

SPME/GC/Q-ToF-MS and Chemometric Approaches for Detecting Adulteration in Ground Roasted Coffee

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ABSTRACT

In the world, adulteration of coffee might have been observed for years owing to dishonest food manufacturers. Today, different analytical techniques have been utilized for food fraud detection. In the current research, the potential use of solid-phase microextraction (SPME)-*gas chromatography-time-of-flight mass spectrometry* (GC/Q-ToF-MS) combined with chemometrics was evaluated to detect coffee adulteration. The aroma profiles of ground roasted coffee were compared with some commonly used adulterants (ground roasted barley, corn and soybean) to identify marker aroma compounds that could separate ground roasted herbal adulterants from ground roasted coffee. The SPME fiber assembly DVB/CAR/PDMS was utilized to collect and concentrate the headspace volatiles of ground roasted coffees and adulterants, and the volatile profile analyses were performed by GC/Q-ToF-MS. Non-adulterated and adulterated samples were successfully separated after applying some chemometric tools (principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA) and *hierarchical cluster analysis* (HCA)) on the obtained chromatographic data. Two volatile compounds (1H-imidazole-4-methanol and benzene-2-(1,3-butadienyl)-1,3,5-trimethyl) were determined as potential markers for determining adulterants (ground roasted barley, corn or soybean) in ground roasted coffee (*p*-value cut-off<0.001 and fold change (FC) cut-off>10). Also, 2-furanmethanol and 2-formyl-1-methylpyrrole were found as marker candidates for roasted coffee powder. This analytical method allowed the detection of selected herbal adulterants (5% w/w) found in ground roasted coffee.

Key words: Coffee adulteration; volatile profiles; SPME; GC/Q-ToF-MS; chemometrics.

1 INTRODUCTION

Food adulteration is a serious problem, which all of us have faced commonly from time immemorial (Banerjee et al., 2017). Adulteration may cause both health and economic problems. Techniques of adulterating foods have become more complicated, thus efficient and reliable methods are necessary for detecting these frauds (Schieber, 2018). Adulteration deteriorates product quality, which leads to deception of consumers by incompliance with product claims and legal standards (Oliveira et al., 2009). Today, it is not easy to find unadulterated food because nearly all foods, including fats and oils, dairy products, honey and coffee etc. are prone to adulteration (Haji; Desalegn; Hassen, 2023).

Globally, coffee is a widely consumed drink and countries that produce and export it achieve considerable economic gains (Toci et al., 2016). The shortage of coffee beans and its economic value cause vicious food manufacturers to adulterate coffee by changing the quality coffee beans and adding less expensive plant materials (coffee husks, barley, rye, soybean etc.) to coffee blends (Cheah; Fang, 2020). Coffees from *Coffea Arabica* L. are sold at higher prices than coffees from *Coffea canephora* var. *Robusta* owing to their more desirable sensory profile and other agronomical reasons (Wang; Lim; Fu, 2020). Therefore, the incorporation of considerably cheaper Robusta coffees in claimed 100% Arabica coffees leads to food fraud. Furthermore, it has been found that plant materials like roasted

soybeans can be a suitable adulterant for coffee (Cheah; Fang, 2020). It is known that some chemical groups named pyrazines, furans, aldehydes, ketones and pyrroles are in charge of the aroma characteristics of coffee (Angeloni et al., 2021). Similar aroma compounds can be found in roasted barley, soybean and corn (Wang; Kato; Fujimaki, 1969; Doi et al., 1980; Kim; Lee; Kim, 1998; Puviprom; Chaiseri, 2012). Maillard and Strecker reactions between reducing sugars and amino acids and caramelization play a key role in the formation of these compounds during the roasting process of herbal products (Cui et al., 2020).

Physical properties of ground roasted coffee like particle size, texture and color make it highly vulnerable to adulteration by processed plant materials (Oliveira et al., 2009). It is hard to differentiate genuine coffee from adulterants with simple visual inspection. Microscopy is generally the preferred technique to detect adulterants in coffee. Different roasted and ground cheap fillers are used as adulterants in coffee, so it is hard to generate a method which is distinguishing between various marker ions (Pauli et al., 2014).

Spectroscopy, chromatography, digital image processing and electrophoresis are often used in studies for detecting markers of adulterants in coffee (Ebrahimi-Najafabadi et al., 2012). Souto et al. (2015) offered a methodology based on an ultraviolet-visible (UV-Vis) spectroscopy to identify adulterants (husks and sticks) in the aqueous extracts of grinded roasted coffee. The data were evaluated using Soft

Independent Modelling by Class Analogy (SIMCA), partial least squares discriminant analysis (PLS-DA) and Successive Projections Algorithm-Linear Discriminant Analysis (SPA-LDA). In another study, digital images and SPA-LDA were used to find adulterations (husks and sticks) in coffees by Souto et al. (2014). Song et al. (2019) generated a high-performance liquid chromatography (HPLC) method to determine some herbal products (roasted barley, wheat and rice powders) used as adulterants in ground roasted coffee. Monosaccharides, trigonelline and nicotinic acid were determined chemical indices and glucose could be the best chemical index to discriminate non-adulterated coffee from studied adulterants. Similarly, Domingues et al. (2014) determined fraud in coffee by two different HPLC systems based on carbohydrate profile. Moreover, Cai, Ting and Jin-Lan (2016) developed a chromatographic method based on oligosaccharide profiling for detecting fraudulent food products (rice and soybean) found in grinded coffee. 17 characteristic oligosaccharide markers were used to identify adulterants in ground coffee (5% adulterants). Daniel et al. (2018) offered a methodology based on capillary electrophoresis-tandem mass spectrometry to detect adulterants (soybean and corn) in ground roasted coffee. The monosaccharides profile was used as a quality marker. The monosaccharide profiles of samples were assessed by principal component analysis (PCA). Pauli et al. (2014) utilized carbohydrate contents of samples to discriminate ground roasted coffee from adulterants (roasted soybean and wheat). In the study, HPLC-high performance anion-exchange chromatography (HPAEC)-pulsed amperometric detection (PAD) combined with chemometrics (PCA and LDA) was used. Sezer et al. (2018) managed to detect corn, wheat and chickpea adulteration in coffee (<0.6%) employing laser-induced breakdown spectroscopy. Spectra obtained by analysis were analysed using various chemometric tools (PCA and PLS). Combes, Joët and Lashermes (2018) developed a DNA-based method to detect Robusta adulteration in Arabica products.

As can be seen from the literature, most of the coffee adulteration studies were based on carbohydrate contents. However, several fraud detection studies for coffee were conducted using an untarget metabolomics approach and SPME to identify marker volatile compounds of adulterants. Untarget metabolomics has become a common and useful technique to specify metabolites (known and unknown) in food studies owing to challenges in identifying compounds such as expense of standards (Xi et al., 2021). For instance, Oliveira et al. (2009) managed to detect adulterated ground roasted coffee using SPME/GC-MS and chemometrics (PCA). This methodology could detect 1% (w/w) roasted barley in roasted coffee samples. They identified aroma compounds that can be used as chemical markers for coffee fraud detection. Furthermore, De Carvalho et al. (2024) reported marker

volatile compounds for separating main adulterants (soybean, rice and coffee husks) from ground roasted coffee, and PCA, *hierarchical cluster analysis* (HCA) and *PLS-DA* approaches and SPME/GC-MS were used. Nonetheless, more studies are needed for the multi-detection of various adulterants in ground roasted coffee. It is clear that finding marker volatile compounds that can distinguish roasted coffee from potential herbal adulterants is not easy work because of the complexity of ground roasted coffee and herbal adulterants' matrix. The purpose of this study is to generate a multi-detection method for fraud materials (ground roasted barley, corn and soybean) in ground roasted coffee using SPME/GC/Q-ToF-MS and chemometric approaches.

