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FEASIBILITY STUDY TO ESTIMATE THE TDS OF COFFEE FROM NIR SPECTROSCOPIC MEASUREMENT OF ROASTED COFFEE BEANS AND BREW.

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1. INTRODUCTION AND OBJECTIVES

From its obscure origins in the highlands of Ethiopia, the coffee plant has garnered international admiration like no other. Indeed, coffee remains the most traded plant-based commodity internationally, with a global production output of 175 million 60 kg bags in 2020 (International Coffee Organisation, 2024). Moreover, it holds the status of the most consumed beverage after water (United States Department of Agriculture, 2023). Given its significance, assuring quality along the coffee value chain is imperative. In this regard, quality assurance for various aspects from cultivation through processing to the final brew are well established (Vieira, 2008a).

The principal target of quality assurance is consumers who are drawn to the beverage for its unique sensory attributes and cognitive effects (Samoggia and Riedel, 2018). One such sensory attribute is brew strength (Frost et al., 2020). The term describes all components found in the brew which influence the sweetness, bitterness and several sensory perceptions elicited by the specific proportions of the chemical constituents in the brew (Batali et al., 2020). Brew strength is quantified as the mass concentration of all dissolved components, otherwise known as total dissolved solids (TDS) (Sunarharum et al., 2014). TDS is applied in conjunction with extraction yield (EY), which is defined as the ratio of mass extracted from coffee to the weight of the coffee grounds used (Sunarharum et al., 2014).

According to mass conservation arguments, there is a linear correlation between the EY and TDS, with the slope as the brew ratio (Cordoba et al., 2020; Ristenpart and Kuhl, 2015). This relation was first developed by the seminal work of Lockart (1957) and forms the basis of Brewing Control Charts used by coffee brewers worldwide. The chart proposes that the ideal coffee brew has TDS and EY in the ranges of 0.79 - 1.25% and 18 - 22% respectively (Lingle, 2011; Lockhart, 1957; Ristenpart and Kuhl, 2015). Despite recent revisions and expansion of the charts to accommodate modern sensory preferences, it remains an integral part in assessing the quality of coffee brew (Batali et al., 2020; Frost et al., 2020).

As a mass concentration, estimating coffee TDS requires the preparation of a brew from which an aliquot is either oven-dried or subjected to refractive-index-based estimations with appropriate correction factors (Kimball, 1991; Petracco, 2001b; Wang and Lim, 2023). Moreover, TDS is strongly influenced by brewing methods and associated parameters such as percolation time, temperature, water quality and quantity, and pressure among others (Batali et al., 2020; Cordoba et al., 2020; Frost et al., 2020; Lingle, 2011). This multitude of potential variables often translates into differences in TDS estimated from the same coffee sample (Belitz et al., 2009; Petracco, 2001b). It is, therefore, necessary to explore non-destructive secondary analytical methods of estimating TDS as this will yield lesser variations and also allow for routine application with minimal sample preparation (Reh, 2008).

Near infrared spectroscopy (NIRS) stands out as a viable alternative to explore in this regard. It is based on the unique interactions of electromagnetic radiation in the NIR range (12500-4000 cm $^{-1}$) with matter (Sandorfy et al., 2006). The interaction manifests as absorbance of frequencies of polychromatic light that corresponds to the molecular vibrational transition of the material (Ozaki et al., 2006). The chemical and physical characteristics of the materials are thus deduced from the resulting spectra (Sandorfy et al., 2006). Chemometric methods are required when applying NIRS to complex sample matrices (Ribeiro et al., 2010)

Indeed, NIR spectroscopy has been extensively explored in the coffee industry with applications ranging from the estimation of caffeine content of roasted beans (Zhang et al., 2013), discrimination of defective coffee beans (Craig et al., 2012), and predicting the sensory scores of roasted beans (Ribeiro et al., 2010).

Thus, this study seeks to explore the feasibility of estimating the TDS of coffee samples from the NIR spectra of roasted coffee beans and brew prepared from the beans with two reference methods. The aims of the study were:

1. Measure the TDS of coffee samples using two reference methods: oven-drying and Brix°-derived measurements.
2. Collect the NIR spectra of roasted coffee bean and brew made from the beans

3. Investigate the relation between the two-reference methods to gain a deeper understanding on the potential effects on the calibration models.
4. Build two calibration models from the two reference methods to predict reference TDS measurement.

2. LITERATURE REVIEW

2.1. Botanical classification

The *Coffea* genus comprises over 100 species (Davis et al., 2006). Coffee may grow as a perennial shrub or tree depending on the species (Rena et al., 1987). In the case of arabica coffee (*C. arabica* L.), it typically has a single main trunk above ground while robusta coffee (*C. canephora* Pierre ex A. Froehner) grows with multiple trunks (Alves et al., 2017). These two species represent about 98% of the coffee market (Alves et al., 2011). The difference in morphology extends to their mature fruits. In arabica coffee, mature fruits known as "berries" can be either red or yellow, and Robusta plants exhibit a wider range of hues in their fruits (Herrera and Lambot, 2017). The shape of the fruit, ranging from round to oblong, varies depending on the Coffea species. Moreover, the size of both the fruit and its endosperm (referred to as the "bean") is influenced by the specific cultivar, as well as cultivation conditions (Herrera and Lambot, 2017). Typically, each fruit yields two beans. The bean itself contains proteins, caffeine, oils, sugars, dextrin, chlorogenic acid, and various other substances that contribute to the characteristics of the resulting beverage (Pinheiro et al., 2021).

2.2. Coffee Production

The compositional differences of the two varieties makes them suitable for various applications. *Coffea arabica* L. is the most cultivated constituting about 65% to 75% of global coffee production (International Coffee Organisation, 2024). It is known for its superior taste qualities but contains lower levels of total soluble solids (Sera, 2001). *C. canephora* Pierre, on the other hand constitutes 10% to 25% of global coffee production. While Robusta is perceived as having inferior taste characteristics relative to Arabica, it contains double the caffeine content and yields higher levels of extractable solids (Ferrão, 2009). Furthermore, Robusta exhibits greater resistance to diseases such as leaf rust (*Helimeia vastatrix*) and is employed to increase the quantity of coffee drinks like espresso coffee and instant coffee (Alves et al., 2011; Manzocco et al., 2019).

2.3. Cultivation and processing

The quality of cup coffee predominantly hinges on the physical and chemical attributes of green coffee, shaped by a blend of three key categories: environmental factors, genetic factors, and agricultural practices (Herrera and Lambot, 2017). Coffee harvesting practices has a strong influence on the quality of beverage obtained (Vieira, 2008a). It is recommended to limit the number of unripe cherries to no more than 20% due the negative impacts on brew quality (Vieira, 2008a). This is because, at peak ripeness, there is increased level of sugar and other elements that can enhance the desirable qualities like flavour, aroma, sweetness, acidity, body and balance in the beverage post roasting (Giomo, 2012).

Following harvesting, berries undergo either dry or wet processing. In dry processing, debris and damaged berries are separated through flotation in washing channels (Vieira, 2008a). Subsequently, the berries are spread out on terraces and regularly turned until they uniformly dry under the sun (Giomo, 2012). Dehydration of coffee is essential for safeguarding the beans during storage, constituting a crucial phase in the post-harvest process aimed at achieving a high-quality end product (Resende et al., 2011). The drying process reduces the moisture content of coffee beans from 60% to levels ranging between 11% and 13%, thereby mitigating the risks of oxidation as well as fungal and bacterial proliferation (Pinheiro et al., 2021). In the wet processing method, debris and some damaged berries are removed in washing channels. Mechanical removal of the outer layer and a portion of the berry's pulp occurs, and the remaining pulp is eliminated through fermentation and washing (Wintgens and Zamarripa C., 2004). Consequently, in this method, it's the coffee beans, not the berries, that are sun-dried (Ismayadi et al., 2005). Dried beans undergo additional processing such as hulling, polishing, cleaning, sorting by various criteria such as size, density, or colour, grading, as well as roasting and grinding (Santos et al., 2009) Upon completion of drying, coffee can be stored either on the farm or in external facilities (Ribeiro et al., 2012)

2.4. Chemical composition of the green beans

Green coffee consists of carbohydrates, nitrogen-containing compounds (primarily proteins, trigonelline, and caffeine), lipids, organic acids, and water. Virtually all components of green coffee serve as potential precursors for flavour and colour development (Baggenstoss et al., 2008). Among these constituents, sugars, proteins, free amino acids, trigonelline, and chlorogenic acids (CGA) stand out as the principal flavour precursors (Poisson et al., 2017).

While the overall composition of Arabica and Robusta species is quite similar, their relative proportions vary significantly. Arabica coffees are distinguished by higher levels of carbohydrates (such as sucrose, mannans and oligosaccharides), trigonelline, lipids, organic acids (including citric, malic, and quinic acids), and 3-feruloyl-quinic acid (3-FQA) (De Maria et al., 1996). Conversely, Robusta coffees exhibit higher concentrations of caffeine, proteins, arabinogalactans, chlorogenic acids (except 3-FQA), total phosphate, ash (comprising calcium salts), and transition metals (such as Al, Cu, and Fe). These notable differences in composition play a pivotal role in shaping the distinct qualities and characteristics of roasted coffee (Poisson et al., 2017).

2.4.1. Carbohydrates

Carbohydrates account for approximately 40-65% of the dry weight of green coffee, comprising both water-soluble and water-insoluble carbohydrates (Martinez et al., 2018). The soluble polysaccharides and the insoluble fraction consist of polymers of arabinose, galactose, glucose, and mannose (Bradbury and Halliday, 1990). Furthermore, cellulose, galactomannan, and arabinogalactans collectively represent about 45% of the dry weight of coffee beans with the remaining portion composed of sucrose (3-8%) (Trugo, 1985). The soluble fraction of green coffee carbohydrates is believed to be the primary source of precursors for the development of coffee aroma, taste, and colour (De Maria et al., 1996; Nunes and Coimbra, 2001). These precursors readily engage in various reactions, evidenced by their rapid depletion in the early stages of roasting (Poisson et al., 2017). Water-soluble carbohydrates are categorized into two fractions: high molecular weight (HMW) and low molecular weight (LMW) fractions (De Maria et al., 1994).

HMW polysaccharides in green coffee mainly consist of galactomannans and arabinogalactans, with the latter constituting 14-19% of the dry matter (De Maria et al., 1994; Illy and Viani, 1995).

The water-soluble low molecular weight (LMW) fraction contains significant flavour precursors such as free sugars (De Maria et al., 1994). While mono- and disaccharides are present in minor quantities, they play essential roles in aroma development through caramelization and Maillard reaction (Poisson et al., 2017). Sucrose, the predominant disaccharide constitutes approximately 8% of Arabica green coffee and about half that amount in Robusta (3-6%) (Belitz et al., 2009). The higher sucrose content in Arabica has been suggested to contribute to its complex aroma and overall flavour (Farah, 2012).

Oligosaccharides (such as stachyose and raffinose) and monosaccharides (including arabinose and glucose) are present in trace amounts in green coffee (De Maria et al., 1994). The insoluble portion comprises high molecular weight (HMW) polymeric components located in the dense cell wall complex of the bean and comprises mannans, hemicellulose, and cellulose, and more abundant in Arabica than in Robusta coffee (Belitz et al., 2009; Illy and Viani, 1995).

2.4.2. Nitrogen-containing substances

Nitrogen compounds, primarily proteins, constitute approximately 11-15% of the dry coffee material, with a total protein content of around 10% for both Arabica and Robusta green coffee (Poisson et al., 2017). Some proteins are bound to arabinogalactan, forming arabinogalactan proteins (AGPs) (Belitz et al., 2009). Moreover, free amino acids constitute less than 1% of green coffee, these include aspartic acid, glutamic acid, and asparagine among others (Wong et al., 2008). They play crucial roles as reaction partners in Maillard chemistry and Strecker degradation, generating numerous potent odorants (Wong et al., 2008). In addition to proteins and free amino acids, coffee contains the alkaloid caffeine, which is perhaps the most widely recognized and extensively studied alkaloid in plants (Poisson et al., 2017). Trigonelline is another important nitrogen-containing component. It is classified as an N-methyl betaine and can be found in arabica green beans at levels ranging from 0.6% to 1.3%, and in robusta green beans at levels from 0.3% to 0.9% (Macrae, 1985).

2.4.3. Lipids

Lipids make up approximately 15-18% of Arabica and 8-12% of Robusta (Viani and Petracco, 2007). This lipid fraction consists of coffee wax and triglycerides, predominantly composed of linoleic acid (40-45%) and palmitic acid (25-35%) (Belitz et al., 2009). Additionally, diterpenes such as cafestol and kahweol, along with sterols in both free and esterified forms, contribute to the total lipid content (Viani and Petracco, 2007).

2.4.4. Acids

The acidic fraction in green coffee consists of both volatile and nonvolatile aliphatic and phenolic acids, collectively constituting 8% of the raw bean (Maier, 1993). Major nonvolatile acids include chlorogenic acid (CGA), malic acid, citric and quinic acid (Maier, 1993). Volatile acids, primarily formic and acetic acids, originate from the fermentation process during postharvest treatment but can also be formed through Maillard-type reactions during roasting (Davídek et al., 2006; Viani and Petracco, 2007).

CGA are a group of phenolic compounds formed from the esterification of hydroxycinnamic acids with quinic acid (Farah, 2012). Caffeoyl-quinic acid (CQA) constitutes about 80% of the total CGA (Farah, 2012). Among CGA, the 5-CQA isomer is the most abundant and is continuously degraded during roasting, followed by 4- and 3-CQA (Clifford et al., 2003; Farah et al., 2005). CGA serve as important precursors of bitter taste compounds but can also decompose into their constituents, quinic acid and hydroxycinnamic acid, which may further degrade into volatile and non-volatile phenolic compounds (Dorfner et al., 2003; Tressl et al., 1976). Reported levels of CGA in green coffee vary from 8% to 14.4% dry matter for Robusta and 3.4% to 4.8% for Arabica (Ky et al., 2001).

2.4.5. Minerals

As with most plant materials, potassium is the primary component in green coffee ash, constituting 1.1%, followed by calcium (0.2%) and magnesium (0.2%) (De Maria et al., 1994). The main anions are phosphate (0.2%) and sulphate (0.1%). Various other elements are present in small, trace amounts (Pinheiro et al., 2021).

2.5. Coffee roasting

Coffee roasting is a unit operation that converts green beans into roast coffee. The process is aimed at achieving roasted coffee with the desired flavour profile, as well as imparting a dark colour and a brittle, porous texture suitable for grinding and extraction (Schenker and Rothgeb, 2017). Throughout the roasting process, coffee beans are subjected to hot air, causing their temperature to rise thus triggering extensive chemical reactions, dehydration, and significant alterations in the microstructure (Schenker and Rothgeb, 2017).

The process is carried out within the temperature ranges of 200-250°C for a roast time of 3 to 20 minutes (Yeretzian et al., 2002). It is worth mentioning that the temperature at which roasting occurs is often a representation of the temperature of the convectional heat used and the bean surface in contact with the temperature probe (Schenker and Rothgeb, 2017). Consequently, the comparison of roasting temperatures across different systems is not straightforward.

During the roasting process the coffee beans gradually change colour from green to and darker shades of brown (Yeretzian et al., 2002). The change in colour provides an objective basis to assess the degree of roasting. The colour is quantified with scales like the Agtron "Gourmet Scale" and the L*a*b colour space (Schenker and Rothgeb, 2017).

Additional changes include expansion of the volume of the bean by over 50%, accompanied by one-fifth loss in mass due to moisture loss and the release of volatiles and carbon dioxide (Pinheiro et al., 2021). The continued increase in internal pressure ultimately yields fissures in the cell wall tissue, known as "crack" (Yeretzian et al., 2002). Moreover, the expansion coupled with dehydration and chemical reactions modifies the microstructure of the beans form dense to porous (Schenker, 1999). Consequently, the native cell structures are replaced with "hollow" cells which results in a bean with gas-filled void at its centre thus facilitation easy grinding (Schenker, 1999). Moreover, the structural changes break up oil bodies and mobilize coffee oil to the surface of the beans aided by the built-up pressure (Schenker and Rothgeb, 2017).

The early stages of roasting are characterised mainly by moisture loss (Yeretzian et al., 2002). Hence, dark roasted beans experience a higher rate of moisture and organic matter loss relative to light roasted beans (Schenker and Rothgeb, 2017). Furthermore, the line between the loses across roasting degrees are blurred owing to natural fluctuations in the composition of green beans (Yeretzian et al., 2002). Thus, the similar beans roasted under the same parameters (temperature and time) may exhibit differences in composition (Schenker, 1999).

