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Article

Ambient Mass Spectrometry Employed for Direct Analysis of Intact Arabica Coffee Beans

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As técnicas de ionização ambiente na espectrometria de massas: ionização de dessorção por eletrospray (DESI) e ionização ambiente por spray sônico (EASI) foram exploradas como uma forma simples e rápida para analisar diretamente a superfície intacta de grãos de café arábica tratados pelas vias seca, semi-seca e úmida. Cinco substâncias foram identificadas, incluindo três componentes da camada de cera que recobre os grãos verdes de café ($^{\beta}$*N*-araquidonoil-5-hidroxitriptamida, $^{\beta}$*N*-behenoil-5-hidroxitriptamida e $^{\beta}$*N*-lignoceroil-5-hidroxitriptamida) e geralmente associadas com irritações estomacais que a bebida do café provoca em indivíduos sensíveis. Além disso, os processos de pós-colheita empregados nos cafés puderam ser diferenciados através da ferramenta estatística multivariada análise de componentes principais (PCA) usando dados de perfil químico das amostras. Nenhum processo de extração ou preparo de amostra foi necessário nas análises de DESI e EASI e os resultados obtidos sugerem portanto a possibilidade de uso dessas duas técnicas para um rápido controle qualitativo e processos de certificação de amostras de café.

The ambient ionization mass spectrometry techniques: desorption electrospray ionization (DESI) and easy ambient sonic-spray ionization (EASI) were explored as fast and simple ways to directly analyze the surface of intact green Arabica coffee beans treated by the dry, semi-dry and wet post-harvest methods. Five compounds were identified, including three components of the waxy layer that covers the green coffee beans ($^{\beta}$*N*-arachinoyl-5-hydroxytryptamide, $^{\beta}$*N*-behenoyl-5-hydroxytryptamide, and $^{\beta}$*N*-lignoceroyl-5-hydroxytryptamide) and that are commonly related to related to stomach irritations caused by coffee beverage consumption in sensitive people. Moreover, the multivariate statistical tool principal component analysis (PCA) was employed to differentiate the coffee post-harvest methods using data from the mass spectrometry fingerprinting analyses. Extraction procedures or sample pretreatment steps were not required for DESI and EASI analyses and the results obtained suggest therefore that these techniques could be used for rapid quality control and certification processes of coffees samples.

Keywords: ambient ionization, mass spectrometry, coffee, 5-hydroxytryptamides

Introduction

Ambient sampling/ionization mass spectrometry (MS) comprises a family of techniques that operate under ambient conditions and allows the direct analysis of samples with minimal or no sample pretreatment.[1] The first technique to broadly demonstrate this concept of ambient MS was desorption electrospray ionization (DESI)[2] introduced in 2004, followed by direct analysis in real time (DART)[3] and easy ambient sonic-spray ionization (EASI).[4] After the introduction of DESI, a rapid growth in the field of ambient MS was observed and today, ten years later, more than thirty different ambient MS techniques have been described showing the success of this new field.[1]

DESI and EASI are usually classified as spray-based desorption/ionization ambient techniques. They are capable of desorbing and ionizing molecules for MS analysis directly from sample surfaces at open-air conditions using very little or no sample preparation. The analysis is done in seconds to minutes by just spraying a solvent onto the

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sample surface, where secondary scattered droplets are generated and evaporated, and their constituents analyzed by mass spectrometry (Figure 1).[5]

Although being spray-based techniques, they greatly differ in the ionization mechanism. In DESI, the application of high voltage to the spray capillary, generally 3-5 kV, results in charged droplets either positive or negative with a relatively high charge load that will promote the desorption/ionization of the analytes.[5] In EASI, however, there is no voltage applied and bipolar charging (both positively and negatively) results from a natural statistical imbalance distribution of ions present in tiny droplets formed during sonic spraying.[4]

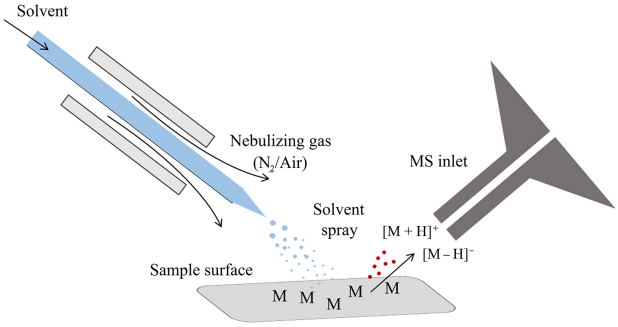


Figure 1. Schematic representation of typical EASI-MS experiments. Unlike DESI, no voltage is applied to the spray capillary in EASI and a higher-velocity nebulizing gas is used.