2 MATERIAL AND METHODS

2.1 Raw materials and chemicals

Coffea Arabica L. beans (Huila, Colombia) (Caturra variety) and plant materials (barley (*Hordeum vulgare*), dent corn (*Zea mays indentata* L.) and soybean (*Glycine max* L.) were purchased from local markets in Bursa, Türkiye. Nonanal (99% pure) analytical standard was from Aromsa (Türkiye). The manual SPME holder (57330-U) and SPME 50/30 µm fiber coated by divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) polymer (57328-U) were purchased from Supelco Inc. (USA). A ZB-WAXms (30 m×0.25 mm; 0.25 µm) column was from Agilent (USA).

2.2 Roasting conditions

Roasting process was applied to 180 g samples using a coffee roaster (Bar Well, China) and roasting conditions were given in Table 1. Roasted samples were ground at the finest level with a coffee grinder (Delonghi KG521.M, Italy).

Table 1: Roasting process conditions.

Sample	Roasting temperature (°C)	Roasting time (min)
Green coffee beans	180	20
Barley	180	25
Soybean	180	20
Corn	180	20

2.3 Determination of volatile compound profile by SPME-GC/Q-ToF-MS

Considering the methodologies proposed by Marin et al. (2008) and Sari et al. (2012), volatile aroma compounds were isolated from samples using the SPME 50/30 µm fiber coated by DVB/CAR/PDMS polymer. A ground roasted sample (0.6 g) and magnetic stirring bar were placed in a glass vial (20

3 RESULT

mL). 60 μ L internal standard (100 mg/L nonanal in methanol) was added to each sample. The headspace vial was closed immediately and was heated for 30 minutes at 45°C with an agitation speed of 250 rpm for prewarming. Then, the needle attached to the manual SPME holder was inserted into the vial at 45°C for 30 min at the same agitation speed. GC/Q-ToF-MS (Agilent 7890B GC and 7200 Accurate Mass Q-TOF MS, USA) was employed to determine volatile compounds in the samples. After extraction, the fiber was thermally desorbed in the GC injection port for 10 min at 250°C in a splitless mode. A ZB-WAXms column and helium as carrier gas (1.6 mL/min) were used. The GC oven temperature was programmed from 40°C (5 min) to 180°C at the rate of 2°C/min, then to 250°C (5 min) at 10°C/min. Electron ionization (EI) mass spectra were obtained at 70 eV. The run time was 87 min.

2.4 Volatile component identification

Identification of volatile compounds was done by comparing mass spectra of samples with commercial libraries (W9N11, Flavor2, OIL ADAMS and NIST17). Volatile compounds were listed when the scores of libraries were higher than 70.

2.5 Adulterant concentrations

The detection capability of the marker ions was tested by preparing coffee/adulterant mixtures at a level of 2.5%, 5% and 10% (w/w).

2.6 Chemometric analysis

The GC/Q-ToF-MS data were evaluated with the help of the Agilent Mass Profiler Professional Version 13.0 (MPP) software (Agilent, USA). MPP software is a useful chemometrics platform designed to be used in any mass spectrometry. GC data was firstly converted to a compound exchange format (CEF) and was transferred to MPP software. A higher quality data set was obtained by filtering (minimum absolute abundance: 5000 and number of ions required: 2). Alignment parameters (retention time tolerance: 0.05 min, match factor: 0.3 and delta MZ: 0.005) were applied. Studied samples were divided into adulterant (10 samples (3 corn, 3 barley and 4 soybean samples)) and coffee (10 samples) groups in the MPP software. Then, PCA, *PLS-DA* and HCA were conducted. PCA was implemented to decrease the dimensionality of a data set. The first principal component having maximum variance is orthogonal to the second principal component having the second maximum variance and so on. By this means, projections offering maximum statistical information can be seen. *PLS-DA* unites dimensionality reduction with group information consideration. HCA is one of the qualitative classification methods in which tree-structured clusters of data samples are created (Franca et al., 2009).

A GC chromatogram of volatile compounds for ground roasted coffee is presented in Figure 1. Figure 2, 3 and 4 show GC chromatogram of volatile compounds for ground roasted corn, barley and soybean, respectively. In all roasted samples, an extensive number of volatile compounds were detected. Among isolated volatiles, 2-furanmethanol, 5-methyl-2-furancarboxaldehyde, 3-furaldehyde, 3-formylpyrrole, 3-hydroxy-2-methyl-4H-pyran-4-one (maltol), 1-(1H-pyrrol-2-yl)-ethanone (2-acetylpyrrole), 2-methoxy-4-vinylphenol, 2-formyl-1-methylpyrrole, 2-ethyl-3-methyl-pyrazine, pyrazine, 1-(6-methyl-2-pyrazinyl)-1-ethanone, pyridine, 2,5-dimethyl-pyrazine, 2-ethyl-3,5-dimethyl pyrazine, 2-(methoxymethyl)-furan, 3-pyridinamine, 2-vinyl-5-methylfuran, ethyl-pyrazine, 2,3-dimethyl-pyrazine, benzaldehyde, caffeine, phenol, N-furfuryl pyrrole, 2-furanmethanol acetate (furfuryl acetate), 2-methoxy-phenol (guaiacol), 3-methyl-phenol, 4-methoxy-benzenamine, 4-hydroxypyridine, 1H-Indole, 2-amino-4-methyl-phenol, 2,2'-Bifuran, 2-hexylfuran, 1-(2-furanyl)-ethanone and 5-hydroxymethyl-2-furaldehyde (HMF) were the most abundant compounds in ground roasted coffee. 2-furancarboxaldehyde, 5-methyl-2-furancarboxaldehyde, 1-decyne, 1H-imidazole-4-methanol, 4-pyridinamine, phenylglyoxal, 2-ethyl-5-methylfuran, 2-ethyl-3,5-dimethyl-pyrazine, methyl-ethyl-pyrazine, ethyl-pyrazine, phenol, pyrazine, 2,5-dimethyl-pyrazine, 2,3-dimethyl-pyrazine, acetylpyrrole, 4-vinyl-guaiacol, benzenemethanol and 1H-pyrrole-2-carboxaldehyde were detected abundantly in ground roasted corn. In ground roasted barley, 3-furaldehyde, 2,5-dimethyl-pyrazine, 2,6-dimethyl-pyrazine, 2-acetyl-3-methylpyrazine, methyl-ethyl-pyrazine, 2,6-dimethyl-pyrazine, 5-methyl-2-furancarboxaldehyde, 3-formylpyrrole, pyrazine, benzaldehyde, acetylpyrrole, N-furfuryl pyrrole, 2-methoxy-phenol, propanoic acid, 3-methyl-2-butenic acid, 4-vinyl-guaiacol, 3-pyridinamine, 4-hydroxypyridine, 1H-Imidazole-4-methanol and HMF. Moreover, 2-furancarboxaldehyde, 5-methyl-2-furancarboxaldehyde, 2,5-dimethyl-pyrazine, 3-formylpyrrole, 2-ethyl-3,5-dimethyl-pyrazine, methyl-ethyl pyrazine, 2-acetyl-pyrazine, benzaldehyde, pyrazine, 2,6-diethyl-pyrazine, 2-furanmethanol, 2-amino-4-methyl-phenol, 1H-imidazole-4-methanol, N-furfuryl pyrrole, acetylpyrrole, 1-ethyl-2-formyl pyrrole, 4-hydroxypyridine, ethyl-benzene and 1-ethynylcyclopentanol were the most plenty aroma compounds in ground roasted soybeans.