Among the notable reaction that yield compounds of interest to coffee quality is; Maillard Reaction (which gives rise to melanoidins), the reaction of hydroxyamino acids undergoing decarboxylation and dimerization and the degradation of proteins, chlorogenic acid, and polysaccharides, among others (Moreira et al., 2012). The Maillard reaction produces various volatile compounds, including pyridines, pyrazines, dicarbonyls like diacetyl among many others (Dorfner et al., 2003). Figure 1 depicts the various flavour precursors in coffee beans and their products.

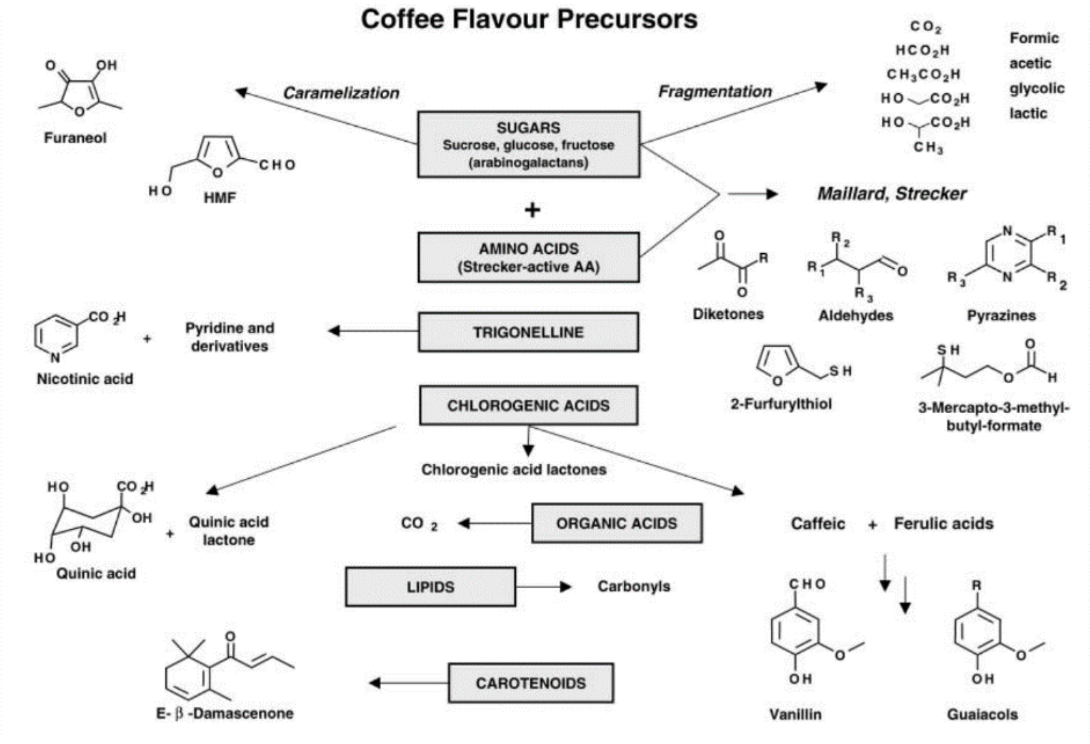

Figure 1.: Coffee flavour precursors (Yeretzian et al., 2002)

2.5.1. Effect of roasting on bean composition

2.5.1.1. Carbohydrates

Approximately 12-24% of polysaccharides are degraded in light-roasted coffee, increasing to 35-40% in dark-roasting (Bradbury, 2001). The degradation primarily involves the breakdown of arabinogalactan side chains into arabinose, while cellulose and mannans largely remain intact (Bradbury, 2001). While polysaccharides may not directly contribute to aroma formation during roasting, they influence relevant organoleptic properties of coffee brews, such as viscosity and mouthfeel (Redgwell et al., 2002).

As observed with arabinogalactans, roasting also induces structural alterations in AGPs, leading to the depolymerization of main and side chains with the release of free arabinose (Oosterveld et al., 2003; Wei et al., 2012). Most of the liberated arabinose combines with CGA to form melanoidins (Bekedam et al., 2006; Moreira et al., 2012; Nunes et al., 2012). Additionally, arabinose residues may contribute to the formation of formic and acetic acid (Ginz et al., 2000). While free galactose, another component of arabinogalactans, is primarily present in significant amounts in green beans, it undergoes rapid degradation during roasting (Redgwell et al., 2002)

Reducing sugars like glucose and fructose concentrations increase in the initial stages of roasting due to sucrose degradation (Wei et al., 2012). However, nearly all free sugars are lost during roasting due to Maillard reactions and caramelization, contributing to water, carbon dioxide, colour, aroma, and taste formation (Poisson et al., 2017).

2.5.1.2. Nitrogen containing compounds

Although free amino acids (aspartic acid, glutamic acid and asparagine) constitute less than 1% of green coffee, their significance in shaping the final flavour of roasted coffee is considerable (Yeretzian et al., 2002). They play crucial roles as reaction partners in Maillard reaction and Strecker degradation, generating numerous potent odorants (Wong et al., 2008;

Yeretzian et al., 2002). Proteins and peptides can also serve as aroma precursors by breaking down into smaller reactive molecules (De Maria et al., 1996b). However, free amino acids are almost entirely degraded during roasting.

Throughout the process of roasting, trigonelline, undergoes demethylation, leading to the production of niacin (Trugo, 2003). Moreover, trigonelline contributes to the formation of volatile compounds such as pyridines and pyrroles during the roasting process, enhancing the final aroma of the beverage (Monteiro and Trugo, 2005). The trigonelline concentration in roasted coffee is influenced by the roasting duration, with more intense roasting resulting in lower trigonelline levels in the beverage (Monteiro and Trugo, 2005). Commercial coffee samples have been found to contain trigonelline levels ranging from 0.2 to 0.5 g per 100 g of roasted coffee (Monteiro and Trugo, 2005). Alkaloids like caffeine exhibit relatively high stability and are not affected significantly by the level of roasting (Viani and Horman, 1974).

2.5.1.3. Lipids

During the roasting process, lipids can undergo thermal degradation to form aldehydes, which may react with other compounds present in coffee (Belitz et al., 2009). The oxidation of unsaturated fatty acids results in the production of potent aldehydes like hexanal, nonenal, and other enals, along with dienals (Belitz et al., 2009). However, these aldehydes are not considered key contributors to the aroma of coffee (Sanches-Silva, 2004). They can undergo further reactions such as cyclization or interaction with other coffee constituents (Spadone and Liardon, 1989). Hexanal is commonly used as an indicator of lipid oxidation in various food products and has also been associated with coffee staling, among other compounds (Spadone and Liardon, 1989).

2.5.1.4. Organic acids

CGA undergo significant degradation during coffee roasting. This degradation results in the formation of hydrolysis products such as quinic acid and phenolic acids like ferulic acid, which further break down to produce important phenolic odorants like guaiacol and 4-vinyl guaiacol

(Jaiswal et al., 2012). Approximately 90% of total CGA, equivalent to 7% of green coffee solids, react after 9 minutes of roasting (Farah et al., 2005). Recently, the identification and formation pathways of bitterness components in roasted coffee have been elucidated by Jaiswal et al (2012). CGA lactones, the breakdown products of CGA (CQAs), have been recognized as major contributors to bitterness in coffee (Jaiswal et al., 2012). Moreover, the decarboxylation of CGAs during roasting leads the increase in phenolic compounds such as vinyl guaiacol, phenol and guaiacol (Moreira et al., 2000). Guaiacols are the main phenolic representatives of roasted coffee flavour (Arruda et al., 2012)

2.6. Coffee extraction methods

Coffee preparation is a solid-liquid extraction where both soluble and insoluble compounds in coffee migrate to the coffee brew (Wang and Lim, 2023). The process coffee extraction process, benefits from increased surface area per unit volume of extractable solids and decreased particle radial distances within the solids, both of which are facilitated by smaller particle sizes (Cordoba et al., 2020). The mass transfer mechanisms involved in these steps are intricate and heavily influenced by the microstructures developed during the coffee bean roasting process, as well as the inherent properties of the coffee grounds (such as variety, roast profile, grind size) and brewing conditions (including temperature, extraction time, brewing pressure, and brew ratio) (Wang & Lim, 2023).

The extraction process can be categorized into three broad methods: decoction methods (such as Turkish coffee, boiled coffee, percolator coffee, and vacuum coffee), infusion methods (including Napoletana and filter coffee), and pressure methods (like Moka, Plunger, and espresso) (D’Agostina et al., 2004).

Different brewing methods (Figure 2) significantly impact the strength of coffee by influencing various factors such as the extraction process, temperature, and contact time with water (Wang and Lim, 2023). Furthermore, the brewing temperature, time, and extraction process play crucial roles in determining the strength of coffee, with variations in these parameters leading to differences in the chemical composition and sensory characteristics of the brewed beverage (Orent et al., 2011; Petracco, 2001a).

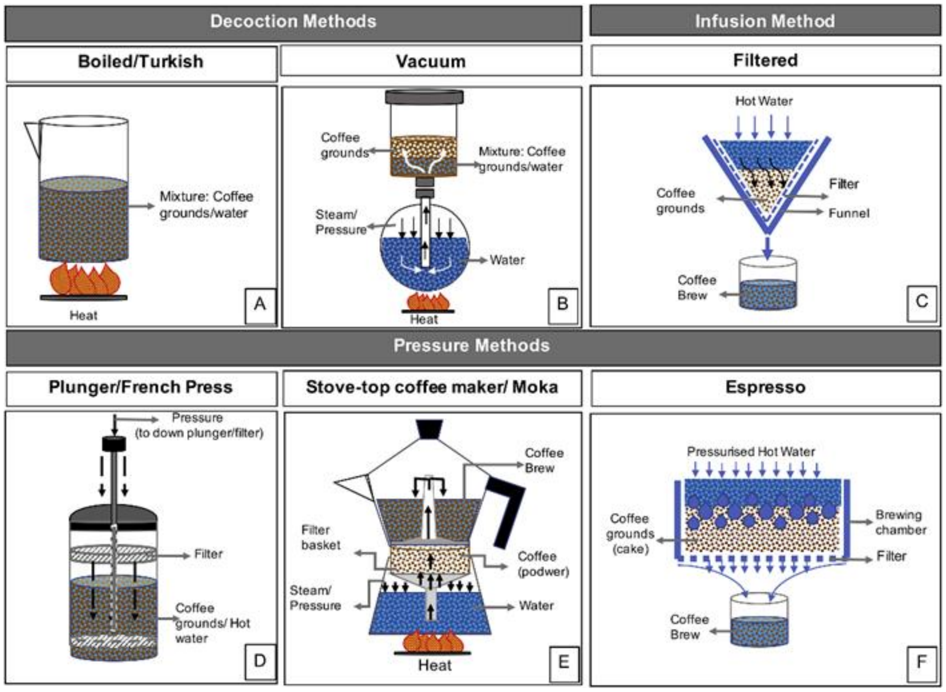

Figure 2: Different coffee extraction methods (Cordoba et al., 2020)

2.6.1. Pour-over extraction and the V60

The pour-over coffee method is often referred to as drip coffee or filter coffee (Mestdagh et al., 2017). It requires coarse to medium fine particle-sized coffee grounds (600µm) to enable water to pass through the coffee bed solely by gravity (Frost et al., 2020; Mestdagh et al., 2017). The ground coffee is placed in a holder with a filtration device (Chen et al., 2023). Various filter sizes, shapes, and materials can be employed to regulate the filter bed's shape and level of filtration (Frost et al., 2020; Mestdagh et al., 2017). The filtered water then collects in a serving vessel while retaining the grounds in the filter.

The shape and depth of the filter and the coffee bed are subjects of considerable discussion as they significantly influence extraction quality (Chen et al., 2023; Frost et al., 2019, 2020a). Many filter coffee systems, like the V60, utilize cone-shaped filters, which create a conical coffee bed that optimizes the extraction of specific flavours, ultimately affecting the taste of the final brew (Chen et al., 2023; Frost et al., 2019). Besides, the concentration of lipids in filtered coffee may be considerably reduced due to the retention of lipophilic molecules in the filter paper (Rendón et al., 2017). This was supported by Chen et al (2023), who found significant differences in TDS, EY and fat content of the same coffee samples brewed with filters of different shapes and materials were. Furthermore, the concentrations of volatiles as well as chlorogenic acids were different across filter types. Figure 3 a) illustrates a model of the V60 and b) the set-up in use.

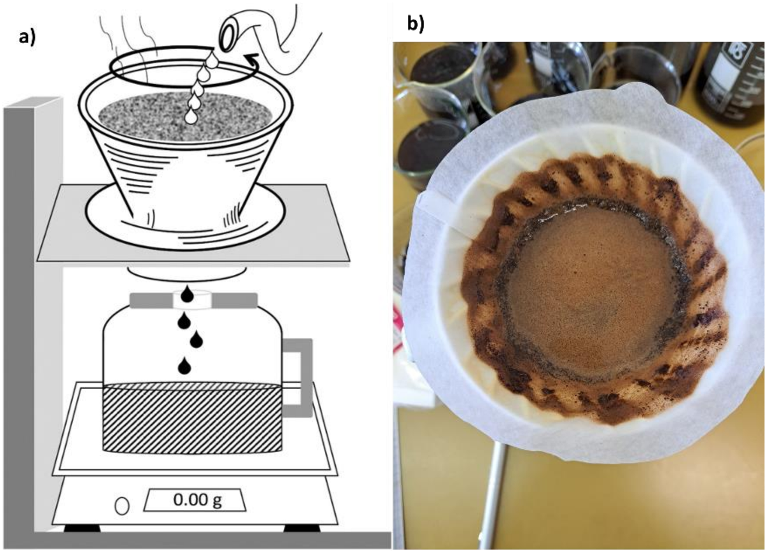

Figure 3: a) 3d model (Chen et al., 2023), and b) actual V60 set-up

2.6.2. Extraction parameters and their impact on brew strength

2.6.2.1. Effect of Water temperature

The temperature of the water plays a crucial role in achieving a well-balanced extraction of roasted coffee. The recommended brewing temperature range for hot coffee is typically between 91°C and 94°C, which represents a compromise aimed at achieving both a good extraction yield and a balanced sensory profile (Mestdagh et al., 2017)

Lower temperatures result in inefficient extraction of certain compounds whiles higher temperatures tend to favour the extraction of less polar compounds, such as bitter, astringent, and phenolic compounds (Severini et al., 2016). Higher water temperatures increase the kinetic energy of water molecules, enhancing their mobility and increasing the likelihood of leaching compounds from the coffee bed due to greater physical forces (Severini et al., 2016). Moreover, higher temperatures lead to lower viscosity, allowing water to penetrate the coffee bed more easily and access intercellular spaces to solubilize coffee compounds (Mestdagh et al., 2017). Hence, it can be inferred that the level of TDS of coffee brew is higher at elevated temperatures. This relationship, however, is not linear for all components, as observed in the solubility differences between caffein and citric (Albanese et al., 2009; Salamanca et al., 2017).

2.6.2.2 Particle Size of ground coffee

Grinding roasted beans increases the surface area available for extraction and aids in the transfer of soluble and emulsifiable substances into the water during brewing (Rodrigues et al., 2019). Hence, controlling the grinding conditions is crucial as it directly impacts the resulting flavour of the brew (Rodrigues et al., 2019).

During the grinding process, a variety of particle sizes and shapes can be generated within the same sample, characterized by the particle size distribution (PSD) (von Blittersdorff and Klatt, 2017). The PSD is influenced by moisture content of the roasted beans and the roasting protocol (von Blittersdorff and Klatt, 2017). Shorter roasting protocols are associated with increased porosity and brittleness of coffee beans due to loss of cell wall elasticity (Illy and Viani, 2005; von Blittersdorff and Klatt, 2017). Conversely, coffee beans roasted slowly tend to form a matrix with more uniform pore sizes and higher density resulting in a more homogeneous PSD (Von Blittersdorff & Klatt, 2017). The result of which is uniform and consistent extraction.

Ground coffee with larger coffee particles have less total surface area available for contact with water, resulting in a faster but less efficient extraction process (Rodrigues et al., 2019). On the other hand, smaller particles allow for a more efficient extraction due to increased surface area, resulting in a slower flow of water through the coffee grounds (Andueza et al., 2003; Cordoba et al., 2020, 2019; López-Galilea et al., 2007; Rodrigues et al., 2019; Walston et al., 2022).