In these techniques, analytes are often ionized as protonated $[M + H]^+$ or deprotonated $[M – H]^-$ molecules with low energy content, hence, fragmentation is normally minimal or fully avoided. This feature favors the analysis of complex mixtures in their natural environment without extraction procedures.[6] The versatility of DESI and EASI analyses have been proven by its use in different areas, for example, natural products,[7] pharmaceutical products,[8] illicit and counterfeit drugs,[9] fuels,[10] and forensics,[11] with upmost simplicity.[12]

Coffee is an extremely important agricultural commodity for many developing countries, including Brazil, the largest coffee producer and exporter.[13] Besides the large number of non-ambient MS techniques employed to investigate coffee samples, ambient ionization techniques such as DART,[14] low-temperature plasma (LTP) probe,[15] and paper spray[16] have also been successfully used for this purpose.

To obtain high-quality coffees, several factors have to be considered, from choice of the right species/cultivar, edaphoclimatic conditions and post-harvest treatments, to process of packing, roasting and coffee brew preparation. The step of coffee fruit processing after harvesting is very important and, depending on the method employed (dry, semi-dry or wet), coffees will display great variation in body, acidity and flavor.[17] The dry method (natural coffee) is mostly employed in Brazil, and different from the other two methods that are mainly used for Arabica beans (*Coffea arabica* L.), the dry method is applied for both Arabica and Robusta (*C. canephora* P.) coffees. Basically, it consists of drying the whole coffee fruits in mechanical dryers or under the sun on large patios, followed by pulp removal to obtain the "green" coffee beans. In the semi-dry method (pulped natural coffee), the pulp removal occurs before the drying process. Finally, the wet process (washed coffee) consists of removing the fruit pulp followed by the mucilage removal using chemicals or fermentation, and then drying.[18] The semi-dry and wet methods usually require restrict fruit maturation control and extra process steps compared to the dry method, and commonly result in coffees with higher market prices.

Investigations on coffee post-harvest treatments usually deal with analysis and comparison of target compounds using elaborated techniques or time-consuming protocols for both sample preparation and analysis.[19] Hence, they normally do not allow high-throughput analysis. Reports on the use of non-target fingerprinting analyses for coffee post-harvest methods differentiation are also scarce.[20] Therefore, the improvement or development of new, simple and fast methods to control the post-harvest processes and to guarantee the coffee quality would be highly beneficial.

With all these in mind, we decided to explore the ambient ionization MS techniques DESI and EASI as simple and fast ways to directly analyze intact green beans of Arabica coffees from three post-harvest treatments (dry, semi-dry and wet) as well as try to differentiate these treatments using the unsupervised multivariate statistical tool principal component analysis (PCA).

Experimental

Coffee samples

Six samples of green Arabica coffee beans from crop 2011/12 and processed by the dry, semi-dry and wet post-harvest treatments (two samples from each treatment) were obtained from coffee producers of the Região Serrana of Rio de Janeiro State, Brazil. Samples were stored in a freezer at –4 °C and the defective beans were manually removed before mass spectrometry analysis.

Ambient ionization mass spectrometry

Six intact coffee beans from each sample were placed in front of the mass spectrometry inlet and were directly analyzed by spraying its surface. No additional

sample preparation was required and the experiment was performed under ambient conditions. Full scan mass spectra were recorded in positive ion mode over the range of *m/z* 150-1000 using a LCMS-2010EV single quadrupole mass spectrometer (Shimadzu Corp., Japan) and a Thermo LTQ mass spectrometer (Thermo Fisher Scientific, USA) equipped with a lab-built EASI and DESI ion sources, respectively, described elsewhere.[21]

The experimental conditions for DESI were as follow: spray voltage of 5 kV, incident spray angle of 52°, N_2 gas pressure of 100 psi, and methanol (HPLC grade; Fisher Scientific, Whitby, Canada) at flow rate of 5 μL min^{-1}. No spray voltage is employed for EASI and it was used an incident spray angle of 30°, compressed N_2 pressure of 120 psi, and methanol at flow rate of 20 μL min^{-1}.