Moreover, the aroma profile of ground green coffee beans, barley, corn and soybean was also studied by SPME-GC-Q-ToF-MS to determine volatile compounds in the unroasted form of samples. Benzaldehyde, 2-pentyl-furan, methyl-(1-methylethyl)-benzene, octanal, dodecanal, 3-furaldehyde, hexanoic acid, benzenethanol, benzenemethanol, 2-hydroxy-benzoic acid, 1,10-decanediol were abundantly found in ground

green coffee beans. Hexanal, hexanoic acid-methyl ester, 2-pentyl-furan, dodecane, 1-octanol-2-butyl, 1-octanol-2,7-dimethyl, 1-octadecanol, 1-octen-3-ol, dihexysulfide, hexanoic acid, nonanoic acid, phenol and 1,10-decanediol were detected in ground corn. In ground soybean, methyl ester-hexanoic acid, 2-pentyl-furan, 2-methyl-1-hexene, 1-nonen-3-ol, benzoic acid, 1-ethynylcyclopentanol, 1,2,3,4-tetramethyl-benzene, 1-octen-3-ol, phenylglyoxal and 1,5-hexadiene-3-methyl were determined. 4-ethyl-2-methoxy-phenol, 5-methyl-2-furancarboxaldehyde, 1-tetradecanol, 3-formylpyrrole,

1H-pyrrole, 2-furanmethanol, oxalic acid, 2-methoxyphenol, acetylpyrrole, pentyl-benzene, tetradecane, 5,5-dimethyl-hexanal, 2-furancarboxaldehyde, benzenemethanol, 1-furfuryl-2-formyl-pyrrole, 1-ethynylcyclopentanol and 2-phenoxy-ethanol were found in ground barley.

Peak detection was performed in MassHunter using integration (Figure 5). Then, CEF files were generated using the MassHunter export tool. A higher quality data set was obtained by filtering. The mass versus retention time plot in Figure 6 showed that 1073 unique entities were found

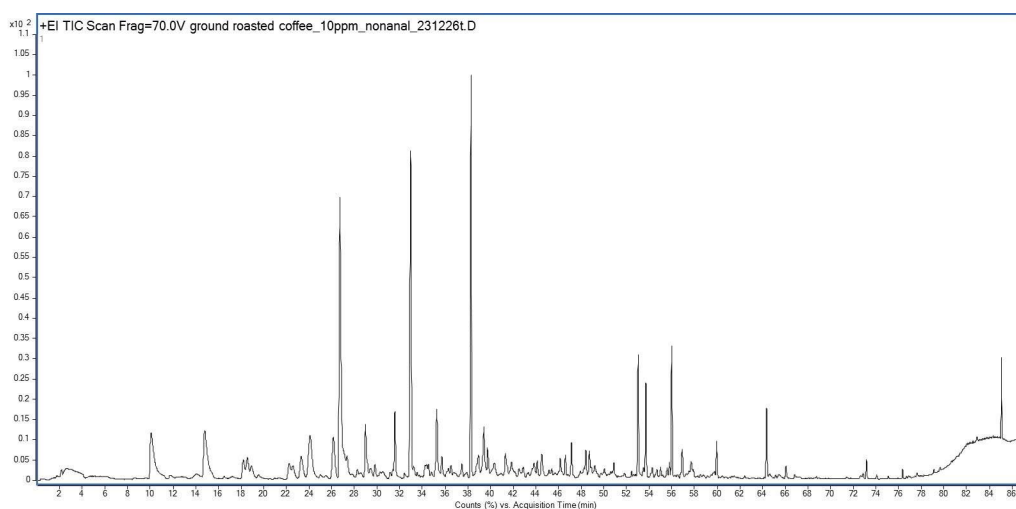


Figure 1: Typical chromatogram of ground roasted coffee by GC-Q-ToF-MS.

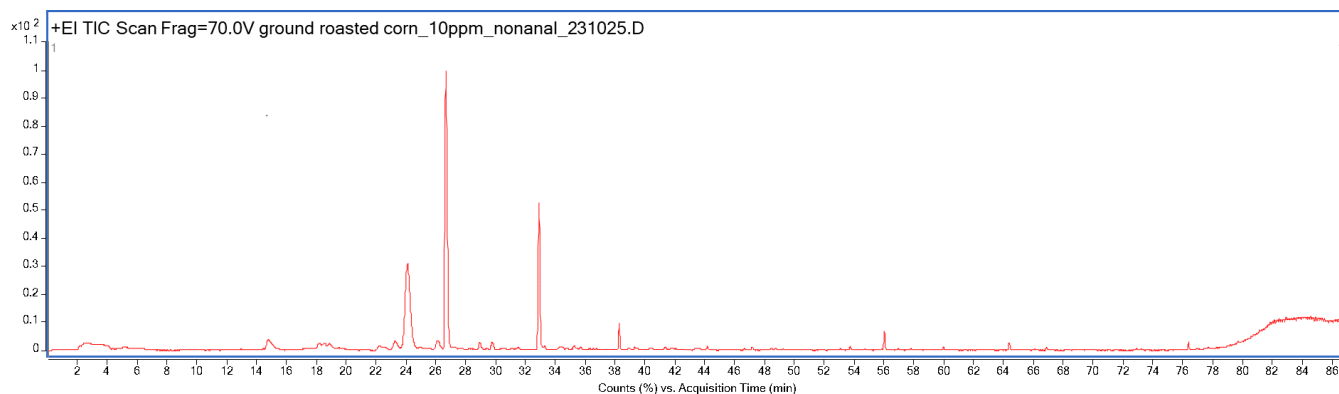


Figure 2: Typical chromatogram of ground roasted corn by GC-Q-ToF-MS.

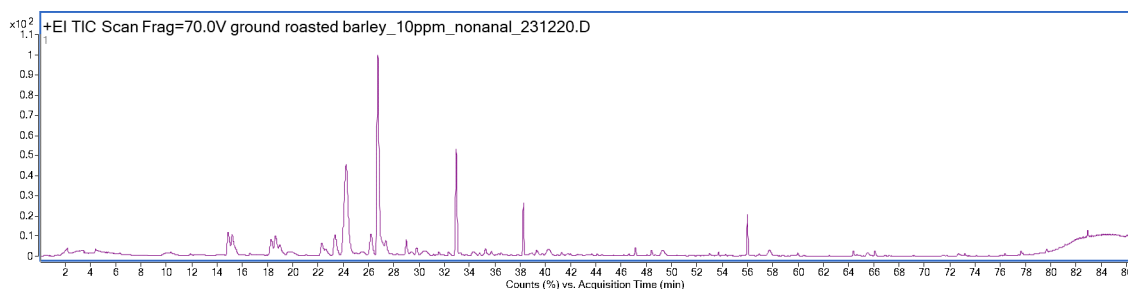


Figure 3: Typical chromatogram of ground roasted barley by GC-Q-ToF-MS.

in the studied samples. The retention time and molecular mass relationships of compounds were evaluated for the separation of coffee and potential adulteration products, and the frequency of these compounds was determined according to the number of times they could be detected in the samples. Volatile compounds with a low frequency of occurrence in the samples were shown in red, and volatile compounds with a high frequency of occurrence were shown in blue.

