# High-Performance Liquid Chromatography Analysis of Coffee-Based Products

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Coffee is a very popular beverage worldwide. However, its composition and characteristics are affected by a number of factors, such as geographical and botanical origin, harvesting and roasting conditions, and brewing method used. As coffee consumption rises, the demands on its high quality and authenticity naturally grows as well. Unfortunately, at the same time, various tricks of coffee adulteration occur more frequently, with the intention of quick economic profit. Many analytical methods have already been developed to verify the coffee authenticity, in which the high-performance liquid chromatography (HPLC) plays a crucial role, especially thanks to its high selectivity and sensitivity.

coffee targeted analysis non-targeted fingerprint HPLC

## 1. Introduction

The coffee tree belongs to the Coffea genus of the Rubiaceae family, including more than 100 species, of which Coffea Arabica (Arabica) and Coffea Canephora (Robusta) are the most consumed, and therefore the most economically important [1][2][3]. Arabica differs from Robusta in several aspects, such as morphology, size and colour of the beans, chemical composition, and sensory properties [4][5][6], as well as growing, cultivation, and brewing properties [7]. Robusta provides very good body and foam, is richer in chlorogenic acids, and contains approximately 40–50% more caffeine than Arabica, which accounts for 65% of global production, is more acidic, less bitter, and has a more refined and pronounced taste and aroma [7][8][9][10][11]. For this reason, Arabica is much more appreciated by coffee consumers, hence its market price is approximately 20–25% higher compared to Robusta [12].

The phytochemical profile of green coffee beans is currently known to be very complex and provides a wide range of health benefits [13][14]. Coffee has been valued for years for its stimulating effect on the central nervous system, associated primarily with caffeine [15][16][17]. Nevertheless, studies show that consumption of two to three coffee cups a day brings many other potential health benefits, including prevention of cancer, type 2 diabetes, cardiovascular and liver diseases, and Alzheimer's and Parkinson's diseases [16][17][18][19][20][21][22][23][24][25][26]. In addition to caffeine, the most important bioactive compounds responsible for these effects are mainly polyphenols [13][27][28][29], of which esters of caffeic and quinic acids, known as chlorogenic acid isomers, are the most abundant [15][16]. While caffeic acid has anticancer effects [30], chlorogenic acids (CGA, **Figure 1**), including the isomers of caffeoylquinic (CafQA), dicaffeoylquinic (diCafQA), feruloylquinic (FQA), and p-coumaroylquinic (pCoQA) acids, exhibit antibacterial, antifungal, antiviral, antioxidant, and chemoprotective properties [26][31][32]. Coffee polyphenols,

together with caffeine, also balance cholesterol and arrhythmia, reduce lipid oxidation and risk of obesity, hypertension, hyperglycemia, or heart and liver failure [22][33][34][35][36][37]. However, caffeine is also associated with stomach irritation, insomnia, and increased breathing and heart rate [26]. As regards the organoleptic characteristics of the coffee beverage, polyphenols are considered to be responsible for its acidity, bitterness, and astringency [38][39].

