip reflects the higher mobility of electrons relative to that of much more massive positive ions, but it could also depend on the composition of the coffee itself. Note also that the balanced ionizer is overall less efficient than a properly tuned unipolar corona ionizer in its capacity to reduce charge. This observation is aligned with experiments in silos which show that the most effective neutralization of negatively-charged powders occurs not under balanced ionization, but when the positive ion density is higher than the negative one by a factor of 2-3.¹⁴²

2.2.5 Aggregate formation. For ionizing strategies, charge mitigation occurs at the chute exit, not in the grinder itself. Conversely, the water addition evidently passivates charging throughout the grinding process. These differences may have important effects on particle-wall adhesion, material loss, and clump formation, especially since previous work has shown that particles adhered to the wall can have Q/m ratios several dozen times larger than those forming the bulk.¹⁴³

Whether a particle of radius r with charge q will electrostatically adhere to a surface depends in part on its electrostatic-to-gravitational force ratio (EGR),

$$EGR = \frac{F_e}{F_g} = \frac{3}{4} \frac{kq^2}{\pi g \rho_p r^5}. \quad (2.2)$$

where k is Coulomb's constant, ρ_p is the particle's density, and g is the acceleration due to gravity. Because $EGR \propto 1/r^5$, smaller particles are much more likely to adhere to surfaces than larger ones (for a given q). Thus, dry, charged coffee exiting the grinder tends to be depleted in small particles. Retained fines within the grinder must be knocked out mechanically. This segregation can be readily observed in **Figure 18a**, where we plot the size distribution of grounds directly expelled by the grinder (solid, brown curve) and that of grounds retained within the grinding cavity (dotted, brown curve) when 10 g of whole coffee is ground with no charge mitigation technique.

From Figure 16c, our data shows that adding moisture to whole coffee reduces charging by at least 50%. This reduction would result in a 4-fold decrease in the EGR , possibly allowing small particles to overcome electrostatic adhesion and become reincorporated in to the bulk. The effect is reflected in our data where the addition of 100 μL of water added to 10 g of whole beans produces an

appreciable shift in particle size distribution toward smaller diameters, **Figure 18a** (dashed, blue curves). In fact, we observe a decrease in the mean particle size of expelled grounds up to water contents of $50 \mu\text{l g}^{-1}$ (see **Figure 18b**). However, at higher extrinsic moisture levels, the mean particle size again moves toward larger diameters due to the formation of moisture-promoted aggregation driven by capillary forces, rather than electrostatic ones.¹⁴⁴

For the high-voltage ionization system, we do not see an analogous shift toward smaller particles sizes with increasing ion density (see **Figure 18c**). Comparing the masses of coffee retained under high-voltage ionization and the water addition technique, **Figure 18d**, even a modest $10 \mu\text{l g}^{-1}$ reduces retention to $\sim 2.5\%$, whereas the high-voltage ionization method has retention percentages indistinguishable from those of no-treatment grinding ($\sim 12\%$).

2.2.6 The effect of charge mitigation on espresso quality. In principle, charge mitigation during grinding should provide a better control on the characteristics of the grounds are used during coffee brewing. However, as evident from **Figure 18**, disparate charge reduction methods, while generally effective at reducing a material’s Q/m ratio, do not necessarily generate granular materials with equatable properties. How do these differences influence brewing?

In our previous work,¹²³ we demonstrated that adding small amounts of water to beans prior to grinding changed the brewing behaviors when preparing espresso. **Figure 19a** exemplifies such behaviors. There, we plot the shot time (left panel) and flow rate for espresso brewed with and without added water, following the espresso preparation method discussed in the Methods section. For these experiments, we employed the dark roasted Temascaltepec. Mitigating charge with extraneous water results in extended shot times, decreased flow rates, and

increased percentages of total dissolved solids (%TDS) as compared to no charge mitigation. We interpreted these findings to reflect the breaking or rearrangement of electrostatically-bound aggregates, resulting in a particle bed with smaller average grain size and, thus, reduced permeability. The data in **Figures 18a and d** suggest that an additional mechanism may also be operative: added water dislodges a large number of small particles that would otherwise remain trapped within the grinder.

The impact of shifting the distribution finer is enormous. Keeping all variables the same, a remarkable 16% increase in coffee concentration is achieved. Such increase in accessible coffee material in comparable brew times, **Figure 19a**, poses significant financial implications for the coffee industry, allowing for more efficient use of dry mass coffee, at the cost of adding less than 0.5 mL of water to the whole beans during grinding.

Conversely, charge reduction using an ionizing source at the grinder chute does not produce a reduction in the mean particle size, nor does it decrease grinder retention (see **Figures 18c and d**). As evident in **Figure 19b**, we observe nearly indistinguishable differences in espresso shots prepared with or without the ionizers. The modest increase in %TDS from 7.76% to 8.02% (average over five replicates) is still notable, and can be attributed to some fine particles being liberated from boulders. These data suggests that ionization techniques perhaps do cause some aggregates to break up as these exit the chute, but the effect is limited. However, they do not propitiate the reincorporation of small particles bound electrostatically to the interior surfaces of the grinder and burrs. Thus, unlike the addition of water, discharging coffee at the nozzle produces limited changes to the physical

characteristics of the grounds used to brew coffee compared to the untreated samples.

For dark coffees, added water prior to grinding can generate appreciable differences in espresso brew characteristics, **Figure 19**. Similar experiments with a lightly roasted sample of the same coffee (Temascaltepec) do not reveal significant changes to espresso brew characteristics, either with extrinsic water or ionization (**Figure S3**). As noted in our previous work,¹²³ darker roasted coffees not only charge negatively, but also acquire the highest absolute charge-to-mass ratios. Lighter roasts charge more ineffectively, with coffees with $\sim 2\%$ residual water acquiring Q/m ratios near 0 nC g^{-1} . Consequently, electrostatic effects like clumping and sheeting are markedly less present when grinding lighter roasts. That the addition of extrinsic water or ionization do little to modify the properties of the bed is, thus, not surprising.

2.2.7 Conclusion. We have assessed the performance of a range of electrostatic reduction techniques in the context of coffee grinding. Added moisture and high-voltage ionization effectively counteract charging generated through fracto- and triboelectric charging. At minimum, both techniques have the potential to decrease the gravimetric charge by at least 50 %. Unipolar ionization methods can reduce the Q/m ratios of expelled coffee to near zero if appropriately tuned to a given coffee. Bipolar or balanced ionization may be less effective than unipolar ionization, but can produce charge reductions comparable to those afforded by water addition. However, ionization generally does not address electrification processes and adhesion dynamics within the grinder. As such, ionization methods at the grinder chute do not mitigate material loss (retention) which, for a grinder like the EK43, can be hundreds of milligrams of dry material. Conversely, the

charge reduction afforded by water addition (volumes ranging from 0-50 $\mu\text{L g}^{-1}$ dry mass coffee) has the capacity to resolve aggregation effects across the entire grinding system, even if particles retain some charge. Because particle-wall aggregates comprise smaller grains, we find that reincorporating this material into the bulk significantly changes the espresso brewing behavior (slower shots and smaller flow rates) and resultant increase in coffee solubility. And while our experiments conclusively demonstrate the economic upside of water incorporation during grinding for espresso, we suspect a similar effect will be observed for all percolation brewing techniques, as liberation of fine particles will not only clog void space in the coffee bed, but also fill voids in filter paper in pour-over embodiments.

2.2.8 Limitations of the study. Although the selected coffees do span a range of origins and processing methods, and were roasted to span roast colors commonly found in the specialty coffee sector, there may be coffee samples that fall outside the typical parameter space considered here (*i.e.*, initial and post-roast moisture, bean color, origin, and even species). Furthermore, in our hands we consistently observe the impact of reduced flow and increased extraction as a function of shift in particle size distribution. However, there may exist some parameter space where a coffee requires different volumes of water added to the coffee to observe the effect. Similarly, the rate of delectrification achieved by grinding and waiting may be impacted by subtle variables such as grind size and humidity.

2.2.9 Supplemental Files. Video S1: Temascaltepec ground at grind setting 2.0, without any static treatment, related to Figure 2c that shows the electrification of coffee ground without water. Captured using a Canon 100 mm f/2.8 USM lens at 1000 frames per second (25 fps playback)

Video S2: Temascaltepec ground at grind setting 2.0, with the addition of 0.01 mL of water per g of coffee, related to Figure 2c that shows the electrification of coffee ground with water. Captured using a Canon 100 mm f/2.8 USM lens at 1000 frames per second (25 fps playback)

Video S3: Temascaltepec ground at grind setting 2.0 and exposed to the high voltage ionizer at a radius of 3 cm, related to Figure 3b that shows the electrification of coffee ground in the presence of the ionizer. Captured using a Canon 100 mm f/2.8 USM lens at 1000 frames per second (25 fps playback)

Additional Supplemental Information can be found in Appendix B.

Table 1. Characteristics of in-house roasted coffee used in this work.

	Yirgacheffe Zero Defect	Temascaltepec	Yogondoy
Origin	Ethiopia	México	México
Producer	Tamrat	Federico	García
	Alemayehu	Barrueta	Luna
Process	Washed	Washed	Washed
%H₂O (initial)	12.0	8.9	9.3
%H₂O (dark)	1.0	1.3	1.1
%H₂O (light)	2.8	3.0	3.0
Agtron (dark)	62.1	58.4	60.2
Agtron (light)	88.7	70.1	93.1

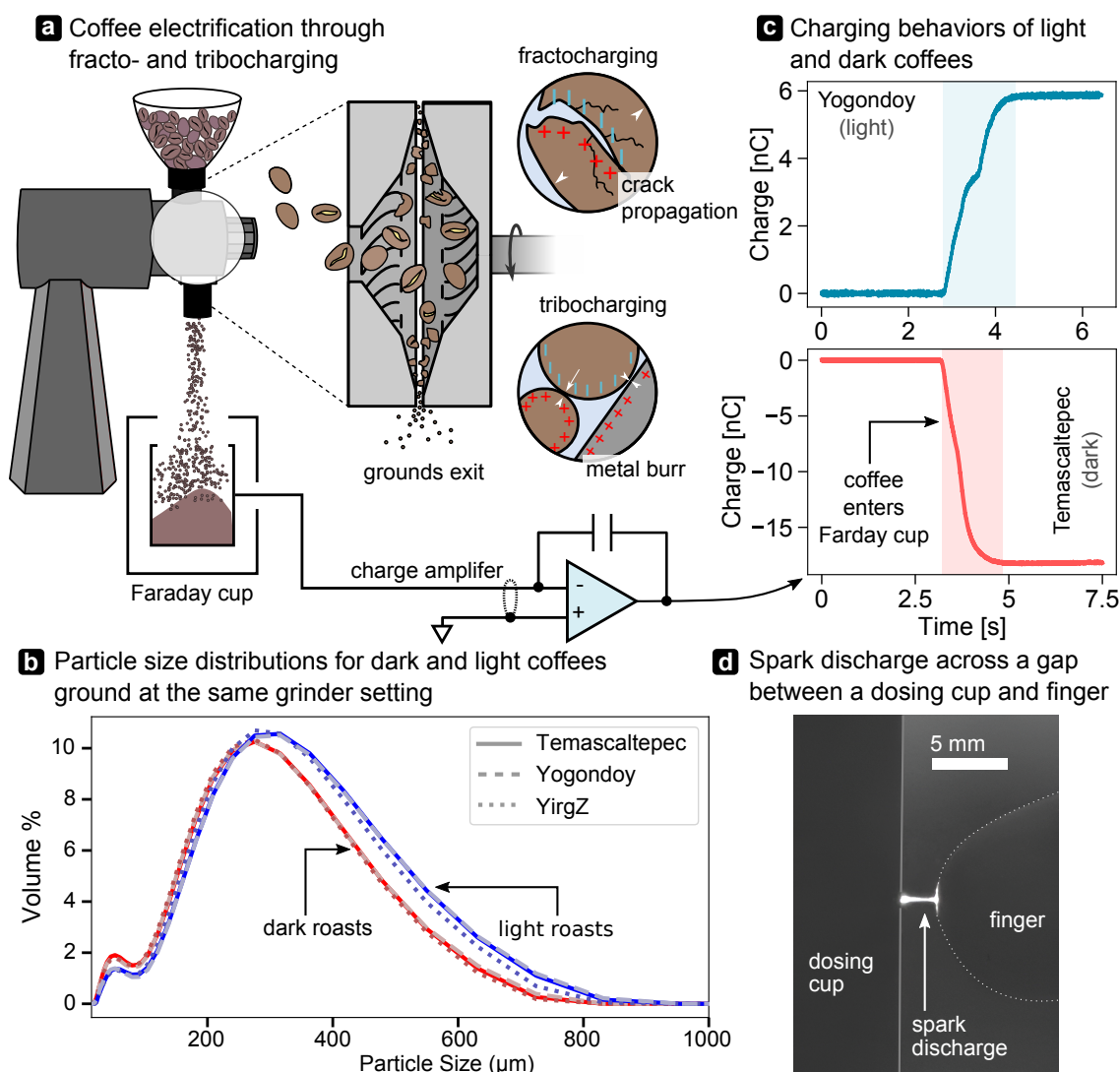


Figure 15. Electrification of coffee during grinding. **a)** Schematic of the setup used to assess the electrification of coffee during grinding. During fracture, coffee particles accumulate charge from the burr-coffee and coffee-coffee interfaces (tribocharging), as well as fracture points (fractocharging). Charge-to-mass ratios can be measured with a Faraday cup and scale. **b)** Particle size distributions for our in-house roasted coffees ground at setting 2.0 on our Mahlkönig EK43. **c)** Example charging curves (raw data from Faraday cup) for lighter/wetter and darker/drier coffees. **d)** Photograph of a spark discharge spanning the gap between a metal cup containing freshly ground coffee and the lead author's finger. Assuming a breakdown field of 3 MV m^{-1} (air at 101 kPa), the potential difference between the two surfaces is $\sim 7.5 \text{ kV}$.

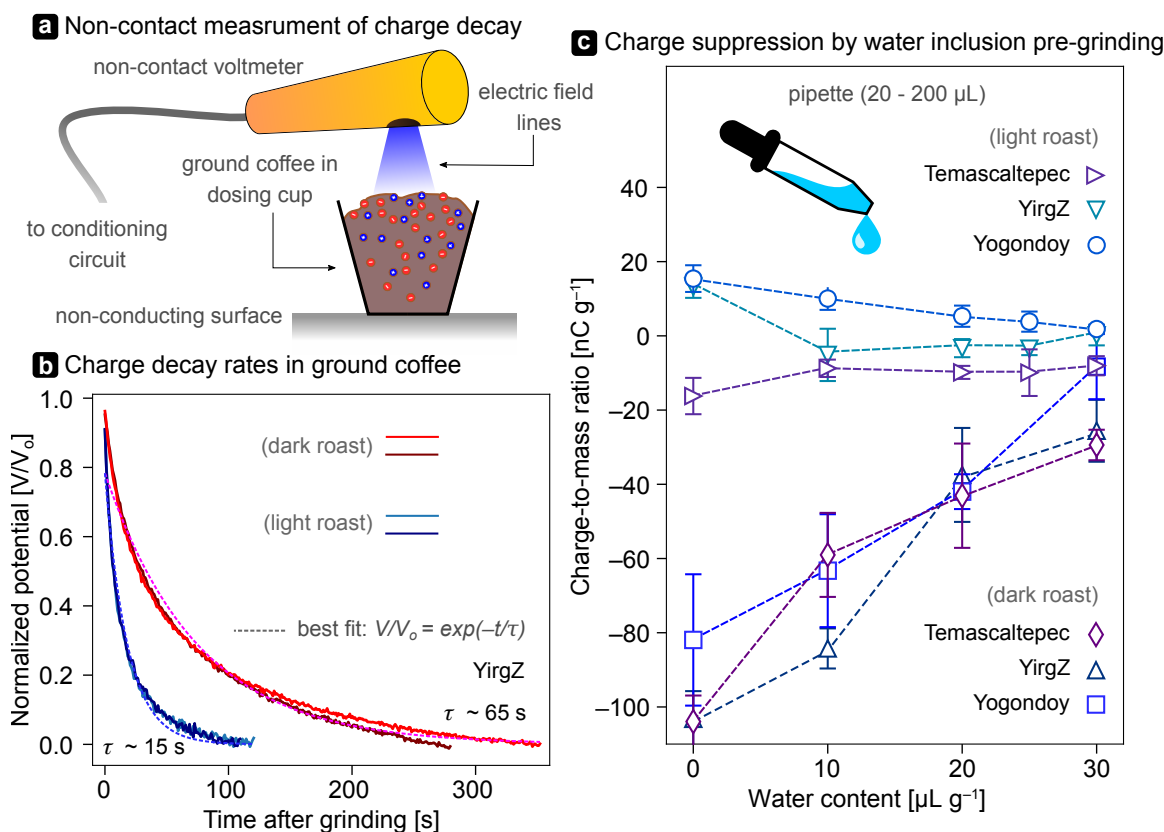


Figure 16. Time-resolved and water-mediated charge reduction strategies.

a) Schematic of setup used to measure the charge decay in freshly ground coffee. A non-contact voltmeter was placed 5 mm above 10 g of ground coffee and its potential was measured every 0.5 sec. **b)** Charging dissipates with time as charge-carriers recombine with each other through surface and bulk conduction. Some charge may also be lost directly to the atmosphere. Charge in lighter roasts decays faster than in dark coffee. **c)** During the grinding process, charge accumulation is hindered by the addition of small amounts of water ($0 - 30 \mu\text{L g}^{-1}$) to the whole beans prior to grinding.