PCA, PLS-DA and HCA techniques were used to determine discriminant volatile markers for the detection of corn, soybeans and barley in roasted coffee. Using MS data of a total of 20 roasted and ground samples, coffee and herbal products commonly used as adulterants were separated through PCA based on aroma profile. According to the PCA of coffee and adulterants, the first three components (PC1:46.75%, PC2:20.55%, PC3:10.56%) explained 77.86% of the variation of analyzed samples (Figure 7). HCA structure can be seen in Figure 7. Then, analysis of variance (ANOVA) was utilized to specify

whether the variations between identified compounds ensuring the fold change (FC) criteria (>10) were statistically significant. 1073 compounds were lowered to two significant compounds for adulterants and two significant compounds for coffee using a probability p value (<0.001) and FC criteria (>10). The two aroma compounds having the lowest p -values and highest FC values were chosen for the construction of the classification model. The adulteration model was constructed using PLS-DA (Figure 8).

Potential aroma markers of coffee adulteration were specified. Two marker volatile compounds (1H-imidazole-4-methanol and benzene-2-(1,3-butadienyl)-1,3,5-trimethyl) were determined for adulterants and two marker volatile compounds (2-furanmethanol and 2-formyl-1-methylpyrrole) were detected for coffee, which met the mentioned criteria (Table 2). Agilent MassHunter Qualitative Analysis 10.0 Software was used to apply find by integration and clean spectra were extracted from interfering peaks. These EI mass spectra were searched in the library database (Figure 9).

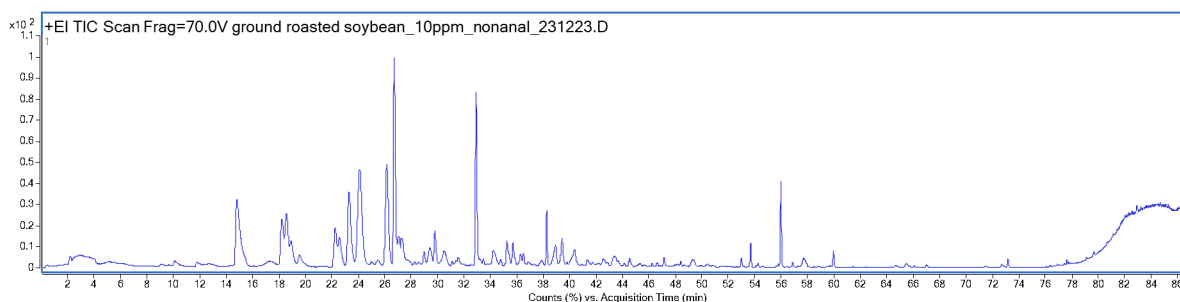


Figure 4: Typical chromatogram of ground roasted soybean by GC-Q-ToF-MS.

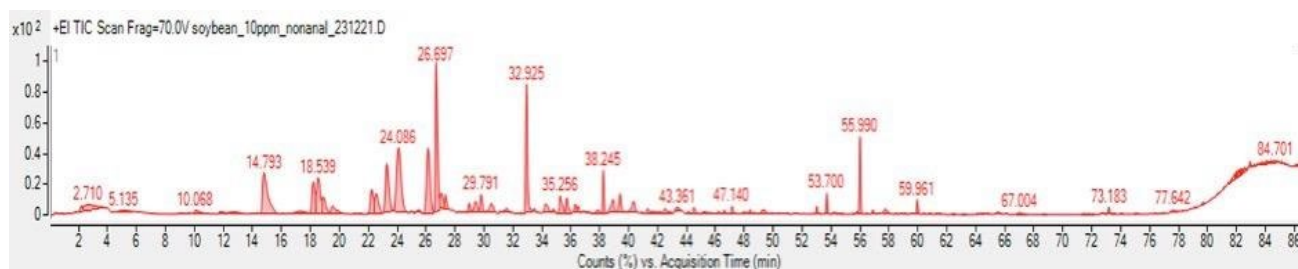


Figure 5: Peaks were identified by integration.

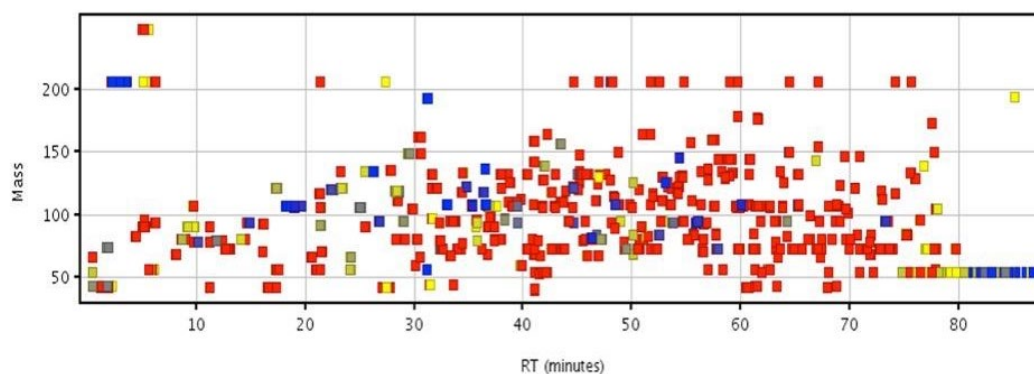


Figure 6: The mass versus retention time plot indicated that 1073 compounds were differentiated by integration.

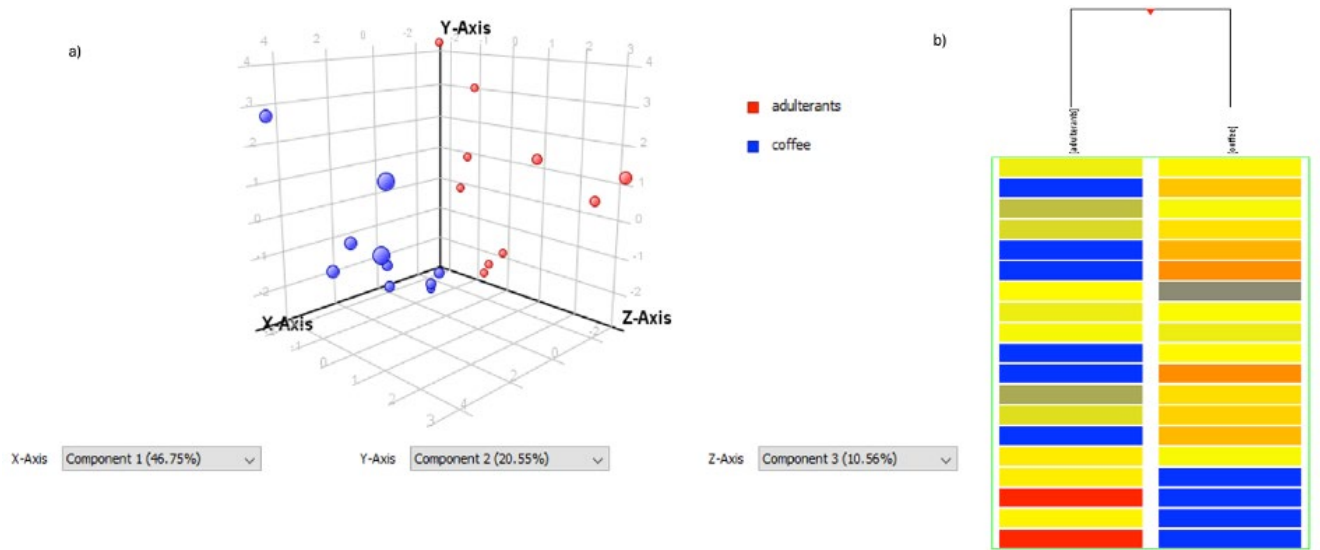


Figure 7: Separation of adulterants and coffee groups by PCA (a) and HCA (b).