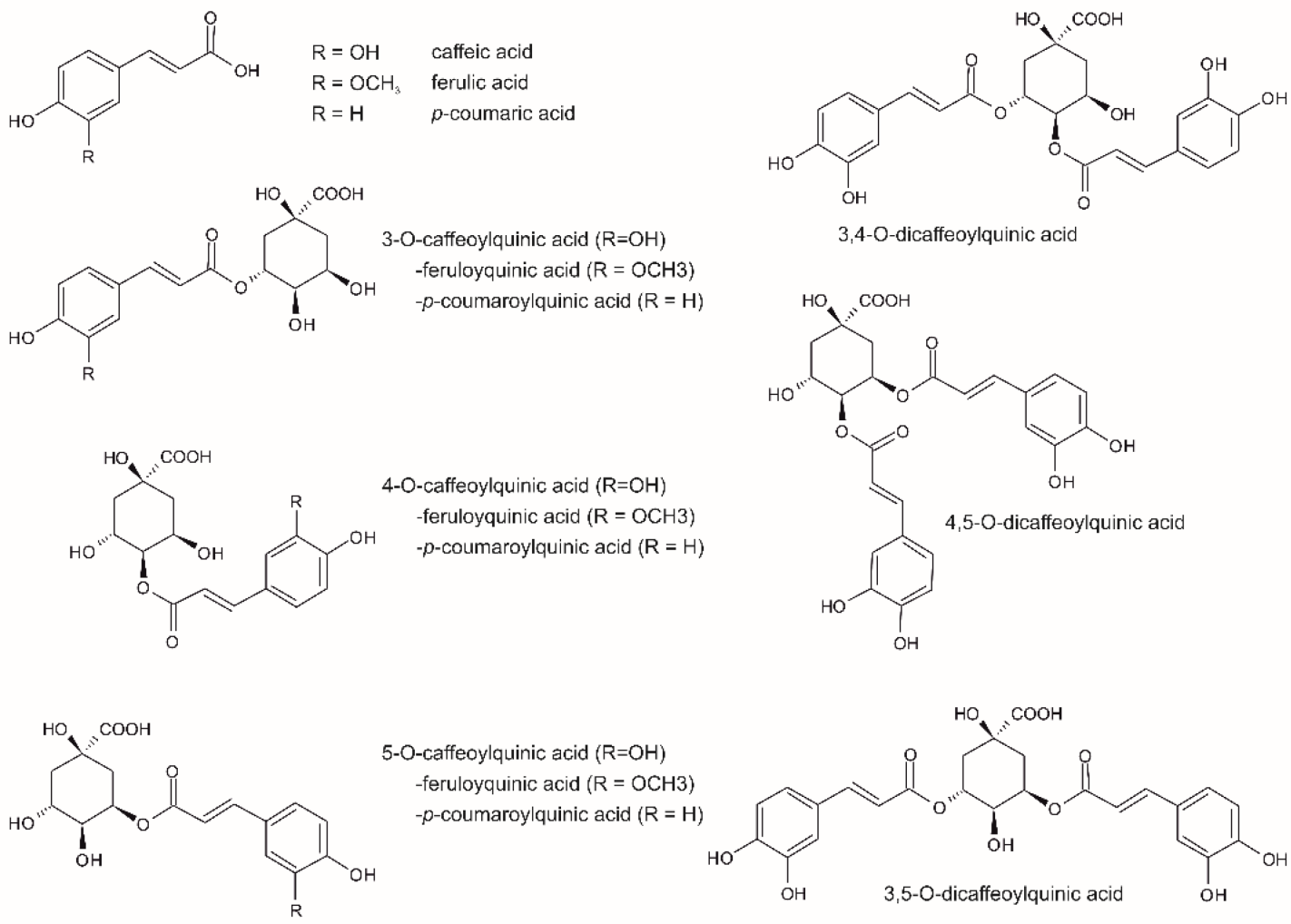


**Figure 1.** Structures of the most important chlorogenic acids present in coffee.

## 2. Coffee Adulteration

According to the European Commission, food products are adulterated if their composition and/or quality do not match their description or labelling [40]. Adulterated food products are usually not harmful to health (sometimes the nutritional value may even be increased), but consumers have a right to know what exactly they are buying and consuming. Moreover, a potential risk of food allergies caused by additives has to be considered [41].

Coffee has been adulterated since time immemorial and today even ranks high at the top of the list of the most adulterated foods [42]. A very common method of coffee adulteration is to mix beans of different economic value.

The undeclared, and thus illegal, addition of cheaper Robusta to Arabica is therefore considered a fraud. Therefore, many researchers have successfully studied the distinction between Arabica and Robusta in coffee blends [1][5][10][12][43][44][45][46][47][48][49][50][51][52][53][54][55][56][57][58][59]. As coffee quality is linked to specific growing areas, incorrect geographical indications are also considered illegal and have been verified by several teams of scientists [10][44][60][61][62][63][64][65][66][67][68][69]. The last common way of coffee adulteration is the blending of roasted coffee with undeclared materials. The list of coffee adulterants is very long and includes roasted and unroasted coffee husks and stalks, cereals (e.g., chicory, corn, barley, wheat, rye, oats, rice, buckwheat, triticale, bran, and malt), legumes (e.g., soybeans, peas, chickpeas, and carob), roots (e.g., chicory or dandelion), vegetables (e.g., potatoes, carrots, and beetroots), fruits (e.g., figs, bananas, acai, and prunes), nuts (e.g., almonds, peanuts, and chestnuts), and seeds (especially cocoa and sunflower seeds). Several techniques have also been developed to detect these impurities [10][41][68][70][71][72][73][74][75][76][77][78][79][80].

