Combining ion mobility spectrometry and chemometrics for detecting synthetic colorants in black tea: A reliable and fast method

Mina Sobhaninia [a], Ahmad Mani-Varnosfaderani [b], Mohsen Barzegar [a],[*], Mohammad Ali Sahari [a]

[a] Department of Food Science and Technology, Faculty of Agriculture, Tarbiat Modares University, P. O. Box 14115-336, Tehran, Iran
[b] Department of Chemistry, Faculty of Basic Sciences, Tarbiat Modares University, P. O. Box 14115-175, Tehran, Iran

ARTICLE INFO

ABSTRACT

Black tea (*Camellia sinensis*) is a widely consumed beverage and is subjected to adulteration. In this study, the combination of ion mobility spectrometry and machine learning techniques was employed to detect synthetic colorants in black tea. To accomplish our objective, six synthetic colorants (carmine, carmoisine, indigo carmine, brilliant blue, sunset yellow, and tartrazine) were added to pure tea at different concentrations. A qualitative model was built using partial least squares discriminant analysis (PLS-DA) for the collected data and exhibited 100% accuracy in identifying synthetic colorants in black tea. For quantitative analysis, a PLS regression model was employed. The R^2 values obtained for the test set ranged from 0.986 to 0.997. The method developed in this study has proven to be reliable and effective in detecting synthetic colorants in black tea. Also, this method is a simple, rapid, and trustworthy tool for identifying adulteration in black tea.

Introduction

Tea, derived from the *Camellia sinensis* plant, is a widely enjoyed beverage worldwide. It is produced using fresh sprouts, delicate leaves, mature leaves, and stems of the tea plant. With its distinct flavor and reputed health benefits, tea ranks among the top three non-alcoholic beverages globally. Black tea, accounting for more than 70 % of global tea consumption, is particularly popular. Aside from its delightful taste, tea offers therapeutic properties that combat various ailments, such as its anti-inflammatory and anti-cancer effects (Huang et al., 2024; Isemura et al., 2000; Qin et al., 2023).

The perception of taste, texture, and freshness in foods and beverages is significantly influenced by their color, which also plays a vital role in consumers' decision-making process when selecting food and beverages. To enhance attractiveness, compensate for colorant loss during processing, and mask undesirable changes in the natural colorants, food products often incorporate synthetic edible colorants. These colorants can be categorized as natural, synthetic, and mineral (Amchova et al., 2015).

The quality of brewed tea is determined by its color. Research by Munim Khan et al. (2023) on the evaluation of the organoleptic quality of Bangladeshi black tea found that the brewed color of tea has a significant ($p < 0.01$) and positive correlation with its quality. However,

tea can be exposed to harmful substances such as synthetic dyes, including azo and coal tar dyes, intentionally or unintentionally. Deceptive methods involve adding synthetic colorants like carmine, carmoisine, indigo carmine, brilliant blue, sunset yellow, and tartrazine (either alone or in combination) to enhance the appearance of tea brewed from damaged leaves or lower-quality sources (Deb Pal and Das, 2018; Sharma et al., 2011; Wei et al., 2020). These colorants have gained popularity in the food industry due to their cost-effectiveness, efficiency, and improved stability compared to natural colors (Ali, 2010; Alves et al., 2008). However, concerns have arisen about the potential adverse effects of synthetic colorants on human health. Synthetic edible colorants exhibit stronger binding capabilities with human serum albumin compared to natural colors. This enhanced affinity may impact the physiological functions of albumin, which is a crucial transporter for various molecules such as drugs, fatty acids, cholic acids, and steroids (Basu and Suresh Kumar, 2015; Masone and Chanforan, 2015).

Furthermore, numerous colorants contain aromatic rings and azo functional groups (N═N─) in their chemical structure. These compounds can be metabolized by intestinal microbes into carcinogenic byproducts through the reduction of azo groups, ultimately impacting human health with potential side effects. Potential side effects may include facial itching, hives, swelling around the eyes, hyperactivity in

children, DNA alterations, activation of estrogen receptors, and an increased risk of early-onset biliary cirrhosis in postmenopausal women (Amchova et al., 2015; Feng et al., 2012; Garkani Nejad et al., 2022; Wei et al., 2020).