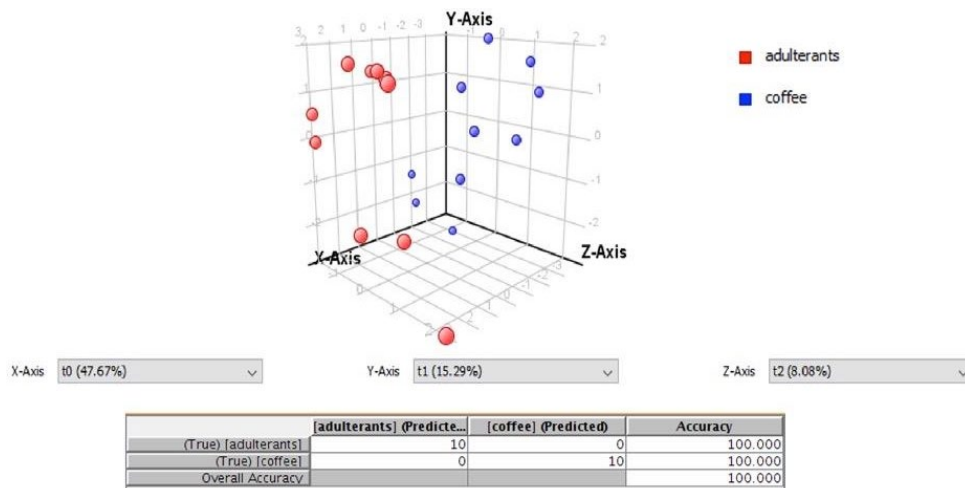


Figure 8: PLS-DA scores plot and prediction results.

Table 2: List of potential volatile marker compounds that can be used to detect coffee adulteration

Compound	Retention time (min)	m/z of the most intense ions (ratio)	p	p (corr)	FC
Adulterants					
1H-imidazole-4-methanol	38.26	98 (100), 97 (146.3), 69 (53.8), 42 (36.1)	2.08×10^{-32}	3.96×10^{-31}	-35035148.00
Benzene-2-(1,3-butadienyl)-1,3,5-trimethyl	43.38	157 (100), 142 (59.2), 172 (14.0), 141 (24.1)	1.44×10^{-22}	1.37×10^{-21}	-9390840.00
Coffee					
2-furanmethanol	38.20	98 (100), 41 (17.2), 53 (46.1), 81 (74.2)	8.67×10^{-10}	4.12×10^{-9}	69043408.00
2-formyl-1-methylpyrrole	37.40	108 (100), 109 (12.1), 53 (37.0), 80 (42.9)	3.58×10^{-10}	2.27×10^{-9}	19387480.00

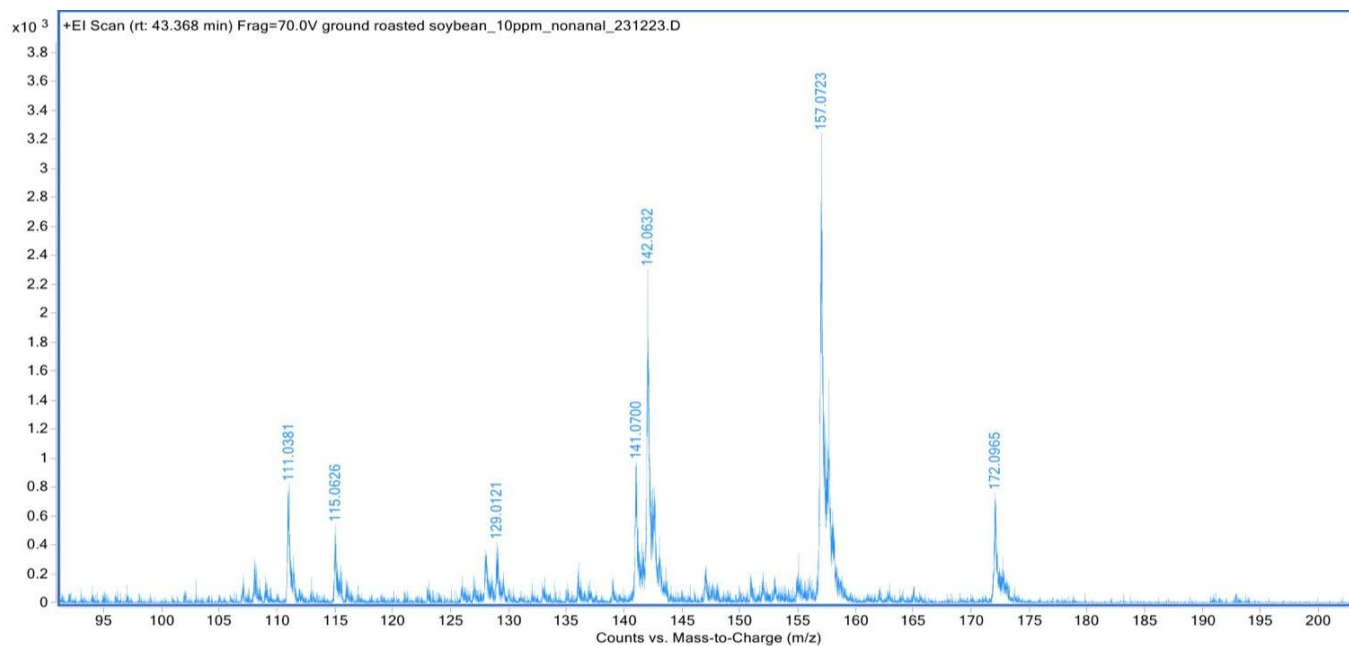


Figure 9: EI mass spectra of benzene-2-(1,3-butadienyl)-1,3,5-trimethyl in ground roasted soybean.

4 DISCUSSION

The determined aroma profile of ground roasted coffee was in parallel to the study on ground roasted coffee by Choe et al. (2023) and on Turkish coffee by Dadalı (2021). Puviprom and Chaiser (2012) reported similar aroma compounds in roasted corn. Aroma compounds detected in ground roasted barley showed similarities with the study done by Kim, Lee and Kim (1998) on roasted barley extract. Lee et al. (2023) detected similar volatile compound groups in ground roasted soybeans. Similar compounds were reported in green coffees by Headspace-SPME/GC-MS analysis by Vezzulli, Lambri and Bertuzzi (2023). When the aroma profiles of ground roasted and unroasted herbal products were compared, it was observed that pyrazine, furan and pyrrole derivatives were formed during roasting of herbal products. Alike, Keawkim and Jom (2022) stated that Maillard reaction products, named pyrazine, furan and pyrrole, increased during roasting at 180°C.