As indicated, adulteration practices are diverse and include many tricks to reduce production costs and thus increase the profit from the final product [78][81][82]. However, adulterated coffee products not only mislead consumers, but can also affect their health [71][73]. Therefore, it is essential that analytical techniques are able to detect various forms of adulteration (the use of poor-quality coffee beans, such as unripe, burnt, defective, etc. [10], presence of specific adulterants, degree of dilution, and unauthorized use of geographic origin of coffee beans [78][81][82]) to find whether the product label claims are based on the truth. For these reasons, various spectroscopic [12][50][60][62][63][67][68][69][79][83][84][85][86][87][88][89][90][91][92][93], electrophoretic [74][75], electrochemical [76][80], and biological [56][75][77][94] techniques have already been developed, but chromatographic techniques, especially high performance liquid chromatography (HPLC), have become the most dominant [1][39][45][46][51][66][72][73][95][96][97][98][99] for their more versatile use, reliability, reproducibility of results, possibility of automatization, identification of a large number of qualitative biomarkers in complex matrices, and low sample consumption [13][95][98][100][101].

# 3. Analysis of Antioxidants in Coffee Products Using HPLC

## 3.1. Sample Preparation

Prior to chromatographic analysis, the samples of green, as well as roasted coffee beans, have to be always grinded to a powder from which the target analytes can be subsequently extracted. The contact surface, particle size, weight of the sieve, extraction technique used, as well as time, temperature, and pressure of extraction, are the most significant extraction variables [102]. Depending on the analyte, various extraction methods have already been developed. A simple solid–liquid infusion using hot water [11][26][39][96][102][103][104][105][106][107] or organic solvents [32][99][108][109] is the most common technique of PPs and caffeine isolation. Other extraction techniques, namely percolation [110], ultrasound-assisted [108][111][112] or microwave-assisted extractions [111], QuEChERS [108], and deep eutectic solvent-based extraction [113] have been used rarely. Since the coffee brewing method plays an essential role in the composition and health properties of the resulting beverage, many studies dealing with this issue have already been published [11][106][114][115][116]. In the study of Budryn et al. [114], the influence of coffee genotypes (Arabica vs. Robusta) on the efficiency of various extraction methods (brewing with boiling water and boiling in water at normal and elevated pressure) was investigated. The most efficient extraction methods of

chlorogenic acid isomers from ground Arabica and Robusta green coffee beans were boiling with water at normal and elevated pressure, respectively.

## 3.2. Targeted Analysis

HPLC with spectrophotometric detection (HPLC-UV/VIS), combined with multivariate data treatment, was used to distinguish between specialty and traditional coffee beans in the study by Alcantara et al. [39]. Using PCA, all seventeen samples were very successfully divided into two groups (special versus traditional coffee) according to the quantity of caffeine, chlorogenic, nicotinic, and caffeic acids. This recognition of samples is useful for consumer protection because traditional coffees are of lower quality and, therefore, these can be purchased more cheaply. The main difference was the number and amounts of compounds that were responsible for the organoleptic properties of coffee. Traditional coffees, usually representing blends of Arabica and Robusta, contained higher caffeine and lower polyphenol contents than specialty coffees, which are typically composed of entirely 100% Arabica and roasted to a lower degree, resulting in less degradation of biologically active substances and, consequently, less loss of sensory properties.

The assessment and the comparison of antioxidant potential and content of selected biologically active substances (caffeine and coumaric, ferulic, caffeic, and chlorogenic acids) between green coffee samples and food supplements, based on green coffee extracts, was the aim of the work of Brzezicha et al. [112]. In fact, food supplements are not subject to any quality control or analytical verification of their composition before they are placed on the market. There are not even uniform procedures for verifying their authenticity. For this reason, many questions arise about their quality, efficacy, and safety, as well as whether a supplement or a food is a better source of biologically active substances. Brzezicha et al. [112] ascertained that green coffee samples have comparable or even higher antioxidant properties than dietary supplements. The amount of 5-CafQA in food supplements was very diverse (0.33–329 mg/g) compared to green coffee samples (32.7–47.6 mg/g). Moreover, the green coffee samples contained lower levels of caffeine. The scholars found discrepancies between the determined and the manufacturer’s declared values (the amount of chlorogenic acid was in all cases below the declared value and, conversely, the amount of caffeine was higher in some samples than indicated on the packaging). The quality of food supplements could therefore be summarized as unsatisfactory.