Despite the stability and efficiency of synthetic colorants, several research studies have been conducted to extract, detect, and quantify these compounds in food and beverages due to potential health concerns. Sha et al. (2015) employed liquid–liquid microextraction (LLE) combined with HPLC to extract and detect five synthetic colorants (tartrazine, sunset yellow, amaranth, ponceau 4R, and brilliant blue) in various food samples. The extraction efficiency was found to exceed 95 %, and the detection limit ranged from 0.074 to 0.051 ng/ml. Wei et al. (2020) employed UV/Vis spectrometry and HPLC, along with machine learning techniques, to detect the presence of carmine in black tea. They employed a multi-layer perceptron (MLP) feedforward neural network model to quantify the amount of carmine added to tea, achieving R^2 values of 0.988 and 0.972 for UV/Vis spectrometry and HPLC methods, respectively. Martin et al. (2016) employed electrospray ionization liquid chromatography coupled with mass spectrometry to detect 18 synthetic colorants in confectionery products and ice creams. A correlation coefficient of $R^2 \geq 0.98$ was obtained between the response and concentration of 12 of these colorants. The detection limits ranged from 10 to 1000 μg/kg.

While spectrophotometric methods are commonly used for quantitative analysis due to their affordability and ease of use, they have limitations in identifying or detecting additives in specific food products. Factors such as spectral overlap or the absence of significant absorption features pose challenges (Nath et al., 2013; Yamjala et al., 2016). For separating, identifying, and quantifying edible colorants with high sensitivity and accuracy, HPLC is a commonly used analytical technique. Additionally, the liquid chromatography-mass spectrometry method is especially effective in detecting illegal and toxic dyes at trace levels. However, these methods come with some drawbacks, including expensive equipment, time-consuming processes, high solvent consumption, and complex sample preparation (Bonan et al., 2013). Therefore, there is a demand for food fraud detection methods that are simple, sensitive, selective, cost-effective, environmentally friendly, and fast (Esteki et al., 2018; Rovina et al., 2017).

Ion mobility spectrometry (IMS) is a highly efficient method for separating chemicals based on their gas-phase ion mobilities. In IMS, the movement of ions under the influence of a strong electric field and against the drift gas flow enables their separation. The IMS spectrum represents the intensity of detected ions against their drift times, allowing separation not only by mass but also by size, spatial structure, and charge-to-mass ratio (Eiceman et al., 2013; Tabrizchi et al., 2000).

These advanced spectrometry instruments provide highly accurate and reproducible data, serving as a vital foundation for techniques with low quantitation limits. When combined with chemometric analysis, these methods can be further enhanced, making them increasingly popular in spectrometric quantitation. Chemometric methods are especially valuable when faced with the challenge of isolating a single peak that corresponds to a specific metabolite. In such complex cases, where multiple peaks with differing times or intensities are observed, chemometric methods can be employed to identify these distinct peaks and determine their respective contributions to the spectrum. This information is then utilized for constructing calibration or classification models (Esteban et al., 2020; Frost, 2017; Sarker and Nahar, 2015).

Jafari et al. (2012) conducted a study on the presence of nitrite and nitrate ions in food and drinking water samples. They used an electrospray ionization source (ESI-IMS) in conjunction with IMS for analysis and determination. The results of their research indicated that nitrite could be detected at a concentration of 3.8 μg/l, while nitrate could be detected at 4.7 μg/l. IMS spectra were also used in two independent research studies to evaluate the quality and purity of extra virgin olive oil and sesame oil. The IMS system was used to identify and analyze volatile substances in extra virgin olive oil, with the objective of

detecting any impurities. When adding lower-cost oils such as sunflower and corn, an R^2 value greater than 0.72 could be distinguished. Furthermore, (Garrido-Delgado et al., 2018; Zhang et al., 2016) conducted an IMS analysis on sesame oil and developed models using the recursive support vector machine (R-SVM) technique to identify counterfeit samples with a precision of 94.2 %.

Fattahi et al. (2023) used IMS-CDI⁻ in conjunction with chemometric analysis to detect the presence of four synthetic edible colorants (Tartrazine, Sunset Yellow, Ponceau 4-R, and Erythrosine) in saffron. The researchers successfully determined the concentrations of these colorants in adulterated saffron using the variable importance in projection (VIP) and PLSR model (VIP-PLSR). The VIP-PLSR model provided root mean square error (RMSE) and R^2 values ranging from 2.39 % to 3.53 % and 0.880 to 0.954, respectively.

The primary goal of this study is to develop a highly accurate method of identifying pure black tea and distinguishing it from six different synthetic colorants by establishing their unique fingerprints. Additionally, this study aims to employ advanced machine learning methods to analyze the ion mobility spectra of adulterated black tea samples. This analysis will enable the detection of the concentrations of synthetic colorants in the samples and identify any variations in the levels of colorants added to pure black tea. The ultimate goal of this study is to improve the accuracy of detecting synthetic colorants added to black tea, which will help to ensure the safety and quality of tea products.