An electrospray ionization-high resolution Fourier transform ion cyclotron resonance mass spectrometer (ESI FT-ICR MS) was employed in the positive ion mode to perform MS/MS experiments and to obtain *m/z* values with mass errors lower than 1 ppm using a coffee extract and MS conditions as described by Garrett *et al.*.[22]

Multivariate statistical analysis

Lists containing the rounded *m/z* to integer values and relative abundances of the thirty most intense ions from the mass spectra of each sample were exported from the mass spectrometers software to Microsoft Excel. Data were manually aligned, filtered by removing the ions that appeared in less than three replicates from each sample, and treated by Pareto scaling to reduce the differences between large and small peaks.[23] The resulting matrix, where each line represented a sample and each column a variable (*m/z* values), was then submitted to PCA using the software The Unscrambler version 9.1 (CAMO Software). Internal leave-one-out cross-validation was employed to choose the optimum number of PCs.

Results and Discussion

The intact coffee bean has an elliptical, plane-convex shape. Thus, the surface of both convex and flat sides of the coffee bean were analyzed by DESI and EASI. However, it was not possible to obtain a mass spectrum from the convex bean side using EASI-MS. The design of the EASI ion source used required solid samples to have a flat surface for the correct spray hit angle, which is necessary to desorb the ions from sample surface as well as to collect them by the MS inlet. Differently, the lab-built DESI ion source used was more flexible and equipped with a platform that enabled to hold the coffee beans and move it in the xyz axes. This flexibility helped the right adjustment of the spray hit angle and, consequently, the analysis of both coffee bean sides.

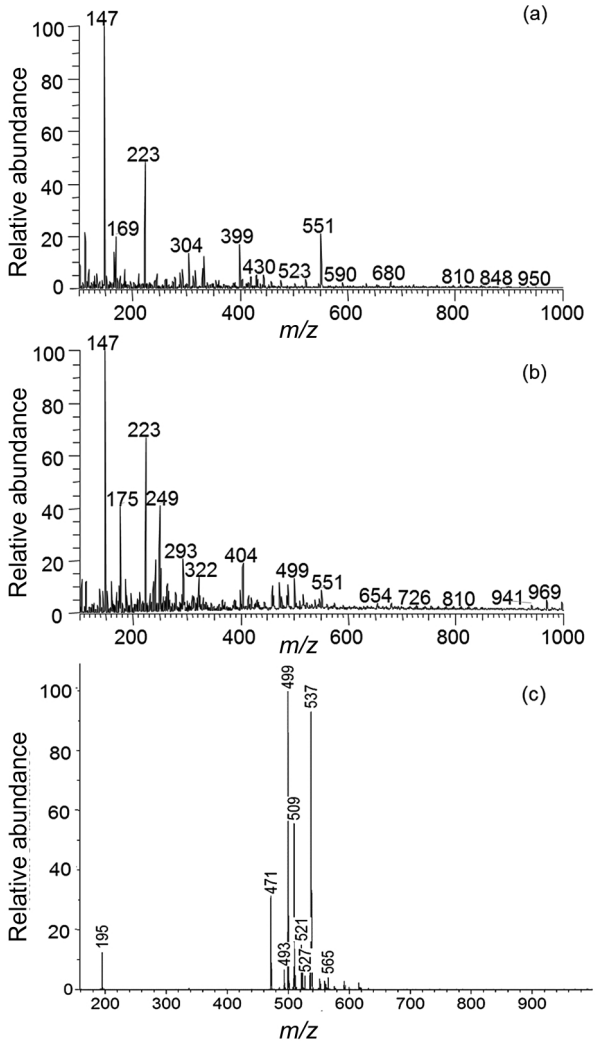
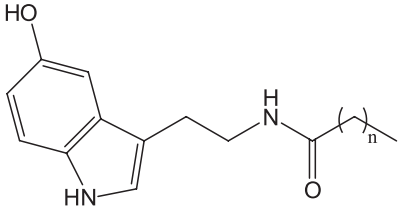


Figure 2. DESI(+)-MS fingerprinting of the (a) convex and (b) flat coffee bean sides, and EASI(+)-MS fingerprinting of the flat coffee bean side (c). These mass spectra are from an intact coffee bean processed by the dry post-harvest method.