The effect of the coffee roasting process on selected compounds was investigated by Macheiner et al. [109] and Schouten et al. [105] using HPLC-UV/VIS and HPLC-MS/MS instrumentation, respectively. Macheiner et al. [109] examined changes of CafQA and diCafQA isomers present in Arabica and Robusta coffee samples during different degrees and temperatures of roasting, batch size, and roaster designs, while Schouten et al. [105] focused on changes in antioxidant capacity (FRAP, DPPH, and ABTS methods), total phenolic content (Folin-Ciocalteu method), weight loss, water activity, density, moisture, and colour, as well as concentration changes of acrylamide, trigonelline, and nicotinic and caffeic acids in Arabica and Robusta coffee samples roasted to five different roasting degrees (light, medium-light, medium, medium-dark, and dark). Regardless of the botanical origin of the sample, the antioxidant capacity was highest in the first two stages of coffee roasting. With a higher degree of roasting, the antioxidant capacity decreased, but because of the formation of other antioxidant molecules, such as free quinic

acid, melanoidins, or other low molecular weight phenolic compounds, the decline was only moderate [105]. Analogous findings concerning isomerization and other compositional changes occurring during the roasting process were also reported in the study by Klikarová et al. [96]. Further, Schouten et al. [105] presented that the total CGA content was higher in green and light roasted samples. The most abundant CGAs were 5-CafQA (about 80%), followed by 3-CafQA and 3,5-diCafQA. The content of 3-CafQA was increased by light roasting, while 5-CafQA was reduced or stagnated. Decreases in 5-CafQA, 3-CafQA, and 3,5-diCafQA of about 90%, 70%, and 70%, respectively, were observed in dark roasted samples. No significant differences in antioxidant capacity were found between the Robusta and Arabica green samples. However, after roasting, Robusta samples showed considerably higher values, probably due to higher caffeine content. In contrast, total CGA and trigonelline levels were higher in Arabica samples [105]. According to Macheiner et al. [109], chlorogenic acid isomerization reactions were detected at comparable stages of the coffee roasting process, regardless of species, variety, batch size, or roaster design. Degradation of 3-CafQA and 4-CafQA due to isomerization reactions were slower and occurred later in Robusta beans than in Arabica beans. Concentrations of 3,4-diCafQA and 4,5-diCafQA remained almost unchanged until the first crack, while 3,5-diCafQA degraded very rapidly regardless of Coffea species, batch size, and roaster designs. Thereafter, the concentrations of all diCafQA isomers observed continued to decrease until the end of the roasting process.

## 3.3. Non-Targeted Analysis

Recently, numerous non-targeted analysis approaches have been developed, dealing not only with the HPLC fingerprints [1][117][118][119][120][121][122][123][124][125][126][127], but also, less frequently, with profiling using techniques such as gas chromatography coupled to mass spectrometry [101][128][129], nuclear magnetic resonance (NMR) [57][81], UV/VIS spectroscopy [130], or inductively coupled plasma optical emission spectrometry [61][62]. These techniques are predominantly combined with multidimensional statistical methods, such as PCA, factor analysis (FA), discriminant analysis (DA), partial least squares regression (PLS), and their combinations (e.g., PLS-DA), in order to obtain as much information from the measured data as possible.

Strategies of non-targeted chromatographic fingerprinting are based on recording instrumental signals as a function of retention time, but without knowing any further information (identification or quantification) about the compounds providing these signals. For this purpose, simple sample processing procedures are usually used to obtain as many compounds of different families as possible [118]. Thus, non-targeted analysis represents a very simple, rapid, and inexpensive method that could be advantageously used to verify the authenticity and quality of coffee.