Materials and methods

Pure tea sample preparation

Samples of pure black tea were purchased from Lahijan Tea Company in Iran. The collected samples were stored under controlled conditions at 4 °C to maintain their quality, while protecting them from light and moisture, until analysis.

To prepare the tea infusion, 1 g of finely powdered tea was mixed with 19 ml of double distilled water. The mixture was then heated in a boiling water bath for 10 min and rapidly cooled by placing the container in a cold-water bath until it reached a temperature of 4 °C. Subsequently, centrifugation was performed at 10,000 g for five minutes to separate any solid particles present. The resulting supernatant was further clarified by passing it through a nylon syringe filter (Sigma-Aldrich Co (St. Louis, MO, USA)) with a pore size of 0.45 μm (Wei et al., 2020).

Adulterated tea samples preparation

Synthetic carmine, carmoisine, indigo carmine, brilliant blue, sunset yellow, and tartrazine colorants were provided by the Iran Institute of Standards and Industrial Research (ISIR). All colorants had a purity higher than 95 %. To produce adulterated tea samples with edible synthetic colorants, these colorants were added to pure tea at 13 different levels, ranging from 0.03 % to 3.6 % of the dry tea weight. The resulting mixtures were then brewed and filtrated as described in the previous section.

Spectrometric analysis

The ion mobility spectrum was obtained using an advanced IMS (IMS-CDI-300, TOF Tech Pars Co., Ltd, Isfahan, Iran) equipped with a corona discharge ionization source. The device was supplied with compressed air from a capsule (Mana Mehrgan gas, Tehran, Iran) containing 80 % oxygen and 20 % nitrogen, which served as the carrier gas and drift gas (purity 99.999 %). When a small amount of water vapor is introduced with this gas into the ionization zone, it forms three reactant ions (H_3O^+, NO^+, and NH_4^+) through a positive corona discharge ionization source.

A 2 μL liquid sample was injected into the injection port of the IMS. It

was then converted into gas vapor at a temperature of 200 °C. To introduce the vaporized molecules into the ionization zone, the carrier gas flow was set at 180 ml/s. In the ionization zone, the vaporized molecules from the sample collided with the reactant ions, which resulted in the formation of secondary ions, also known as product ions. These product ions were then directed to the drift zone (180 °C, 8000 V) through the ion shutter, which was opened for 40 μs. The ions moved towards the collector plate for 20 ms due to the electric field, opposing the direction of the drift gas movement. The signals were then converted to a visible spectrum using Picoscope 2204 software (Pico Technology Co., UK).

Chemometric analysis

Distinct fingerprints were obtained for pure tea and each of the six synthetic colorants by recording a total of 112 ion mobility spectra. To achieve this, 16 measurements were taken for each sample.

In order to determine the quantity of synthetic colorant added to pure tea, each colorant was added at 13 different levels, with 16 measurements for each level. This resulted in a total of 208 ion mobility spectra for each colorant.

After acquiring the spectra, sections that did not have metabolite peaks (such as the beginning and end of the spectrum) and those that contained reactant ions were removed (4.67–5.77 ms). The remaining data (5.78–13.50 ms) was then analyzed using various multivariate analysis methods, including principal component analysis (PCA), partial least squares discriminant analysis (PLS-DA), hieratical clustering, and partial least squares regression (PLSR).

After the preliminary analysis, the less significant drift times were eliminated, reducing the size of the data matrix and enabling a focus on identifying the important drift times in the ion mobility spectrum. The analysis was then repeated using only the selected drift times, as depicted in Fig. 1.

To construct PLSR and PLS-DA models, the dataset was randomly split into a 75 % training set and a 25 % test set. The calibration model was developed using the training set through a 10-fold cross-validation approach. External validation was carried out on an independent test set. The optimal number of components was determined by selecting the model with the smallest root mean square error (RMSE) and the highest coefficient of determination (R^2). All multivariate data analysis (PCA, hieratical clustering followed by heatmap, PLS-DA, PLSR, and Venn diagram) was conducted using R software (Version: 2023.06.2 + 561).

Results and discussion

Fingerprinting pure tea and synthetic colorants by using IMS

Each food item is composed of a complex matrix containing various types and quantities of biological metabolites. These natural compounds are responsible for providing distinct flavors, aromas, and nutritional content. The composition and concentration of metabolites in each food item are influenced by factors such as genetics, environment, and processing methods. Consequently, the metabolite profile of each food item becomes unique and differentiates it from others (Sales et al., 2017).