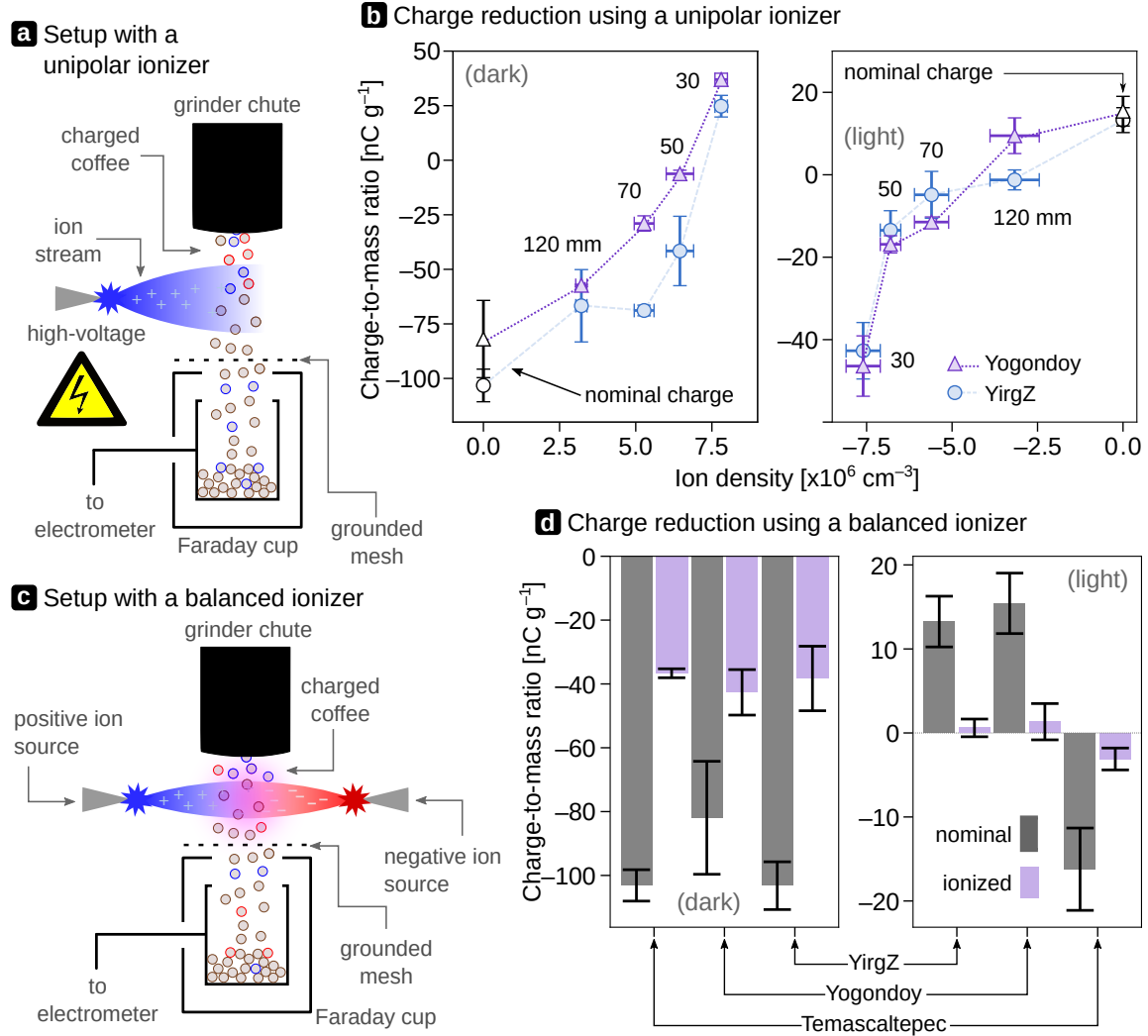


Figure 17. Ion beam charge reduction strategies. Charging may be counteracted by ionizing the air around the coffee grounds as these exit the grinder. Free negative and/or positive ions adhere to solid particle surfaces, tuning their charge. **a)** Ionization may be accomplished via high-voltage gaseous breakdown. **b)** While potentially effective, the number of positive and negative ions generated must be adjusted to balance the charging characteristics of a coffee. The nominal charging behavior of coffee with no de-electrification is presented in white. Dark coffees generally natively charge negatively, while light coffees charge positively. The distance between the ionizer and coffee is presented in mm. **c)** Negative and positive ions may also be generated via a bipolar high-voltage source. **d)** Exposing negatively charging coffee to a balanced ionizer reduces its charge by at least 50 %.

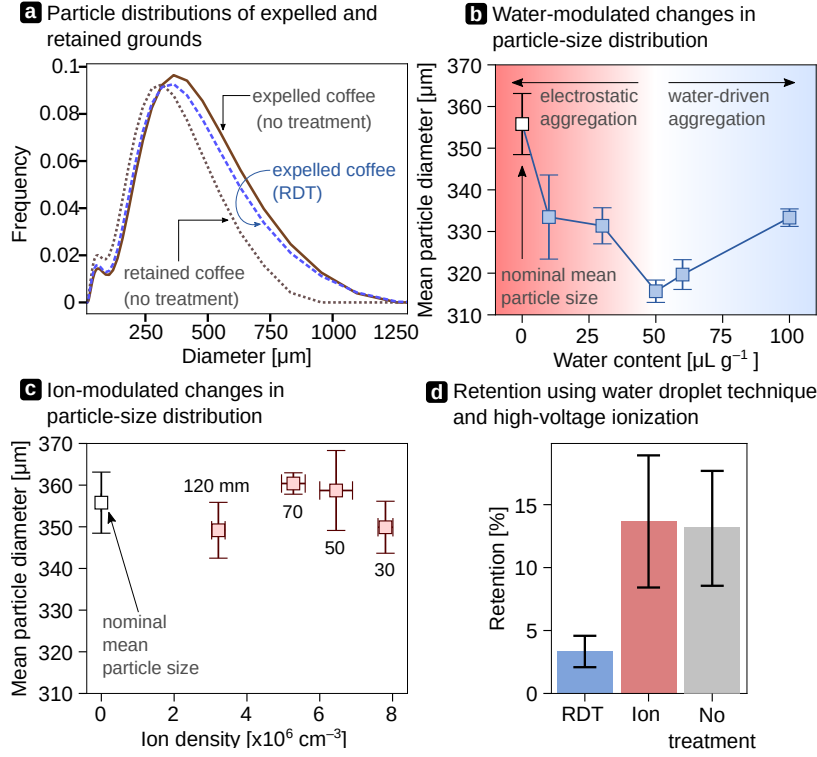


Figure 18. Particle aggregation and grinder retention **a)** For dry-ground coffee (Yogondoy [dark]), expelled grounds follow the particle size distribution is presented in brown. Grounds retained within the grinding cavity concentrate fines (dotted, brown curve). Fines have higher electrostatic-to-gravitational ratios, meaning they are more likely to adhere to surfaces when charged. Adding even a small amount of water ($10 \mu\text{L g}^{-1}$) can significantly reduce electrostatic aggregation, reducing retention and shifting expelled ground particle sizes toward smaller diameters (dashed, blue curve). **b)** Water contents in the range of $0\text{--}50 \mu\text{L g}^{-1}$ continue to shift particle sizes toward smaller mean diameters. Water contents above $50 \mu\text{L g}^{-1}$ again increases the mean particle size, indicating the activation of wet (capillary) aggregation processes. **c)** A linear shift in mean particle size and ion density is not observed for coffee treated with a unipolar corona ionizer at different chute-ionizer distances. These data suggest that fine particles within the grinder are not included in the measurement sample (that is, they remain electrostatically adhered to the inner surfaces of the grinder), and the aggregates are formed before deionization, which is to be expected since the corona ionizer is placed after the chute. **d)** Because the water addition technique (RDT) hinders electrification throughout the grinder, the wet method (using $10 \mu\text{L g}^{-1}$) has the ability to greatly reduce retention. Ionization ($7.8 \times 10^6 \text{ cm}^{-3}$), addressing static only at the grinder chute, involves retention masses similar to those of grinding with no static mitigation treatment. Grind data in panels **a–c** were collected in triplicate and the averages are presented.

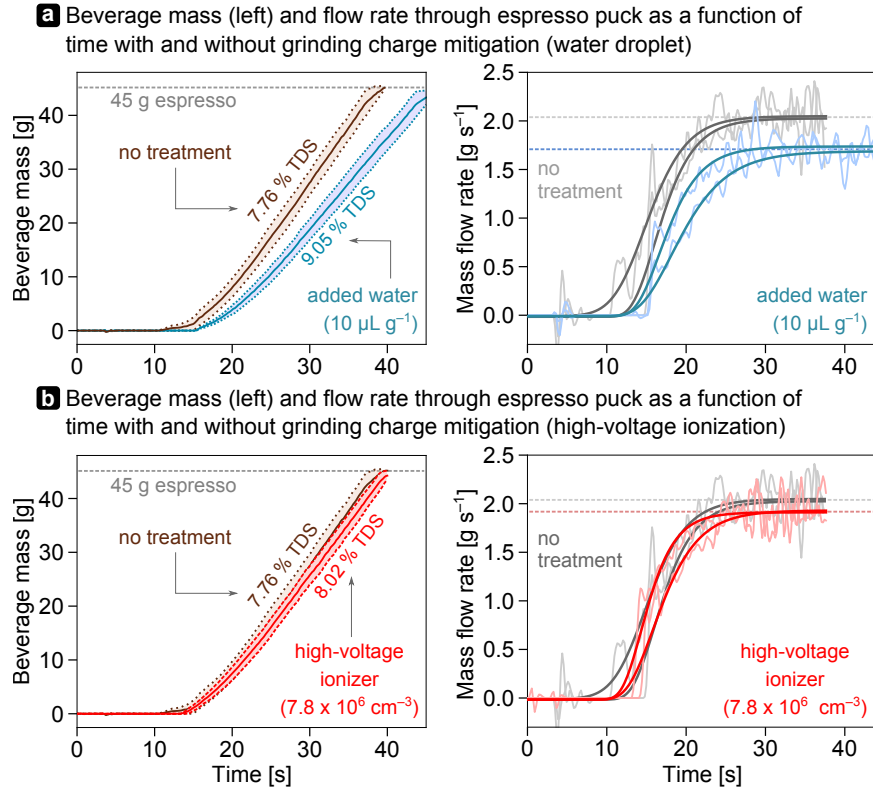


Figure 19. Espresso shot time and flow rate dependence with and without charge mitigation for a dark roast (Temascaltepec) **a)** Without changing any brewing parameters, coffee prepared using the addition of water to whole beans during grinding produces consistently longer shots (left panel) with reduced flow rates. The shot flow rate can be fit using a generalized logistic function such that the permeability of the bed approaches a constant (right panel). Note that the time it takes an espresso prepared with water to reach this plateau is significantly longer than that of an espresso brewed conventionally. **b)** Using a positive high-voltage ionizer, we do not observe an appreciable increase in shot time or a reduced flow rate. We do observe a modest increase in % TDS. The departure from the behavior observed with the Ross droplet technique highlights the fact that ionization methods at the grinder chute do not address electrostatic effects within the grinder cavity and highlights the importance of de-electrification during grinding. Shots were run in triplicate, and compared to the untreated samples. For a p-value of 0.05, the ionization treatment is not significantly different from the native charging sample (t-value of -1.625). However, the water addition treatment was found to be significantly different (t-value of 6.059) at the same p-value.

CHAPTER III

DETERMINING ROAST DEGREE

3.1 An electrochemical descriptor for coffee quality

3.1.1 Author Contributions. The study was conceived by CHH and REB. Coffee samples were roasted and brewed by REB. Cyclic voltammetry and quartz crystal microbalance measurements were performed by REB. Laser diffraction measurements were performed by EJR. DFT calculations were performed by DP. Data analysis was performed by REB, ZSW, and LSW. Liquid chromatography and high resolution mass spectrometry was performed by JW. REB and CHH wrote the manuscript and all authors contributed to the final version.

3.1.2 Experimental Methods. *Electrodes and Electrode Cleaning.* A three-electrode setup consisting of a working electrode (WE), counter electrode (CE) and reference electrode (RE) was used for cyclic voltammetry (CV) and quartz crystal microbalance (QCM) experiments. Figure 20 shows examples of each type of electrode. Figure 20a shows the platinum wire CEs as purchased, left, and as used, right, from CH Instruments. The CE wire was coiled to maximize surface area while allowing for variation in sample holder configuration. CEs were cleaned during the normal procedure for cleaning the platinum dot WE, detailed below.

Figure 20b shows a used, left, and new, right, silver/silver chloride RE. Discoloration from coffee material can be seen in the internal KCl fill solution and in the porous frit at the bottom. RE regeneration was performed when the fill solution began to leak out, when the silver wire became white with silver chloride deposits, or when the RE performance was suspected to be subpar. RE regeneration was performed by gently separating the wire and holder (white) from

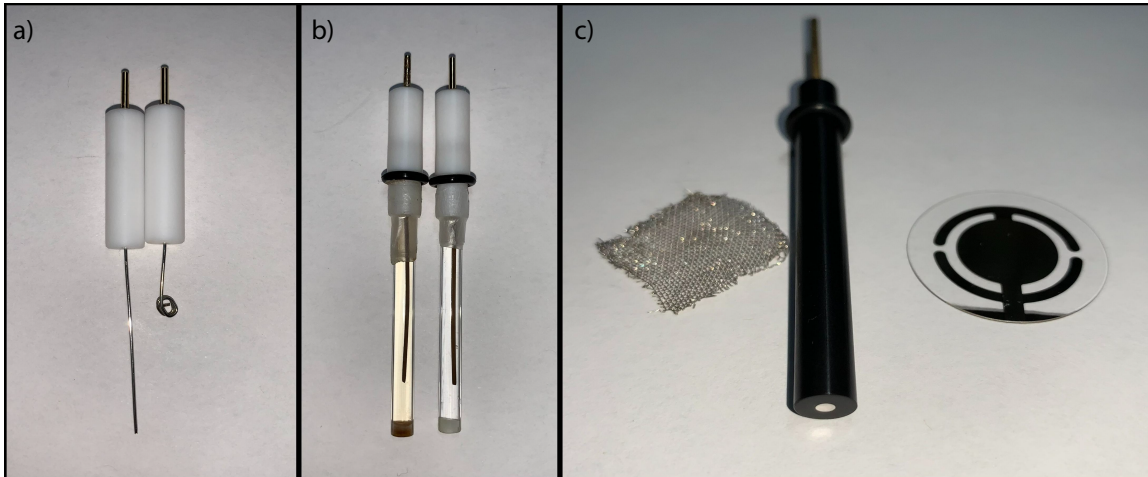


Figure 20. Electrodes used in experiments. a) Platinum wire counter electrodes. Left, as purchased from CH Instruments. Right, coiled to maximize surface area. b) Silver/silver chloride reference electrodes. Left, used and right, new. c) Platinum working electrodes. Left, platinum mesh electrode. Middle, platinum dot electrode. Right, platinum quartz crystal microbalance electrode.

the tube casing. The fill solution was flushed and replaced with fresh saturated KCl solution, and the silver wire was polished with sandpaper until shiny. The two pieces were then carefully reconnected, taking special care that the porous frit did not become dislodged. Finally, the regenerated RE was reoxidized using a two-electrode setup where the regenerated RE was attached to the working and working sense leads and a platinum CE was attached to the CE and RE leads. The potentiostat was then used to run chronopotentiometry at 0.001 amps for 10 minutes in saturated KCl solution. The regenerated RE was then checked against an unused RE to determine any unexpected voltage offset.

Different platinum WE configurations were needed depending on the type of experiment. Figure 20c shows three platinum WE configurations. The leftmost WE is a platinum mesh with a surface area of 5 cm². The mesh WE was used for experiments in conjunction with high resolution mass spectrometry. Normal cleaning of the mesh WE consisted of CV cycling in 50 mM H₂SO₄ for

30 cycles with a scan window of -1.1 V to 1.1 V and a scan rate of 1 V/s. This was also considered the normal cleaning method used for the platinum dot WE (middle). If the CV features showed decreased current from the expected values, additional cleaning methods were employed. The platinum mesh WE was cleaned via a 5–10 minute soak in freshly prepared piranha solution. Additional cleaning of the platinum dot WE entailed hand polishing using the polishing kit from CH Instruments. The platinum dot WE was held vertically with light, even pressure and moved in a figure-eight pattern in a slurry of 0.3 μm alumina with ultrapure water for 30–60 seconds. The electrode surface was then rinsed with ultrapure water and the process repeated in a slurry of 0.05 μm alumina and rinsed thoroughly again. Electrochemical cycling was then repeated to ensure current levels had returned to expected values. The rightmost WE in Figure 20c is a 5 MHz titanium/platinum QCM electrode (QM1004) purchased from FilTech for QCM experiments. The QCM WE was cleaned via soaking in isopropyl alcohol for at least one hour and dried with N_2 immediately before use.

Sample Preparation. A green coffee named El Tambo from Cauca, Colombia was sourced from Tailored Coffee Roasters, Eugene, OR. This coffee is representative of an average specialty coffee, and costs approximately \$10/kg. The coffee was roasted in 50 g sample batches using an IKAWA Pro50. Sample batches were roasted following the roast profiles presented in Figure 23a. These roasts canvassed industrially relevant light, medium, and dark roasts (spanning whole bean Agtron values of 75.8 (lightest) to 55.7 (darkest), Table C.1). The coffee was allowed to rest for three days before being ground with a Mahlkönig EK-43 grinder (particle size distributions are presented in Figure C.1) and brewed via cupping method with a brew ratio of 1:13.5 using 93°C water (filtered Eugene

tap water using a Pentair Everpure Conserv 75E Reverse Osmosis system with remineralization to 30 mg/L CaCO_3). The coffee was allowed to contact the water for 4 minutes, without agitation or stirring. The samples were then filtered through paper and allowed to come to room temperature (21.6°C). The samples were stirred before each aliquot was taken to ensure homogeneity. The cumulative concentration of solvated coffee material (total dissolved solids as a mass percentage, %TDS) was calculated from the measured refractive index following a literature procedure.¹⁴⁵

Cyclic Voltammetry Measurements. A three-electrode electrochemical setup was employed for all voltammetric measurements. Cyclic voltammetry (CV) was performed using a Gamry 1010B potentiostat, controlling platinum working and counter electrodes, and a silver/silver chloride reference electrode, purchased from CH Instruments. Prior to data collection, the working and counter electrodes were polished using a modified literature approach¹⁴⁶ (10 scans at 300 mV/s scan rate in 50 mM H_2SO_4 , until key H_2SO_4 redox features overlaid, Figure C.2). Measurements were made directly on as-brewed coffee, with no supporting electrolyte or buffer. The bulk resistivity in all samples was found to be 700 - 2100 Ω and the pH of each solution is noted in Table C.2. Since most coffee is a solution of weak acids, the solutions are self-buffering to a pH of around ~ 5.0 , aligned with previous literature reports¹⁴⁷.

Particle Size Distribution. Particles created by the EK-43 were measured using the Malvern Mastersizer 2000 laser diffraction system. The solid samples were dispersed into an airstream (2.0 bar) of compressed breathing-quality air and passed through a laser beam of He-Ne at 633 nm and of solid-state blue light at 466 nm. The particles interfere with the laser beam and scatter the light at different angles based on their sizes. The scattered light is then detected and analyzed by

the instrument to give the particle size distribution of the sample. Ground coffee samples were run in triplicate and the average particle size distributions are plotted in Figure C.1.