Non-targeted HPLC-MS metabolic profiling was effectively used to elucidate the relationship between metabolites and the cupping score indicating the beverage quality [119]. In total, thirty-six varieties of green beans from Guatemala were subjected to the analysis. Using an orthogonal partial least squares (OPLS) regression model, two metabolites (from a total of 2649 valid peaks) were found to be strongly correlated with a high cupping score, and can therefore be utilised as universal quality indicators. The metabolites were first purified and then

spectroscopically identified as isomers of 3-methylbutanoyl disaccharides (i.e., precursors of 3-methylbutanoic acid that is known to enhance the coffee quality).

For characterisation and evaluation of the coffee authenticity and quality, a total of five papers concerning the non-targeted HPLC fingerprint strategies using UV/VIS or fluorescent detection (FLD), combined with chemometrics, were published by the Spanish researchers in 2020–2021 [1][118][122][123][124]. In 2020, they analysed a total of 306 commercially available coffee samples, of which 240 were Nespresso-type products of various origins (Nicaragua, Brazil, India, Uganda, Ethiopia, Central/South America, Columbia, or Indonesia), purchased in supermarkets in Barcelona (Spain), and brewed directly by using an espresso machine [1]. The next 66 samples were purchased in bean form in Vietnam and Cambodia and, after grinding, these were brewed using a moka pot coffee maker. All samples differed in variety (Arabica, Robusta, or their mixture) and degree of roasting (1–5). Selected samples were also used for adulteration studies where the original coffee was mixed with “adulterant” coffee (Colombia vs. Ethiopia, Colombia vs. Nicaragua, India vs. Indonesia, Vietnam-Arabica vs. Vietnam-Robusta, Vietnam-Arabica vs. Cambodia, and Vietnam-Robusta vs. Cambodia) in various ratios ranging between 100:0–0:100 (original coffee: adulterant coffee; *w*/*w*). HPLC-UV/VIS fingerprints were subjected to statistical analysis (PCA, PLS-DA, and PLS regression) and found to be sufficient chemical descriptors to classify coffee by geographical origin (even for nearby countries such as Vietnam and Cambodia), varieties, and degree of roasting (**Figure 2**). Regarding botanical origin (variety), the differences are mainly based on the relative intensities of the peak signals, as the fingerprint profiles are similar. Additionally, PLS regression could reveal coffee adulteration down to 15% of adulterant coffee (coffee of a different geographical or botanical origin than declared) [1]. All 66 Vietnamese and Cambodian samples, together with half of the Nespresso-type samples, both processed as before, were also analysed by HPLC-FLD to obtain fingerprints that were consequently subjected to PCA and PLS-DA statistical analysis as well [122]. HPLC-FLD fingerprints of only two Vietnamese, one Cambodian, and five Nespresso-type coffee samples were again used to reveal adulteration cases related to different production regions. For this purpose, the same pairs of original coffee and adulterant coffee (Colombia vs. Ethiopia, Colombia vs. Nicaragua, India vs. Indonesia, Vietnam-Arabica vs. Vietnam-Robusta, Vietnam-Arabica vs. Cambodia, and Vietnam-Robusta vs. Cambodia) were compared [123]. From these two papers, the identical conclusions as in the previous work published in 2020 were interpreted.