2.6.2.3. Pressure

The application of pressure within a fluid generates potential energy, which can readily be converted into kinetic energy, imparting velocity to tiny masses of fluid (Cordoba et al., 2020). This process drives micron-sized solid particles or oil droplets into the cup, potentially altering the properties of the beverage and enriching its sensory characteristics (Petracco, 2001b). One benefit of using pressure is that aromatic compounds are less prone to evaporate from the coffee bed compared to non-pressurized or low-pressure extraction methods. Instead, these compounds are retained in the cup to a greater extent (Sánchez López et al., 2016).

2.6.2.4 Water quality and quantity

Water is the second most essential ingredient after roasted coffee beans. Its characteristics such as hardness, acidity, and cation composition can directly impact the sensory outcome of the extract (Hendon et al., 2014). Highly soluble compounds like caffeine, organic acids and sugars are extracted rapidly, often reaching over 90% extraction yield within the first few seconds of brewing (Severini et al., 2016; Stadler et al., 2002). Consequently, a lower extraction yield (under-extracted coffee) tends to result in a cup profile characterized by water-soluble compounds, leading to a sweeter and more acidic taste profile (Andueza et al., 2007). For instance, in drip coffee brewing, like the V60, it's estimated that approximately 90% of the caffeine is extracted within the initial minute of brewing (Mestdagh et al., 2017). Conversely, less soluble compounds require more time (or water volume) for extraction. Figure 4 illustrates the scheme of extraction and the influencing process variables.

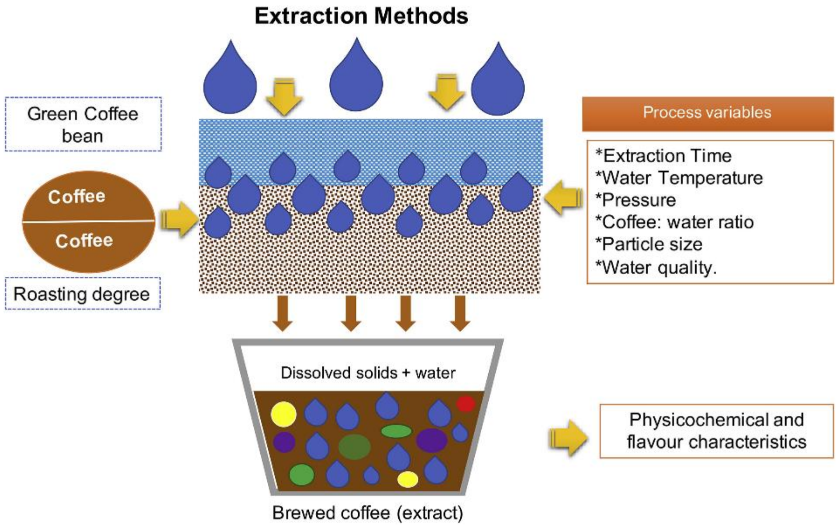

Figure 4: Extraction and associate process variables. (Cordoba et al., 2019)

2.7. Chemical composition of brew

Coffee brew contains volatile and non-volatile components as well suspended particles from fines (Belitz et al., 2009). As stated earlier, the concentration depends on the brewing methods and the various process variables such time, temperature, percolation time, water quality among others (Belitz et al., 2009).

2.7.1. Non-volatile constituents

The non-volatile constituent comprises carbohydrates, lipids, organic acids, minerals, melanoidins, chlorogenic acids, nitrogen-containing substances as well unidentified chemical constituents (Ludwig et al., 2014). Polysaccharides make up approximately 24 % of the dry weight of arabica brew (medium roast), composed mainly of galactomannans and arabinogalactans (Belitz et al., 2009; Moreira et al., 2011). They serve many flavour functions including foam stabilisation (Nunes et al., 1997), increase viscosity (Arya and Rao, 2007) and bind aroma compound (Clifford, 1985).

The second class of non-volatile components found in coffee brew comprise organic acids, mainly formic, acetic, malic, and phosphoric acid, and CGA (14% of dry brew weight) (Belitz et al., 2009; Cordoba et al., 2020). These acids are linked to the astringency, bitterness, and acidity of the beverage, particularly those with higher concentrations, like caffeoylquinic acid and feruloylquinic acid (Farah, 2019).

Nitrogen-containing compounds make up the third class of major non-volatile compounds with the most abundant being caffein and trigonelline (Belitz et al., 2009; Cordoba et al., 2020). Additional alkaloids found in coffee beverage are furan-2-yl methylated benzene diols, triols and phenylindanes (Frank et al., 2007; Kreppenhofer et al., 2011).

Melanoidins round off the major non-volatile components of coffee brew. In addition to providing colour, melanoidins influence flavour release through the presence of diverse functional groups (Bekedam et al., 2006; Hofmann et al., 2001; Moreira et al., 2012; Nunes and Coimbra, 2007). As mentioned earlier, the lipid concentration in filtered coffee brew is much less due to the retention of lipophilic molecules to the filter papers (Rendón et al., 2017). According to Petracco (2001), paper filters excel in capturing oil droplets, permitting approximately 10 mg/l to pass into the brew.

2.7.2. Characterization of Coffee Brew

Coffee brew consists of a solution matrix containing salts, acids, sugars, and specific compounds such as caffeine, alongside various dispersed phases (Lyman et al., 2003). These dispersed phases include emulsions (consisting of oil droplets), suspensions (comprising solid particles), and effervescence (consisting of gas bubbles) (Petracco, 2001b).

Coffee is characterized by parameters such as viscosity, density and refractive index among others (Moreno et al., 2015; Petracco, 2001a). According to Viani and Petracco (2007) the density of coffee brew with high lipid content like those characteristics of expresso, are lower than water.

Characterizing coffee brew by refractive index is challenging due to the polyphasic nature of the brew (Viani and Petracco, 2007). Filtered brews typically have refractive index values ranging from 1.333 to 1.338 in contrast to the index of pure water (1.333 at 20°C) (Petracco, 2001b). Measures of refractivity on filtered aliquot of espresso exhibit no major difference concerning the influence of solutes and dispersed phases (Petracco, 2001b).

In a recent study by Moreno et al (2015) characterised coffee brew by refractive index and Brix° using diluted freeze-dried coffee samples. This suggests that the inconsistencies encountered by Petracco (2001b) could be attributed to the volatiles and gases. This has not been confirmed by an independent.

2.8. Cup Quality and Total Dissolved Solids (TDS)

In the quest to comprehend the interplay between coffee quality factors, cupping taste analysis stands as a globally recognized and utilized method, despite its inherent subjectivity (Cardoso et al., 2017). Various studies have endeavoured to establish a correlation between the physicochemical properties of coffee and sensory perception of quality aiming to enhance sensory analysis with greater standardization and precision (Borém et al., 2008; Pereira et al., 2018). This is essential because the chemical composition of coffee is intricately linked to consumer perception of brew quality. Chemical components of coffee brew of interest include caffeine, trigonelline, 5-caffeoylquinic acid, minerals, and sucrose among others (Barahona et al., 2020; Bicho et al., 2013; Lacerda, 2014; Martinez et al., 2018; Morales-Ramos et al., 2020; Pinheiro et al., 2021). Despite the immense progress made in mapping chemical components to desirable sensory attributes, quantifying these components individually is cumbersome (Gloess et al., 2013).

Estimations of the TDS of brew with simple instruments like a refractometer is a more practical approach to assessing in-cup quality due to its strong correlation with brew “strength” and relative ease of estimation (Petracco, 2001b). Furthermore, it aids in control of other cup-quality parameters like balance. TDS is defined as the mass concentration of all dissolved species in a brew expressed as a percentage (Sunarharum et al., 2014). Moreover, TDS allows for mass conversion arguments to calculate the extraction yield (EY), which is the ratio of mass extracted from coffee to the weight of the coffee grounds used (Sunarharum et al., 2014).

According to mass conservation arguments, there is a linear correlation between the EY and TDS, where the slope is related "brew ratio", which is the ratio of the mass of water used to the mass of coffee grounds (Cordoba et al., 2020; Ristenpart and Kuhl, 2015). This relationship forms the basis of Brewing Control Charts of the Specialty Coffee Association used to estimate coffee brew flavour profile (Lockhart, 1957). TDS values 0.79 - 1.25% and EY between 18 - 22%, according to the Brewing Control Charts, represent ideally brewed coffee (Lingle, 2011; Lockhart, 1957; Ristenpart and Kuhl, 2015).

The nine superimposed areas on the Brewing Control Chart represent distinct levels of brewing quality (Lockhart, 1957). Brews below 18% are perceived as under-extracted or lacking in development, resulting in overly sweet and acidic flavours (Lockhart, 1957). Conversely, brews exceeding this range are considered over-extracted, leading to unpleasant bitter and astringent tastes (Lingle, 2011). Furthermore, brew characterized by low EY and high TDS is categorized as "strong underdeveloped" coffee, while one with high PE and low TDS is labelled "weak bitter." The central zone is recognized as "ideal" for all brewed coffee. These delineated quality zones serve as widely accepted guidelines in the coffee industry to facilitate the production of coffee with enhanced consistency and quality (Lockhart, 1957).

The Brewing Control Chart has been expanded in recent years by Frost et al (2022) and Betali et al (2020a). They demonstrated in their studies that high TDS was strongly correlated with bitterness, roast-like aromas, and smokiness; while high TDS coupled with low EY was correlated with sourness and citrus, lower TDS is associated with high sweetness and tea-like.

It is noteworthy, however, that TDS is composed of soluble (about 90%) and suspended particles (about 10%), hence, brewing techniques that utilize a filter like the V60, may yield lower values of TDS (Petracco, 2001b). Figure 5 illustrates the coffee brewing chart.

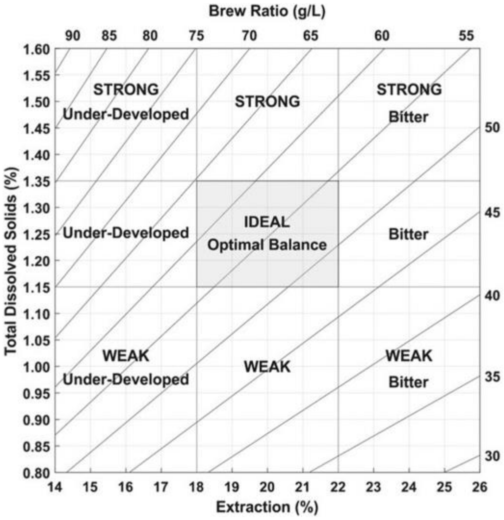

Figure 5: Brewing control chart (Lockhart, 1957)

2.9. TDS estimation

TDS is measured with gravimetric methods such as oven-drying, electrical conductivity, refractive index-based TDS meters and hydrometers (Gajdoš Kljusurić et al., 2015; Pinheiro et al., 2021; Wang and Lim, 2023). Oven-drying and refractive index-based estimates are predominantly used for routine analysis and research purposes (Moreno et al., 2015; Pinheiro et al., 2021; Wang and Lim, 2023).

2.9.1 Oven-drying method

The determination of coffee TDS by the oven drying method involves drying a sample in an oven until all moisture is removed (Petracco, 2001b). The oven drying method can be time-consuming, taking several hours, as well as associated loss of volatile compounds (Wang & Lim, 2023). Drying protocols that incorporate microwave ovens significantly reduce drying time (Carlson et al., 2013; Hemphill and Martin, 1992; Marquez et al., 1995; Van Wychen and Laurens, 2023).

2.9.2. Refractive Index and Brixº measurement

The TDS of coffee brew can be accurately measured using a refractometer calibrated for the coffee matrix (Wang & Lim, 2023). The refractometer utilizes a prism-sample interface to refract light towards a photodetector, determining TDS based on the index of refraction of the brew and its temperature (Fedele, 2012). According to Moreno (2015), components such as melanoidins and sediments of coffee extract affect the diffraction of light. Measurements obtained from refractometers and Brixº meters (refractometer calibrated on the Brixº scale – 1 Brixº equals the refractive index of 1% W/W sucrose at 20ºC) cannot be used for direct estimation of TDS of coffee without a correction factor (Kimball, 1991; Moreno et al., 2015).

This is due to the low sucrose and high organic acids in coffee brew (Kimball, 1991; Sunarharum et al., 2014). In pursuit of a correction factor, several independent studies (Aloe, 2022; Gómez, 2019) have proposed the equation; TDS% = 0.85*(Brixº) + Af, where Af is the temperature adjustment factor required for analogue refractometers (Gómez, 2019). It is worth noting that the TDS and Brixº values used for the analysis were estimated with digital refractometers with a predefined coefficient for converting Brixº to TDS.

In a peer-reviewed study by Moreno et al (2015), they proposed TDS% = 0.87*Brixº at 20ºC. This lends credence to the conversion factor, but the potential influence of coffee roasted across various levels of intensity in combination with different extraction methods remains unanswered. As noted earlier, estimating the refractive index of coffee brew is particularly challenging due to the polyphasic nature of the brew (Viani and Petracco, 2007). Moreover, refractive index and by extension Brixº measurements are sensitive to temperature fluctuations which necessitates a temperature correction (Kimball, 1991).

2.10.1. Role secondary analytical methods and NIRS

Secondary analytical methods have been applied extensively in the food industry to estimate raw material quality, undertake process control, rapid analysis and product development

(Reh, 2008) The primary drivers behind the mass adoption are cost reduction and efficiency, which allows for improved product quality, reduction of waste, routine analysis and increased production capacity among others (M. M. Ali & Hashim, 2022; Odabaş & Çakmak, 2021; Shao et al., 2022).

The various methods of estimating TDS of coffee require the preparation of coffee brew from roasted coffee beans (Wang and Lim, 2023). Hence, exploring secondary analytical techniques in this regard will be immensely beneficial to the coffee industry. NIRS stands out as a major secondary non-destructive analytical method that has been applied extensively in the coffee industry to estimate quality parameters of coffee (Baqueta et al., 2020; Budiastra, 2020; Esteban-Dıez et al., 2004; Grassi et al., 2023; Kumaravelu & Gopal, 2015; Mutz et al., 2023; Ribeiro et al., 2012; Zhang et al., 2013).

NIRS is based on the unique interaction of electromagnetic radiation in the NIR range with matter (Sandorfy et al., 2006). According to Sandorfy et al (2006) the interaction manifests as the absorbance of frequencies of polychromatic light that corresponds to the molecular vibrational transition of the material. The chemical and physical characteristics of the materials are thus deduced from the resulting spectra (Sandorfy et al., 2006)

2.10.2. Theoretical background

NIR spectra are generated primarily by the weak, broad overtones and combination bands of fundamental vibrational transitions linked to C-H, O-H, S-H and N-H functional groups (Teye et al., 2013). The NIR region covers a wavenumber range of 12500cm^{-1} - 4000cm^{-1}, where absorption bands primarily correspond to overtones and combinations of fundamental vibrations (Blanco and Villarroya, 2002).

Vibrations of the molecules have been described with the harmonic and anharmonic oscillator models with the latter offering a more robust explanation of the behaviour of observed molecules (Sandorfy et al., 2006). The anharmonic model is represented by the equation;

$$E_{vib} = hv\ [1 - (2\nu + \Delta\nu + 1)\gamma] \tag{1}$$

where E_{vib} is the energy of vibration, v is the vibrational quantum number, ν is the fundamental vibrational frequency, γ is the anharmonicity factor (Teye et al., 2013). The anharmonicity factor accounts for transitions between non-adjacent vibrational states which results in overtones; multiples of fundamental vibrational frequency (Kumaravelu and Gopal, 2015)

According to Kumaravelu & Gopal (2015) at typical room temperature, the transition from the ground state to the first excited state strongly absorbs light in the infrared (IR) region, generating intense fundamental bands (Kumaravelu and Gopal, 2015). They added that the transition from the ground state to the second excited state, involving the absorption of near-infrared (NIR) light, results in weak bands known as the first overtone. Similarly, the transition from the ground state to the third excited state, also absorbing NIR light, leads to weak bands of the second overtone (Ozaki et al., 2006). Third and fourth overtone bands occur based on transitions to the fourth and fifth excited states, respectively, with the absorption of NIR light (Sandorfy et al., 2006).

In molecules with multiple atoms, the interaction of two or more vibrational modes can lead to simultaneous energy changes, resulting in absorption bands known as combination bands (Ozaki et al., 2006) These bands have frequencies that are the sums of multiples of each interacting frequency (Kumaravelu and Gopal, 2015; Ozaki et al., 2021).