Fig. 2 illustrates the ion mobility spectra of pure tea and six synthetic food colorants. The initial three peaks correspond to reactant ions (H_3O^+, NO^+, and NH_4^+), while the subsequent peaks represent metabolites with a higher proton affinity as compared to the reactant ions (Tabrizchi et al., 2000). An important aspect of ion mobility spectrometry is that peaks with shorter drift times indicate smaller metabolites or those with higher charge density. Conversely, larger ions with lower charge density move more slowly, resulting in longer drift times and
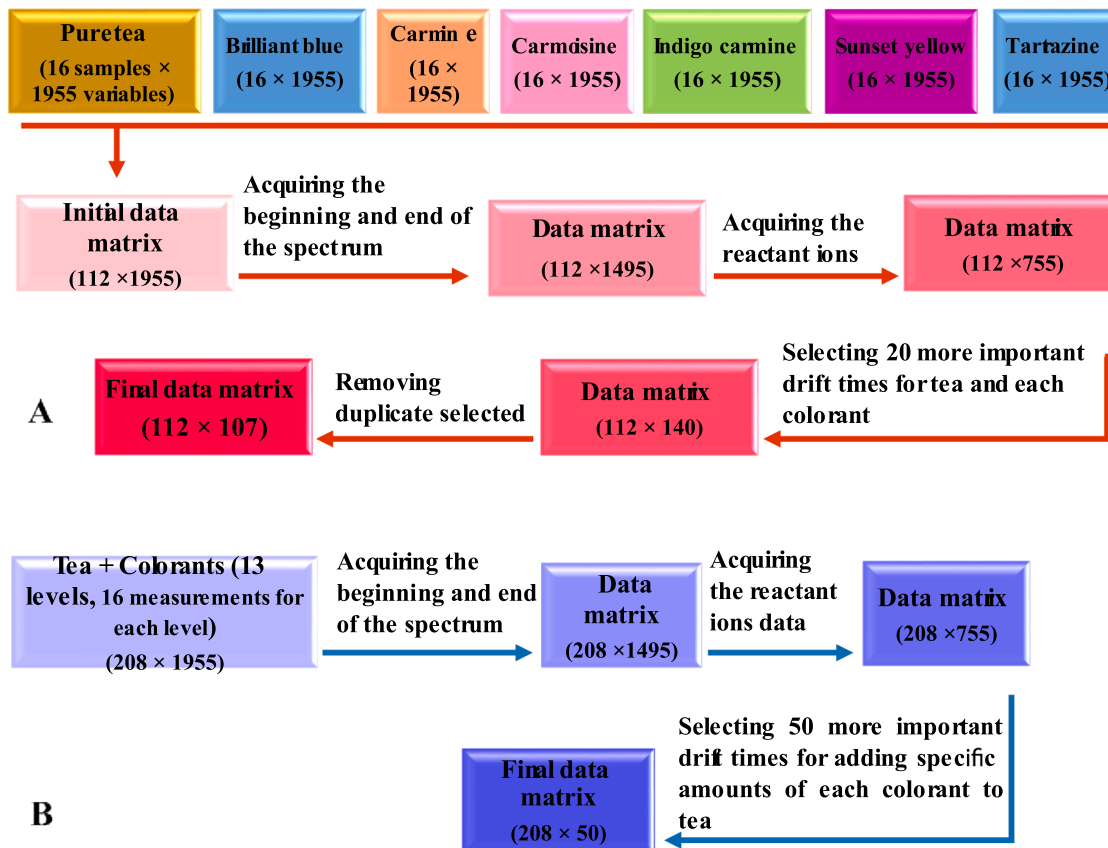