The direct DESI and EASI mass spectra in the positive ion mode of a representative green coffee bean processed by the dry method is shown in Figure 2. The MS profiles obtained for both coffee sides analyzed by DESI were more similar comparing them to the EASI-MS profile, with most of the analytes and background ions from sample and solvent located within the range of *m/z* 100-500. In a different way, EASI-MS analysis of the flat bean side resulted in a mass spectrum with more pronounced analyte ions within the range of *m/z* 450-600 and improved signal-to-noise ratio, that is, with much lower background. These profiles were also observed for coffees processed by the semi-dry and wet methods. In EASI, likely due to the low charge load of the spray droplets, it is usually

observed less intense ion currents but lower chemical noise compared to DESI.[24]

The ions of *m/z* 471, 499 and 527 from the EASI mass spectrum (Figure 2c) were identified as protonated molecules $[M + H]^+$ of the fatty acid amides of serotonin: $^{\beta}N$-arachinoyl-5-hydroxytryptamide ($C_{30}H_{50}O_2N_2$; experimental *m/z* value of 471.39454; error: 0.06 ppm), $^{\beta}N$-behenoyl-5-hydroxytryptamide ($C_{32}H_{54}O_2N_2$; experimental *m/z* value of 499.42587; error: 0.12 ppm), and $^{\beta}N$-lignoceroyl-5-hydroxytryptamide ($C_{34}H_{58}O_2N_2$; experimental *m/z* value of 527.45715; error: 0.08 ppm), respectively (Figure 3), by their common fragment ions of *m/z* 177 and 160 in MS/MS experiments, which corresponded to losses of fatty acid units from the protonated molecules, and also by their high accuracy *m/z* values obtained by ESI(+) FT-ICR MS analysis of a methanolic coffee extract.[25] These three compounds are considered the major 5-hydroxytryptamine derivatives (C-5HTs) in green coffee beans and are located in the waxy layer that covers the beans.[26] Along with other C-5HTs, they are suspected to account for stomach irritations related to coffee beverage consumption by sensitive people.[27] Dewaxed and "stomach-friendly" coffee brands in which C-5HTs are claimed to be partial or completely removed to avoid indigestibility are available on international market, reaching higher prices than regular coffees. The easy detection of these three compounds by EASI-MS suggests that this ambient ionization technique could be employed for their rapid detection and, therefore, for qualitative control of the dewaxing processes. The main advantage of EASI-MS compared to other analytical techniques that employ, for instance, chromatographic separations to analyze dewaxed coffees would be the direct and no sample preparation analysis.



n	Compounds	*m/z*
18	$^{\beta}N$-arachinoyl-5-hydroxytryptamide	471
20	$^{\beta}N$-behenoyl-5-hydroxytryptamide	499
22	$^{\beta}N$-lignoceroyl-5-hydroxytryptamide	527

Figure 3. Chemical structure and *m/z* values of 5-hydroxytryptamine derivatives identified on the surface of intact Arabica green coffee beans by positive ion mode EASI-MS and DESI-MS.

The ion of *m/z* 537 $[M + H - H_2O]^+$ displayed fragment ions of *m/z* 281, 147 and 131 by MS/MS experiments and was tentatively identified as the coffee diterpene cafestol palmitate (experimental *m/z* value of 537.43030; error: 0.15 ppm).[28] The ion of *m/z* 195 $[M + H]^+$ was identified as caffeine by its high accuracy *m/z* values (experimental *m/z* value of 195.08765; error: 0 ppm).