2.10.3 Modes of NIR spectra acquisition

NIR measurement techniques can be categorized into two main methods: transmittance and reflectance (Barbin et al., 2014; Fontes et al., 2022). Transmittance is suitable for clear liquids or thin solid samples like solutions, suspensions, fibres, powders, films, and gases (Dahm and Dahm, 2021). Transmittance further divides into regular transmittance and transflectance methods which can be used for bulk materials such as clear suspension (Barbin et al., 2014).

Reflectance, on the other hand, is applicable to solid samples like whole and ground coffee beans, fabrics, pastes and powders, relying on the reflection from the rough surfaces of scatterers (Ikehata, 2021). In diffuse reflection, the incident ray undergoes partial reflection by the surface of the sample and partial transmission beneath it (Pasquini, 2003). The transmitted ray is refracted and reflected multiple times on the surfaces of particles, with a portion exiting the scatterer. The process bears similarity with transmitted light as it travels within the absorptive material (Pasquini, 2003). As the rays disperse in various directions upon exiting the object's surface, a gold-evaporated integrating sphere is commonly employed to efficiently capture them (Pasquini, 2003). For swift measurements, a detector is positioned at an off-angle side of the standard reflection to avoid direct contact with the sample (Ikehata, 2021).

For solutions and suspensions with low turbidity like coffee brew, transflectance measurement is preferred for obtaining efficient spectra absorption (Ikehata, 2021; Lyman et al., 2003; Ozaki et al., 2006). To achieve this, it is essential to use window materials with optimum path length and refractive index as well as applicability in the wavelength region of interest (Ikehata, 2021; Ozaki et al., 2006)). The temperature at which measurements are obtained is important as NIR spectrum is highly sensitive temperature (Williams, 2007).

Both transmittance and reflectance methods require a background measurement, involving the measurement of the intensity, I_0, of the transmittance or reflectance light from the background (Osborne, 2006; Osborne et al., 1993; Pasquini, 2003). This intensity, I_0, can be measured either before each sample or at convenient intervals during routine analysis (Osborne, 2006). Subsequently, the intensity of the sample light, I, is measured. The absorbance of the sample is then determined using the formula $A = -\log(I/I_0)$ for transmittance measurements (Osborne, 2006). In the case of reflectance measurements, the reflectivity, $R = I/I_0$, is obtained, and the absorbance of the reflectance is expressed as $\log(1/R)$ (Ikehata, 2021)

2.10.4 Interpretation of NIRS

The foundation of spectral analysis in NIR spectroscopy relies on band assignments, yet, these assignments are typically intricate due to the overlap of numerous bands stemming from overtones and combinations which complicates the task (Illy & Viani, 1995; Lyman et al., 2003; Ozaki et al., 2021; Wang et al., 2012). For samples with complex spectrum like coffee, detailed band assignments might not always be essential but remains important to discern the various functional group from which a band originates (Illy and Viani, 1995; Ozaki et al., 2021; WANG et al., 2012)

The strength of light absorption is heavily influenced by the extent of change in dipole moment during vibrational transitions as observed in X-H (where X is C, O, N or S), C=O and C≡N (Czarnecki et al., 2015). Consequently, the vibrations of heteronuclear diatomic molecules dominate the NIR spectra (Czarnecki et al., 2015; Ozaki and Morisawa, 2021). In addition, the multiple vibrational modes of polymeric molecules are either interconnected or coupled, which results in broad overlapping combinations bands complicates direct functional group assignments (Ozaki and Morisawa, 2021; Siesler, 2007).

For samples with high moisture, it is important to note that the first overtone bands of O-H and N-H stretching modes in monomeric species exhibit much higher intensity compared to the corresponding bands in polymeric species (Ozaki et al., 2021). Thus, the spectra of water have an intense foot observed at 4000 cm^{-1} (Ozaki et al., 2006). Furthermore, two strong bands useful for investigation are observed at 5235 and 6900 cm−1 (Ozaki and Morisawa, 2021). These are the result of combination of H-O-H antisymmetric stretching mode (second overtone) and bending mode (first overtone) and that of H-O-H symmetric (fundamental) and antisymmetric (second overtone) stretching modes, respectively (Ozaki and Morisawa, 2021). Hence, the spectra of samples with high water content like coffee brew are often dominated by bands origination from first overtone O-H stretch modes and may overshadow bands from terminal functional groups like O-H in organic acids (Hu et al., 2006).

Lastly, NIR spectrum is affected by variations in particle size distribution and density. These cause differences in the path length travelled by photons before reaching the detector (Martens, 2001). These physical discrepancies between samples induce light-scattering effects, resulting in shifts in the baseline and variations in intensity (Martens, 2001).

2.10.5. Chemometrics applied in assessing coffee quality.

The NIR spectra of complex materials like roasted coffee beans possess broad overlapping NIR absorption bands which are influenced be the chemical and structural properties of the sample (Teppola, 2002). This renders the spectra acquired multivariate and requires chemometric procedures to filter information of interest by describing how multivariate spectral features (independent variable) relate to the properties of the analyte of interest (dependent variable) (Teppola, 2002)

2.10.6 Preprocessing techniques

As note earlier, physical and chemical differences in samples translate to unwanted variations in NIR spectra (Martens, 2001), thus a major goal of pre-processing is to linearize spectra in accordance with the Lambert–Beer law (Ozaki and Morisawa, 2021). One such unwanted variation in NIR spectrum is baseline shift, which is the result of multiplicative and additive effects (Teppola, 2002). The Savitzky-Golay (SG) derivatives has found extensive applications in this regard (Esteban-Dıez et al., 2004; Pizarro et al., 2004; Teófilo et al., 2009). The pretreatment method diminishes baseline shift by employing a low-degree polynomial fit around a given point within a spectrum (Savitzky and Golay, 1964). One downside of derivative methods is that the signal-to-noise ratio of the spectrum may worsens with derivative step (Savitzky and Golay, 1964).

Further methods for correcting baseline shift are multiplicative scatter correction (MSC) and standard normal variate (SNV) (Esteban-Dıez et al., 2004). MSC addresses additive (vertical) baseline variations and multiplicative baseline shifts by applying a basic linear univariate fit to a standard spectrum to enhance linearity of the spectra (Sørensen et al., 2021). While generally beneficial, using MSC requires caution as it may inadvertently introduce unwanted artefacts (Esteban-Dıez et al., 2004; Shimoyama et al., 1998). The Standard Normal Variate (SNV) method is another effective technique for rectifying the vertical baseline drift in a series of spectra (Barnes et al., 1989). SNV operates by computing and standardizing the mean and standard deviation of the intensities within each spectrum (Barnes et al., 1989).

Noise remains a major part of undesired variations in NIR spectra (Sørensen et al., 2021). High-frequency noise is the most encountered and is generally associated with the NIR instrument's detector and electronic circuits (Ozaki et al., 2021). Noise can be mitigated by incorporating accumulation-average processing into the spectrum data collection process (Ozaki et al., 2006) . While Savitzky-Golay (SG) derivative can be used to eliminate high-frequency noise, it's important to note that increasing the smoothing intensity by adding more smoothing points may cause distortion, resulting in reduced resolution and band intensity (Savitzky and Golay, 1964). Other preprocessing methods include cantering, normalization, orthogonal signal correction (OSC) and other (Esteban-Dıez et al., 2004). The preprocessing method is often tied to the aim of the aims of study.

2.10.7. Data reduction and classification

NIR spectrum contains data collected across hundreds of different wavelengths, which makes dimension reduction processes imperative (Pizarro et al., 2004). Furthermore, NIR spectrum often exhibits a high correlation among adjacent variables (absorptions at various wavelengths), known as multicollinearity (Sørensen et al., 2021). The phenomenon complicates linear regression models used for calibration and prediction, hence the need for dimension reduction (Sørensen et al., 2021).

Principal Component Analysis (PCA) is applied extensively to this effect as a data compression tool and an unsupervised pattern recognition technique in qualitative NIR analysis (Hotelling, 1933). The model works by decomposing correlated variables into a smaller set of uncorrelated latent variables called principal components (PCs) (Wold et al., 1987). The first PC ideally captures the most variance in the data, with subsequent PCs capturing the remaining variance while being orthogonal to previous components (Wold et al., 1987).

Furthermore, each principal component comprises a linear combination of original variables, with scores indicating the orientation of each variable to the PC, and loadings characterizing the orientation of the PC vector (Wold et al., 1987). The score plots aid in interpreting PCA results, facilitating outlier detection and analysis (Pizarro et al., 2007; Wold et al., 1987).

2.10.8 Quantitative analyses of NIR data

The objective of multivariate calibration involves developing a predictive model that establishes a relationship between the NIR spectra and the analyte concentration (Wold et al., 1983) In this process, calibration aims to model analyte concentrations (y-variables) as linear combinations of absorption spectra (x-variables) (Wold et al., 1983). This enables the prediction of analyte concentrations in unknown samples solely based on absorption spectra (Sørensen et al., 2021). PCR and PLS are the most encountered because they allow for incorporating more information into the calibration model and are not hindered by multicollinearity like in MLR (Wold et al., 1983). In PLS, the largest covariance between independent variable (spectral data) and dependent variable is used as a weight vector to guide the regression in the direction of the highest systematic variance in the dependent variable as function of the dependent variable (Smilde et al., 2004). The scores in PLS are derived from projecting the dependent variable onto the weight vector, followed by determining the loadings through the regression of scores on independent variable (Smilde et al., 2004).

The performance of multivariate models always has to be validated. Typically, validation focuses on assessing the models' ability to extrapolate the values of new samples (Sørensen et al., 2021). The process involves separating the dataset into calibration and test sets where the calibration set is used to build the model and the test set to evaluate model performance (Martens et al., 1987). In splitting the data into validation and calibration sets, it must be ensured that they are independent of each other, that is, the same physical sample cannot appear in both datasets, either as individual measurements or as replicates. (Smilde et al., 2004). In cases where the dataset isn't large enough to partition, cross-validation, can be utilized (Smilde et al., 2004). The process involves sequentially excluding one or more samples from the dataset to create a calibration model with the remaining samples and then using that model to predict the values of the excluded samples (Wakeling and Morris, 1993; Wold, 1978).

Model performance is evaluated with Pearson’s correlation coefficient ® and the coefficient of determination (R^2) between known dependent variables and their associated predicted variables (Wakeling and Morris, 1993).’It's important to note that these metrics are considered alongside the root mean square errors of calibration and prediction (RMSEC and RMSEP) (Wakeling and Morris, 1993) The optimal model is one with a sufficiently high correlation (R and R^2) as few as possible components, and low prediction error (root mean squared error of prediction) (Sørensen et al., 2021).

2.10.9. Assessing coffee quality characteristics with NIRS

NIR spectrometry has been used to assess the multitudes of coffee quality characteristics (Baqueta et al., 2020; Budiastra, 2020; Esteban-Dıez et al., 2004; Grassi et al., 2023; Kumaravelu & Gopal, 2015; Mutz et al., 2023; Ribeiro et al., 2012; Zhang et al., 2013).

Discriminating and classifying arabica and robusta varieties is one such major field. These include; discriminating between arabica and robusta samples (Downey et al., 1997), and distinguishing coffee samples from different lots and producers (Santos et al., 2012) ; discriminating Kona coffee from adulterants (Wang et al., 2009).

NIRS has also seen application assessing degree of roasting and associated changes in quality characteristics. Examples include; discriminating roasted coffee beans by the level of roasting (Ribeiro et al., 2010); and relating roasting level of coffee to quality attributes like total acidity, chlorogenic acids, and colour (Esteban-Díez et al., 2004a)

Perhaps the most relevant applications of NIR spectroscopy in relation to this research are those aimed at predicting coffee composition from the NIR spectra of beans and brew (Barbin et al., 2014). These applications include predicting; the moisture content of green beans (Morgano et al., 2008); caffeine content of roasted ground coffee (Garrigues et al., 2000; Huck et al., 1999, 2005; Zhang et al., 2013), effect of roasting conditions on flavour profile of coffee brew (Lyman et al., 2003); and determination of plant fat and sugar content in coffee beverage (Wang et al., 2012).

As demonstrated, the feasibility of applying NIRS to assess the TDS of roasted coffee remains unexplored. We therefore aim to conduct a feasibility study to estimate the TDS of coffee from NIR spectra of the roasted beans and brew.

3. MATERIALS AND METHODS

3.1. Coffee samples

Green coffee beans (48 *Coffea arabica* and 2 *Coffea canephora*), originating from five regions; South America; Asia; Central America and Africa.

3.2. Roasting Protocol

The fifty original samples (300g) were roasted on a small scale, using a predefined protocol (reference). Three levels were set for the first crack (start of roasting): light, medium and dark roasted. This generated 150 samples which were stored at -80°C until testing. Since different coffees behave differently during roasting, the boundaries between the distinct levels may be blurred. To produce light roasted coffees, the process was stopped 40 seconds after the first crack, while for the other two levels, the time was changed to 60 and 90 seconds. The starting temperature was about 150°C and the final temperature was 190°C. A Probat sample roaster was used for roasting (Leogap, Curitiba, PR, Brazil).

3.3. Grinding and Brewing

The roasted beans (20 g) were ground using an electric grinder with a fine setting (4) to a median particle size distribution of 600µm. The particle size distribution was determined using a VWR EML 200 Remote Sieve with parameter: amplitude=1.5, interval=10 sec and time 10 minutes.

The brewing in this study was carried out using a V60 dripper (Hario, Japan). The setup consists of a ceramic cone, filter paper (pore size 203 ± 21 µm) and a scale. The filter paper, folded into a cone shape and then along the seam onto itself, was wetted with hot water (98 °C). The setup was then mounted on a beaker and placed on the scale. About 16 g of the previously weighed ground coffee was transferred into the V60 dripper. Subsequently, 40 g of hot water (96°C) was poured over the mass and swirled gently until a slurry formed. The slurry stood for 45 seconds from the first pour. More hot water was poured in a horizontal and vertical circular motion for 1 min 15 seconds from the first pour to yield 230 g of water. The setup was then manually swirled gently and allowed to stand until the coffee bed appeared visibly dry. The resulting brew was then covered with wax and allowed to cool to ambience overnight.

3.4. Total Dissolved Solids and Extraction yield

3.4.1. Oven drying method

The total dissolved solids (TDS) of the coffee brew were determined using oven drying method (TDS-OD) adopted from a similar study (Andueza et al., 2007; Wang et al., 2019). TDS for this method refers to the residue of drying the eluent obtained from the V60 dripper (the pore size of filter paper for brewing is 20µm. Brew samples were pipetted (10ml) into previously weighed Petri dishes (dried at 105°C for 30 minutes). The weight of the samples was recorded and then dried at 105°C for 4 hours until constant weight was attained. The TDS was calculated using the formula:

$$TDS(\%) = \frac{m_{dried\ brew\ -}\ m_{petridish}}{m_{brew}} * 100\% \qquad (2)$$

m_{brew} is weight of the pipetted brew; $m_{dried\ brew}$ is the weight of petri dish with the dried brew; $m_{petridish}$ is the weight of the petri dish.

3.4.2. Measurement of Brix°

A digital refractometer (HANNA instruments® H196801) was used to measure the Brix° of the coffee brew. A single-point calibration of the instrument was conducted with 200µL of distilled water. The Brix° was measured by pipetting 200µL of coffee brew into the stainless steel well of the refractometer and recording the corresponding values. The measurements were conducted at ambient temperature (20 - 25°C). Temperature correction of the Brix° was performed by the instrument. The Brix° readings obtained were converted to TDS by the formula (Moreno et al., 2015):

$$TDSBC = 0.87 * Brix \qquad (3)$$

Where TDSBC is Brix°-corrected TDS.

3.5. Recording of NIR Spectra and data pre-processing

3.5.1. Coffee brew

The near-infrared Spectra of the coffee brew were collected between the range of 15798-3554 cm^{-1} in transflection mode with Bruker MPA™ multi-purpose FT-NIR analyser (Bruker, Ettlingen, Germany). Brew samples were pipetted (1 ml) into a quartz cuvette (22mm). Instrument control and spectra collection were conducted using software, Opus 7.2 (Bruker, Ettlingen, Germany), which was supplied by the device manufacturer (Bruker, Ettlingen, Germany). Care was taken not to introduce bubbles into the brew samples during pipetting as it would increase the noise in the measured spectra. Background scans were recorded with a gold-coated integrating sphere after which the spectrum was collected at room temperature (20-25 °C). The spectra were smoothed with twenty-five points after which the triplicates were averaged for each sample. The spectra were collected over two months.