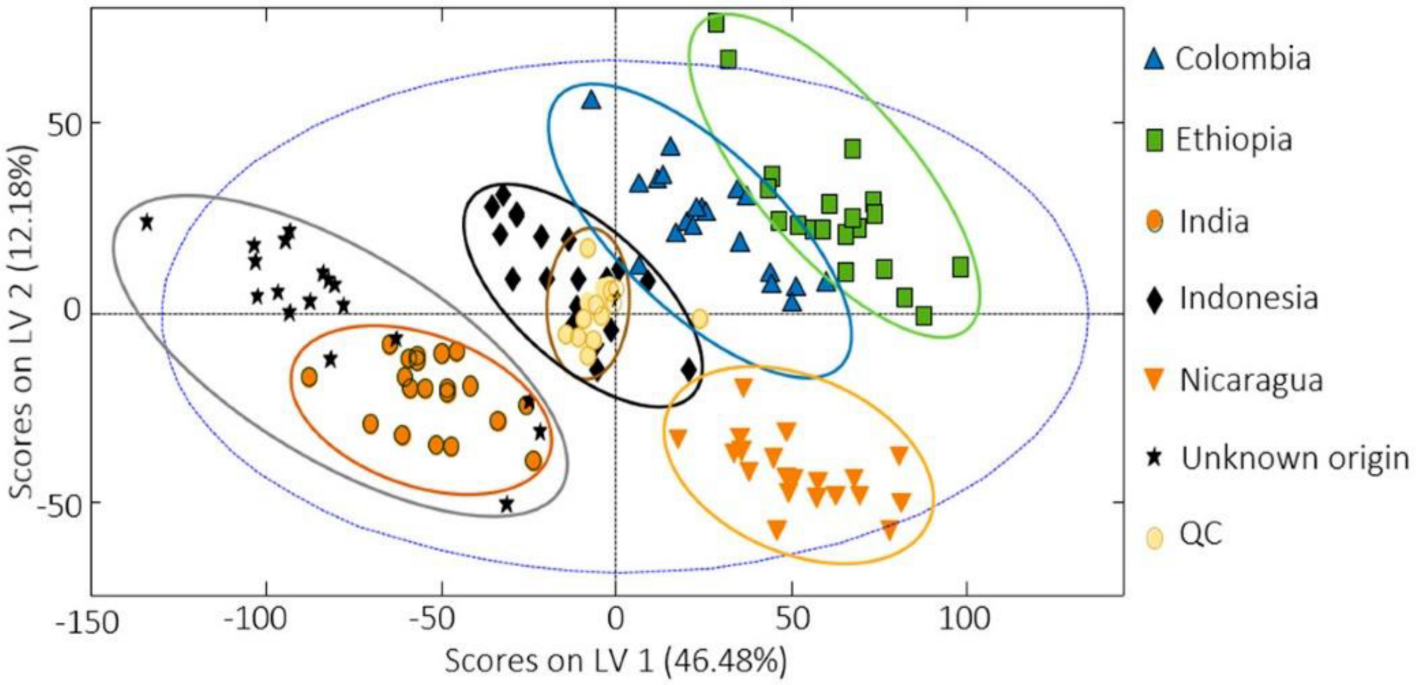


**Figure 2.** PLS-DA differentiation of coffee samples based on their geographical origin [1].

Further, both HPLC-UV/VIS and HPLC-FLD fingerprints of only 54 previous samples of Vietnamese and Cambodian coffee, together with 69 samples of chicory, flour (wheat, rice, cornmeal, rye, and oatmeal), and barley, which were subsequently mixed into coffee as adulterant in ratios ranging between 100:0–0:100 (coffee:impurity; *w*/*w*), were evaluated using PLS-DA to determine the adulteration level [118]. Various extraction solvents (water, methanol, ethanol, acetonitrile, acetone, and organic-aqueous mixtures containing 20, 50, and 80% of each organic component examined) were tested to obtain the maximum number of signals. The highest extraction capacity was achieved by using $H_2O$:acetonitrile (50:50, *v*/*v*) and $H_2O$:methanol (50:50, *v*/*v*) for FLD and UV/VIS detection, respectively. Coffee adulterants provided completely different fingerprints than coffee samples, and their amount could be detected down to 15%. Comparing both fingerprint techniques (**Figure 3**), HPLC-FLD fingerprints did not completely distinguish coffee from barley samples, while all samples were perfectly discriminated by HPLC-UV/VIS fingerprints [118].