The five molecules detected by EASI-MS (cafestol palmitate, caffeine and three C-5HTs) were also observed on the flat side of coffee beans by DESI-MS, however, with much lower signal intensity (Figure 2b). For DESI-MS analysis of the convex bean side, these compounds were not observed in all samples, and perhaps this occurred due to ion suppression caused by other coffee compounds present in the convex bean side. The ion of *m/z* of 551 observed in Figure 2a and b corresponds to a solvent contaminant.

To try to differentiate the coffee post-harvest treatments, PCA was carried out using a matrix of 36 samples and 41 variables from fingerprinting analysis of the flat bean side by EASI-MS and a matrix of 36 samples and 55 variables from fingerprinting analysis of the convex bean side by DESI-MS. A better cluster separation was achieved after applying the Pareto scaling. As Figure 4a shows for PCA analysis of DESI-MS data, three groups were formed, representing the dry, semi-dry and wet post-harvest treatments. Six PCs were used and the first two were responsible for 69% of the

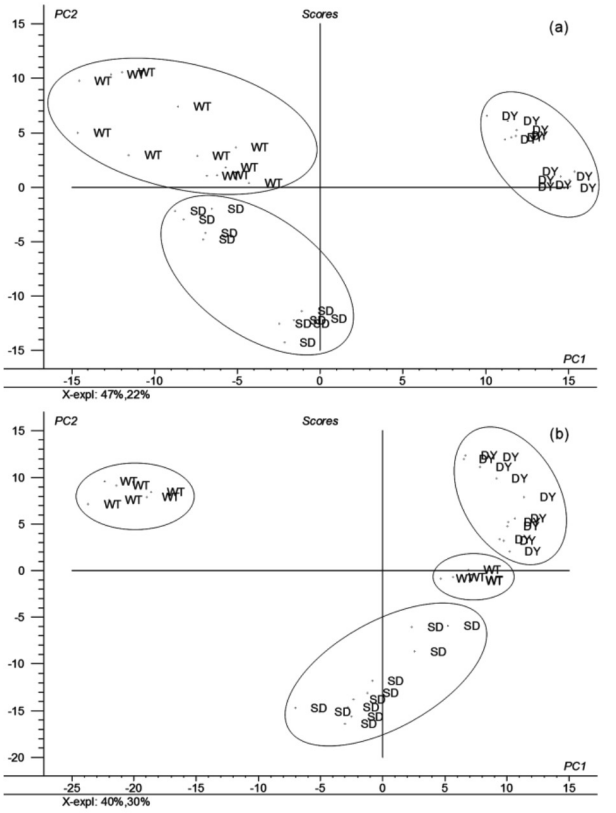


Figure 4. PCA score plots showing the clusters formation according to the coffee post-harvest methods by (a) DESI-MS and (b) EASI-MS analyses of intact green coffee beans (WT: wet, SD: semi-dry, and DY: dry post-harvest methods).

explained variation. A similar clustering was observed for EASI-MS data, although two clusters were formed for the wet treatment (Figure 4b). Five PCs were used and the first two explained 70% of the data variation.

Comparing the dry, semi-dry and wet post-harvest treatments, the wet treatment is the one that suffers with much more variations or adaptations among different coffee producers, mainly because of the step of removing the mucilage before the drying process. In most of the cases, is the expertise of coffee producers that determines the exact point where all the mucilage has been removed from the coffee bean in the water fermentation tanks, and this may explain the dispersion of samples from this treatment observed by PCA.

The variables (*m/z* of ions) with high absolute loading values in the loading plot (not shown) for DESI-MS analysis were: 104, 152, 172, 223, 288, and 316; and for EASI-MS: 471, 493, 499, and 509. It is interesting to note that variables 471 and 499, two high abundant ions in EASI-MS analyses and identified as the waxy components $^{\beta}$*N*-arachinoyl-5-hydroxytryptamide and $^{\beta}$*N*-behenoyl-5-hydroxytryptamide, respectively, were positively correlated with coffees processed by the dry method. In this treatment, coffee fruits are dried in its intact form, followed by pulp removal. Hence, it may keep more efficiently the waxy layer that covers the coffee bean comparing this treatment with the semi-dry and wet, where the steps of pulp removal before the drying process might led to losses of compounds due to lixiviation or exogenous metabolism. Further investigations are required to try to identify and correlate the other discriminant variables revealed by PCA with the post-harvest treatments.