3.5.2. Roasted Beans

The near-infrared spectra of the roasted beans were obtained from a previous study using the same samples using the same instrument (Benes, 2023). The collection of spectra data was conducted with whole roasted bean samples (40-60 g) in a rotating cuvette (Ø85 mm) in six replicates. The spectral data were collected in diffuse reflection measurements mode within the range of 12500 – 3800 cm^{-1} (resolution 16 cm^{-1}; scanning speed 10 kHz), using the OPUS 7.2 (Bruker, Ettlingen, Germany) software. Each spectrum was calculated as the average of thirty-two subsequent scans. Background scans were recorded with a gold-coated integrating sphere.

3.6. Statistical Methods

3.6.1 Sample size calculation

The minimum sample size required for Repeated Measures (RM) ANOVA was calculated a priori with G*Power (v3.1.9.7). The parameters used are as follows; [f (effect size) = 0.4, alpha error probability = 0.05, power (1- beta error probability) = 0.95, number of groups=1, number of measurements = 3, correlation among repeated measures = 0.5, non-sphericity correction =1)]. This resulted in a minimum sample size of 18, which is below the sample size used for the analysis (38 samples) (Faul et al., 2007).

3.6.2 Chemometric evaluation

The near-infrared spectra data was exported from Opus 7.2 (Bruker, Ettlingen, Germany) into The Unscrambler® X Version 10.4 (Camo Software As. Oslo Science Par Guastalleen 21 0349 Oslo Norway) for chemometric analysis. The spectra data of the coffee brew and roasted beans was trimmed to the range 12489.48 – 4381.73cm^{-1} and 7004.598 – 3803.157 cm^{-1} respectively. Principal Component Analysis (PCA) was used for exploratory analysis of the spectra. Descriptive statistics (box plot and line plot) revealed variations and swoops across the various wavenumbers as well as baseline shifts. This is indicative of additive and chemical effects which are associated with the spectra of complex samples like coffee (reference). This prompted the decision to use Savitzky-Golay first derivative (FD) and second derivative (SD), Multiple Scatter Correction (MSC) and Standard Normal Variate (SNV) and their combinations; MSC and SD for the TDS-OD model of both brew and roasted beans spectra; SNV and SD for the TDS-BC model (coffee brew) and SD and SNV for the TDS-BC model (roasted beans).

3.6.3 Partial least squares regression (PLSR)

To estimate the TDS of the coffee samples, Partial least square regression (PLSR) was used to test two models for the two reference methods (TDS-OD and TDS-BC). Performance of the models were evaluated on different statistical indices such as RMSE, R^2, among others. Model validation was performed with random seven-fold cross validation. Statistical tests and visualizations performed with the Unscrambler® X Version 10.4 (Camo Software, Oslo, Norway) and for data interpretation, various statistical software was used, such as SPSS Statistics 23 (IBM, New York, USA) and R statistical software package (Version 4.2.3.).

4. RESULTS AND DISCUSSION

4.1 Data inspection and Cleaning

The normality of the raw data was checked graphically with a boxplot and density curve. The shape of the density curve of TDS-BC (Fig 1) revealed the shapes of the light and dark roasting levels as bimodal while medium roasted appeared distorted. This prompted further tests for outliers. The density curve of TDS-OD did not show severe signs of distortion Figure 6 shows the Density plots of a) TDS-BC with distortion minor distortions to the left end and b) TDS-OC.

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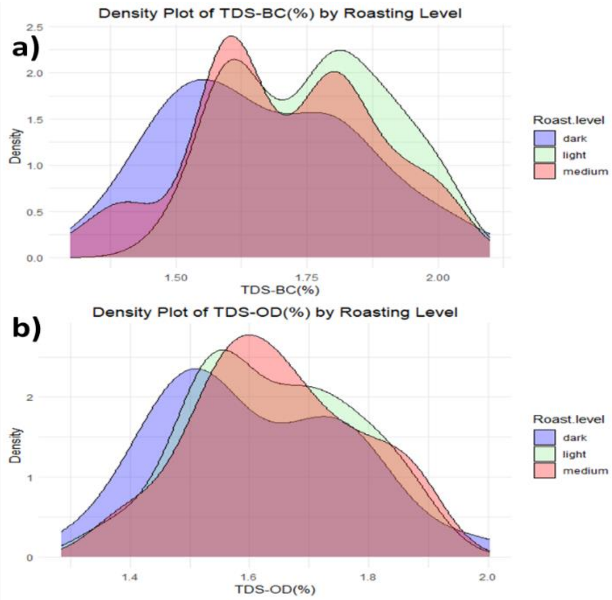

. Figure 6 shows the Density plots of a) TDS-BC with distortion minor distortions to the left end and b) TDS-OC

4.1.1. Testing Outliers

I performed the Mahalanobis distance test on the raw data which resulted in the detection of 12 outliers (Figure 7). The outliers were inspected against the original coffee samples, and it was determined their omission will not impact the aim of the study. At the end of the data cleaning process, I had 38 samples (114 for the three roasting levels).

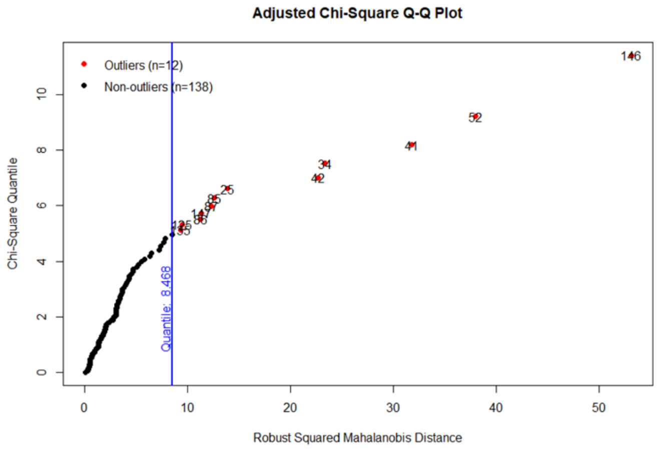

Figure 7.: Result of outlier detection based on the TDS of samples

4.1.2. Effect of Roasting level on TDS

To compare the mean TDS between the three roasting levels, the RM ANOVA model was applied. This model has the assumptions of normally distributed dependent variables and sphericity. The normality of TDS-OD and TDS-BC were tested by skewness and kurtosis and revealed that the assumption was satisfied; TDS-OD (Skewness =0.11; kurtosis = 0.65) and TDS-BC (Skewness =0.4; kurtosis = 0.68). Mauchly's test of sphericity of the RM ANOVA model for both variables revealed that the sphericity was satisfied; TDS-OD [χ^2 (2,74) = [0.95], p = [0.41] and TDS-BC [χ^2 (2,74) = [0.97], p = [0.65].

4.1.3 Linear Regression Model of Brix° and TDS-OD

To investigate the linear relationship between Brix° and TDS-OD, a linear regression model was applied. A previous check for outliers was conducted to ensure accuracy of the model.

$$Y = \beta_0 + \beta_1 * X_1 + \epsilon \quad (4)$$

Where; Y is the dependent variable (TDS-OD),

X_1 is the independent variable (Brix°).

β_0 is the intercept.

β_1 is the slope coefficient.

ϵ is the error term.

The model assumes normally distributed variables and residuals as well as the independence of residuals from the explaining variable (Brix°). Normality of Brix°, TDS-OD and residuals was checked and accepted by the absolute values skewness and kurtosis [TDS-OD (Skewness = 0.11; kurtosis = 0.65, n=114)]; Brix (skewness = 0.09; kurtosis=0.62, n=14); and residuals [(skewness = 0.39; kurtosis=0.5, n=114)]. The mean of the residuals was extremely low (5.512847e-18). The normality of residuals was also tested graphically by density curve. The independence of the residuals from the explaining variable (Brix°) was checked by a scatterplot which showed that the homoscedasticity assumption was satisfied. All statistical tests used were two-sided in the model, and significance level was set at α = 0.05.

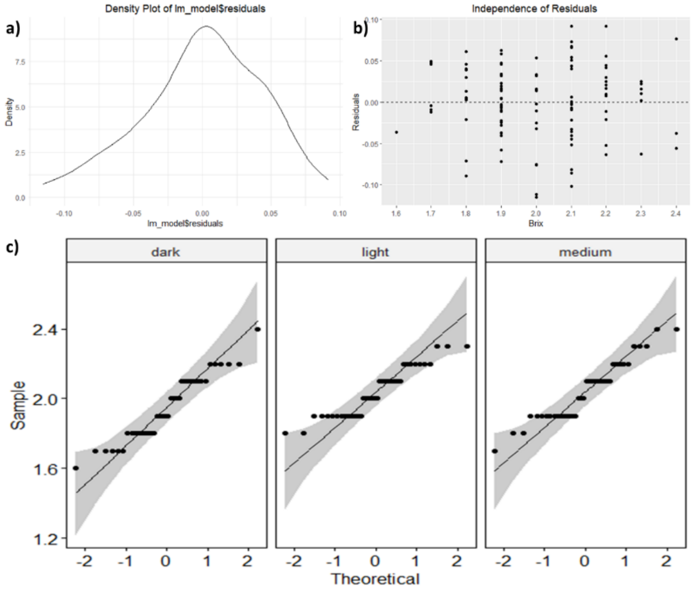

Figure 8.: a) Density plot residuals from the linear regression model, b) scatter plot of Brix vs residuals and c) Normality test of Brix

4.2. Effect of Roasting level on TDS%

The aim of the research is to conduct a feasibility study to predict the TDS of coffee from the NIR spectra of the roasted beans and brew. Hence, the TDS of the coffee samples roasted to three levels; light, medium and dark, were estimated with two reference methods; oven-drying (TDS-OD) and Brix° (TDS-BC). The within-group Repeated Measures (RM) Analysis of Variance did not yield significant differences in the mean TDS% of the coffee samples for both reference methods; TDS-OD (F (2;74) =2.01, p =0.14); and TDS-BC (F (2;74) = 3.11, p= 0.05). Results are summarized in Table 1.

A number of studies have demonstrated the influence of roast degree on the mass concentration of extracted solids (Frost et al., 2020; Illy and Viani, 2005; Petracco, 2001a). The lack of significant difference in average TDS% across roasting levels could be attributed to the synergistic effects of the heterogeneity of the coffee samples, the uneven effect of roasting and the extraction protocol. Firstly, despite the homogeneity in variety, the coffee samples were sourced from seventeen countries across four continents. Moreover, they were subject to different processing procedures (wet and dry). The geographical origin and type of processing influence the composition of green beans (Herrera and Lambot, 2017; Vieira, 2008b).

Furthermore, the impact of roasting on the structure and composition of coffee beans is not linear, hence, the lines separating adjacent roasting levels may be blurred (Schenker, 2000; Schenker and Rothgeb, 2017). In addition, the changes in the microstructure of the beans and the resultant brittleness, which is pronounced in dark roasts, have been shown to impact the particle size distribution and morphology (Schenker, 2000; Schenker and Rothgeb, 2017; Uman et al., 2016)

These differences converge during the extraction process. In the manual V60 setup used in this study, the flow of water through the coffee bed is influenced by factors such as particle size distribution and morphology of ground coffee (von Blittersdorff and Klatt, 2017). These attributes influence the percolation time which in turns may cause variation in the mass concentration of coffee extract (Cordoba et al., 2020, 2019; Fuller and Rao, 2017).

Table 1: Average values of TDS% values from TDS-OD and TDS-BC grouped by roasting level.

method	roast level	mean (n) ± SD	minimum	maximum
TDS-OD (%)	dark	1.61 ± 0.16^{a}	1.28	2.00
	light	1.62 ± 0.13 ^{a}	1.38	1.87
	medium	1.7 ± 0.13^{a}	1.4	1.9
TDS-BC (%)	dark	1.7 ± 0.2^{a}	1.4	2.1
	light	1.7 ± 0.1^{a}	1.5	2.0
	medium	1.7 ± 0.2^{a}	1.5	2.0

*n=38, variables in rows denoted with the same superscript did not yield significant difference (p>0.05). SD-standard deviation of references method is in connection with roasting level (n=114).

4.3 Relationship between Brix° and TDS-OD

The linear regression model resulted in a significant positive linear relationship between Brix° and TDS-OD; (F (1; 112) = 1005; $p < 0.001$; $R^2 = 0.90$; $p < 0.001$). Brix° could account for 90% of the variation in TDS-OD measurement. Moreover, the regression coefficients were significant; β_0 = 0.11(95% CI:(0.01,0.20), β_1=0.75(95% CI: (0.71,0.80) and ϵ (112) = 0.04. This resulted in the following equation for the prediction line:

TDS-OD = 0.11 + 0.75*Brix° at 20C ($t_0(112) = 2.256$ and $t_1(112) = 31.88$; both with $p<0.001$). Thus, one unit increase in Brix° results in 0.86 unit increase in TDS-OD. The calculated root mean square error (RMSE) is 0.04. The results confirmed that refractometers calibrated with a Brix° scale cannot be used for direct estimation of coffee TDS% without a correction. Moreover, the results were strikingly similar to those obtained from previous studies by Gome (2019), TDS = 0.85* (Brix° + temperature correcting factor) and Moreno et al (2015), TDS% = 0.87*Brix° at 20°C (Moreno et al., 2015). The significance of the similarity lies in the different methodologies and samples used. Gomez (2019) used Brix° data from secondary sources while Moreno et al (2015) utilized reconstituted freeze-dried coffee. This suggests that the chemical components of coffee brew responsible refractive index, upon which Brix° is based are not influenced by brewing technique. Results are illustrated in Figure 9.

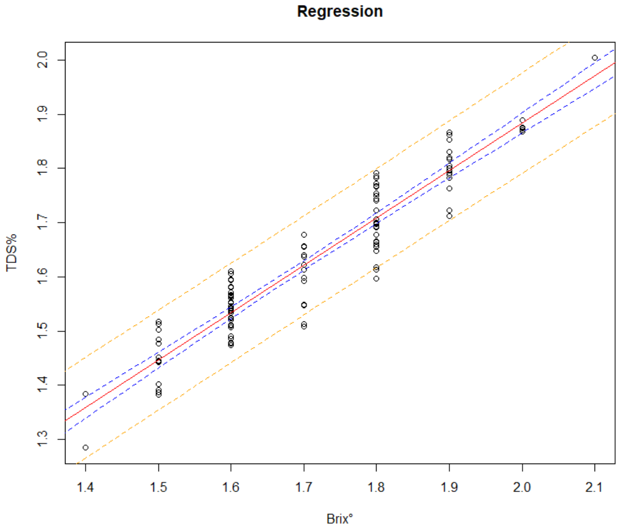

Figure 9: shows dependence of TDS-OD (%) of coffee samples on the Brix° with a linear best fitted line in red, and confidence range for the mean of TDS-OD (in blue) and prediction range of the expected TDS-OD values (in yellow).

4.4 Evaluation of Spectra Coffee beans spectra

The first step in NIR spectroscopic analysis is evaluation of the raw NIR spectra and its associated transformations. There is a pronounced linear baseline shift in the spectra of the roasted coffee samples. In order to linearise the spectra in accordance with Beer-lamberts law, a number of preprocessing techniques were explored. The most effective was a combination of multiplicative scatter correction (MSC) and the Savitzky-Golay second derivative. MSC addresses additive baseline variations and multiplicative baseline shifts by applying a basic linear univariate fit to a standard spectrum to enhance linearity of the spectra (Sørensen et al., 2021). On the other hand, SG second derivative diminishes baseline shift by employing a low-degree polynomial fit around a given point within a spectrum (Savitzky and Golay, 1964). Thus, the maxima of the original spectra become the minima in the transformed spectra (Ozaki and Morisawa, 2021).

Figure 10 illustrates (a) the diffuse reflection NIR spectra of roasted coffees samples in the range of 7000 to 3800 cm^{-1} and (b) the MSC-SG second derivative transformation in the same range. The spectra are grouped by row sets ranges of TDS-BC and TDS-OD in ranges (1.3-1.5, 1.5-1.7,1.7 -1.9,1.9-2.1), however, there was not visual distinction between the two, hence only TDS-BC is illustrated. The high number of compounds found in roasted coffee renders direct inferences of functional groups from the wavelength a near impossible task, however, wavelength ranges most associated with functional groups common to coffee are annotated on the raw and transformed spectra. Assignment of the regions were performed with reference to Table 2.