Quartz Crystal Microbalance. A QCM200 Quartz Crystal Microbalance equipped with a crystal holder was used to perform all quartz crystal microbalance (QCM) experiments. Platinum liquid plating quartz crystals with a titanium adhesion layer and 5 MHz from Fil-Tech electrodes were used. The crystal holder ensures that only one side of the platinum-coated electrode is accessible to the solution and the controller reads the associated frequency. A Biologic SP-300 potentiostat with a platinum wire counter electrode and silver/silver chloride reference electrode was used for collecting CVs corresponding with QCM data. The QCM frequency data was converted to mass values via the Sauerbrey equation as follows:

$$\Delta f = \frac{-C_f \Delta m}{A}$$

where f is the frequency as read from the QCM control box, C_f is the calibration constant which is given to be 56.6 Hz·cm²/μg for the Fil-Tech electrodes, and A is the surface area of the electrode which is 0.4987 cm².

High Resolution Mass Spectrometry. To accumulate mass on the electrode surface for further analysis, a platinum mesh electrode from BASi Research Products with a surface area of 5 cm² was used as the working electrode with a platinum wire counter electrode and a silver/silver chloride reference electrode. The CV scan window was shortened to avoid the oxidation wave where most of the accumulated mass desorbed from the electrode surface. CVs were run in as-brewed coffee with about 1.5 %TDS for 50-100 cycles. Immediately upon CV cycling completion, the working electrode was removed from the sample, patted

dry with a Kimwipe, and submerged into a solution of 80% 18 M Ω ·cm² water and 20% HPLC grade acetonitrile (Sigma-Aldrich). The solution and working electrode were sonicated for 10 minutes and then the electrode was removed and rinsed. This process was repeated a total of four times to ensure that the solution contained enough redissolved residue for mass spectrometry analysis.

LC-MS analysis was performed using a Thermo Scientific system consisting of a Vanquish UPLC coupled with a Q-Exactive orbitrap mass spectrometer. The dissolved residue sample was eluted using an ACE Excel 2 SuperC18 guard column (5mm x 2.1mm, 2 μ m) followed by an ACE Excel 2 SuperC18 analytical column (100mm x 2.1mm, 2 μ m) and the column oven was set to 40°C. A water/methanol/acetonitrile/1M acetic acid gradient, at a flow rate of 0.350 mL/min was used to perform the chromatographic separation. All solvents used were LC-MS grade and included 0.1% formic acid.

Mass spectrometry detection was performed, after chromatographic separation, using electrospray ionization in positive polarity mode. Caffeine was identified as a component of the residue using a standard MS2 DDA scan method (although the DDA threshold was not triggered on the caffeine peak), scanning from 150 m/z to 1000 m/z, revealing the characteristic isotopic peak pattern for protonated caffeine (monoisotopic peak measured at 195.0885 m/z vs a calculated value of 195.0877 m/z, representing an error of < 5 ppm) corresponding to a chromatographic peak in the TIC at approximately 5.1 minutes of retention. This retention time was also consistent with that of the caffeine standards used for quantification. Quantification of caffeine was performed using a SIM method targeted from 194.5876 m/z to 195.5876 m/z, using standards with effective caffeine concentration ranging from 4 to 8 ppm, and resulted in a very linear calibration

curve. The MS instrument was set to a resolution of 70,000 for all measurements in this study.

3.1.3 Introduction. Since the 1950s, coffee consumers have sought quantitative methods to assess beverage qualities beyond those informed by sensory panels. In the meantime, the litany of research on topic has revealed that beverage concentration and bean color are the two primary and independent factors that dictate coffee sensory perception. Dry coffee color is readily determined by spectrophotometry, while the most widely used technique to measure concentration of solvated coffee relates the extracts' refractive index to an effective concentration through an empirically derived polynomial. The latter yields a value generally reported as a mass percentage of total dissolved solids, %TDS, and provides information about strength. From %TDS, the mass efficiency of extraction can then be estimated (i.e., extraction yield). The industry coalesced around the phenomenological observation that dissolution of 20% of the dry mass, yielding a beverage approximately 1.4 %TDS generally produces an enjoyable cup of filter coffee. To date, measurements based on refractive index remain the industry standard despite the refractive index depending on chemical composition, which depends heavily on bean color, which in turn depends on brewing parameters (e.g. temperature, time, grind setting, etc.¹⁴⁸ — a complex thermodynamic and kinetic parameter space. The existing approach cannot discern differences between light and dark coffees with the same refractive index, let alone higher fidelity chemical differences. A quantitative method that reports chemical-specific information beyond %TDS remains a major target for the industry.

There exist numerous other chemical-specific analytical techniques that provide both qualitative and quantitative information about chemical composition,

with the gold standard being chromatography coupled with mass spectrometry. Besides the obvious challenge of identifying which compounds are giving rise to a sensory experience, these techniques also suffer from slow run times, high costs, and yield limited predictive insights. Instead, some research groups have pursued the application of electrochemistry to probe the concentrations of common families of molecules in solution. While this approach is generally sensitive enough to accurately measure the solvated concentration of caffeine, chlorogenic acids, and other molecules, the previous reports have omitted strength in their analyses, precluding the development of a technique which relates preparation variables (e.g. mass of coffee, mass of water, grind setting, water temperature and pressure, contact time, roast color etc.) to the resultant chemical composition of the liquid. Herein, we report a significant advance in coffee quality analysis by demonstrating that a reductive electrochemical feature in unbuffered aqueous cyclic voltammetry of brewed coffee directly correlates with roast color, and the same feature is linearly related to strength (i.e. %TDS). Our electrochemical descriptor of these two coffee qualities provides both qualitative and quantitative insights that reach beyond the limitations of %TDS deduced from a refractive index.

3.1.4 Results and Discussion. Initially, we sought to directly measure the concentration of caffeine ($E_{\text{ox}} = +1.3$ V vs. Ag/AgCl), chlorogenic acids ($E_{\text{ox}} = +0.6$ V vs Ag/AgCl), and other redox active species in undiluted samples, and study their dependence on conventional brew parameters. However, caffeine and chlorogenic acids form an aggregate which terminally impacts their redox activity — they only become well-resolved in acidified, extremely dilute solutions (< 0.01 %TDS) with supporting electrolyte. Other groups have shown that with those adulterants, both boron-doped diamond and glassy carbon

electrodes can provide molecule-specific information,^{41,149–157} but since the primary goal is to instead measure features of as-consumed coffee, we ran exploratory CVs using boron-doped diamond, glassy carbon, and platinum across the range of potentials afforded to liquid coffee, Figure 21a.

As-consumed coffee extracts are reasonable conductors (700–800 Ω resistance), and are self-buffered to pH of ~ 4.8 – 5.2 depending on bean and brewing water composition.¹⁴⁷ Yet, despite the plethora of molecules in coffee extracts, the CV response for a Pt working electrode in 1.56 %TDS coffee is consistent with that of acidic water, Figure 21a.^{158–162} The same is true for coffee extracts at espresso strength (8–12 %TDS). The oxidative Faradaic features map to the response expected for hydrogen adsorption at potentials below H_2 formation (hydrogen underpotential deposition, HUPD) followed by H_2 evolution at negative potentials. At positive potentials, OH adsorption and eventual O_2 evolution are also evident.

The same Pt-surface sites that adsorb water derivatives are also able to physisorb other molecules in solution. In the case of oxidative cycling, some impurities in water compete for the Pt surface resulting in reduced current with subsequent cycling due to limiting the accessible surface area for hydrogen adsorption. Given that Pt is known to interact with caffeine and other molecules in coffee,^{163,164} we expected to see a corresponding decrease in current with sequential cycling. Indeed, the effect was observed, where when scanning from 0 to -1.0 V, the two HUPD features ($E = -0.4$ and -0.7 V) smear together and current decreases with each subsequent scan,¹⁶⁵ Figure 21b. The integrated HUPD feature decreases by $\sim 34\%$ from CV scan one-to-two and $\sim 18\%$ from scan two-to-three.

Further experiments were run to ensure that these features mapped to HUPD variables associated with coffee, rather than fluctuations in dissolved oxygen

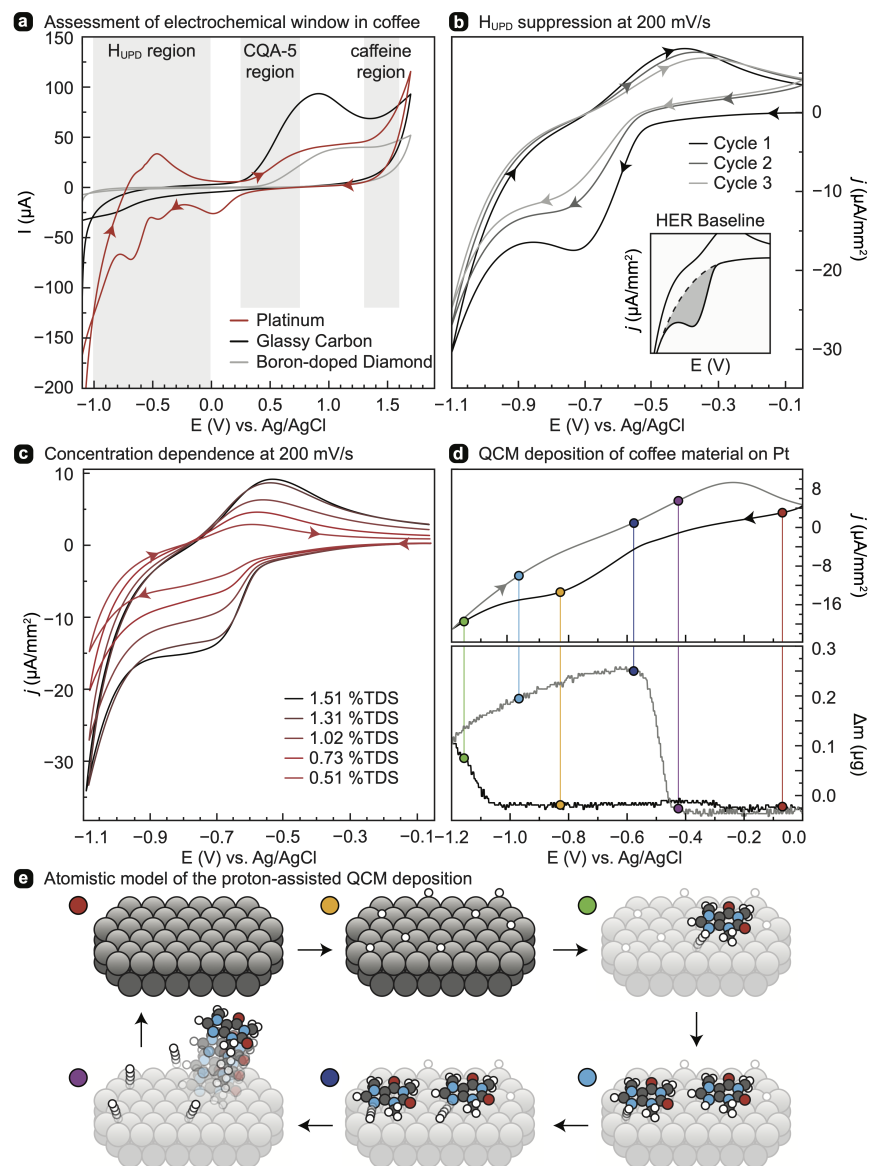


Figure 21. Assessing the voltametric features present in coffee extracts.
a) Cyclic voltammetry performed at 200 mV/s using boron-doped diamond, glassy carbon, and platinum working electrodes. Previously studied potential regions are highlighted in grey and red. The hydrogen underpotential deposition (H_{UPD}) region is highlighted in blue. **b)** H_{UPD} is suppressed with subsequent CV cycling due to deposition of coffee material on the surface of the electrode. **c)** The H_{UPD} region depends on %TDS of the brewed coffee. **d)** Reductive scanning results and mass accumulation on the working electrode, leading to electrode fouling. **e)** Atomistic representation of proton-assisted deposition of coffee material onto the platinum electrode surface.

and other effects, Figure S1. Since the integral of the charge passed depends on activity of protons, the HUPD features indirectly provide insights into the families of molecules in solution, which should depend on roast, brew parameters, and so forth. One proof of this is that HUPD current density decreases with decreasing coffee concentration, Figure c21, due to the reduced number of available protons, and fewer organic molecules competing to bind to the surface of the electrode. As we will show later, the integral of the charge current density of this feature linearly maps to %TDS, but for now we can simply appreciate that HUPD are concentration dependent.

To further support our mechanism that HUPD is being suppressed by adsorbed coffee material, we performed CVs with an electrochemical quartz crystal microbalance (QCM) with a platinum working electrode scanning at 50 mV/s, Figure 21d. Scanning oxidatively, appreciable mass begins to accumulate on the electrode at potentials more negative than HUPD — the balance is insensitive to surface H-adsorption but can detect larger molecule accumulation. Upon cycling back, mass continues to accumulate until the potential falls below -0.5 V, when the electrode liberates most of the adsorbed material back into solution.

Thus, cycling experiments can be designed as to maximum mass accumulation on the electrode, to then be characterized using spectrometric techniques. By cycling 50-100 times from -0.55 to -1.2 V, Figure 22a, sufficient coffee residue was accumulated. The material was then redissolved into a fresh solution of 4 mL of 80% water and 20% acetonitrile. This process was repeated four times to ensure a sufficient amount of material was redissolved in the solution which was then analyzed using liquid chromatography coupled with high-resolution mass spectrometry, Figure 22b. There, a variety of molecules including caffeine (7.3

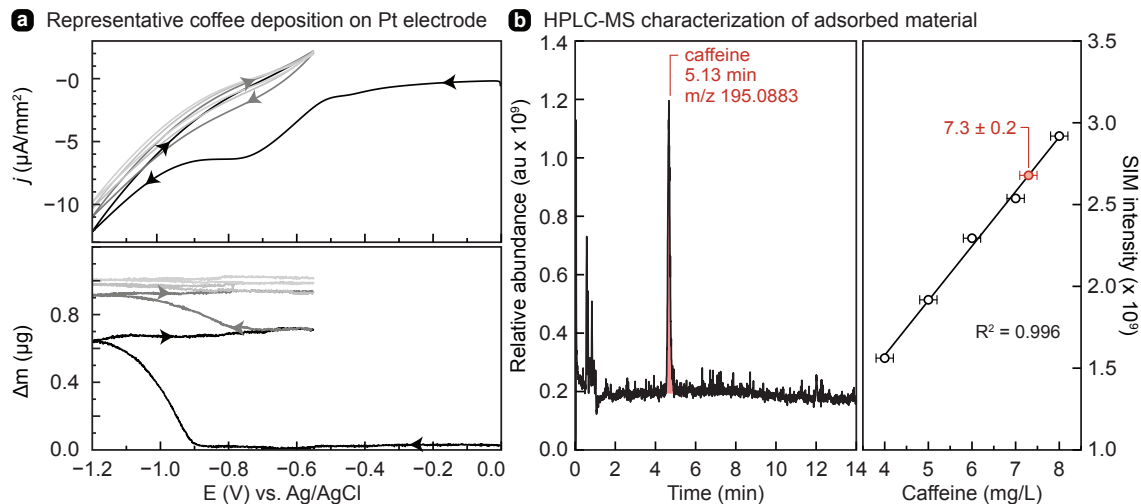


Figure 22. Mass accumulation and determination of Pt-surface adsorbed species. **a)** CV cycles with shortened scan window (upper) and the associated QCM mass increasing (lower). Only four cycles have been shown for clarity; experimental conditions involved 50-100 cycles. **b)** HPLC-MS chromatogram of coffee material collected from QCM electrode showing caffeine present with associated calibration curve of caffeine.

± 0.2 ppm) were detected, suggesting that indeed the electrode gained mass from the coffee material.

To explore using electrochemical analysis as a measure of brewed coffee quality, we roasted a representative specialty coffee sourced from Ethiopia in-house to different degrees and took CVs of each sample. Figure 23a shows the roast profile used for each sample. We chose a simple roast profile with each subsequent sample increasing in overall time by 30 seconds and in final temperature by 2°F . The final sample increase was doubled to 60 seconds overall time and 4°F to ensure that the range of samples covered a reasonable range of gourmet Agtron values. Agtron numbers are used in the specialty coffee industry to describe the intensity of roasted coffee. For the gourmet coffee scale, Agtron values range from 0, extremely dark, to 150, unroasted or green and are given as unitless values. The roast profiles used gave whole bean Agtron values starting at 75.8 (light) for Roast 1a and

ending at 55.7 (dark) for Roast 1f. Following in-house roasting, each sample was rested to allow for CO₂ off-gassing. Each roasted sample was brewed according to cupping technique and then diluted to 1.00 ± 0.02 %TDS. The first CV cycle of each diluted sample can be seen in Figure 23b. As is visible, the overall area of the CV reductive wave decreases with increasing roast degree. Integration of the HUPD reductive wave for each sample supports this visual observation and, in fact, the integrated area decreases by almost 48% between sample 1a to 1f. Therefore, our data supports the use of CV analysis as a novel technique for determining roast differences in a given coffee at the same %TDS.

To further support the use of CV HUPD reductive wave analysis to determine differences in brewed coffee according to the roast degree, each sample was diluted to several different %TDS values and the total charge passed in the HUPD reductive wave during the first CV cycle was calculated. The resulting fit of total charge passed versus %TDS is presented in Figure 23c. Each roast sample shows a linear fit with an R^2 value above 0.9. Notably, the resulting linear slopes decrease with increasingly darker roasts, with a change of 34% between the slope of sample 1a and 1f. Figure 23d combines the total charge passed and %TDS with the whole bean Agtron values to create a predictive landscape tying total charge passed to Agtron number. This thereby yields a new means of resolving differences in roast degree, and therefore coffee quality, which %TDS alone cannot provide.