The coffee bean surface is very irregular and this has a direct effect on the ionization efficiency. Therefore, small variations on chemical profile were observed for coffee beans belonging to the same set of sample (replicates). However, the chemical profile variability among the set of samples were much higher allowing the post-harvest treatment differentiation achieved by PCA analysis.

Conclusions

DESI and EASI are simple, fast, and sample-preparation free open-air ionization techniques capable of analyzing directly a single sample of intact green coffee bean, while preserving its integrity for further analysis. Five compounds were identified, being three of them ($^{\beta}$*N*-arachinoyl-5-hydroxytryptamide, $^{\beta}$*N*-behenoyl-5-hydroxytryptamide, and $^{\beta}$*N*-lignoceroyl-5-hydroxytryptamide) components of the waxy layer that covers the coffee bean and are generally associated with stomach irritations of coffee beverage in sensitive people.

With the combinations of DESI and EASI ambient ionization techniques and PCA, it was possible to follow the differences among the coffee beans according to the post-harvest treatments and this approach could be used for coffee control and certification processes. As a proof-of-concept study, a relative low number of samples were used, but larger variability is expected for the many green coffee beans available on the market. In addition, with the development of portable mass spectrometers,[29] these techniques could be used for field analysis.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

Acknowledgments

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Supplementary Information

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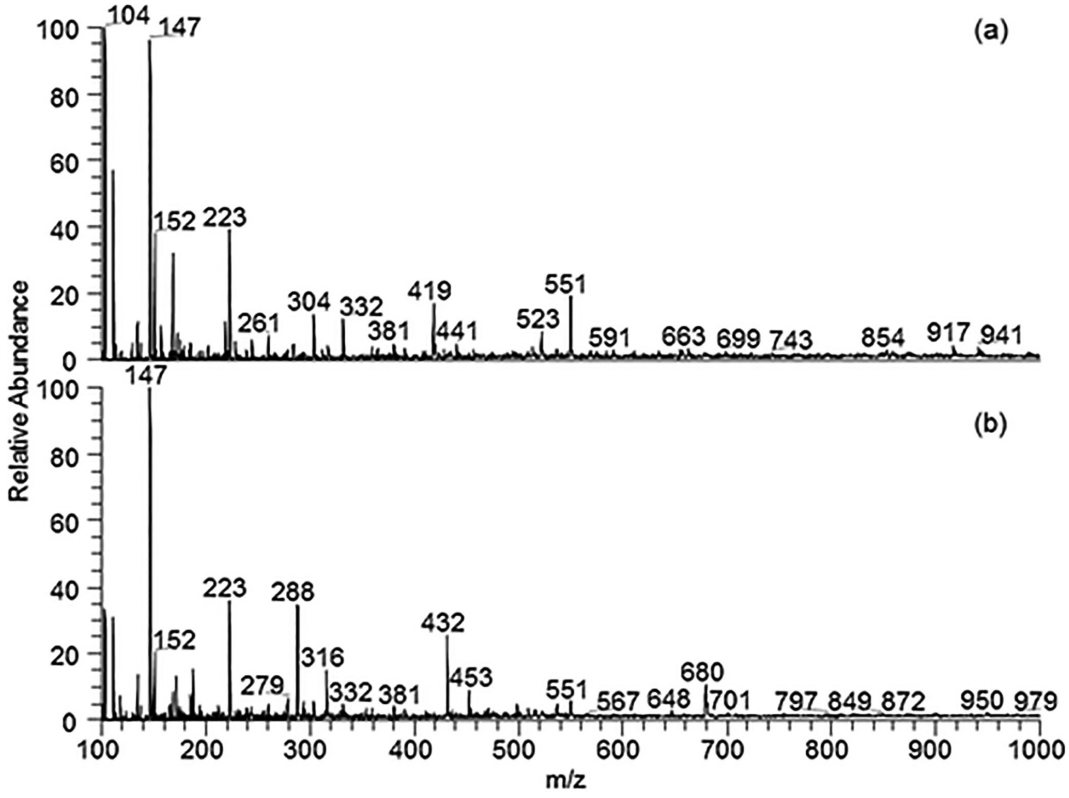

Figure S1. DESI(+)-MS fingerprinting of the convex bean side from coffees processed by the semi-dry (a) and wet (b) post-harvest methods.