A visual inspection of the roasted coffee beans spectra revealed a decreasing trend between 7000 to 3800 cm^{-1}. This observation is attributable to the decrease in moisture content associated with the roasting process. As noted by Yeretzian et al (2002), moisture constitutes the bulk of weight loss encountered during roasting, hence, the rate of moisture loss increases with degree of roasting. This observation was confirmed by similar studies (Alessandrini et al., 2008; Esteban-Díez et al., 2004b).

It worth mentioning that Benes et al (2023), explored the influence of roasting degree on the NIR spectrum of the roasted coffee beans with same coffee samples and roasting protocol used for this study. The result from her PCA analysis showed a strong correlation between roasting degree and NIR spectra of coffee beans.

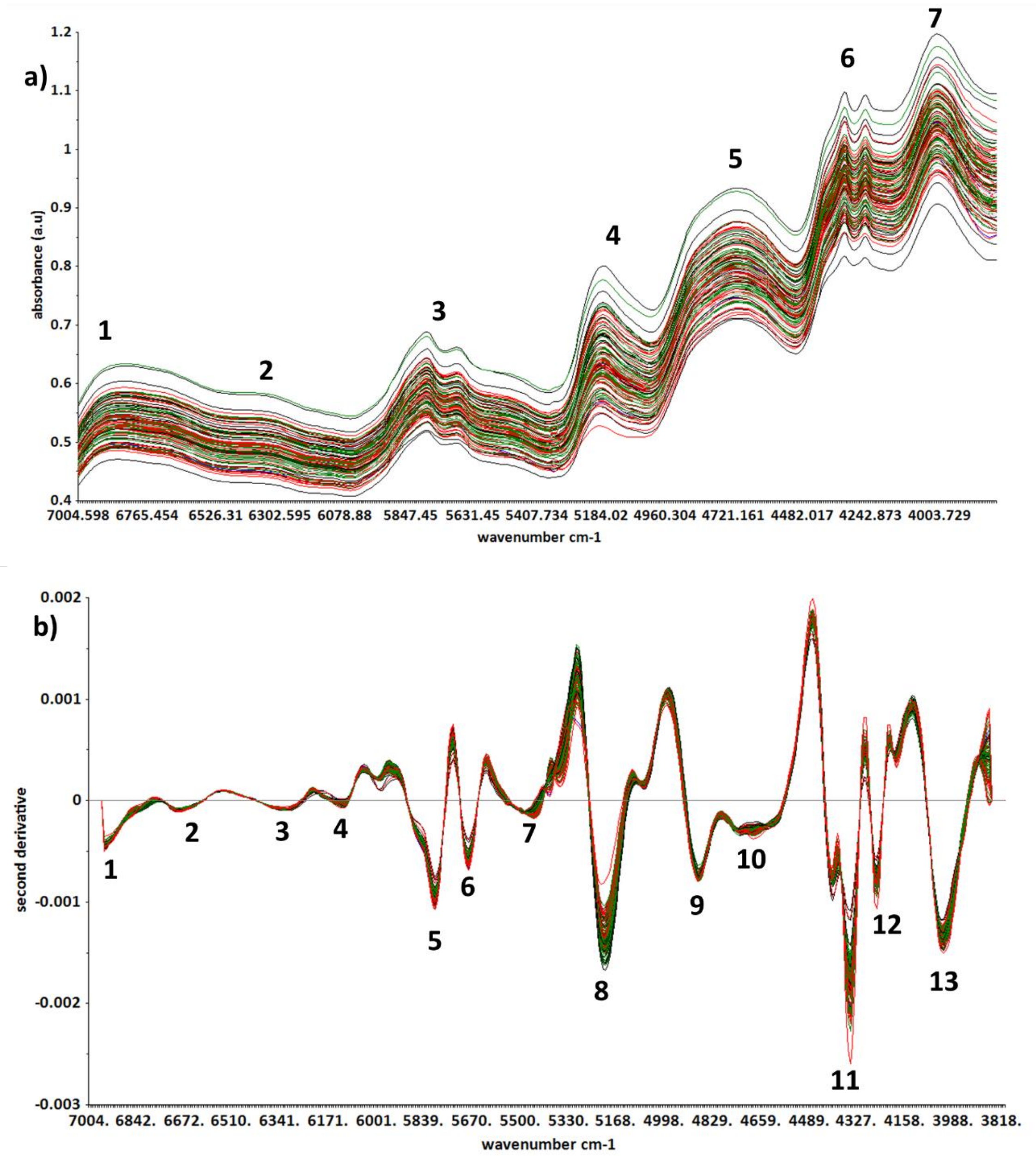

Figure 10 illustrates (a) The diffuse reflectance NIR spectra of roasted coffee beans samples in the range of 7000 to 3800cm. (b) the MSC-SG second derivative transformation in the same range. The roasting degrees is denoted by light (red), medium (green) and dark (blue) for both. The range of TDS-BC coded as (1.3-1.5: blue, 1.5 - 1.7: red, 1.7 - 1.9: red, 1.9 - 2. 1: black). The integers from 1-14 on both (a) and (b) represent wavenumber regions of interest.

Table 2: Typical absorption areas of coffee in the near-infrared region (Buratti et al., 2015; da Silva Araújo et al., 2021; Ribeiro et al., 2011)

Wavenumber [cm^{-1}]	Molecular vibrations	Possible compounds
8586	2nd overtone of C-H valence vibration, HC=CH	lipids
8409	2nd overtone of C-H valence vibration, CH_2	aliphatic hydrocarbons, lipids, caffeine
8243	2nd overtone of C-H valence vibration, CH_3	sucrose
7343	combination of C-H valence and C-H deformation vibration	caffeine, sugars
7020-7006	1st overtone of O-H groups of phenolic compounds; 1st overtone of N-H symmetric valence vibration, (R-C=O-NH_2)	polyphenols, chlorogenic acids
6808	1st overtone of O-H valence vibration	water, chlorogenic acids
6369-6256	1st overtone of N-H valence vibration; 1st overtone of O-H valence vibration	proteins, sugars
5789	symmetric 1st overtone of C-H valence vibration	caffeine, chlorogenic acids
5675	symmetric 1st overtone of C-H valence vibration	lipids, cellulose
5557-5417	O-H combination vibration; combination of 2nd overtone of O-H valence and C-H valence vibration	water, cellulose
5200-5100	combination of O-H valence vibration and HOH deformation vibration	water, chlorogenic acids
5070-5060	combination of N-H asymmetric valence vibration and N-H deformation vibration	proteins, aromatic amines
4866-4850	combination of N-H and C=O valence vibration; combination of asymmetric N-H valence vibration and N-H deformation vibration	proteins, trigonelline
4743	3rd overtone of C=O-O valence vibration; combination of O-H deformation and C-O valence vibration	sugars, trigonelline
4628	combination of C-H valence vibration/C=O valence vibration/ C-H deformation vibrations	lipids, caffeine
4400	combination of O-H and C-O valence vibration	cellulose, glucose
4360-4329	2nd overtone of C-H deformation vibration	proteins, lipids, chlorogenic acids
4246-4232	2nd overtone of C-H deformation vibration; combination of C-H and C-C valence vibration	lipids, chlorogenic acids
4020	2nd overtone of C-H deformation vibration, combination of C-H and C-C valence vibration	aromatic compounds, cellulose

4.5. Exploratory analysis of Beans Spectra

Principal component analysis was used to perform exploratory analysis of both raw and MSC-SG second derivative spectra of coffee beans (6950-3918cm^{-1}). Model validation was performed with a random seven-segment cross-validation. The singular value decomposition (SVD) algorithm was used. The optimal number of principal components for the raw data is 2, however, due the high explained variance rate (PC1:96%, PC2:3%), only PC1 is presented. For the MSC-SG second derivative, the first four principal components describe 96% of the variance in the data (PC1:55%, PC2:23%, PC3:14%, PC4:4%). The first three are illustrated in the correlations loading plot for clarity. The TDS% were categorized into for groups (1.3-1.5, 1.5-1.7,1.7 -1.9,1.9-2.1).

The scores plot of the PCA analysis (Figure 11) for both raw and processed spectra data did not yield clear separation for the groups of TDS for both TDS-OD and TDS-BC. The correlations loading plot of the processed data was selected for further exploration. PC1 showed a strong positive correlation with the following wavenumber range; 6418 to 6200 cm^{-1}, 5300-5000 cm^{-1}, 4500 cm^{-1} and 4000 cm^{-1}. These ranges correspond to the integers 3, 7, 10 and 13 of the MSC-SG second derivative spectra (Figure) which are associated with several components of coffee; 3-protein and sugars, 7 - water and chlorogenic acids, 10 - lipids and chlorogenic acids and 13-aromatic compounds. Due the lack of clear sample clusters in the score plot, we cannot assign direct meaning to these regions of strong correlation with regard to TDS. The relationship between TDS and the NIR spectra was further analyses with PLSR.

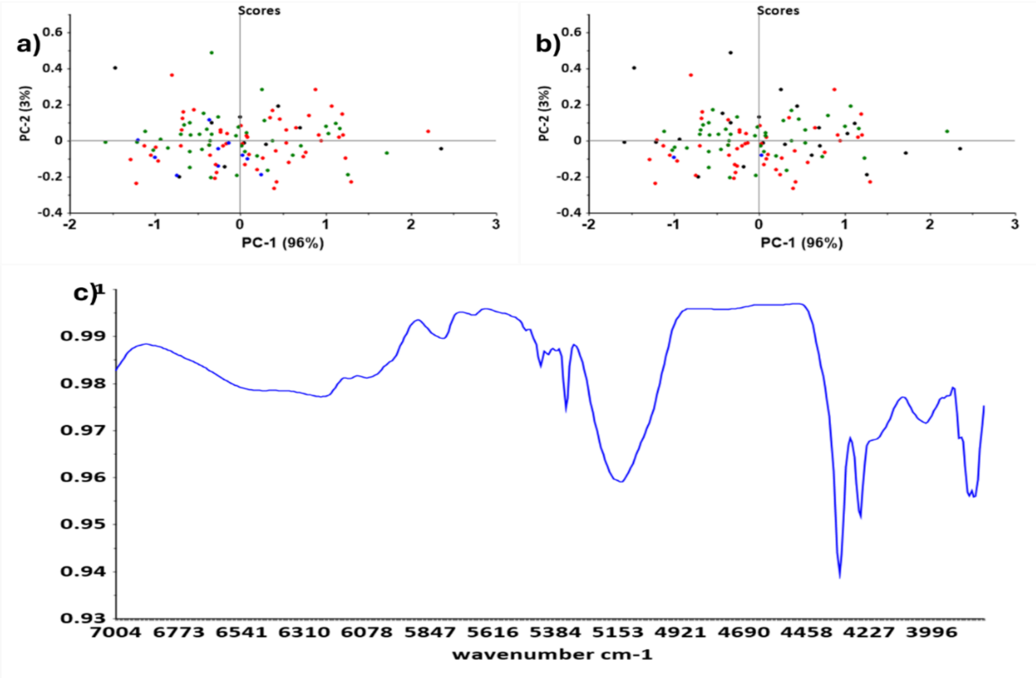

Figure 11: depicts the scores plots of PC1 and PC2 from PCA analysis of raw spectra of coffee beans grouped by a) TDS-OD and b) TDS-BC. The range of both TDS-OD and TDS-BC are (1.3-1.5: blue, 1.5 - 1.7: red, 1.7 - 1.9: red, 1.9 - 2. 1: black). (c) is the correlation loading plot with PC1:blue.

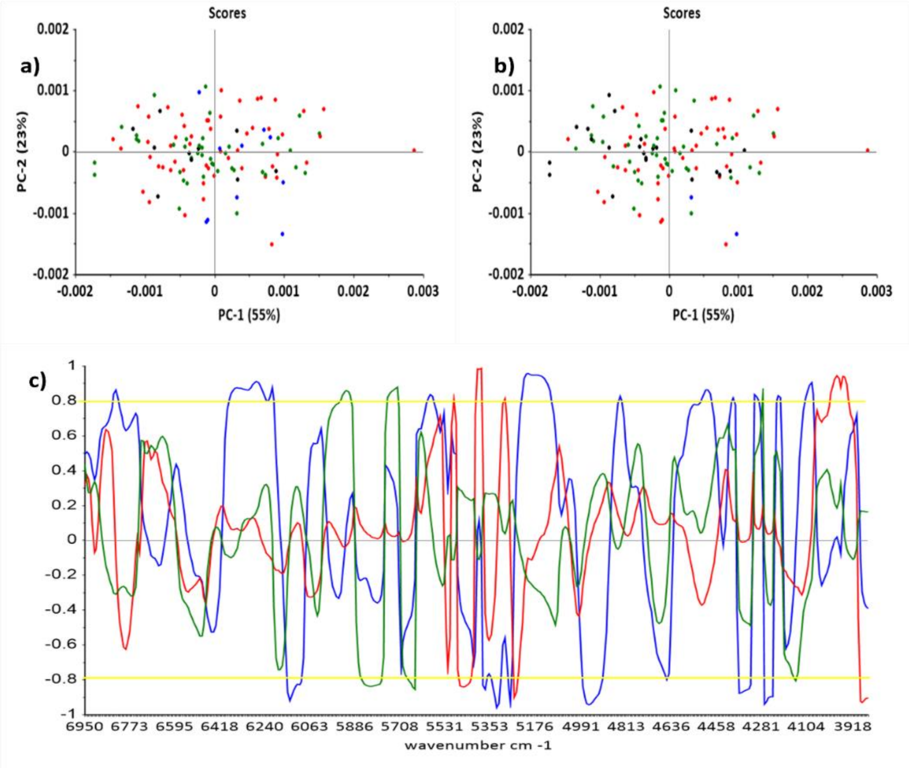

Figure 12: shows scores plots of PC1 and PC2 from PCA analysis of the MSC-SG second derivative roasted beans spectra grouped by (a) The TDS-OD and (b) TDS-BC. The range of both TDS-OD and TDS-BC are (1.3-1.5: blue, 1.5 – 1.7: red, 1.7 – 1.9: red, 1.9 – 2. 1: black). (c) is the correlation loadings plot with three PCs (PC1: blue, PC2: red, PC3: green)

4.6 Coffee brew spectra

The unprocessed transflection NIR spectra of the coffee brew was subjected to a number of preprocessing techniques, with the combination of MSC and the SG second derivative yielding the best results. Figure 1 illustrates (a) the raw transflection NIR spectra of coffee brew in the range of 12500 to 3800 cm^{-1} and (b) the MSC-SV second derivative transformation in the range of 12500 – 4000 cm^{-1}. The spectra are grouped by row sets ranges of TDS-BC and TDS-OD in ranges (1.3-1.5, 1.5-1.7,1.7 -1.9,1.9-2.1), however, there was not visual distinction between the two, hence only TDS-BC is illustrated. The ranges of interest with regard to chemical components most associated with coffee are annotated with integers ranging from 1 to 7 on the processed spectra. They are as follow; 1- lipids, 2 -water and chlorogenic acid, 3- caffein and chlorogenic acid, 4-

water and cellulose, 5 – lipids and caffein, 6 – lipids and chlorogenic acid and 7- aromatic compounds and cellulose. The molecular vibrations at these wavenumber ranges are summarised in Table.

The raw spectra of coffee brews are characterised by a relatively flat trend from 12500 to 8800 cm^{-1}, with peaks at 6900cm-1 and 5235 cm^{-1} and intense foot at 4000 cm^{-1}. These features are typical of the NIR spectra of water as described by Ozaki and Morisawa (2021). The peak at 4000 cm^{-1} is due to the fundamental OH stretching modes. Moreover, the band at 5235 cm^{-1} corresponds to the combination of the H-O-H antisymmetric stretching mode and the bending mode, while the band at 6900 cm^{-1} corresponds to the combination of the H-O-H symmetric stretching mode and the antisymmetric stretching mode (Ozaki et al., 2006). These bands get progressively weaker at higher order overtones as the wavelength shortens which is consistent with the flat trend observed between 12500 and 8800 cm^{-1}.

A visual inspection of the spectra did not reveal a distinct pattern in the separation of by TDS% groups. Further assessment was carried out by PCA.