3.1.5 Conclusion. In this work, we have provided a novel method of assessing coffee quality, specifically roast degree, through a rapid, in-situ, electrochemical technique that expands upon the information regularly provided by %TDS measurements. We find that cyclic voltammetry is an appropriate technique for brewed coffee at as-consumed concentrations and that the HUPD features

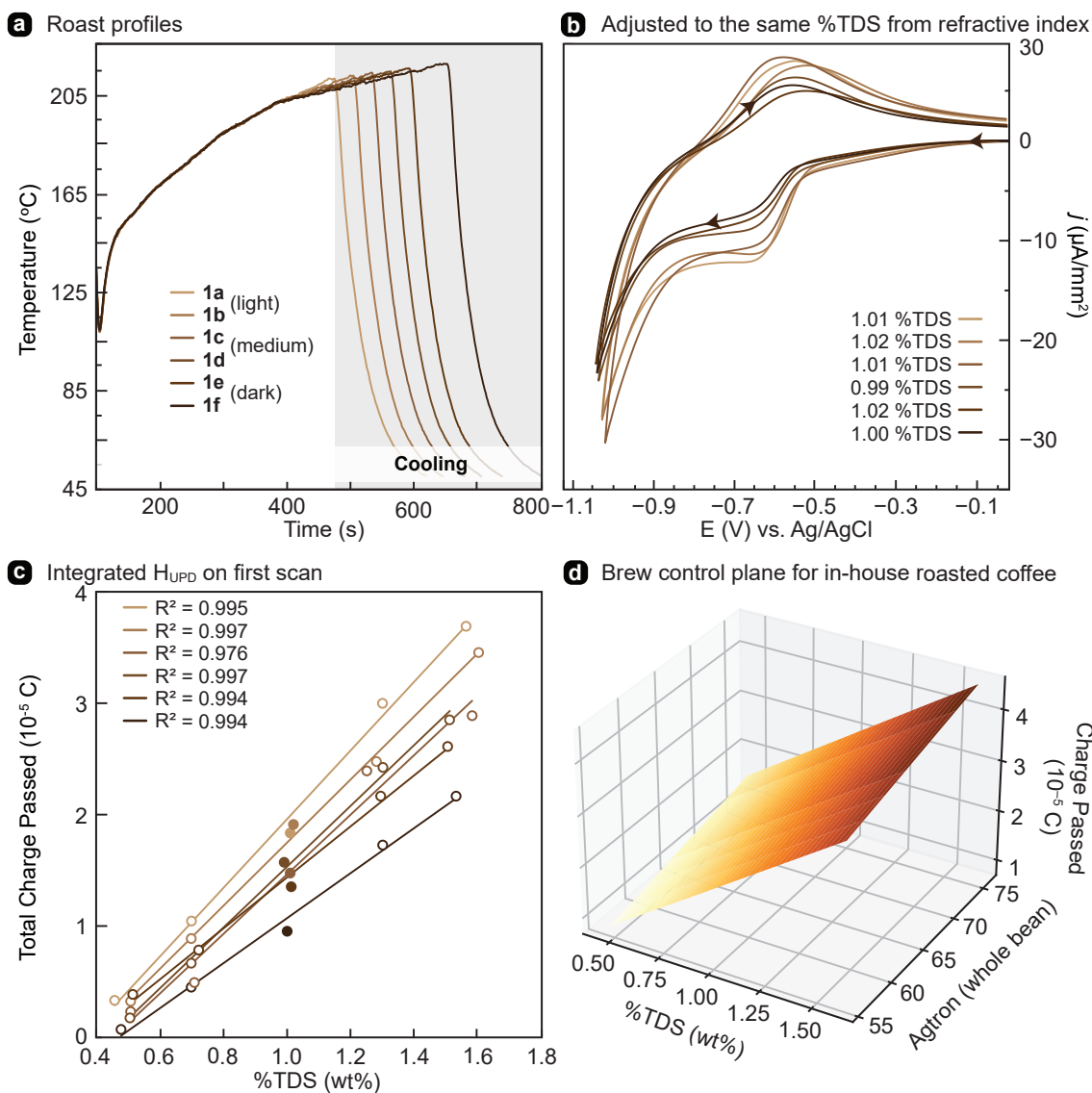


Figure 23. Relating roast profile to hydrogen underpotential deposition suppression. **a)** The temperature profiles used to generate six systematically darker coffees. **b)** The electrochemical response for identically brewed coffee diluted to ~ 1 %TDS. **c)** Subtracting the background hydrogen evolution, the total charge passed is linear with %TDS, but depends on roast color, with darker roasts more effectively suppressing HUPD. **d)** Plotting the total charge and %TDS against the whole bean Agtron value (roast color) to create a “brew control plane” for our in-house roasted coffee.

seen are proportional to the concentration of the sample. HUPD suppression is seen in the form of fouling with subsequent CV cycling due to molecules from the coffee, including caffeine, adhering to the platinum electrode surface. The HUPD reduction wave is also suppressed in coffees with lower concentrations, despite the pH remaining essentially constant, due to increased resistance of the coffee samples. We also find that the HUPD reductive wave integrated area and the slope of the linear fit of total charge passed versus %TDS both decrease with darker roasted coffee. Furthermore, we find that the total charge passed can be related to both the %TDS of the brewed coffee and the Agtron value of the roasted whole beans.

CHAPTER IV

IMPACT OF BREWING PARAMETERS

4.1 A Universal Voltametric Model for Designer Coffee

4.1.1 Author Contributions. The study was conceived by BA, REB, and CHH. Coffee samples were prepared and cyclic voltammetry measurements were performed by REB. Laser diffraction measurements were performed by EJR. Data analysis was performed by REB and BA. REB, BA and CHH wrote the manuscript and all authors contributed to the final version.

4.1.2 Methods. While there are expected differences in chemical composition depending on origin, processing method, and roast, the compounds formed are generally products of the Maillard reaction. Thus, instead of characterizing all compounds in a particular coffee, there is greater value in finding measurables that translate between coffees independent of the bean-related variables. Thus, to be deliberately accessible, we opted to use Starbucks Pike Place blend for this study but note that the approach and results apply to any coffee. Here, the coffees were brewed using the SCA cupping protocol. The coffee (8 or 16 g) was ground on a Mahlkönig EK43, equipped with stock coffee burrs (grind size 8 or grind size 16, see Figure S1 for particle size distributions^{53,166,167}), and placed in a porcelain bowl. The brew water (100 or 150 mL) was produced by filtration through a Pentair Everpure Conserv 75E reverse osmosis system with remineralization to 30 mg/L CaCO₃. The water was heated (to either 70 or 100 °C) and then brewed undisturbed for 2 or 5 min. To arrest the brewing, we filter the coffee through a Hario V60 bleached and tabbed filter paper, into a fresh room-temperature porcelain cup.

Refractive index and subsequent TDS were measured using three commercially available handheld devices (manufactured by Misco, DiFluid, and Atago) following the protocol of filtration through a 20 μm filter, followed by cooling to ambient temperature before measuring. Three devices were included to ensure transferability between common handheld devices used in the industry, see Figure S1. The remaining coffee for each run was transferred to a 20 mL scintillation vial for electrochemical analysis.

Cyclic voltammograms (CVs) were performed using a Gamry Interface 1010B potentiostats, using a three-electrode configuration (platinum button working electrode, a platinum wire counter electrode, and a silver/silver chloride (Ag/AgCl) counter electrode, sourced from CH Instruments). Electrodes were cleaned between each coffee sample by cycling from -1.1 V to 1.1 V at a scan rate of 1000 mV/s for 30 cycles in a 50 mM H_2SO_4 solution. Following cleaning, the electrodes are rinsed with ultrapure water (18 $\text{M}\Omega\cdot\text{cm}$), then with pure acetone, and finally dried with a Kimwipe. The CVs of the unmodified samples are obtained from 0 V to -1.1 V at a scan rate of 200 mV/s for a total of three cycles. CVs were analyzed in OriginPro. Adjacent-average baseline correction was employed to separate the redox features associated with the coffee and, separately, water splitting. Key variables, including peak center (E_p), integrated wave area (A), full-width-half-max (δE), and maximum current (I_p), were then measured.

To measure the impact of brew parameters on the CV features and refractive index-based %TDS of brewed coffee, we employed a screening factorial experiment, in which we varied five factors — brew time τ , water temperature T , coffee bean mass m_b , grind setting g , and water mass m_w — at two levels each. We performed a full 2^5 factorial experiment, with 32 total runs. The factor levels

and randomized run order are shown in Table S1. The data were modeled with a categorical effects model that included up to four-factor interactions,

$$\hat{y} = \beta_0 + \sum_{i=1}^5 \beta_i x_i + \sum_{i \neq j}^5 \beta_{ij} x_i x_j + \sum_{i \neq j \neq k}^5 \beta_{ijk} x_i x_j x_k + \sum_{i \neq j \neq k \neq l}^5 \beta_{ijkl} x_i x_j x_k x_l$$

where $\hat{y}$ is the predicted response, β_0 is the mean response, β_i is the main effect coefficient for the i th factor x_i , β_{ij} , β_{ijk} , and β_{ijkl} are the two-, three-, and four-factor interaction coefficients, respectively. The models were reduced by using an analysis of variance (ANOVA) framework to remove statistically insignificant effects and interactions with an $\alpha = 0.05$ cutoff. We retained insignificant coefficients only when needed to preserve model hierarchy. We then verified the ANOVA modeling assumptions, including normal, independently distributed residuals, and equality of variance (see SI). The analysis quantifies the relative strength of each factor (main effects) and factor interactions (higher-order effects), and determines which factors have no significant effect on the response.

4.1.3 Introduction. The coffee industry generates an annual revenue greater than \$340 B— 1.35% of the United States gross domestic product. At its core, the market is sustained by persistent human enjoyment of the beverage. However, coffee separates itself from most other beverages as it is often prepared at the point of consumption, introducing a high degree of variability. In these ranging preparations, variability in coffee qualities potentially harm the sector, where its growth is driven by predictable and targeted flavor presentation. Tools have been developed to provide insights into coffee quality², and causal relationships have been posited (e.g., increasing brew time typically increases the refractive index of the extract). In that case, total dissolved solids (%TDS, a measure of coffee concentration reported in weight percent) is then computed from an empirically parameterized polynomial and does not depend on any particular

molecule or family of molecules, but rather the ensemble impact on the bulk liquid refractive index¹⁶⁸. While useful for concentration of liquids with known compositions^{169,170}, the technique presents limited value in complex liquids^{171–173} as it cannot provide compositional information, and the composition is highly sensitive to brewing variables. Alternative chromatography-coupled measurements^{17,21,174–179} are intractable in the café setting. Thus, the industry desires a novel approach to measure brewed coffee composition and concentration, while also enabling predictable coffee preparations.

Here, we demonstrate that by varying a five-factor coffee brewing parameter space (brew time, mass of coffee, mass of water, temperature of water, grind size), we can use voltametric measurements to directly probe the composition and concentration of a family of compounds¹⁸⁰ that capture nuanced differences in coffee flavor and their dependence on brew parameters. Unlike other efforts to do the same^{30–32,41,154,181}, our approach requires no sample preparation allowing for direct comparisons of both concentration and composition of coffees brewed in different ways¹⁸². Further, through a careful design of experiments we observe hitherto unprecedented variable interactions, and develop a model to enable predictive coffee brewing, simultaneously allowing for parameter optimization (e.g. minimizing coffee waste) and flavor prediction and measurement.

4.1.4 Results and Discussion. When electrochemically sampling coffee beginning at 0 V and cycling thrice to +1.5 V and back to -1.2 V, filter coffee exhibits redox features attributed to processes associated with hydrogen underpotential deposition (HUPD, Faradaic features appearing between 0 and -1 V when scanning reductively, Figure 24a). In a prior report, we showed that the suppression of HUPD was attributed to organic molecules adsorbing to the surface

of the electrode, blocking the HUPD features. By beginning at 0 V and scanning reductively to -1.1 V, the features homogenize (Figure 24b), and a single broad redox feature can then be extracted using an exponential, interpolated baseline, to reveal the peaks associated with reductive H^+ deposition (Figure 24c). From these data, the maximum current (I_p), integrated area (A), full-width-half-max (δE), and peak center (E_p) are recovered. These features are highly sensitive to the electrode environment and should also directly relate to the concentration of both solvated H^+ and the compounds that preferentially bind to the electrode surface, as well as other heterogeneities associated with the measurement.

To establish the link between the HUPD features in each of the three CV scans and the %TDS as determined from the refractive index, we performed a correlation analysis. Figure 25a shows a clustered multivariate correlation matrix comparing %TDS, E_p , A , I_p , δE for each of the three consecutive CV cycles as well as the difference between cycles (e.g., max current from cycle 1 minus cycle 2, $I_{p1} - I_{p2}$). The data show strong, significant mutual correlations ($|r| \approx 1$, $P \ll 0.05$; see Table SX for numerical correlation statistical values and P-values and Figure SX for full correlation matrix r/P -value heatmap) between %TDS and current-related features including I_p , A , and associated cycle differences. Near unity correlations are established for %TDS and δE for all three consecutive CV cycles and with the cycle differences in total charge passed (A), indicating that %TDS is closely related to total charge passed between cycles and also the full width half max of each individual cycle, indicating that it does not matter which cycle one chooses to use for subsequent sampling, so long as it is consistent. Anticorrelations near negative one (blue) were found for %TDS compared with A and I_p for all CV cycles and %TDS showed correlation near zero (grey) when compared to

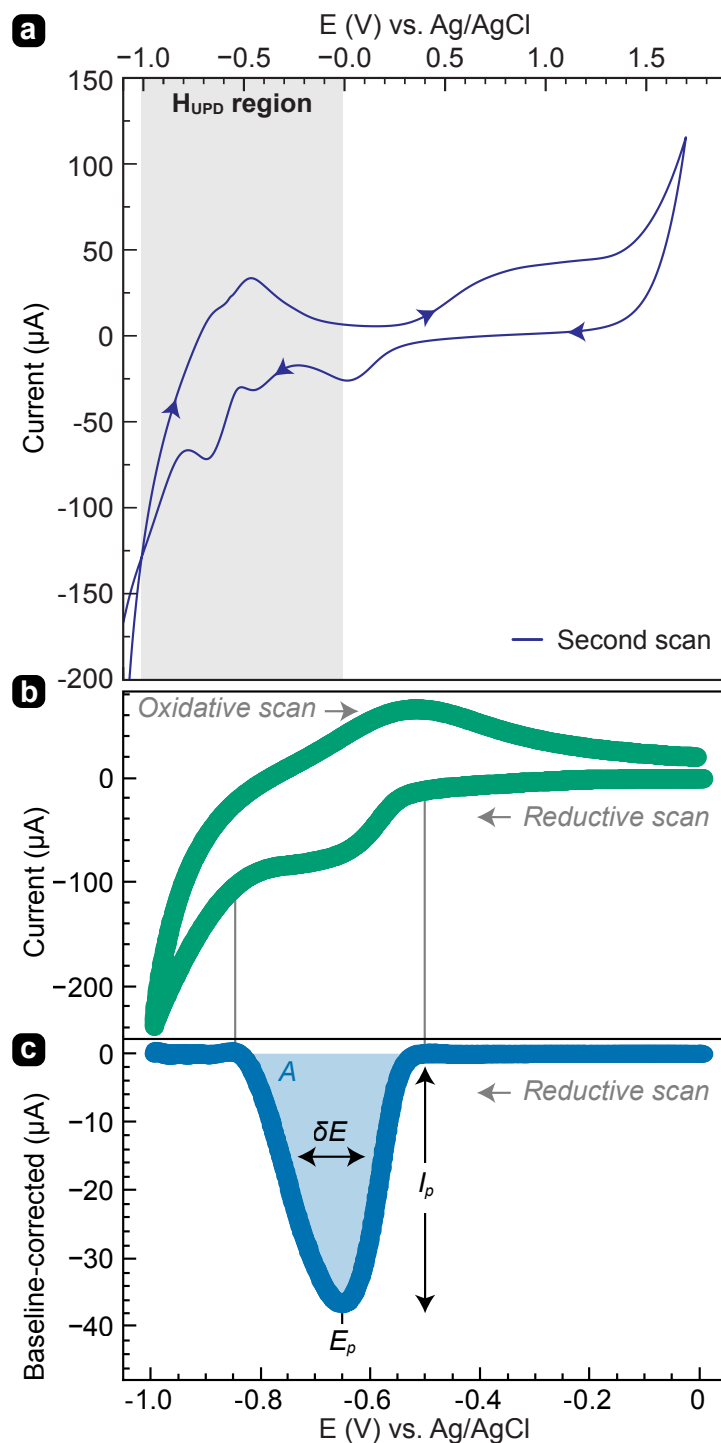


Figure 24. **a)** A typical electrochemical response of filter strength coffee exhibits features like bulk, contaminated acidic water, Pt—Pt—Ag/AgCl. **b)** Beginning at 0 V and cycling reductively to -1.1 V, the hydrogen underpotential deposition feature is probed. **c)** The corresponding background-subtracted reductive feature. Key electrochemical features are labeled.

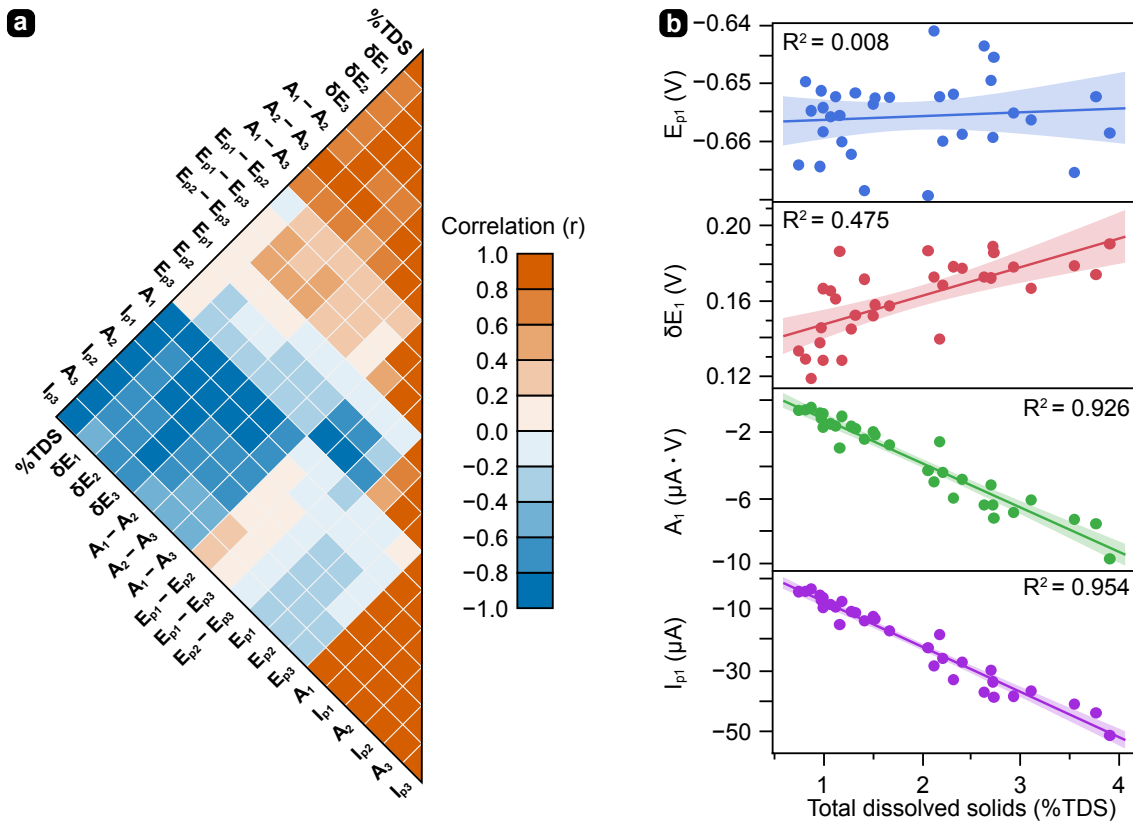


Figure 25. **a)** Clustered multivariate correlation matrix for CV feature vs. %TDS. The heat map represents the statistical correlation r with positive correlation in red and negative in blue, which have been clustered by correlation. **b)** Scatterplots of I_{p1} , A_1 , δE , and E_{p1} vs. %TDS for the entire factorial data set. Linear fits are shown as solid lines with the shaded region giving the 95% confidence interval. The R^2 values for the linear fit are also provided for each plot.

individual and cycle differences of E_p . Figure 25b shows scatter plots of CV features correlated with optical %TDS over 32 measured samples as described in the Methods section, for the ranges discussed in the Appendix D.