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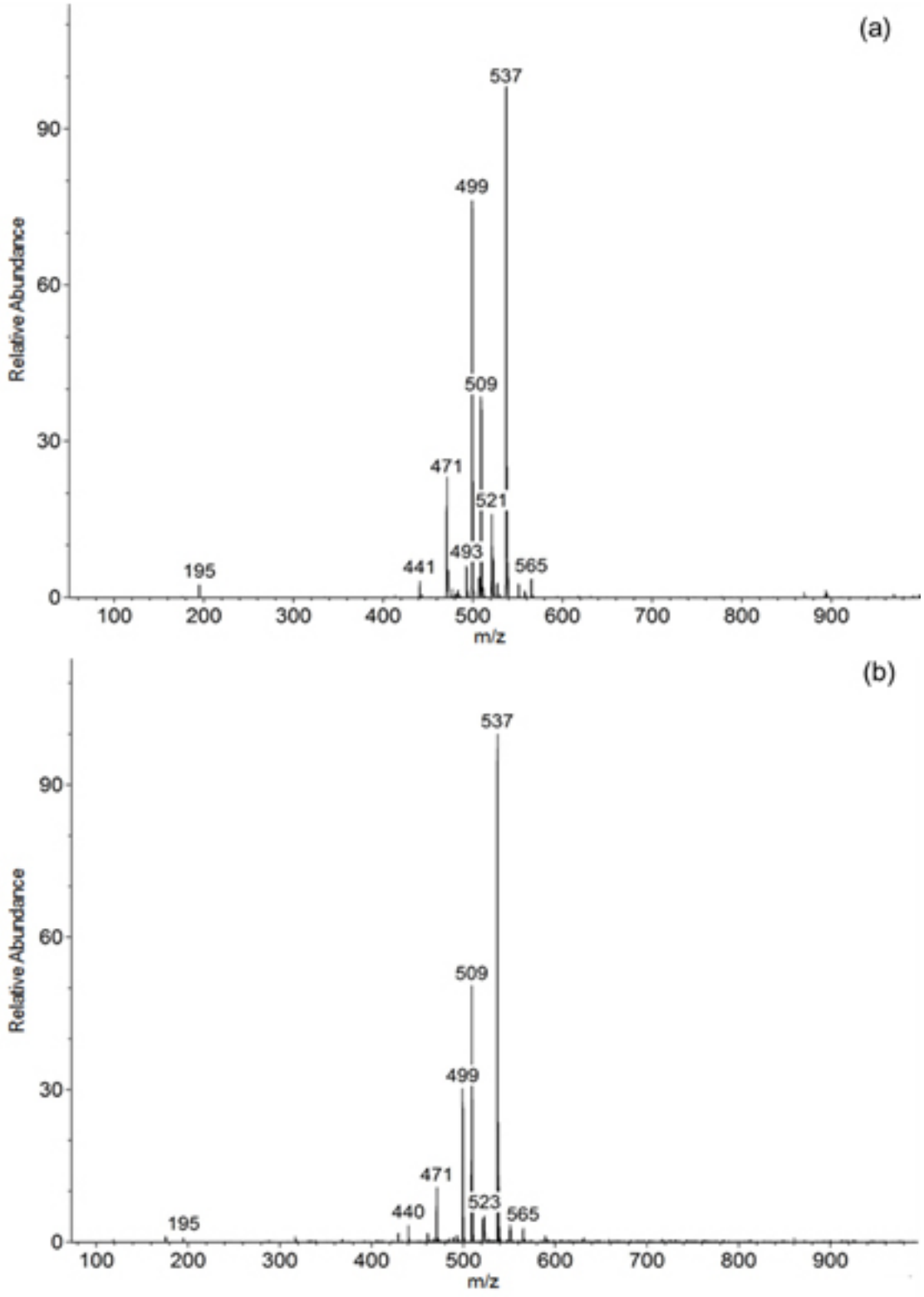

Figure S2. EASI(+)-MS fingerprinting of the flat bean side from coffees processed by the semi-dry (a) and wet (b) post-harvest methods.