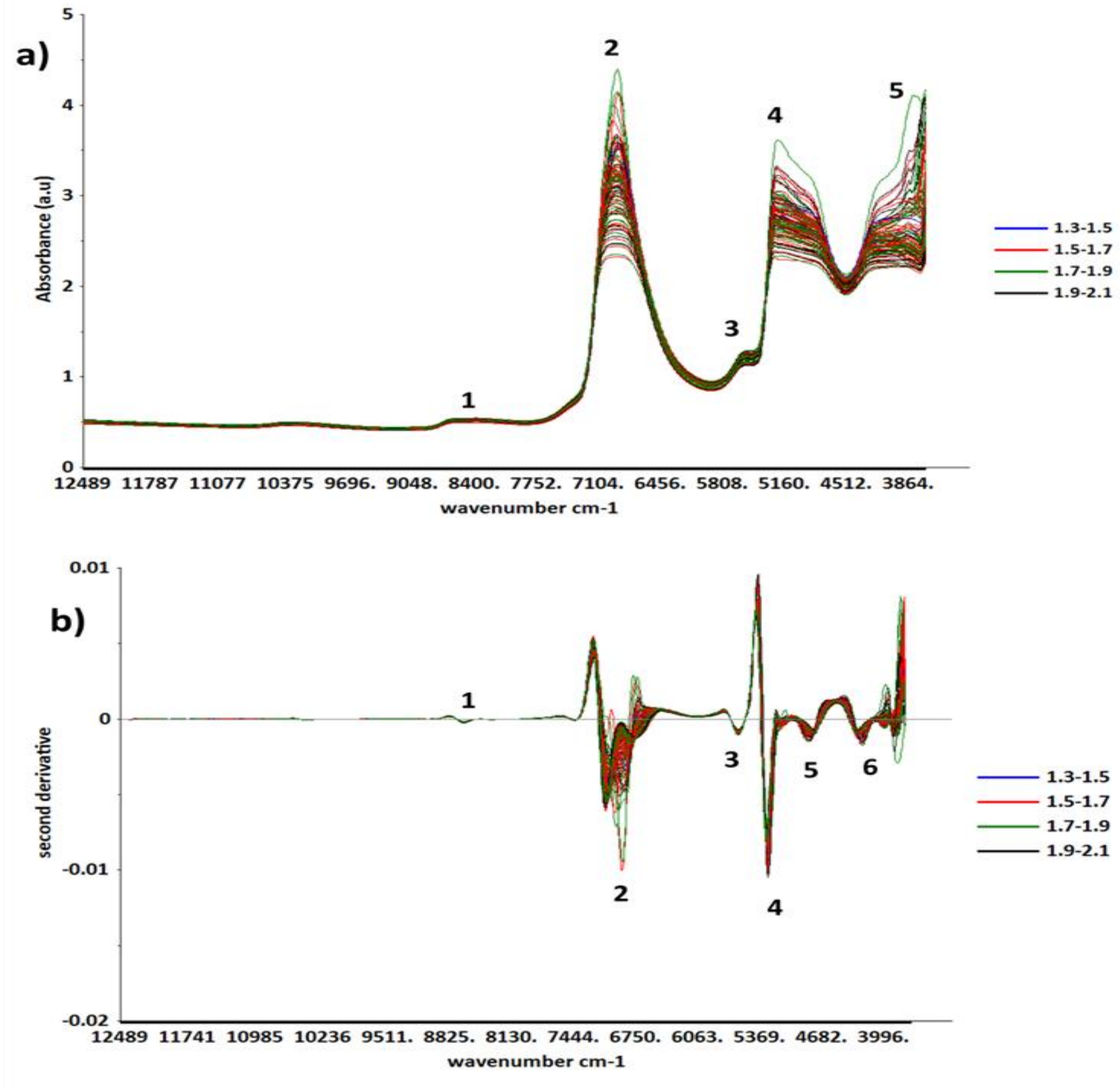

Figure 13: illustrates (a) The transflectance NIR spectra of coffee brew samples in the range of 7000 to 3800cm. (b) the MSC-SG second derivative transformation in the same range. The integers from 1-6 on both (a) and (b) represent wavenumber regions of interest.

(Source: own work)

4.7 Exploratory analysis of Brew Spectra

Principal component analysis was used to perform exploratory analysis of both raw and MSC-SG second derivative spectra of coffee brew in the range of (12500-4000cm^{-1}). As with the coffee beans spectra, model validation was performed with a random seven-segment cross-validation. The singular value decomposition algorithm was also used. The PCA of the unprocessed brew spectra produced four optimal principal components (PC1:74%, PC2:19%, PC3:4% and PC4:1%). For the processed spectra, eight principal components were sufficient to account for the differences in the decomposed variables. However, the first five PCs account for 95% of the variance in the data (PC1:66%, PC2:12%, PC3:9%, PC4:5%, PC5:3%).

As was observed with the roasted beans spectra, the scores plot of the PCA analysis (Figure) for both raw and processed brew spectra data did not yield a clear separation when grouped TDS along the four ranges. Further assessment was carried with the correlations loading plot of the MSC-SG second derivative transformed brew spectra. Despite the lack of clusters, PC1 show a strong positive correlation with the wavenumber ranges of 7945-6850 cm$^{-1,}$ 6330-5245 cm^{-1}. Moreover, PC1 was negatively correlated with the wavenumber ranges 8740-8292 cm^{-1}, 7120-6665 cm^{-1}, 5677-5330 cm^{-1}. These wavenumber ranges are broad and encompass functional groups associated with caffein, lipids, water, proteins, sugars, among others (Barbin et al., 2014; Ribeiro et al., 2011). Also, the ranges overlap at certain points which renders any inferences futile. The PCA results confirmed the lack of visual separation observe form the raw and processed brew spectra. Further tests were carried out with PLSR.

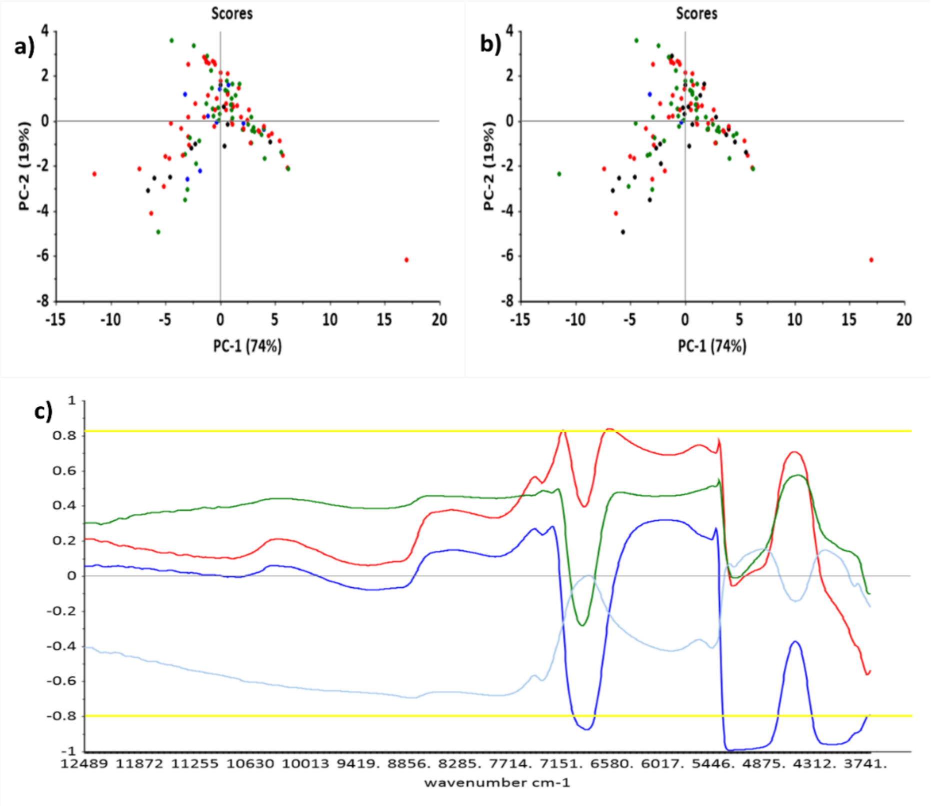

Figure 14: shows scores plots of PC1 and PC2 from PCA analysis of raw coffee brew spectra grouped by (a) The TDS-OD and (b) TDS-BC. The range of both TDS-OD and TDS-BC are (1.3-1.5: blue, 1.5 – 1.7: red, 1.7 – 1.9: red, 1.9 – 2. 1: black). (c) is the correlation loadings plot with four PCs (PC1: blue, PC2: red, PC3: green, PC4: turquoise)

(Source: own work)

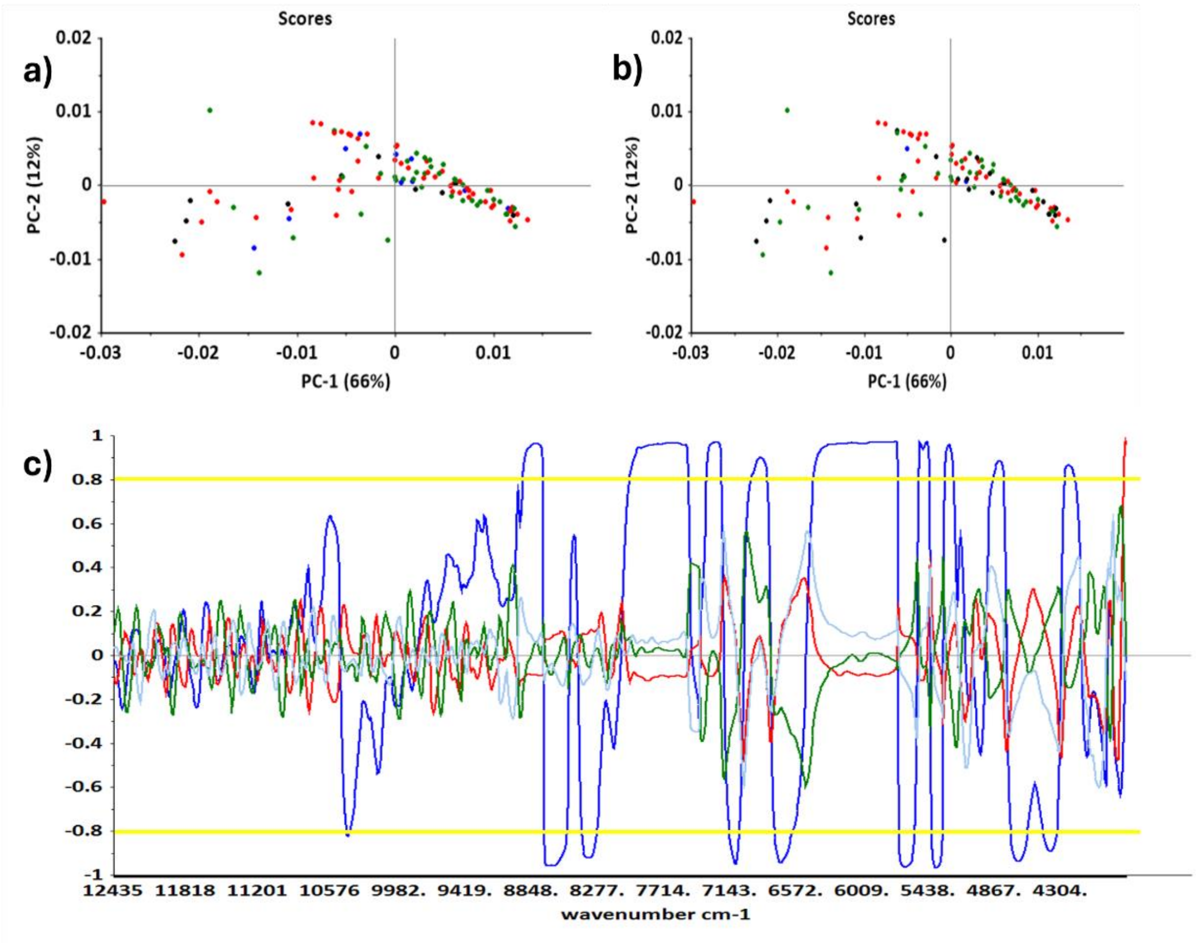

Figure 15: shows scores plots of PC1 and PC2 from PCA analysis of the MSC-SG second derivative roasted beans spectra grouped by (a) The TDS-OD and (b) TDS-OD. The range of both TDS-OD and TDS-BC are (1.3-1.5: blue, 1.5 - 1.7: red, 1.7 - 1.9: red, 1.9 - 2. 1: black). (c) is the correlation loadings plot with four PCs (PC1: blue, PC2: red, PC3: green, PC4: turquoise)

4.8 Results of partial least square regression (PLSR)

4.8.1 Roasted Beans

PLS models were developed using spectral and reference data from 114 samples, with all analyses conducted using averaged values. During the assessment, the spectral range of 7000-4000cm-1 (comprising 416 variables) was used. Additionally, random, seven-segment cross-validation was employed for model validation. The PLS regression model for TDS-BC and TDS-OD was performed on both raw and MSC-SG second derivative processed spectra. Further combinations of various preprocessing methods like standard normal variate (SNV) and first and second SG derivates were explored but yielded poorer models. Only relevant results from MSC-SV second derivative spectra are summarised in Table.

Figure illustrates the results from PLS model for MSC-SD second derivative beans spectra. Section a) shows the Predicted vs Reference TDS-BC% from the calibration and cross validation procedures. The red and blue trendline represent the regression line for cross validation and calibration respectively and the grey trend line is the theoretical trendline line when R^2 is 1.

The strength of PLS regression models are assessed by evaluating R^2/ Q^2, values between above 0.8 are considered strong while those below 0.5 are considered weak (Wakeling and Morris, 1993). It must be noted however, that these ranges are often matrix depend, with lower thresholds for matrices of high complexity (Sørensen et al., 2021). Based on the R^2/ Q^2 values we can conclude that the PLS regression models are considerably weak, TDS-BC (R^2/ Q^2 : 0.12/0.09, RMSEC :0.11%, RMSECV: 0.09%) and TDS-OD (R^2/ Q^2 : 0.16/0.06, RMSEC :0.17%, RMSECV: 0.06%).

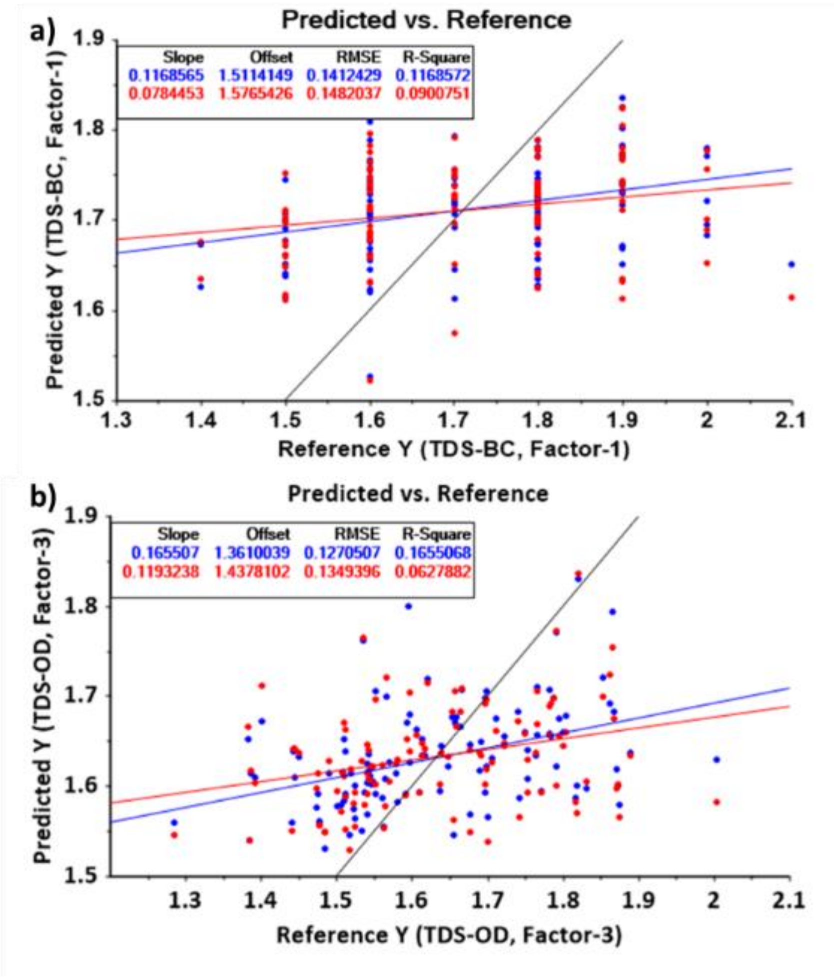

Figure 16: illustrates the results of calibration and cross validation graphs from PLS regression model of MSC-SD second derivative beans spectra a) the Predicted vs Reference TDS-BC regression b) the Predicted vs Reference TDS-OD regression. The red and blue trendline represent the cross validation and calibration procedure respectively. The grey trend line is the theoretical trendline line when R^2 is 1.9

Table3: Summary of results from PLS regression for the processed beans and brew spectra

n is number of reference samples used

Sample	Parameter	Pre-processing	n	Cross validation			
				R^2	Q^2	RMSEC	RMSCECV
Roasted bean	TDS-BC	MSC-SD	114	0.12	0.09	0.14	0.14
	TDS-OD	MSC-SD	114	0.16	0.06	0.13	0.13
Coffee brew	TDS-BC	MSC-SD	114	0.04	0	0.14	0.15
	TDS-OD	MSC-SD	114	0.03	0	0.14	0.15

n is number of reference TDS samples

4.8.2 Coffee brew

The PLS models for coffee brew were developed using spectral and reference data from 114 samples, with all analyses conducted using averaged values. During the assessment, the spectral range of 12500 – 4000cm^{-1} (comprising 1142 variables) was used. Model validation was also performed with random seven-segment cross validation. Both raw and processed coffee brew spectra were used and as with the beans, various combinations of preprocessing methods did not yield better results. Relevant results from the MSC-SG second derivative spectra are summarised in Table.