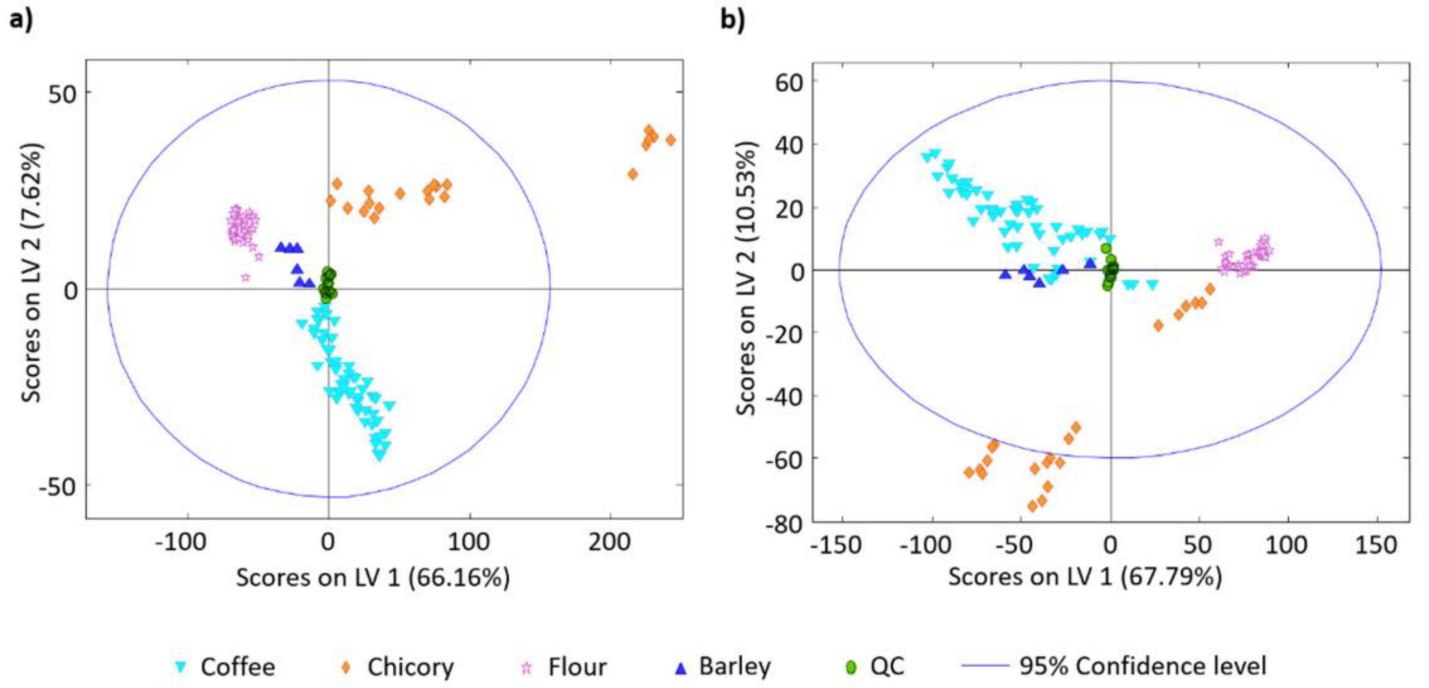


**Figure 3.** PLS-DA classification of the samples using HPLC-UV/VIS (**a**) and HPLC-FLD (**b**) fingerprints [118].

A simple HPLC fingerprint method, together with simultaneous determination of selected bioactive compounds, was developed to evaluate the quality of twenty-four *C. arabica* samples of different geographical origin [125]. About 50 peaks were observed in the fingerprint. However, only thirteen intense peaks with good resolution characterizing the sample were selected. Correlation analysis and PCA analysis proved that the combination of HPLC fingerprint and quantitative analysis can be an effective tool for the evaluation of coffee quality.

# 4. Conclusions

**Figure 4** clearly illustrates the key benefits and drawbacks of targeted and non-targeted analysis. Regarding targeted analysis, it provides very valuable information about the occurrence and concentration of selected (usually significant) analytes in the sample, even without statistical processing of the data obtained. Unfortunately, this qualitative and quantitative determination cannot be performed without the acquisition of frequently expensive analytical standards and the application of any quantitative method requiring additional analyses associated with increased consumption of chemicals. If scholars consider also the time-consuming development of an extraction method suitable for selected analytes (with high recovery), and the long optimization of HPLC separation, which must provide sufficiently separated peaks with good resolution, targeted analysis then represents a relatively time-, financially-, and manually demanding multi-step approach. Although technological progress has made it possible to detect fraudulent practices in coffee by determining specific chemical or biological markers with higher sensitivity than ever before, it can be argued that targeted analysis is unable to reveal all common counterfeiting practices, and thus its application is only limited in this field.