PCA analysis of coffees and adulterants showed that the first three components explained 77.86% of the variation of analyzed samples. The first two or three principal components should at least explain 70% of total variability (Jolliffe; Cadima, 2016), thus the result obtained was acceptable. PCA identified compounds with large abundance gaps between the studied data classes. The samples which are viewed as most similar are placed together on branches in HCA (Tullis; Albert, 2013). According to the HCA dendrogram created in the study, the samples were successfully categorized into two separate parties as adulterants and coffee (Figure 7).

PLS is generally used in conditions where there are fewer observations than measured variables (for example, detected entities m/z). PLS-DA is applied to edge the separation between sample groups (Baumann; Aronova, 2012). Figure 8 showed that coffee and adulterants were differentiated based on their aroma profile. A developed model accurately predicted whether a ground roasted coffee sample would pass the adulteration test.

As an example, the chromatograms of benzene-2-(1,3-butadienyl)-1,3,5-trimethyl in one of the barley and coffee samples were shown in Figure 10 and Figure 11, respectively. As expected, the precursor and product ions of the target compound were found in barley, but they were not found in coffee samples. The detection capability of the marker ions was controlled by preparing coffee/adulterant mixtures at a level of 2.5%, 5% and 10% (w/w). Successful fraud detection was obtained when adulterants were added at level 5% (w/w) to coffee (Figure 12). However, reliable adulteration detection in coffee was not achieved at 2.5% level.

Figure 13 and 14 show precursor and product ions of 2-furanmethanol in ground roasted coffee and corn, respectively. 2-furanmethanol, which is described as caramellic, burnt and smoky (Caporaso et al., 2018), is generated during the roasting process (Hong et al., 2024). According to Choe et al. (2023), 2-furanmethanol is the dominating aroma compound in roasted coffee. Similarly, 2-furanmethanol was listed by Oliveira et al. (2009) as a characteristic aroma of coffee. However, it should be considered that 2-furanmethanol can be formed in roasted grains (Yahya; Linforth; Cook, 2014). Nonetheless, this study demonstrated that it had a considerably lower amount

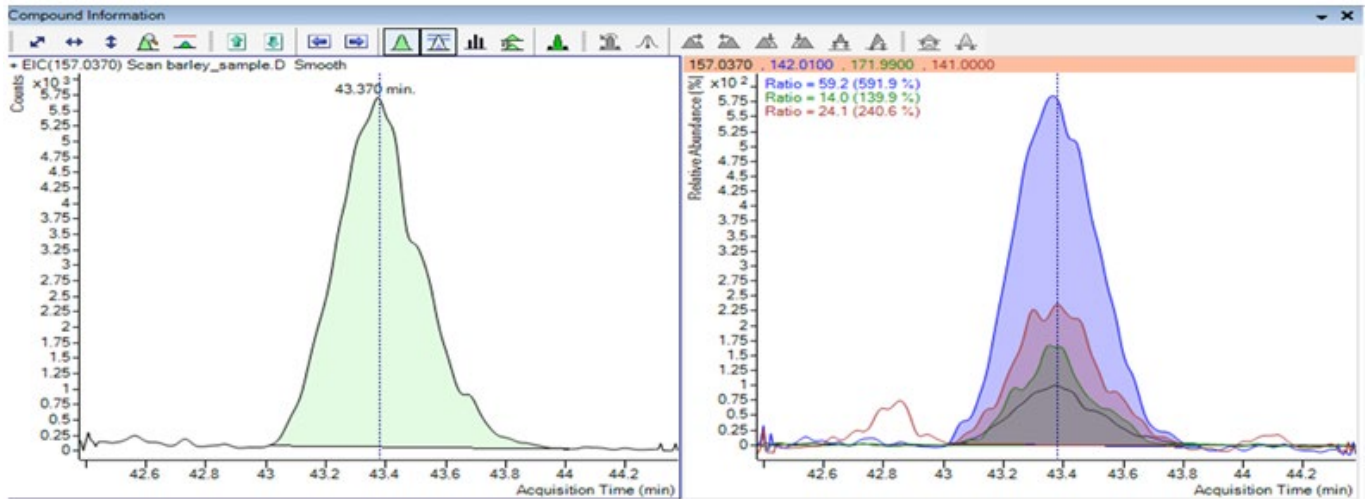


Figure 10: The precursor and product ions of benzene-2-(1,3-butadienyl)-1,3,5-trimethyl in one of the barley sample.

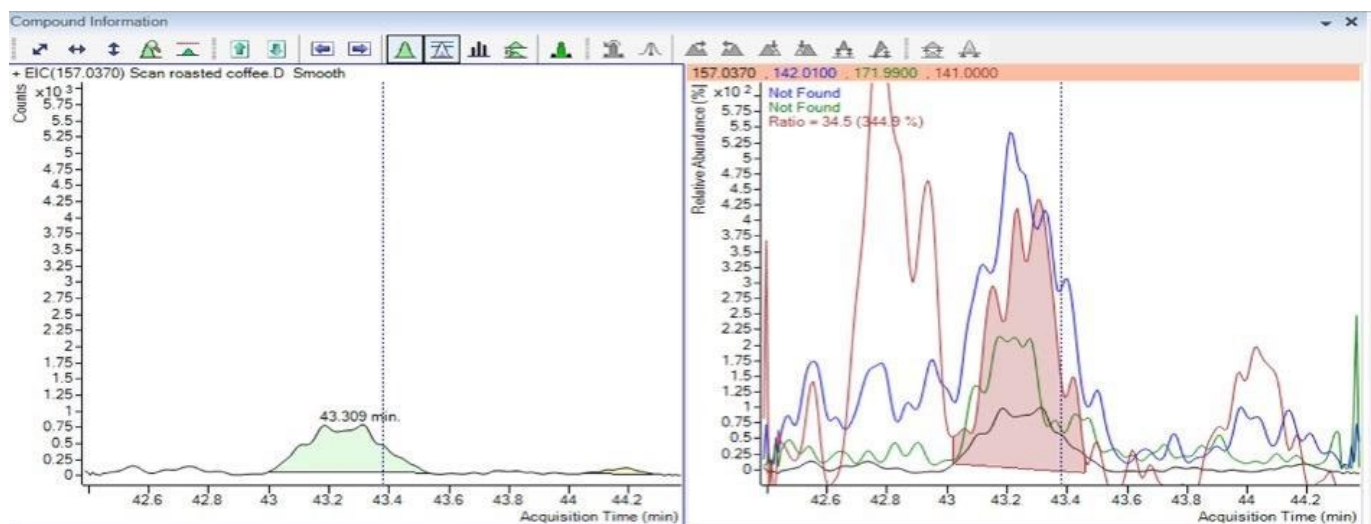


Figure 11: The precursor and product ions of benzene-2-(1,3-butadienyl)-1,3,5-trimethyl in ground roasted coffee sample.