From Figure 25b, a strong correlation between %TDS and either A_1 or I_{p1} indicates that either may be used as a novel, electrochemical method to measure %TDS of brewed coffee. While the correlation between optical %TDS and δE is linear, the decreased R^2 value indicates that only about half of the variation in the measured samples can be explained by the relationship with optical %TDS.

Interestingly, E_{p1} shows zero correlation with optical %TDS, indicating E_p impacts a part of coffee brewing which is not captured by traditional optical %TDS instruments but is captured using our electrochemical characterization.

Since the peak center of the HUPD feature is shifting with varying brew parameters but is uncorrelated with %TDS as reported from a refractive index measurement, we sought to determine which brew factors are impacting the chemistry of the resulting coffee. To do so, we varied the five brew parameters discussed in the methods and modeled their influence on %TDS and CV features (I_p , A , δE , and E_p for each scan). Figure 26a shows the individual brew factors and their interactions from each reduced model with 1% error or less. Each individual brew factor, as well as the interaction between brew time and grind size, were found to be statistically significant in creating the model for %TDS. Here %TDS values were reported logarithmically to normalize residuals for modeling purposes. I_{p1} and A_1 models showed similar dependence on the individual brew factors but also had significant contribution from the interaction of bean and water masses used in the brewing. The bean mass*water mass interaction being significant in the models for both I_{p1} and A_1 , but not for %TDS indicates that these electrochemical variables are more sensitive to changes in composition.

Modeling factors show a marked change for δE , where the only individual brew factors significant below 1% error are bean amount and grind size. Surprisingly, however, the four-factor interaction of time*temperature*bean mass*water mass was found to have significance in the δE model. The significant factors in the model of E_{p1} no longer include water mass and include more multi-factor interactions than the other examined features. Given that the models reveal significant interactions that evade the %TDS approach, the electrochemical

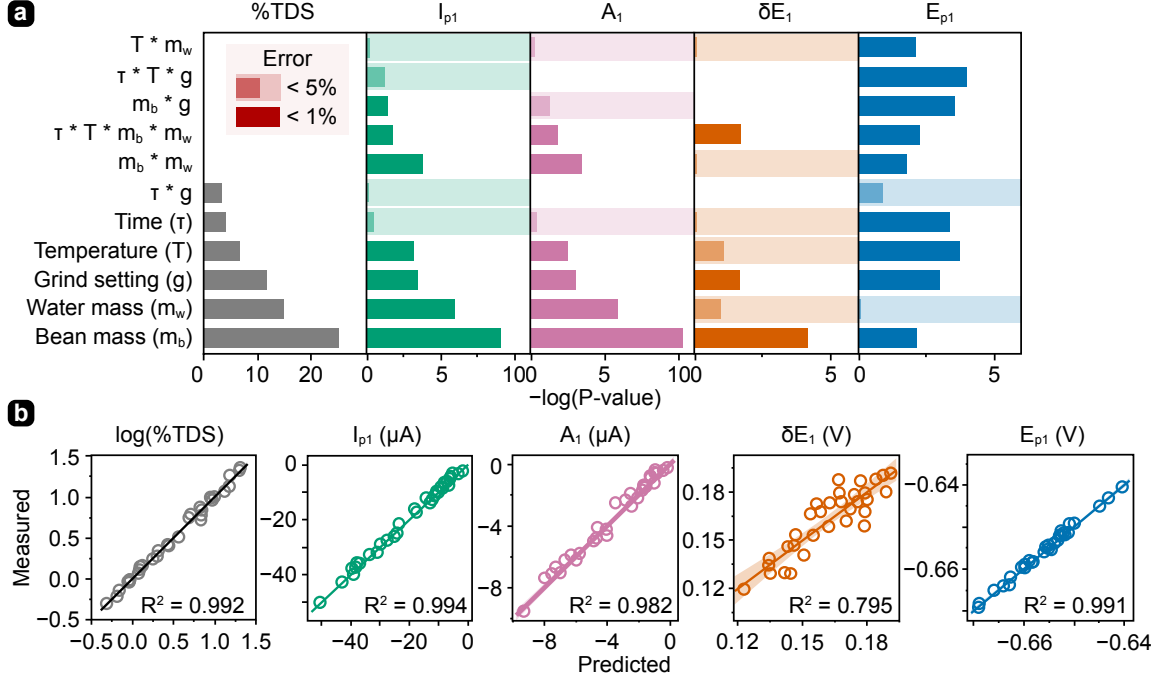


Figure 26. a) Full-effects reduced models for %TDS, I_{p1} , A_1 , δE , and E_{p1} . Each plot shows the $-\log(\text{P-value})$ for sources of the full-factorial experiment, including factors m_b , m_w , g , T , and τ . The plots were filtered to retain sources that had a significance error of $\alpha = 1\%$ (i.e., $-\log(\text{P-value}) = 1$) for at least one response variable (e.g., %TDS); hatched filling indicates sources above $\alpha = 5\%$ (emphasized with transparent boxes). The full reduced model parameter analysis is provided in Appendix D. The %TDS model was transformed to stabilize the variance using $\log(\%TDS)$. *b)* Scatter plots of the measured response versus the predicted response for $\log(\%TDS)$, I_{p1} , A_1 , δE , and E_{p1} using the respective reduced models.

approach described herein is capable of both providing %TDS information through examination of I_p and A , as well as higher fidelity compositional information through δE and E_p .

Figure 26b shows the correlation of the measured values and the predicted values from the model for each of the variables examined. Each of the models have a correlation above 90% except that of δE which has a correlation of almost 80%, meaning that our models provide robust and effective predictive capabilities for analyzing CV features within the conventional coffee brewing parameter space while conclusively showing that simple examination of I_p in the HUPD region is an effective way to measure %TDS and provide rich compositional information beyond concentration alone.

To better understand the influence of individual brew parameters on the resulting electrochemical features, we examined the directionality of the effects plots with respect to the measured variables, Figure 27. Increasing m_b , T , and τ all result in increased %TDS over the large brewing parameter space. This is to be expected, as increasing the dry coffee mass beans should increase the strength of the extract (%TDS). Similarly, increasing temperature increases %TDS, suggesting that the ensemble coffee extraction is endothermic. Additionally, increased brew time permits further solvation of coffee material, increasing strength. Complementary to these data, increasing the mass of brew water and increasing average particle size by grinding coarser both result in decreased beverage strength. These directionality trends seen for %TDS are mirrored in the trends for I_{p1} and may be understood by interpretation of the species partaking in its reduction feature from Figure 24. Since the reduction wave is associated with HUPD on the platinum electrode surface, changes in brew parameters which influence either the

pH, the populations of organic molecules that preferentially bind etc. will manifest as differences in the potential center and current passed. Thus, the relationships between coffee variables and their impact on %TDS is the same as their impact on I_{p1} . A similar trend is observed when examining the full-width-half-max, δE . For example, increasing g decreases δE , likely because more coffee leads to a wider distribution of available compounds in the brewed coffee due to bean-to-bean variation and increasing the coffee particle size decreases overall extraction. Interestingly, however, we find that increasing m_w , T , and τ yields no statistically relevant change in δE .

Interpretation of the effects plots for E_{p1} is less trivial, as electrochemical factors such as electrode surface morphology, electrode surface coverage, mass transport effects, and electrolyte composition and other heterogeneities may influence the peak center of the HUPD feature, E_p ^{183,184}. In our case, we use a polycrystalline Pt button electrode, and surface facets have dissimilar energies of binding adsorbates thereby blocking some exposed facets preferentially over others, see Appendix D for some examples from Density Functional Theory. A similar outcome could be due to a shift in the populations of organic acids in solution, affecting the free proton concentration subtly (below the detection limit of a pH probe). Regardless, a similar effect was observed in prior work where we demonstrated that a variety of molecules are adhering to the working electrode surface during CVs. Instead of examining all possible origins, we find that a simple model of heterogeneity explains the variations in the experimental response of E_p . We can assume that changes in common brewing parameters result in different chemical compositions; an assumption which is supported by the human tongue and other careful quantitative experimentation¹⁸⁵. One such example is the comparison

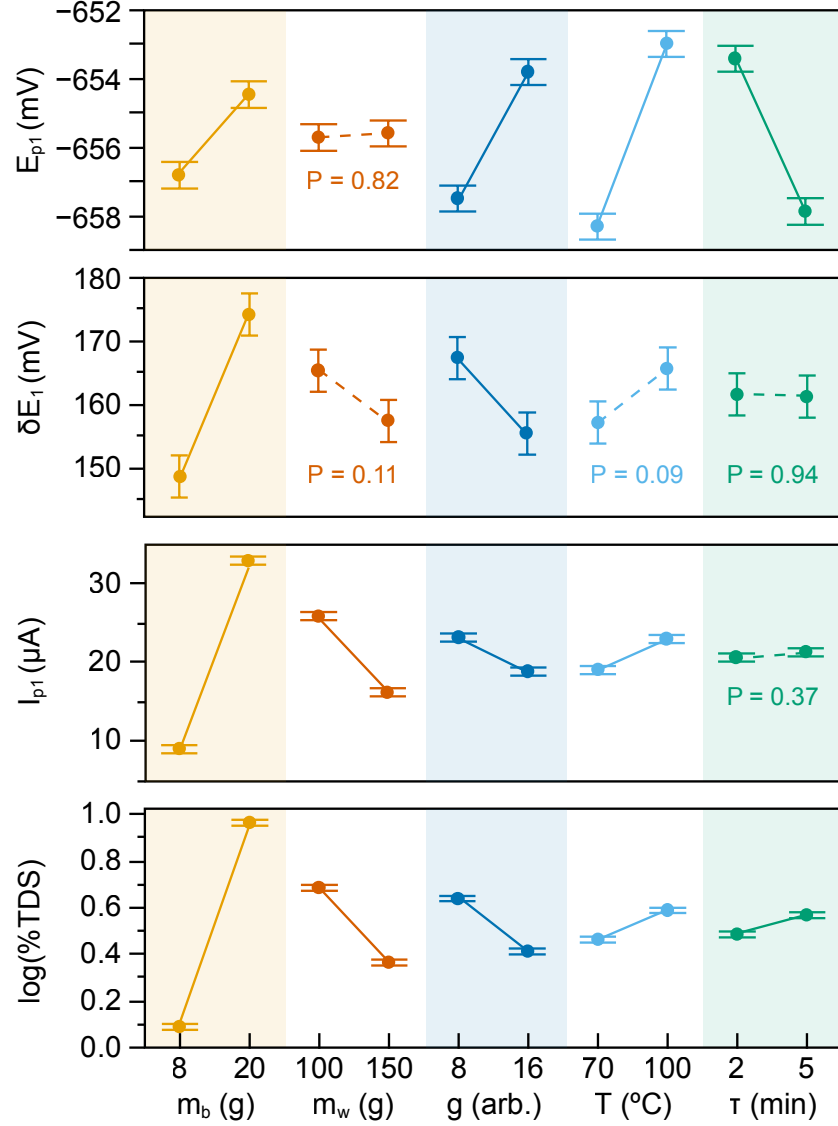


Figure 27. Effects plots for the measured variables $\log(TDS)$, I_{p1} , and E_{p1} with respect to the main experimental factors m_b , m_w , g , T , and τ . The I_{p1} data shows the magnitude of the current; the raw values have a negative sign. The levels for each factor are indicated above the factor label (e.g., m_b levels are 8 g and 20 g). Centers correspond to the mean and the error bars indicate the standard error, which for $\log(TDS)$, I_{p1} , and E_{p1} plots are approximately 0.01, 0.5 μA , and 0.0004 V, respectively. All effects are significant below $P = 0.01$, except those with means connected by a dashed line, whose P -value is given below the effect.

of the four most abundant acids in brewed coffee: chlorogenic acid, quinic acid, citric acid, and acetic acid¹⁸⁶. Each of these acids has a pK_a value of approximately 4. Using a model, varying concentrations of these four acids — which can be experimentally achieved in several ways — can give similar shifts in E_{p1} and δE as those found in this data.

To this point, we have only considered the interactions gleaned from direct measurements of a single CV made on neat coffee samples. However, repeated cycling results in the accumulation of coffee material on the electrode surface. The rate of accumulation depends on a multitude of parameters (including molecule identity, concentration, pH, scan rate, electrode composition, and so forth). Rich information is captured through comparison of electrochemical features from each iteration. Cycling from 0 V to -1.1 V at 200 mV/s results in the HUPD reduction feature decreasing both in I_p and A , while becoming slightly wider in δE , and more negative in E_p , as can be seen in the leftmost panel of Figure 28. A total of three consecutive CV cycles were run for each sample in the five-factor experiment. The scans for the samples with the smallest and largest shifts are presented in Figure SX. The data show the largest difference in CV cycles is between cycle one and two for all electrochemical features, except δE which has no cycle-to-cycle dependence. The cycle-to-cycle decreases observed in both I_p and A are due to differing conditions at the electrode surface during voltammetric cycling. Cycle one is performed on a freshly cleaned electrode and is immediately fouled by the adsorption of coffee material present in the sample, suppressing the observed HUPD reduction wave. However, the rate of fouling decreases after the initial partial surface coverage, leading to the smaller decreases between cycles two and three. The shift in E_p values is found to be significant for all three cycles, indicating that

it is more sensitive to changes in the electrode environment than I_p or A . It is small differences in electrolyte composition – in this case the composition of the brewed coffee itself – and in the molecules fouling the electrode surface which can be discerned through analysis of E_p .

The middle panel of Figure 28 presents the t-ratio between cycles as indicated for paired t-tests. Colored dots that fall on or right of the grey line have a 5% error or less while those on or right of the red line have an error of 0.01%. All paired CV cycle comparisons have an error of about 0.01% for I_p , indicating that changes in maximum current are all statistically significant in paired t-tests. The final panel indicates the fractional change in percentage between paired CV cycles according to the following equation:

$$\frac{I_{p3} - I_{p1}}{I_{p1}} \times 100 = \% \text{Fractional Change}$$

where I_{p3} is the measured variable from the final CV cycle, and I_{p1} is the measured variable from the initial CV cycle. The rightmost panel of Figure 5 shows that the average fractional change between I_{p1} and I_{p3} is about 40%, while that between I_{p1} and I_{p2} is about 30%, and that between I_{p2} and I_{p3} is about 20%. As might be expected due to their physical relationship, A follows very similar trends to I_p . We see decreasing A with cycle number and the connecting letters report indicates that while A_1 and A_3 are distinct, A_2 cannot be distinguished from either A_1 or A_3 . The paired t-test ratios are all above 0.01% error and the fractional changes range from about 38% to about 25%. The changes in δE are more subtle and cannot be found with a simple ANOVA or connecting letters report. However, the paired t-ratios show that there is a small but significant widening of the reduction wave with increasing CV cycle, also supported by the

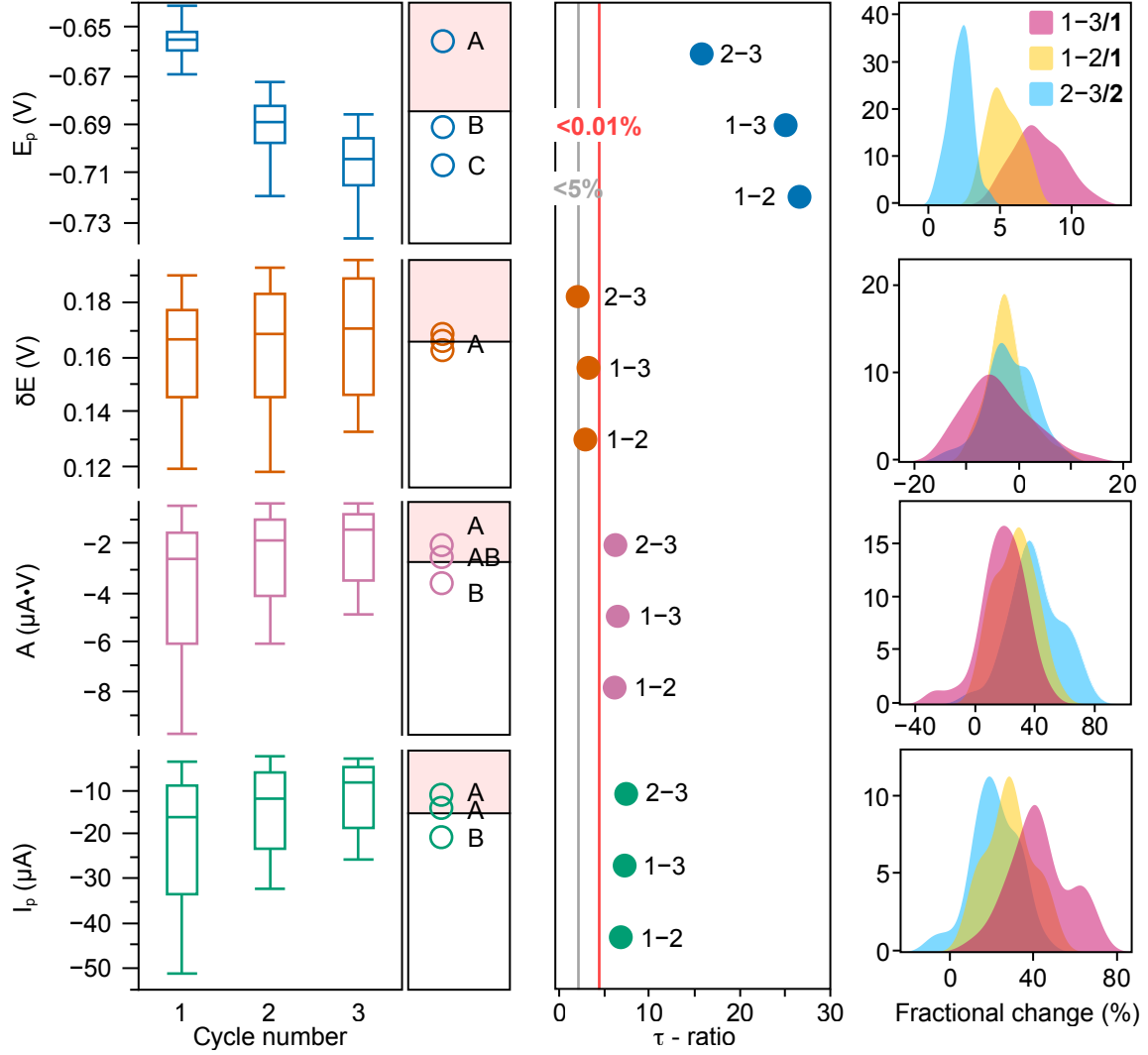


Figure 28. The vertical lines are t-test cutoffs with $N = 32$ for $(\alpha = 5\%, t_\alpha = 2.04)$, $(\alpha = 0.01\%, t_\alpha = 4.48)$. Tukey-Kramer HSD test with 95% confidence rings using family error; circles overlapping with circle centers are not statistically significant below 5%; connecting letter reports: same letter is the same group. Kernel density plots for cycle-to-cycle fractional differences with smoothness factor set to zero; color coding indicates cycle differences as follows: $i'' - j/i$, where i and j are cycle numbers. So $1'' - 2/1$ for E_p data is the distribution for fractional difference $(E_{p1} - E_{p2})/E_{p1}$.

fractional change median values. The biggest change seen by CV cycle can be seen in E_p which becomes increasingly negative with subsequent cycles. Each cycle is distinct in the connecting letters report and the paired t-ratios are all well below 0.01% error^{183–186}.