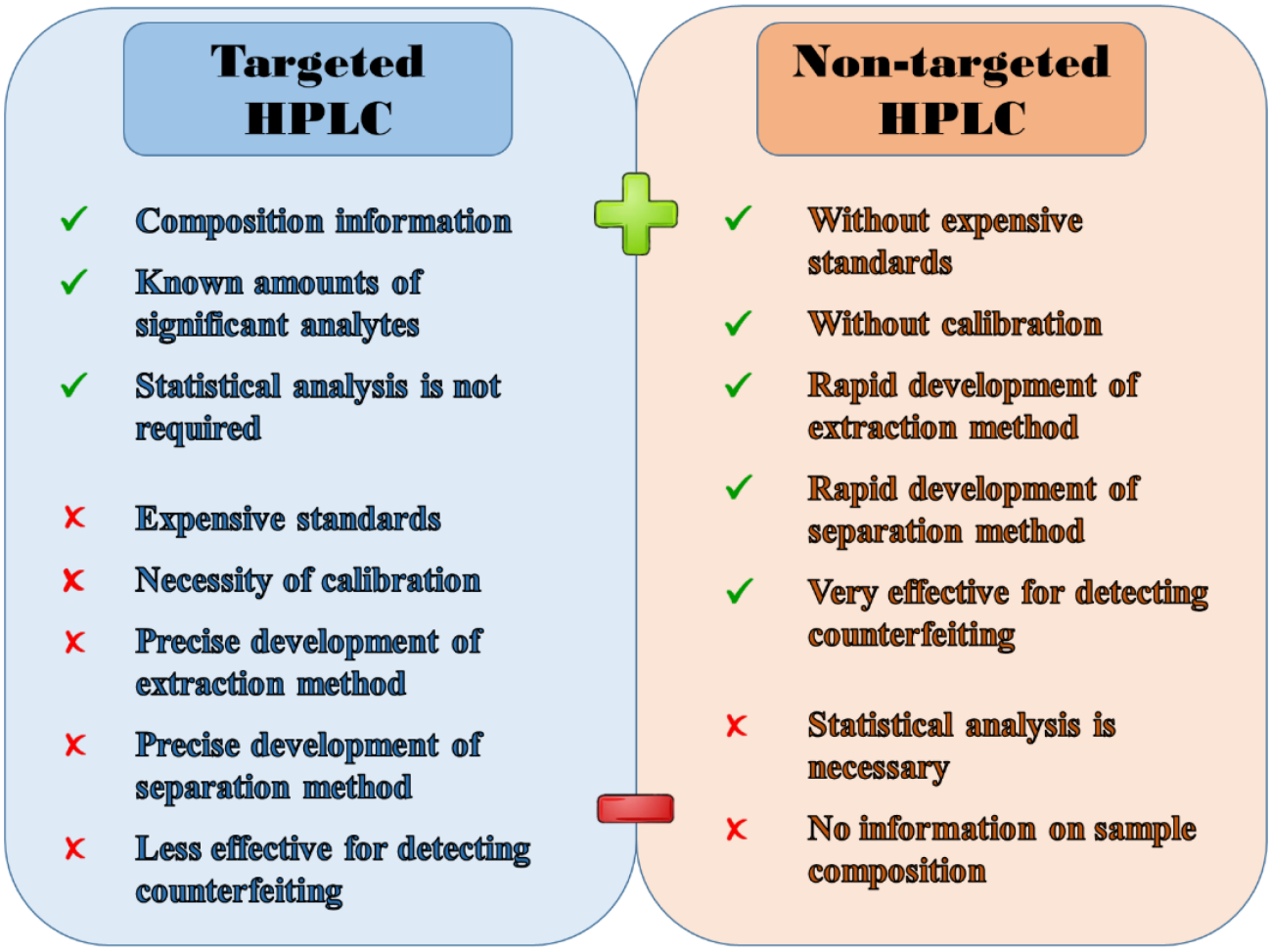


**Figure 4.** Principal benefits and drawbacks of targeted and non-targeted analysis.

On the other hand, in non-targeted analysis (sample fingerprinting/profiling), the traditional procedure of determining analytes in the sample is skipped because it is not crucial to know which analytes the sample contains, let alone in what quantity. This indicates that scholars do not need any analytical standards for the identification of given peaks, nor for their subsequent quantification by some quantitative method (e.g., calibration curve method, multiple standard addition method, method of direct comparison, etc.). In non-targeted analysis, even the optimization of extraction and separation differs from that one used in standard targeted analysis. In this case, the goal is simply to get as many peaks as possible and thus the richest possible chromatogram. Thanks to the easy and rapid optimization of sample pre-treatment and separation, no preparation of calibration solutions, and no identification and quantification of peaks, it significantly reduces the final costs and time.

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