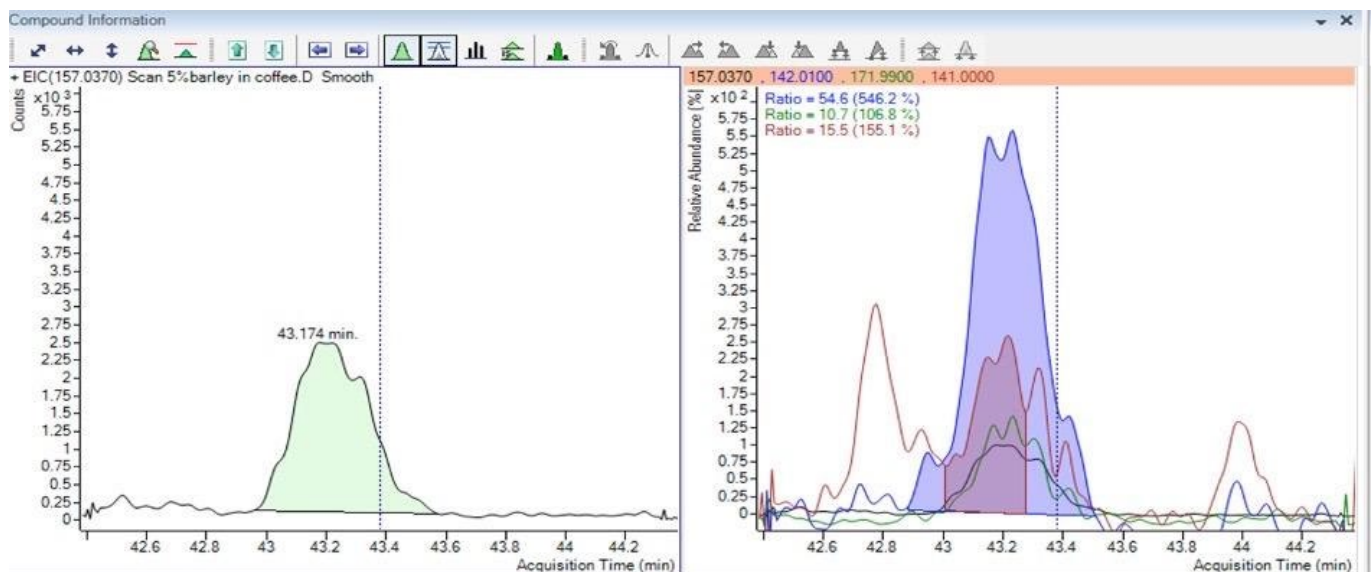


Figure 12: The precursor and product ions of benzene-2-(1,3-butadienyl)-1,3,5-trimethyl in 5% barley in coffee sample.

compared to roasted coffee. Moreover, precursor and product ions of 2-formyl-1-methylpyrrole in ground roasted coffee and soybean were shown in Figure 15 and 16. This compound was detected in roasted coffee, but it is not found in ground roasted herbal adulterants. Pyrroles, which are described as roasted and nutty, are mainly formed thermally, so 2-formyl-1-methylpyrrole could be responsible for the roasted aroma of coffee, as stated by Dippong et al. (2022). Correlatively, 2-formyl-1-methylpyrrole was detected in coffee by Amanpour and Selli (2016) and Caporaso et al. (2018).

It is clear that the identification of specific volatile markers for both coffee and adulterants enhances current detection methodologies, moving beyond traditional carbohydrate-based analyses. However, this study has some limitations related to not detecting adulteration at levels below 5%, not addressing potential variations due to different roasting conditions and a small data set. To maximize its impact, future studies should validate the method across broader coffee varieties and refine detection thresholds for practical industry applications.

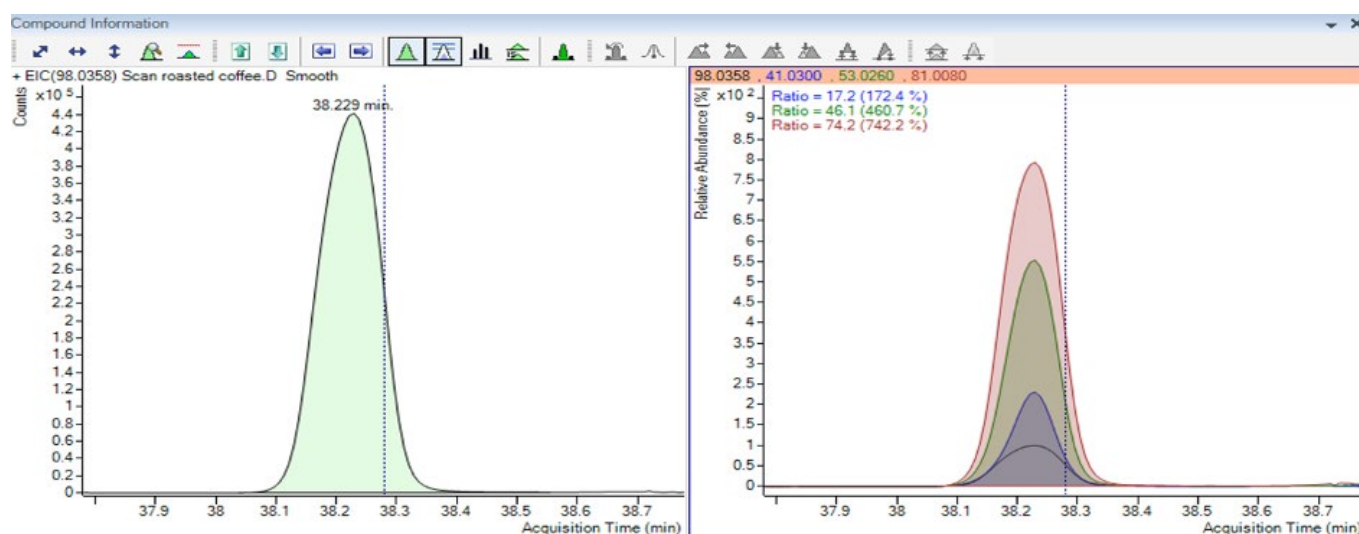


Figure 13: The precursor and product ions of 2-furanmethanol in ground roasted coffee sample.