Of the examined CV features, the most statistically significant differences are found in E_p , as seen in the cycle number differences, each of which is distinct in the connecting letters report and Tukey-Kramer HSD analysis, the large t-ratios found in each cycle comparison, and the large fractional changes by cycle difference. Each of these analysis types indicate that very minor differences found in experimental E_p values are statistically valid and extremely trustworthy. It is the E_p values which provide new insights into minute compositional changes which can be resolved through electrochemical analysis of brewed coffee. E_p values can shift due to many different electrochemical factors, but it is the resolution of these differences, regardless of what gives rise to them, which reaches beyond the traditional information obtained %TDS and, in fact, even beyond the information found via analysis of I_p , A , and δE . Our research into the brewing parameters which change reduction wave E_p values provide a new direction for future electrochemical research into the precise compositional differences which affect the peak potential of HUPD, which has previously been considered a stable, well-studied reaction^{183–186}. This new direction of electrochemistry will surely also provide improved understanding of the chemical composition and matrix interactions occurring in a cup of as-brewed coffee without employing separation techniques.

4.1.5 Conclusion. This work shows a novel application of CVs to gain compositional insight into brewed coffee. Through a five-factor full factorial

designed experiment, we find that the conventional method of measuring brewed coffee concentration, TDS, is highly correlated with I_p of the CV reduction wave. While this work is focused on a single coffee of mixed origin and dark roast, we anticipate that this correlation will hold for other coffees as well since the reduction wave is measuring HUPD from coffee compounds. Full effects reduced models show that each of the five brew factors are significant in predicting TDS, with only one significant interaction between brew time and grind size. All individual brew factors except time are found to be significant at $\alpha = 1\%$ for predicting I_p and A , while only m_b and g are significant for predicting δE . Interestingly, E_p is found to depend on all individual brew factors except m_w and shows no correlation with TDS. Many multiple factor interactions are also significant for predicting E_p , including a four-factor interaction among τ , T , m_b , and m_w . Furthermore, we find distinct changes in the directionality of the effects plots of the main brew factors for E_p compared to the other CV parameters. We propose that the chosen brew parameters are changing the composition of the brewed coffee and that E_p is sensitive to these minute variations. Many possible explanations exist that can describe the observed shifts in E_p including electrode surface morphology and surface coverage, and electrolyte composition^{183–186}. Further investigation is necessary to better understand the competing effects shifting E_p of the reduction wave in coffee CVs to implement using CV as a rapid, non-destructive tool for coffee analysis in café settings.

CHAPTER V

CONCLUSION

The work presented herein is the first to use %TDS as a marker for brewed coffee strength in conjunction with other chemical analyses. Before we can make meaningful measurements on brewed coffee, we must first be able to brew reproducible coffee. In Chapter 2, Electrostatics of Coffee Grinding, we look at the addition of a small amount of water to whole coffee beans immediately prior to grinding. We find that this water addition reduces the electrostatic charge from the grinding process, leading to less aggregate formation among coffee particles and more uniform particle size distribution. This increase in particle size uniformity gives rise to more consistent extraction during brewing. In Chapter 3, Determining Roast Degree, we control the roast profile of several coffee samples and relate the roast degree, as measured by Agtron value, to the %TDS. Additionally, we use CV as a novel technique in as-brewed coffee and find that the integrated area of the reduction wave correlates strongly with %TDS. We confirm that the observed reduction wave is due to hydrogen underpotential deposition (HUPD) on the platinum electrode surface. Furthermore, we find that molecules from the coffee matrix also adsorb to the electrode surface, blocking reaction sites and suppressing the signal from HUPD. Finally, we determine that the total charge passed during the HUPD reduction wave correlates linearly to the %TDS of the sample and the slope of this correlation depends on the roast degree. In Chapter 4, Impact of Brewing Parameters, we vary five common brew parameters (grind size, water temperature, water amount, bean amount, and brew time) and examine their impact on CV characteristics. We further illustrate that the integrated area of the HUPD reduction wave is linearly correlated to %TDS and find that the maximum

peak height follows the same trend. Moreover, we observe that the reduction wave full-width half maximum and particularly the peak center, characteristics inherently related to the sample composition, shift with changes in brew parameters. This research allows us to resolve why a simple scale up of known brew parameters does not result in the same composition and flavor profile.

Reproducible coffee brewing is inherently difficult, based on the bean-to-bean variety that is unavoidable. However, it is these nuances in chemical variation that give rise to many different flavors accessible in brewed coffee. The ability to brew the same cup repeatably is as important to a barista champion as it is to a global organization such as Starbucks. The work illustrated in this thesis gives new insight into how to prepare whole beans in a way that gives a more consistent product. It also allows for predictive optimization of brew parameters which can be tailored to individual goals, such as reducing coffee waste or minimizing energy input. Furthermore, our work directly ties an industrially relevant metric of coffee concentration, %TDS, to roast degree and to brew parameters relevant to all brewing techniques, providing a new framework for quality control that can be applied at the local café level or large scale.

The novel use of CV as a measure of coffee qualities opens a new field of study for electrochemistry techniques in food science. It is likely that monitoring HUPD suppression and peak shifting in other acidic liquids, such as wine or tea, will give similar insight into compositional differences that occur in the cup and might be lost when employing separation techniques. Further studies are necessary to pinpoint the compositional differences that lead to variations seen in E_p values, but it is conceivable that this metric might be used as a marker for quality and for specific flavors in the future. Using the predictive qualities of multifactor analysis

will lead to standard protocols for coffee scale up and scale down and allow for target flavor profiles to be reached in coffee pod technology. Preliminary results of continued research in the Hendon Coffee Lab indicate that the perception of sweetness and of acidity can be appreciably altered through electrolysis of the brewed product. One can easily imagine the inclusion of such electrochemical devices during the brew process, or even a cup designed with electrodes in the bottom that might someday allow the consumer to zap their brewed coffee to increase the acidity to their own preferences. The future of specialty coffee is electric.

APPENDIX A

CHAPTER 2 MOISTURE-CONTROLLED TRIBOELECTRIFICATION DURING COFFEE GRINDING SUPPLEMENTAL INFORMATION

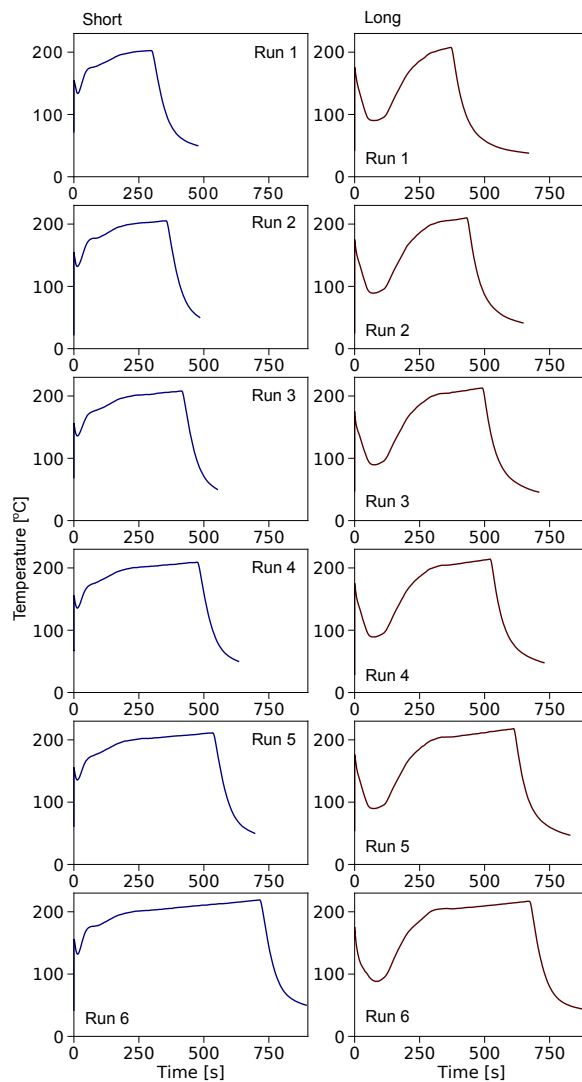


Figure A.1. Roast profiles of the 12 in-house roasts. The temperature versus time plots for each sample roasted on the Ikawa Pro100. The roasts resulted in the numerical values presented in Table A2. Short and long refer to Morse times on the Ikawa.

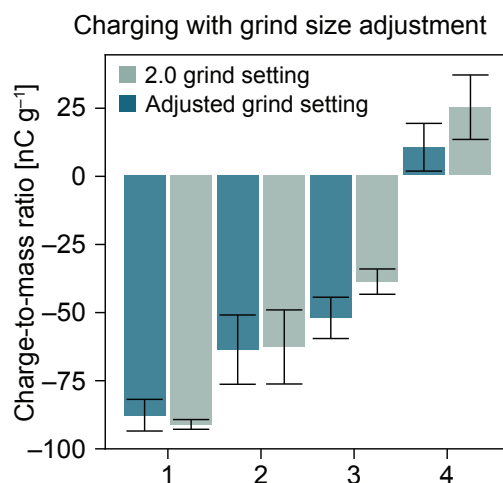


Figure A.2. Empirically correcting for grind size drift due to roast color. Four arbitrary coffees – ranging from dark (1) to light (4) – were first ground at 2.0 and their particle size and charge was measured. To account for the difference in particle size distribution due to roast, the grind setting was then changed so that the particle size distributions of each coffee matched one another. In effect, the was achieved by grinding the darkest coffee 0.3 more coarse. A minor reduction in charging was observed, but most of the charging persists, highlighting that a drift in particle size due to roast is not the determining reason for increased charging in dark coffees.

Table A.1. Details of the commercially sources coffees. * entries were not measured.

Name	Farm/ Producer	Origin	Process	Roaster/ Vendor	Agtron color	% water
<i>Bensa Washed</i>	Small holders	Ethiopia	Washed (W)	Moodtrap	104.2	*
<i>à Lt</i>	Unknown	Vietnam	Washed (W)	Cà Phê	92.2	1.8
<i>Yunnan</i>	Unknown	China	Natural (N)	Super Joy	90.2	2.0
<i>El Vergel Carbonic</i>	El Vergel	Colombia	Natural - Carbonic maceration (N-CM)	Farmers Union	86.3	2.3
<i>Huila</i>	Small holders	Colombia	EA Natural (N-EA)	Heart	82.8	2.9
<i>Reina</i>	Finca Gascón Gold	Guatemala	Washed (W)	Manhattan	81.8	*
<i>Jinotega Rainforest</i>	Mountain Coffee Growers	Nicaragua	Washed (N)	Farmers Union	81.1	1.9
<i>Yogondoy</i>	García Luna	México	Washed (W)	Farmers Union	81.0	1.7

Name	Farm/ Producer	Origin	Process	Roaster/ Vendor	Agtron color	% water
<i>Intro</i>	Small holders	Brazil/ Ethiopia	Natural blend (N-B)	Tailored El	80.8	1.8
<i>Tacámbaro</i>	El Pantano	México	Natural (N)	Apapacho (Mau)	79.6	2.6
<i>Red Brick</i>	La Serrania/ El Palmarito	Colombia/ Guatemala	Washed blend (B)	Square Mile Coffee	77.0	2.0
<i>Bekele</i>	Hache	Ethiopia	Natural (N)	Farmers Union	75.9	1.6
<i>Amatepec</i>	El Equimite	México	Washed (W)	Café Mexiquense	75.6	2.2
<i>Turihamwe Women's Group</i>	JNP Coffee	Burundi	Washed (W)	Mother Tongue	75.2	2.2
<i>Unicycle.com</i>	Unkown	Colombia	Washed blend (B)	L.A. Coffee	75.1	1.8
<i>Kolla Bolcha</i>	Small holders	Ethiopia	Washed (W)	Vesta	75.0	2.2
<i>Temascaltepec</i>	Federico Barrueta	México	Washed (W)	Exploradores de Café	74.2	*

Name	Farm/ Producer	Origin	Process	Roaster/ Vendor	Agtron color	% water
<i>Jinotega</i>	Gold Mountain Coffee Growers	Nicaragua	Natural (N)	Farmers Union	72.5	2.0
<i>Tacámbaro</i>	El Pantano	México	Washed (W)	El Apapacho (Mau)	70.5	2.4
<i>Tarrazú</i>	Small holders	Costa Rica	Washed (W)	George Howell	69.1	1.2
<i>Planadas</i>	Various	Colombia	Decaf (D)	Farmers Union	66.4	1.3
<i>Blonde Espresso</i>	Unknown	Latin America/ East Africa	Washed blend (B)	Starbucks	65.2	1.3
<i>Raku</i>	Unknown	México	Anaerobic natural (N-A)	Exploradores de Café	63.9	1.7
<i>Robusta</i>	Organic Cherry Robusta	India	Washed (W)	Keurig Dr. Pepper	59.2	1.3

Name	Farm/ Producer	Origin	Process	Roaster/ Vendor	Agtron color	% water
<i>Mané</i>	Unknown	México	Washed blend (B)	Mané	57.7	2.2
<i>Sweet Life</i>	Unknown	Indonesia	Washed blend (B)	Farmers Union	56.2	1.1
<i>Pike's Place</i>	Unknown	Latin America	Washed blend (B)	Starbucks	52.0	~1
<i>Kicking Horse</i>	Unknown	Central/ South America	Washed blend decaf (D)	Kicking Horse	42.2	~ 1
<i>Yirgacheffe Zero Defect</i>	Tamrat Alemayehu	Ethiopia	Washed (W)	Farmers Union	green	12%
<i>Yogondoy</i>	García Luna	México	Washed (W)	Farmers Union	green	9%

Table A.2. **Roast profile details of the in-house roasted coffees. Target curves are available for download from DOI:10.6084/m9.figshare.23277320.**

“Short soak” roast - YirgZ (w, 12% initial water content)				
	Time (s)	Temp. (°C)	Color (Agtron)	% water
Run 1	294	203	88.7	2.8
Run 2	354	205	74.0	2.1
Run 3	414	207	72.0	1.5
Run 4	474	209	70.0	1.4
Run 5	534	211	63.8	1.3
Run 6	714	219	62.1	1.0
“Long soak” roast- YirgZ (w, 12% initial water content)				
Run 1	370	206	78.1	2.9
Run 2	430	209	76.3	1.9
Run 3	490	212	71.2	1.4
Run 4	519	213	70.8	1.3
Run 5	610	217	64.6	1.1
Run 6	670	220	61.7	1.0
“Short soak” roast - Rio de Abejas (w, 9% initial water content)				
Run 1	294	203	93.1	3.0
Run 2	354	205	85.8	2.2
Run 3	414	207	78.6	1.6
Run 4	474	209	72.8	1.3
Run 5	534	211	71.0	1.2
Run 6	714	219	60.2	1.1

APPENDIX B

CHAPTER 2 STRATEGIES TO MITIGATE ELECTROSTATIC CHARGING DURING COFFEE GRINDING SUPPLEMENTAL INFORMATION

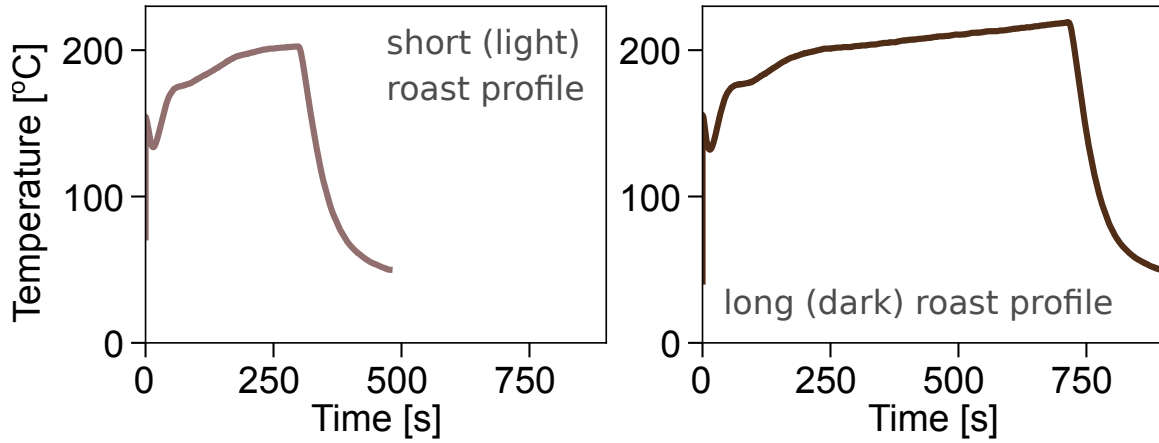


Figure B.1. Temperature profiles used to generate light and dark roasts, related to **Figure 16**. We roasted the coffees listed in **Table 1** using an Ikawa Pro roaster. We roasted coffee in batches of 50 grams. The profiles may be downloaded from [10.6084/m9.figshare.23277320.v1](https://figshare.com/10.6084/m9.figshare.23277320.v1).