Figure 17 depicts the outcomes from the PLS model for MSC-SD second derivative coffee brew spectra. Part a) shows the Predicted vs Reference calibration and cross validation regression graphs for TDS-BC. Part b) shows the Predicted vs Reference calibration and cross validation regression graphs for TDS-OD. The red and blue trendlines represent the regression line for cross validation and calibration respectively and the brow trend line is the theoretical trendline line when R^2 is 1.

The PLS model for the brew was considerably weaker than that of the beans; TDS-BC (R^2/ Q^2 : 0.04/0, RMSEC :0.14%, RMSECV: 0.15%) and TDS-OD (R^2/ Q^2 : 0.03/0, RMSEC :0.14%, RMSECV: 0.15%).

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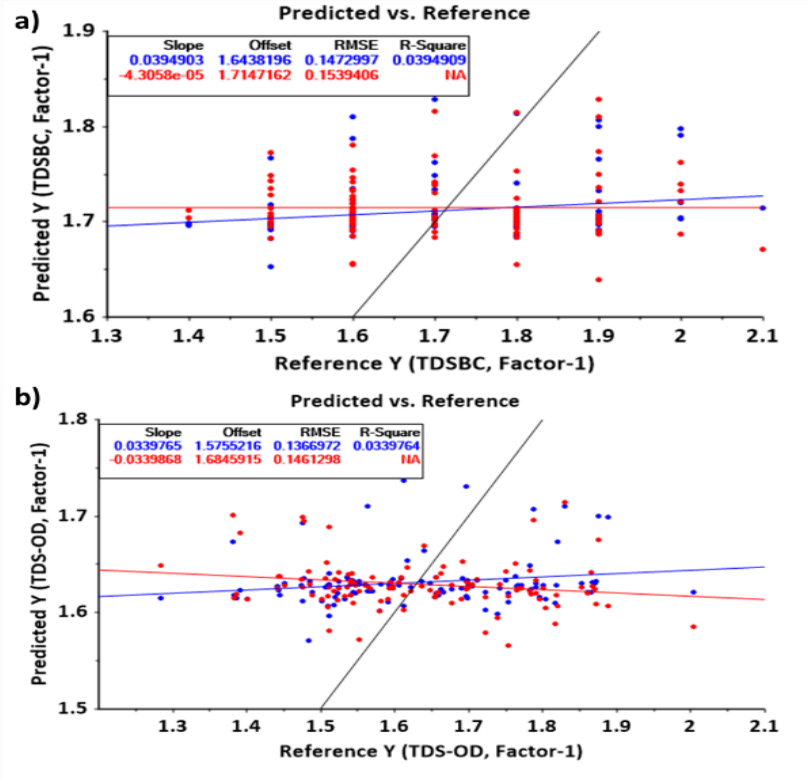

Figure 17: illustrates the results of calibration and cross validation graphs from PLS regression model of MSC-SD second derivative brew spectra a) is Predicted vs Reference TDS-BC regression b) is the Predicted vs Reference TDS-OD regression. The red and blue trendline represent the cross validation and calibration procedure respectively. The grey trend line is the theoretical trendline line when R^2 is 1.

5. SUMMARY AND CONCLUSIONS

Coffee is the most traded plant commodity in the world. The main drivers behind this popularity are consumers who are drawn to its unique sensory attributes and cognitive effects. The strength of the coffee brew is a principal sensory quality attribute that is quantified as TDS. Traditional methods of assessing TDS require the preparation of coffee brew, which is subject to many variations and often leads to inconsistencies across different methods. Secondary analytical techniques such as NIR spectroscopy offer the advantage of minimal sample preparation and routine analysis. The method has seen extensive applications in the coffee industry.

In this study, we set out to estimate the TDS of coffee from the NIR spectra of roasted coffee beans and brew. Fifty original green coffee beans (48 Coffea arabica and 2 Coffea canephora) coffee samples were sourced from four regions: South America, Asia, Central America, and Africa. The samples were roasted with a predefined protocol (light: 40 seconds, medium: 60 seconds, and dark: 90). This generated 150 samples, which were ground (20g) to a median particle size of 600µm. The ground coffee samples were then brewed with a V60 dripper using a predefined protocol. The reference TDS of the coffee samples was then determined using oven-drying: TDS-OD and a Brix°-calibrated refractometer with a correction factor: TDS-BC.

The relation between the TDS-OD and Brix° was tested with a linear regression model which resulted in R^2 and R of 0.90 and 0.95 respectively. Furthermore, Repeated Measures Analysis of Variance (ANOVA) revealed no significant differences in the mean TDS of both reference methods within the three roasting levels; TDS-OD ($F(2;74) = 2.01$, $p = 0.14$); and TDS-BC ($F(2;74) = 3.11$, $p = 0.05$). The NIR spectra of the roasted beans as well as the brew were collected in the range of 12,500 - 3,800 cm^{-1}. The obtained spectra were averaged and pre-processed with multiple scatter correction (MSC), and Savitzky-Golay second derivative.

A visual inspection of both brew and bean spectra grouped by a row set of TDS ranges (1.3-1.5, 1.5-1.7, 1.7-1.9, 1.9-2.1) for both TDS-OD and TDS-BC did not reveal any significant patterns. Further exploratory assessment by Principal Component Analysis (PCA) of the processed spectra resulted in an optimum of 4 PCs for the processed bean spectra (PC1: 55%, PC2: 23%, PC3: 14%, PC4: 4%) and 5 PCs for the brew spectra (PC1: 66%, PC2: 12%, PC3: 9%, PC4: 5%, PC5:

3%). The scores plot from the PCA for both bean and brew spectra did not reveal significant clusters; hence, we could not draw a meaningful conclusion from the correlations loading plot.

Further assessment with Partial Least Square Regression revealed that the calibration models for the transformed bean spectra were not significant for both reference methods; TDS-BC (R^2/ Q^2: 0.12/0.09, RMSEC :0.11%, RMSECV: 0.09%) and TDS-OD (R^2/ Q^2 : 0.16/0.06, RMSEC :0.17%, RMSECV: 0.06%). The results from calibration models for the transformed brew spectra were also not significant; TDS-BC (R^2/ Q^2 : 0.04/0, RMSEC :0.14%, RMSECV: 0.15%) and TDS-OD (R^2/ Q^2 : 0.03/0, RMSEC :0.14%, RMSECV: 0.15%). Due to the lack of robustness of the models, we did not perform a prediction with test sample set. Thus, the results show that estimating TDS from the NIR spectra with the given parameters and experimental design is not ideal.

Indeed, the results from the PLS for the bean spectra were somewhat promising. The experimental design for further studies can employ a roasting protocol that will result in a wider range of TDS values. Moreover, since water is implicated for the relatively weaker PLS model of the coffee brew, further studies may include a freeze-drying step in the sample preparation followed by the collection of the spectra in diffuse reflectance mode.

The results of this research also allow us to conclude that the existing differences in TDS of coffee drinks (prepared with the same brewing method) cannot be purely explained by the obvious differences in the chemical composition (i.e. differences that can be explored by NIRS) of the corresponding coffee beans. Hence, significant TDS range experienced in the case of the same brewing method may however have resulted from the structural differences of the coffee beans. Such can be the hardness, the spatial distribution of key components, and other structural changes that occur as a result of roasting. It can also be assumed that these may even affect the chemical composition of the brew. In other words, a coffee drink with a higher TDS value may differ not only in the amount of solute of the same composition, but the differences in quantity may also be associated with differences in composition. Further NIRS examination of dried, powdered preparations made from such brews may contribute to the understanding of the above dilemma.

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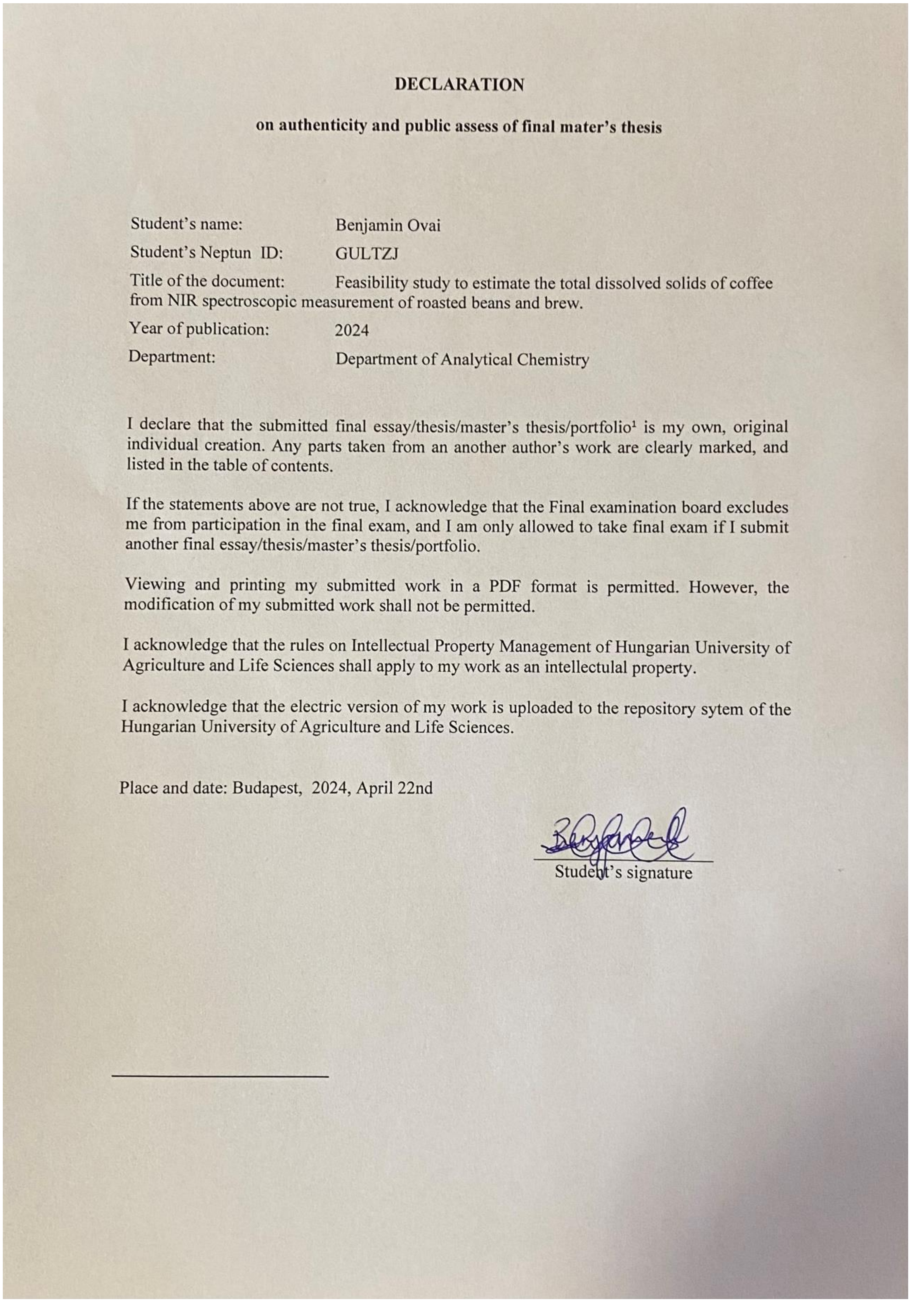

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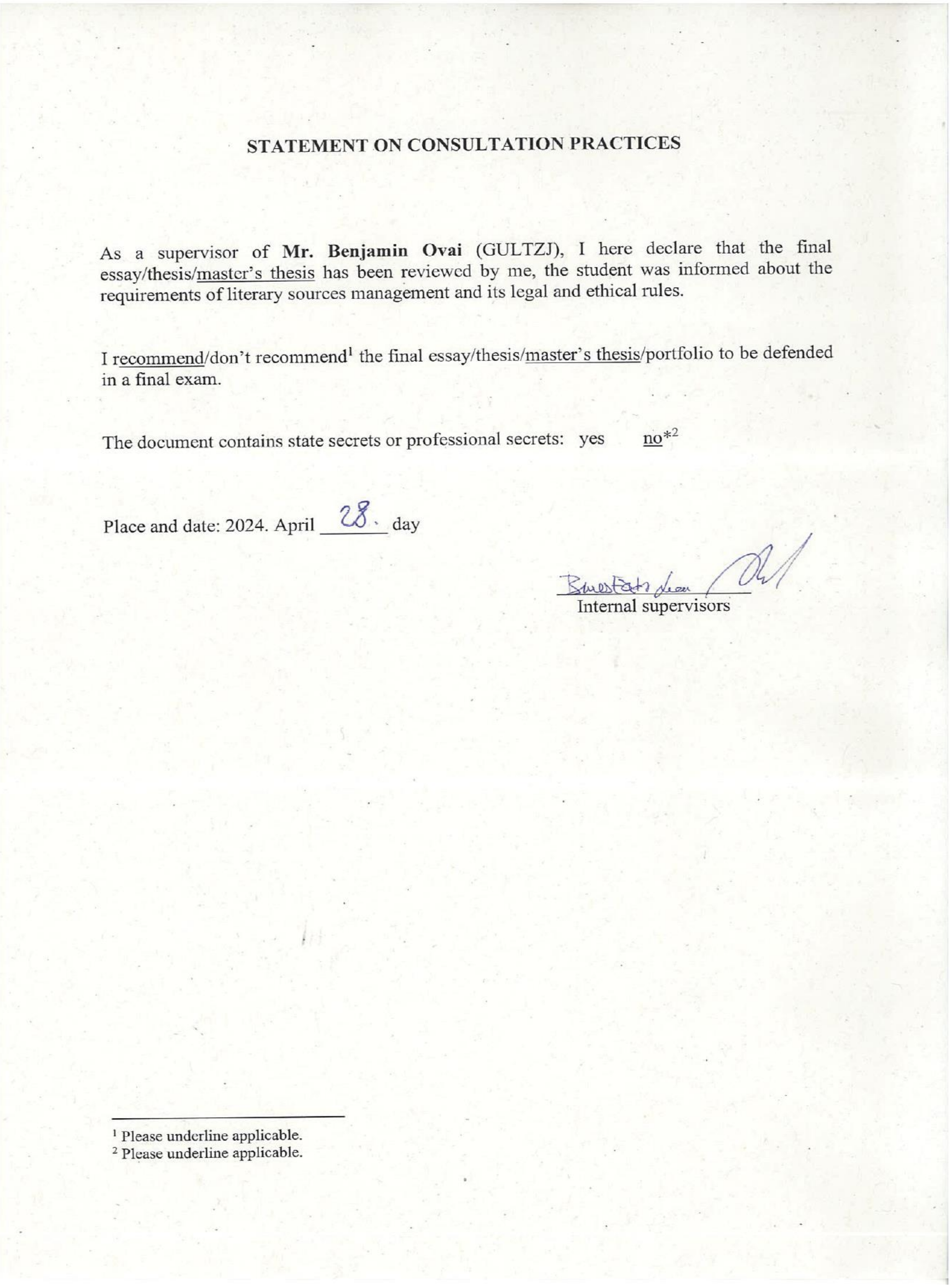

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