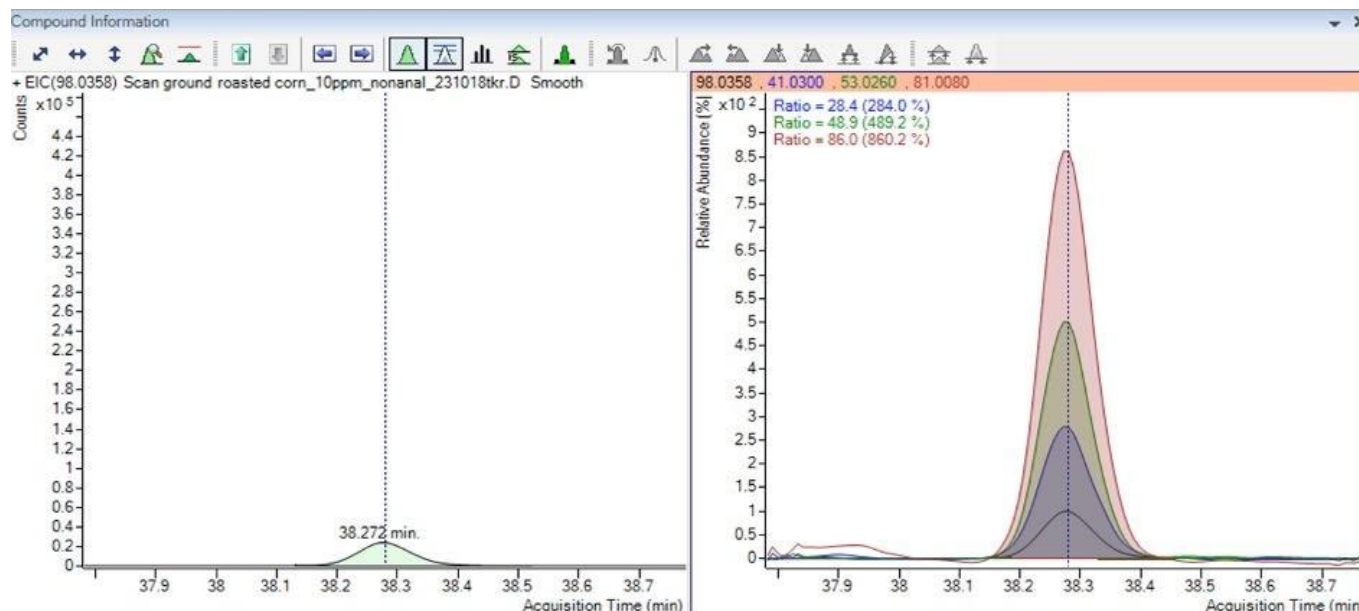


Figure 14: The precursor and product ions of 2-furanmethanol in ground roasted corn sample.

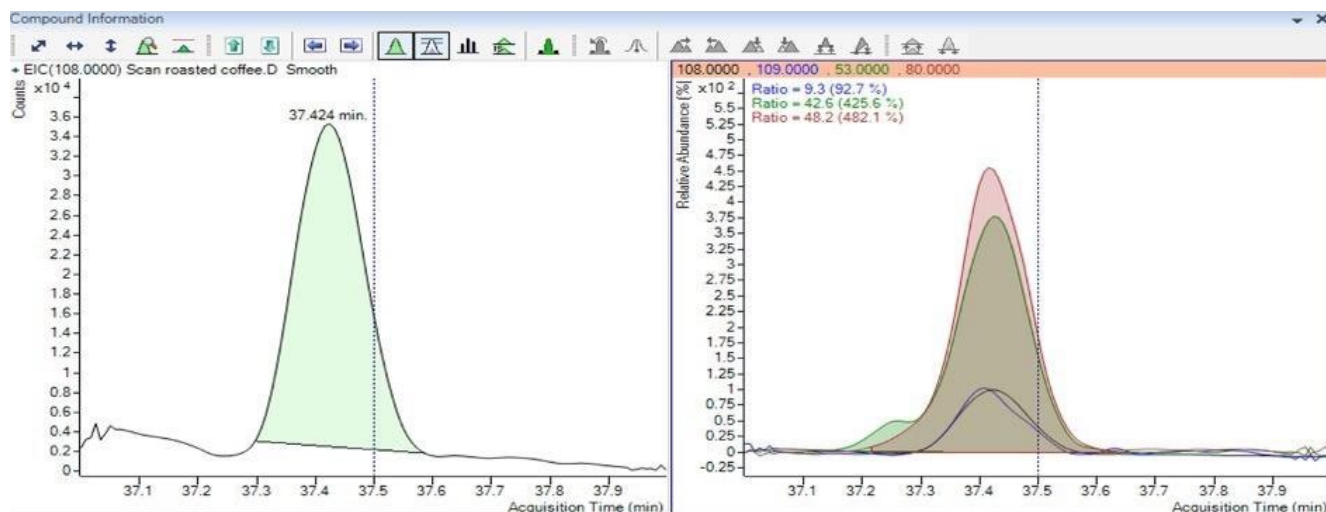


Figure 15: The precursor and product ions of 2-formyl-1-methylpyrrole in ground roasted coffee sample.

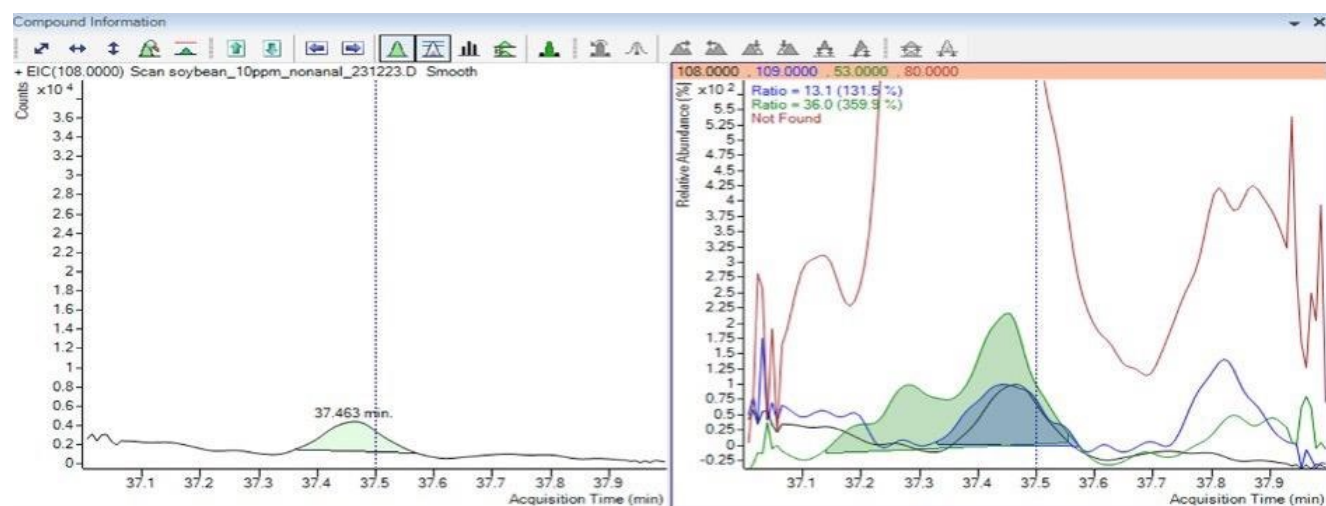


Figure 16: The precursor and product ions of 2-formyl-1-methylpyrrole in ground roasted soybean sample.

5 CONCLUSIONS

SPME-GC-Q-ToF-MS combined with chemometric tools was applied for the determination of adulterants' markers in ground roasted coffee. Two volatile compounds (1H-imidazole-4-methanol and benzene-2-(1,3-butadienyl)-1,3,5-trimethyl) were determined as potential markers for the identification of ground roasted adulterants (barley, corn or soybean). Using methodology, 5% (w/w) adulteration in roasted coffee sample was successfully detected, but a reliable discrimination was not achieved at a lower level (2.5%, w/w). In future studies, the sample size can be increased, and different roasting degrees can be tried.

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GC/Q-TOF MS" supported by General Directorate of Agricultural Research and Policies of the Republic of Turkey the Ministry of Agriculture and Forestry were used. Some parts were presented orally in II. International Food, Agriculture and Veterinary Congress in 2024.

7 AUTHORS' CONTRIBUTION

Conceptual Idea: Akgün, B.; Methodology design: Akgün, B.; Çavuş, F.; Data collection: Akgün, B., Data analysis and interpretation: Akgün, B.; Çavuş, F.; Nurcan A. Güzelsoy, and Writing and editing: Akgün, B.; Nurcan A. Güzelsoy.

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