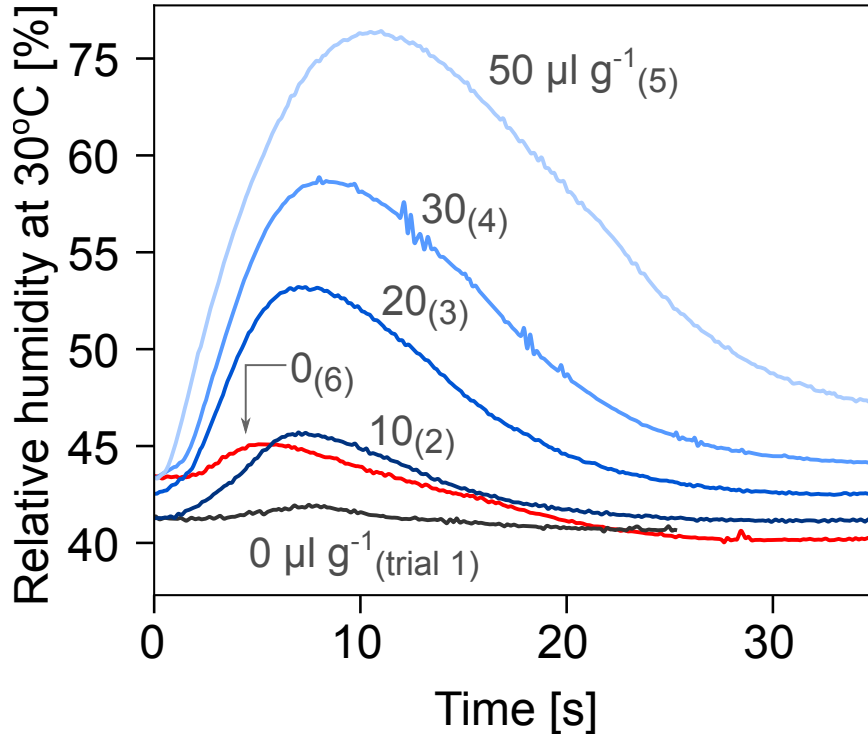


Figure B.2. Changes in humidity within the grinder as function of added water, related to Figure 18. A concern associated with the water droplet technique is that moisture could lead to corrosion within the grinder. Thus, we investigated the manner in which small quantities of water changed the environmental conditions inside the grinding cavity. For these experiments, we inserted a small relative humidity (RH) senso (Honeywell HIH-4030) into the grinder chute and secured it against the stator (non-spinning burr). Relative humidity was then recorded during grinding. Baseline humidity during the experiment was $\sim 40\%$. The curves rendered above show the variation in RH over time for added water contents in the range of $0\text{--}50\ \mu\text{l g}^{-1}$. Experiments were conducted within minutes of each other in the order indicated by the numbers in parenthesis. For low water contents ($\sim 10\ \mu\text{l g}^{-1}$) we find that humidity in the chamber increases by a few percent and then decays back to background in a few seconds. For higher water contents, RH can increase by up to 30%, however we did not register condensation. While the most humid conditions were short-lived, we did find that several minutes were required for the internal RH to return to background for high water contents ($>20\ \mu\text{l g}^{-1}$). This longer-lived excess humidity, however, could be removed effectively by grinding a small amount of dry coffee (red curve, trial 6). Thus, if corrosion is a concern with the water droplet technique, we suggest that a sacrificial "purge" grind be performed when coffee preparation is concluded.

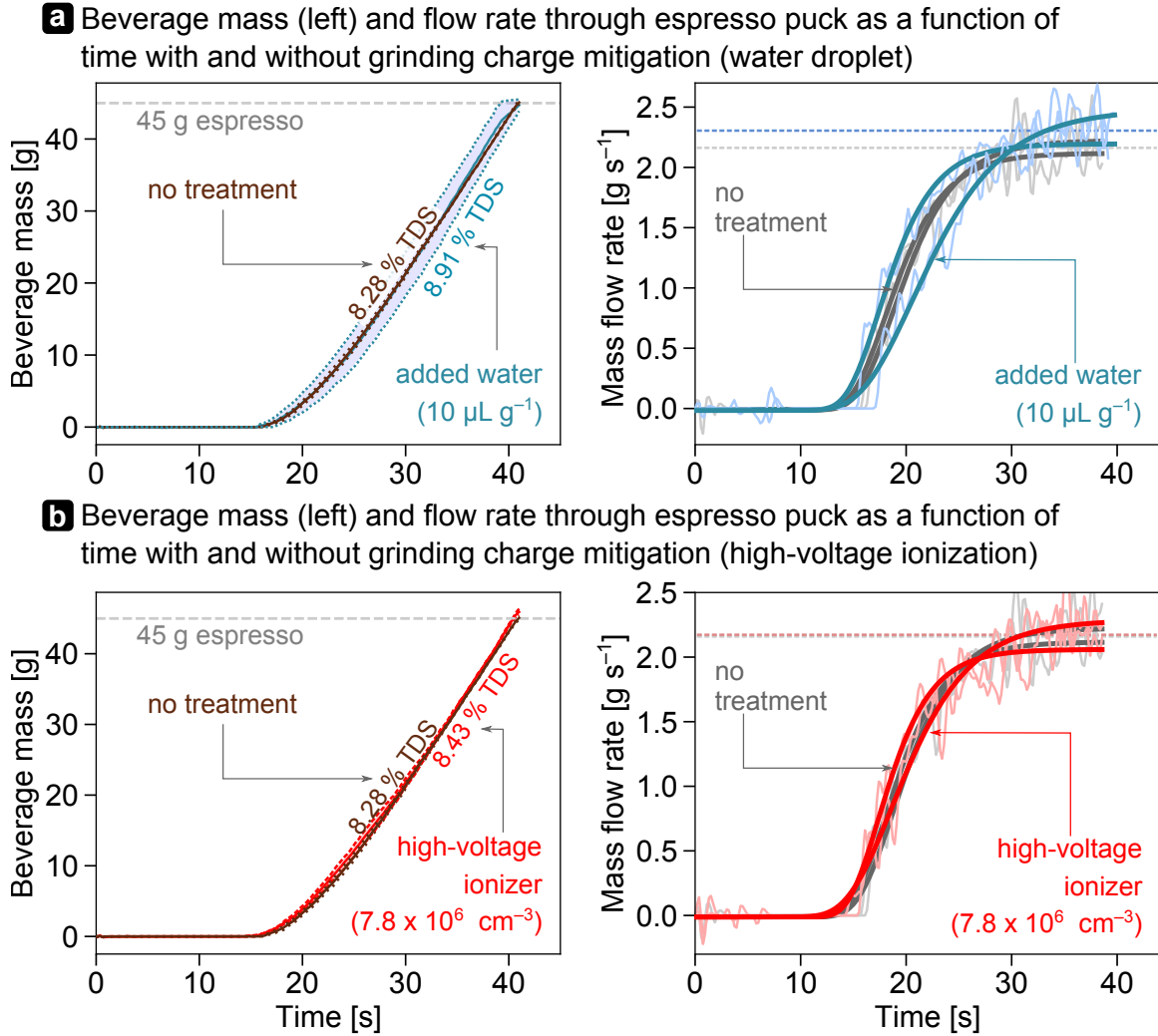


Figure B.3. Espresso shot time and flow rate dependence with and without charge mitigation for a light roast (Temascaltepec), related to **Figure 19**. **a**). Shot dynamics with (blue curves) and without (brown curves) the addition of extrinsic water. **b**) Shot dynamics with (red curves) and without (brown curves) treatment with high-voltage ionization.

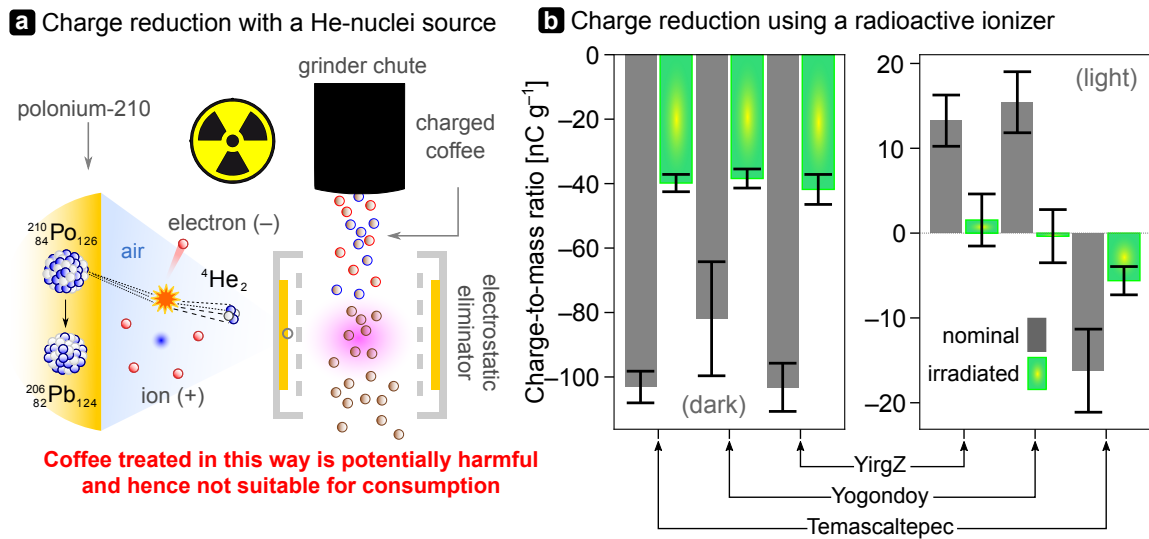


Figure B.4. Although potentially harmful to humans, we also examined de-electrification using helium nuclei, related to Figure 17. a) Negative and positive ions may also be generated via alpha decay. b) Exposing negatively charging coffee, typically dark roasted, reduces charge comparable to the balanced ionizing method presented in the main text. These experiments were conducted for advancement of basic science and, besides being an inferior de-electrification technique compared to conventional ion beams and/or water addition, the risk associated with the use of radioactive elements makes this approach untenable.

APPENDIX C

CHAPTER 3 AN ELECTROCHEMICAL DESCRIPTOR FOR COFFEE

QUALITY SUPPLEMENTAL INFORMATION

Roast	Total Time (min)	Final Temperature (°F)	Whole Bean Agtron	Ground Coffee Agtron
1a	6:17	412	75.8	90.3
1b	6:47	414	72.2	88.8
1c	7:17	416	64.3	83.6
1d	7:47	418	61.2	80.3
1e	8:17	420	58.2	74.6
1f	9:17	424	55.7	76.1

Table C.1. Roasting conditions and their associated Agtron numbers. Grind setting 2 was used on an EK-43 to obtain the ground Agtron values.

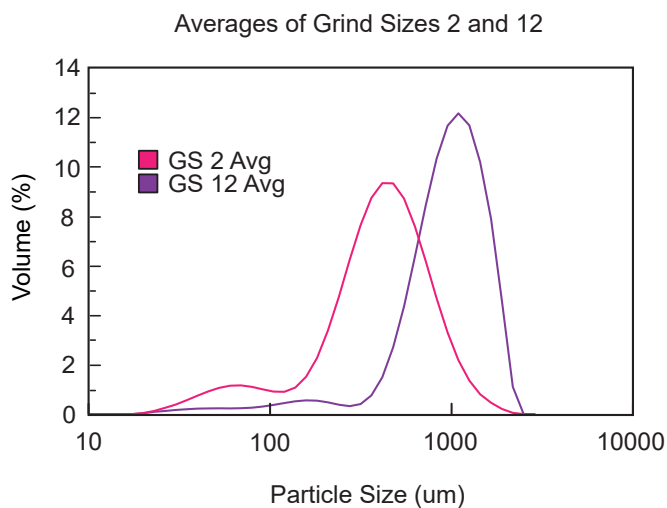


Figure C.1. Particle size distributions for EK43 Mahlkonig grinder settings 2 and 12. Setting 2 was used for ground bean Agtron value assessment and setting 12 was used for coffee cupping brews.

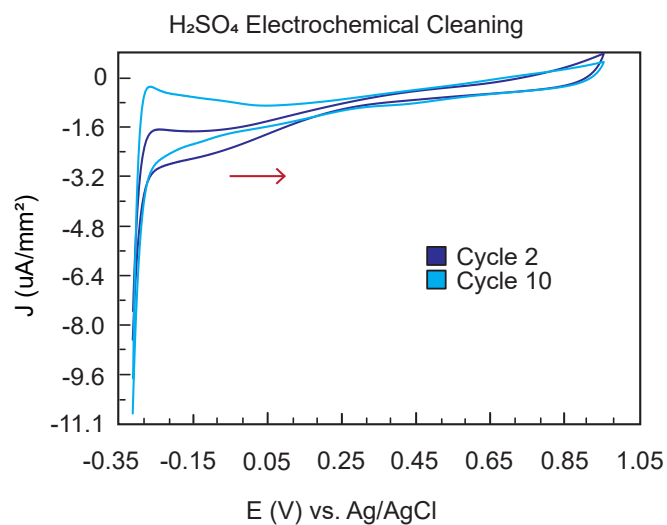


Figure C.2. Example of electrochemical cleaning of platinum working electrode in 50 mM H_2SO_4 . Cycles were repeated until the features visibly overlaid with one another. Scan rate 300 mV/s.

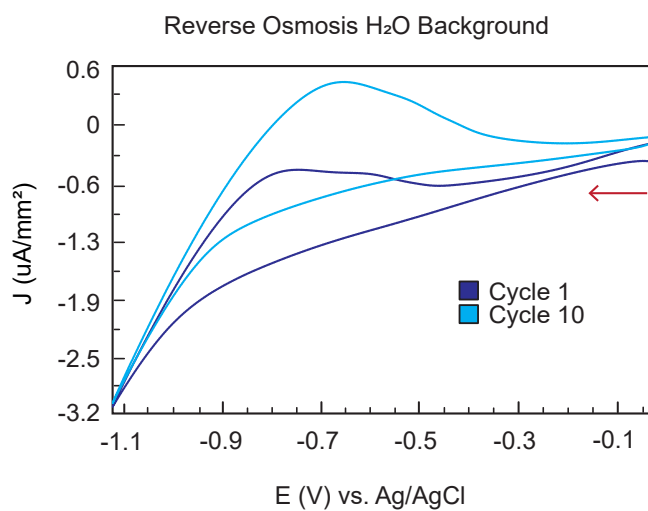


Figure C.3. Background CV of water purified using the Pentair Everpure Conserv 75E Reverse Osmosis system. Scan rate of 200 mV/s.

Roast	Sample	TDS	Resistance (Ω)	pH
1a	Pure	1.56	740.94	4.96
1a	Dil1	1.30	837.57	4.99
1a	Dil2	1.01	1052.93	5.04
1a	Dil3	0.70	1460.61	5.12
1a	Dil4	0.46	2091.03	5.24
1b	Pure	1.60	733.99	5.06
1b	Dil1	1.28	875.55	5.08
1b	Dil2	1.02	1048.32	5.12
1b	Dil3	0.70	1425.42	5.19
1b	Dil4	0.51	1977.29	5.25
1c	Pure	1.58	719.85	5.12
1c	Dil1	1.25	835.85	5.13
1c	Dil2	1.01	1048.65	5.17
1c	Dil3	0.71	1445.79	5.23
1c	Dil4	0.51	1922.64	5.31
1d	Pure	1.51	768.58	5.17
1d	Dil1	1.30	876.40	5.19
1d	Dil2	0.99	1103.23	5.23
1d	Dil3	0.70	1507.73	5.30
1d	Dil4	0.51	1994.35	5.38
1e Run 1	Pure	1.50	789.60	5.30
1e Run 1	Dil1	1.26	861.16	5.29
1e Run 1	Dil2	1.01	1091.62	5.35
1e Run 1	Dil3	0.72	1491.01	5.42
1e Run 1	Dil4	0.51	1992.82	5.50
1e Run 2	Pure	1.50	786.07	5.30
1e Run 2	Dil1	1.31	865.86	5.29
1e Run 2	Dil2	1.01	1090.67	5.36
1e Run 2	Dil3	0.72	1495.26	5.42
1e Run 2	Dil4	0.53	1980.11	5.50
1e Run 3	Pure	1.51	771.35	5.30
1e Run 3	Dil1	1.31	872.56	5.29
1e Run 3	Dil2	1.02	1091.54	5.36
1e Run 3	Dil3	0.73	1489.70	5.42
1e Run 3	Dil4	0.51	1990.33	5.50
1f	Pure	1.53	783.20	5.38
1f	Dil1	1.30	860.28	5.39
1f	Dil2	1.00	1077.01	5.44
1f	Dil3	0.70	1465.19	5.52
1f	Dil4	0.48	2320.41	5.70

Table C.2. %TDS, resistance, and pH values for coffee samples used for cyclic voltammetry.

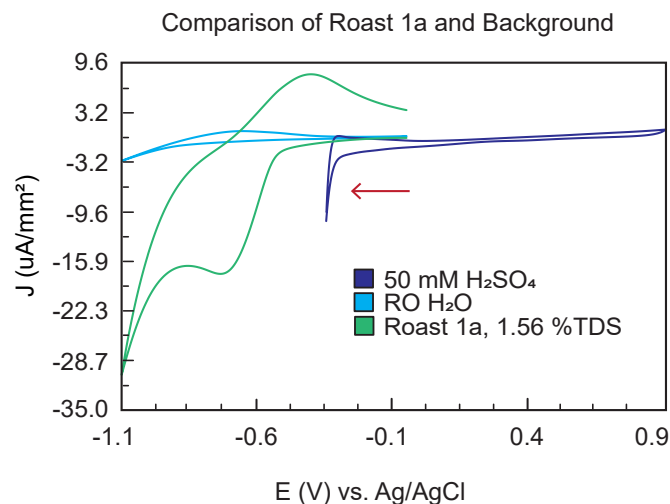


Figure C.4. Overlay of Roast 1a at 1.56 %TDS with a background scan of the reverse osmosis H₂O used for coffee brewing and 50 mM solution of H₂SO₄ used for electrochemical polishing of electrodes. Scan rates for H₂O and coffee were 200 mV/s and 300 mV/s for H₂SO₄.

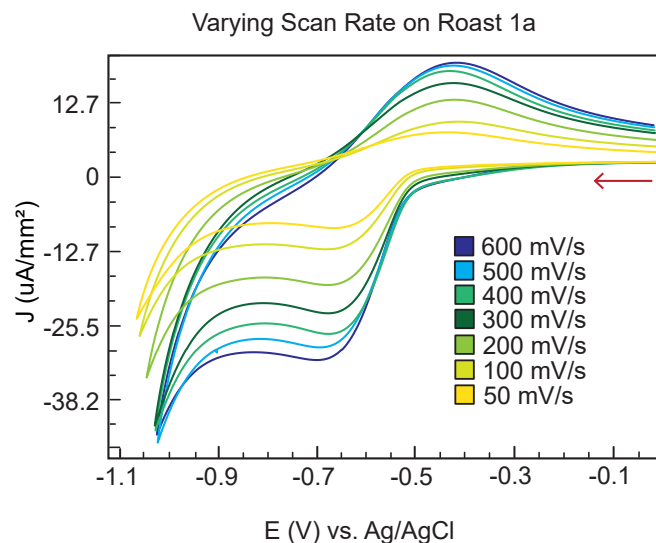


Figure C.5. Scan rate dependence of HUPD peaks in undiluted brewed coffee. Reduction and oxidation peak centers do not correlate linearly with log base 10 of the scan rate, indicating non-Nernstian behavior.

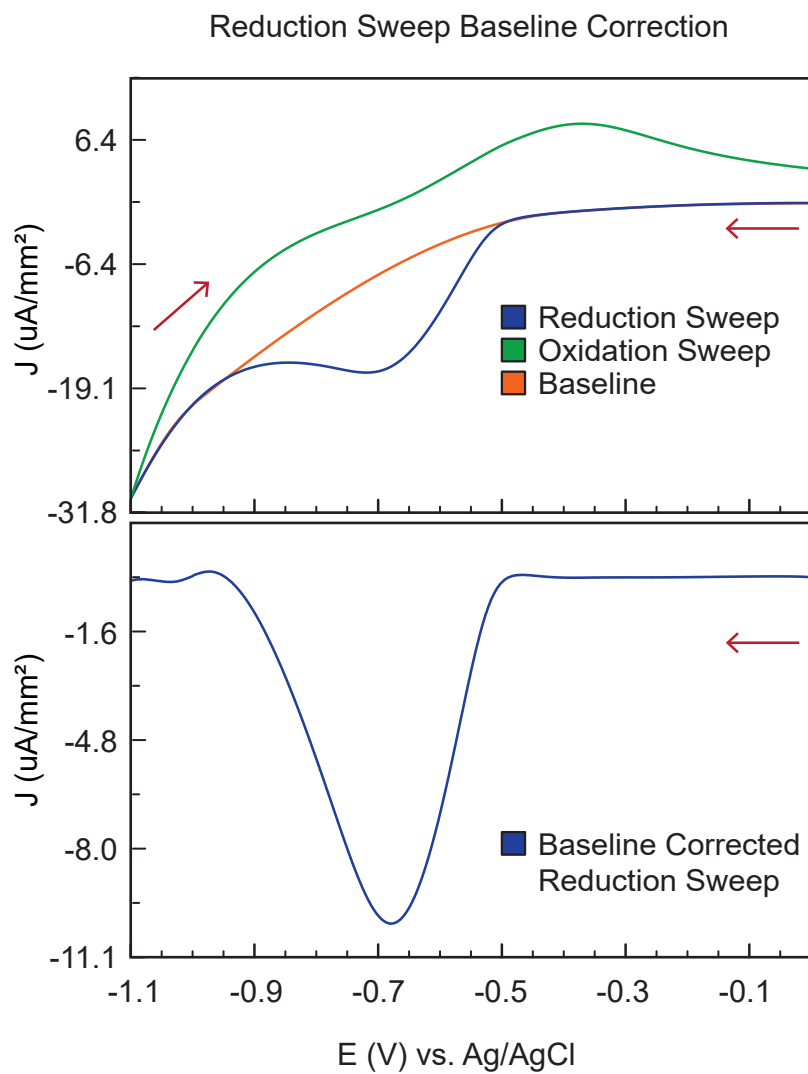


Figure C.6. Example of background subtraction as performed in OriginPro9 to integrate reduction peak area. The top panel shows the first CV curve of roast 1a at 1.56 %TDS. The bottom panel shows the reduction sweep of the CV after the baseline correction was subtracted.

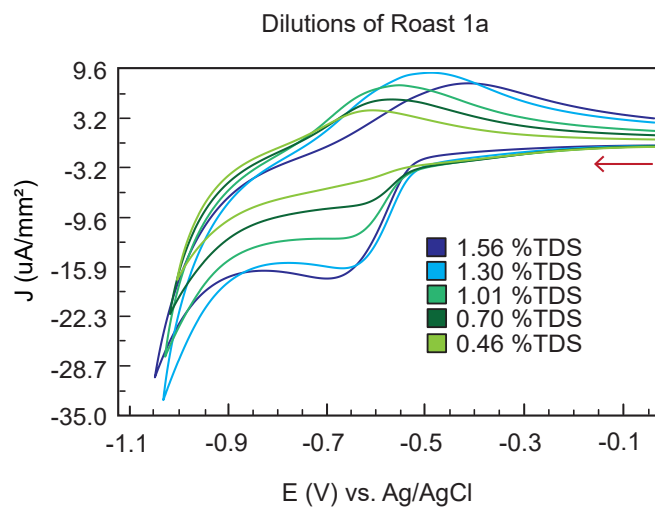


Figure C.7. Overlay of the first CV cycle of Roast 1a via cupping brew method at multiple %TDS values. Scan rate 200 mV/s.

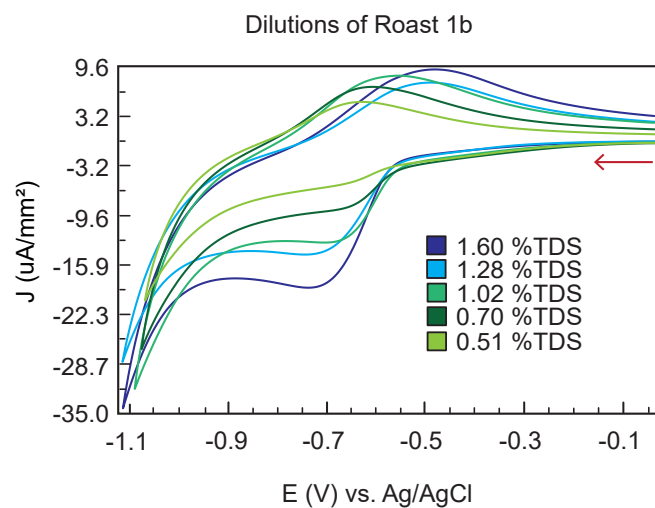


Figure C.8. Overlay of the first CV cycle of Roast 1b via cupping brew method at multiple %TDS values. Scan rate 200 mV/s.

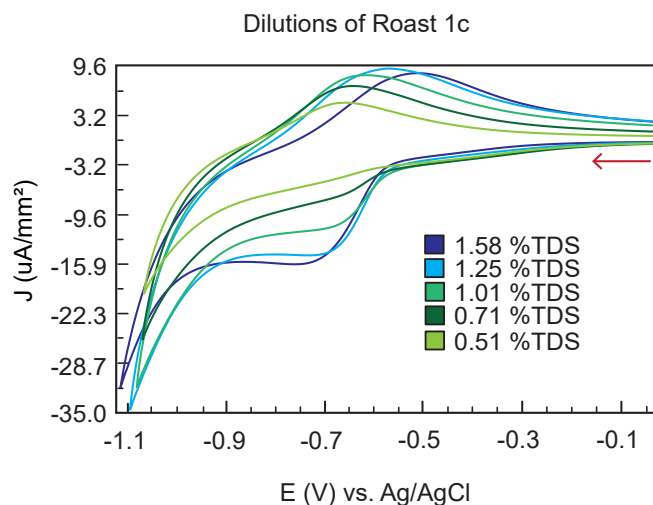


Figure C.9. Overlay of the first CV cycle of Roast 1c via cupping brew method at multiple %TDS values. Scan rate 200 mV/s.

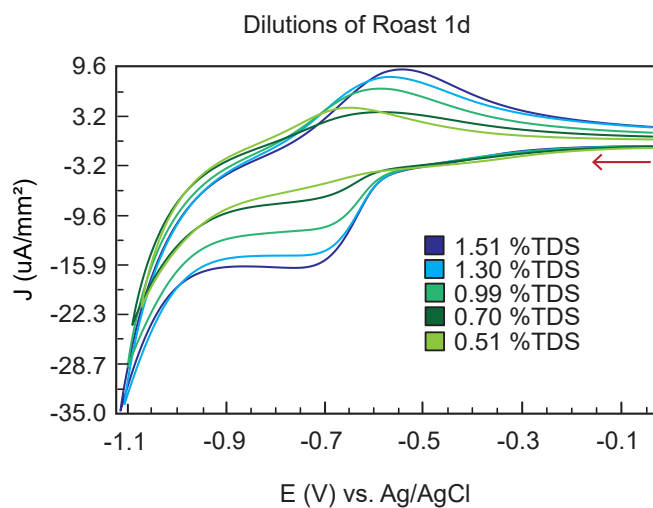


Figure C.10. Overlay of the first CV cycle of Roast 1d via cupping brew method at multiple %TDS values. Scan rate 200 mV/s.

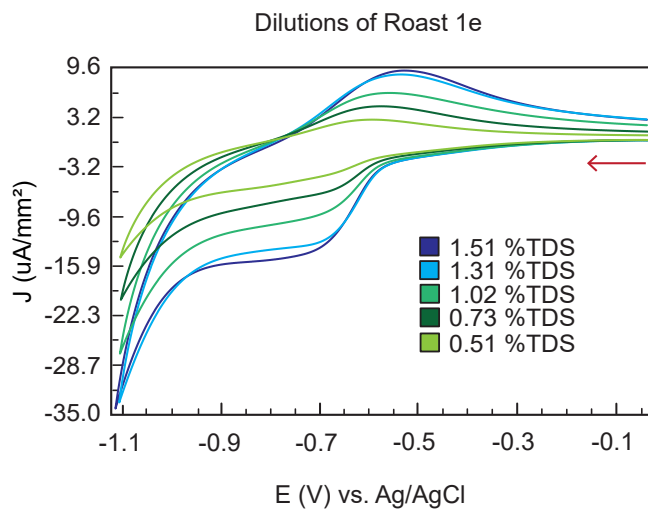


Figure C.11. Overlay of the first CV cycle of Roast 1e via cupping brew method at multiple %TDS values. Scan rate 200 mV/s.

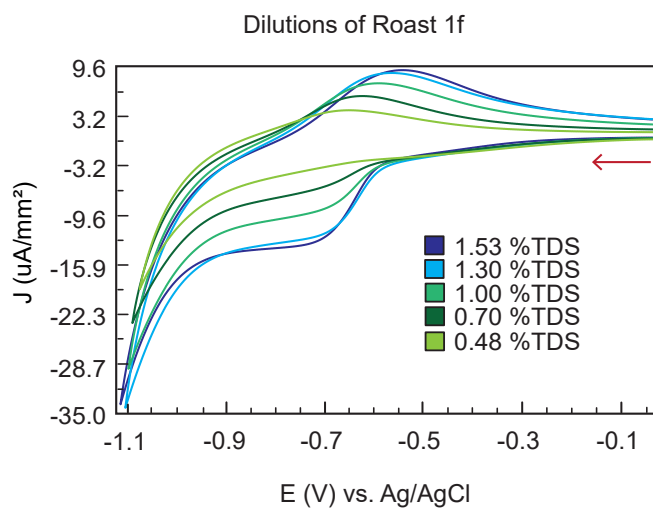


Figure C.12. Overlay of the first CV cycle of Roast 1f via cupping brew method at multiple %TDS values. Scan rate 200 mV/s.

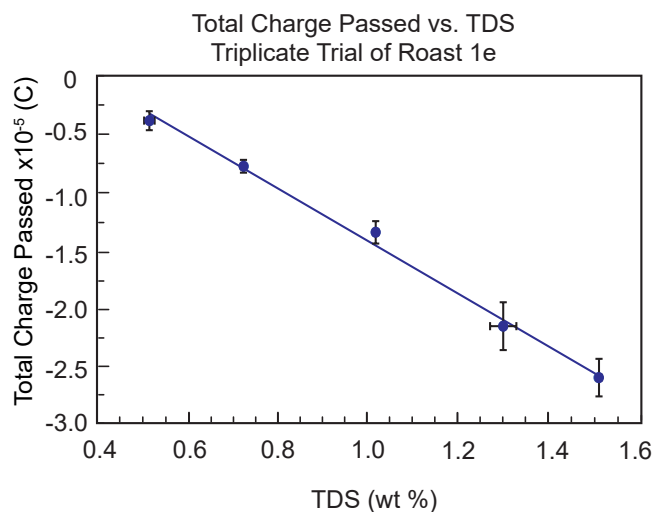


Figure C.13. Total charge passed vs TDS performed in triplicate using Roast 1e with associated error bars.

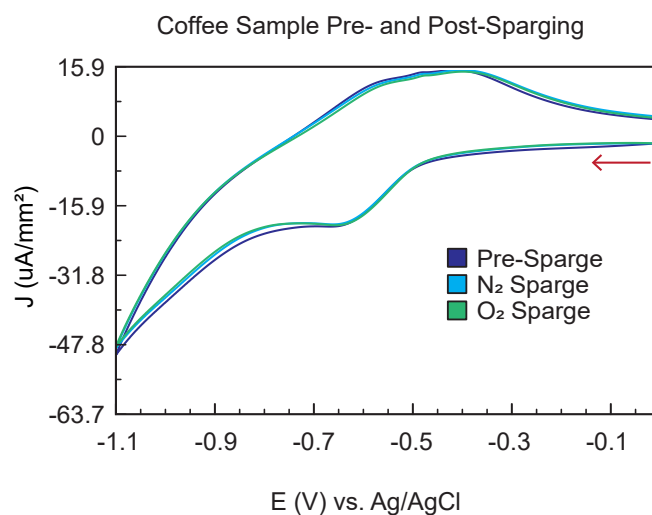


Figure C.14. Overlay of the first CV cycle of brewed coffee with and without sparging. Dark blue trace is the brewed coffee prior to any sparging; light blue trace is following 20 minutes of sparging with N₂, green trace is following an additional 20 minutes of sparging with O₂. Scan rate 200 mV/s.

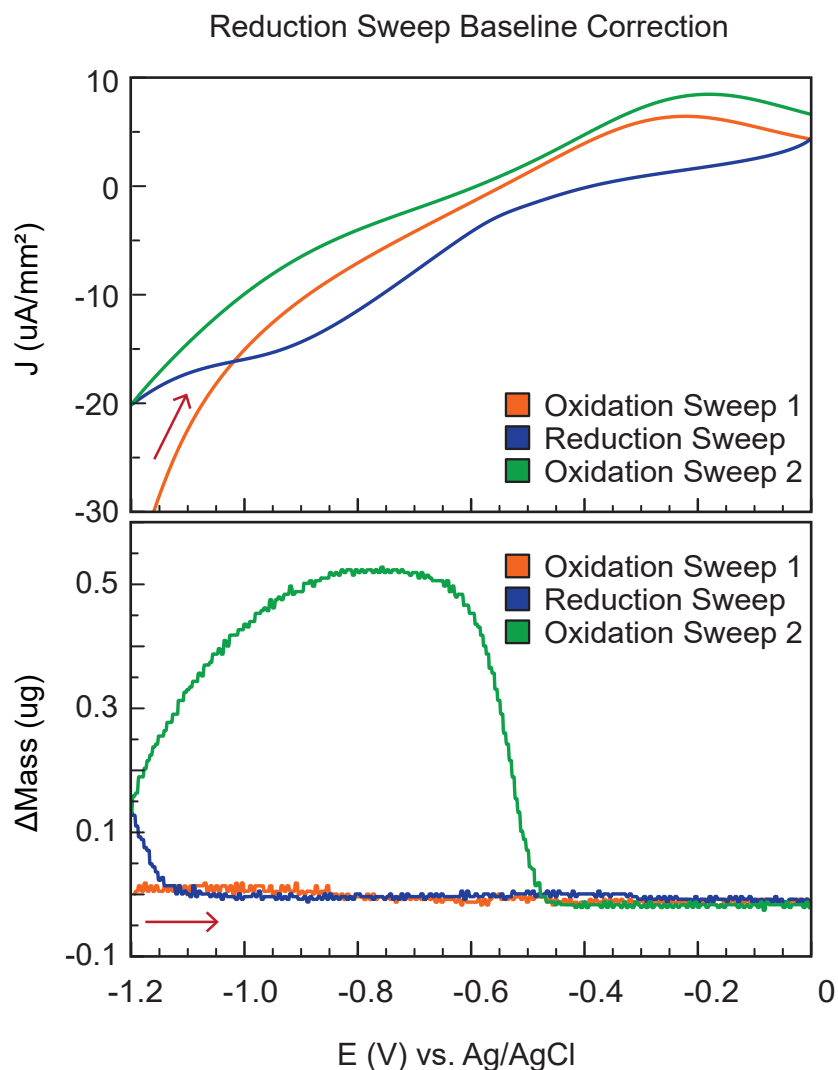


Figure C.15. CV and associated QCM mass data in coffee at 1.36 %TDS. Began at -1.2 V vs. Ag/AgCl and scanned oxidatively, as opposed to starting at 0 V vs. Ag/AgCl and scanning reductively to start. QCM shows no mass gain during the initial oxidative sweep (orange trace). Mass is only accumulated following the onset of HUPD during the first reductive sweep (blue trace) since a build-up of adhered H^+ on the electrode surface is necessary for side reactions that lead to a detectable mass gain.

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