Fig. 1. Steps for reducing data matrix size. A) Data matrix of pure tea and six synthetic colorants spectra; B) Data matrix of adding each synthetic colorant to pure tea at 13 levels.
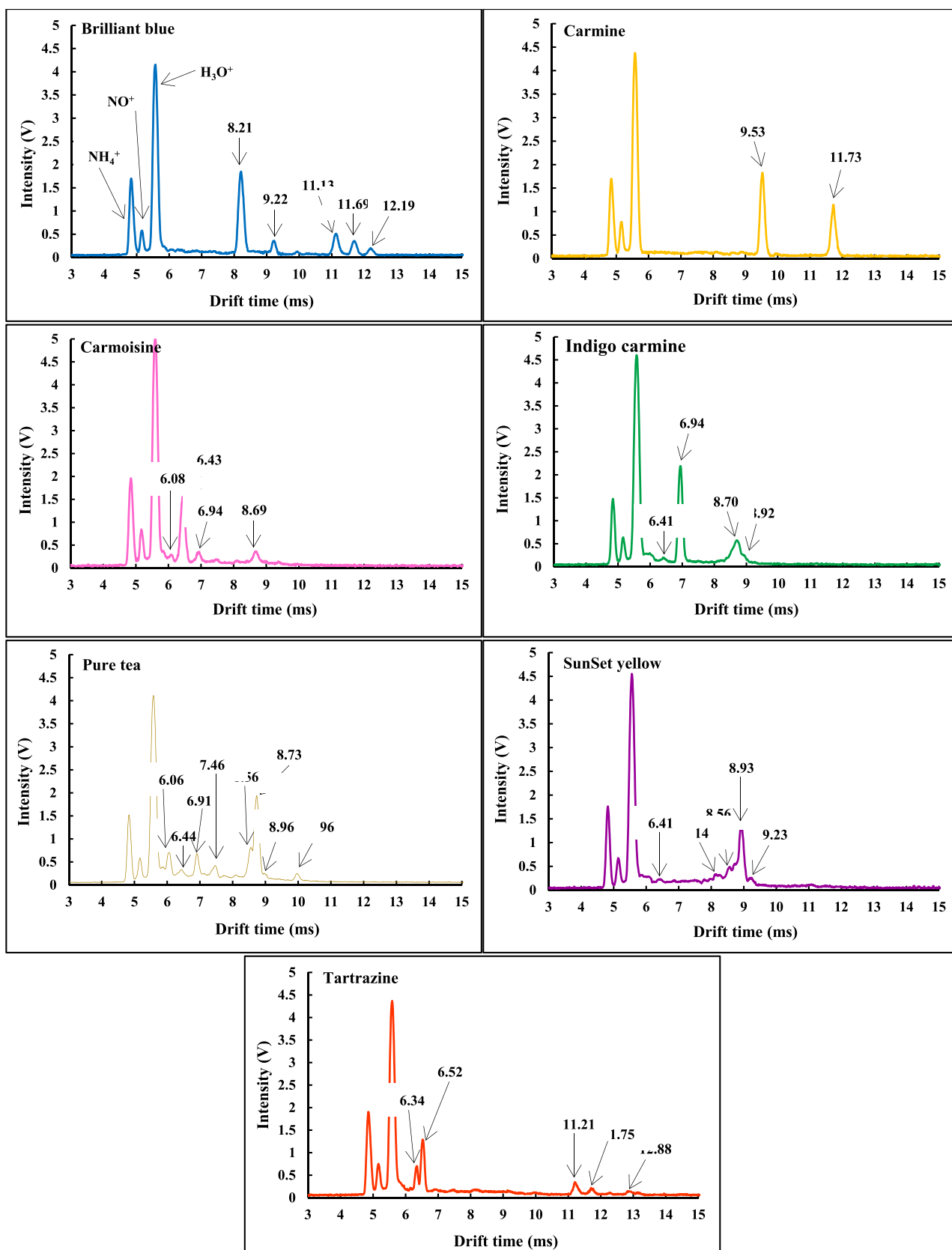
Fig. 2. IMS spectra of pure tea and six synthetic colorants.

reduced peak resolution. This slower movement towards the detector can lead to broader peaks (Chen et al., 2020). As depicted in Fig. 2, it is crucial to emphasize that each sample displays a unique ion mobility spectrum, distinct from the spectra of other samples. This distinctiveness can serve as a discriminating fingerprint for each sample, enabling differentiation and making ion mobility spectrometry a powerful technique for identifying and measuring adulterations.

Discrimination of pure and adulterated tea samples by using PCA and hieratical clustering analysis

This study employed three chemometric methods, namely PCA, hieratical clustering followed by heatmap, and PLS-DA, to differentiate between pure black tea samples and six synthetic colorants. In IMS instruments, there is no tool available for selecting ions that enter the drift tube. As a result, all gaseous metabolites with a higher proton affinity than the reactant ions were ionized during various reactions and subsequently entered the drift tube (Tabrizchi et al., 2000). Each sample possessed a unique chemical ionization fingerprint, allowing for its distinction from other samples. The drift time and intensity of each peak were utilized to differentiate samples. Fig. 3A demonstrates the high reliability and efficiency of the PCA technique in distinguishing between pure tea and synthetic colorants. The first two principal components (PCs) alone explained more than half (51 %) of the total observed variance in the data. Further analysis revealed that only seven components were necessary to explain 91 % of the entire variance in the dataset.

While PCA provided an accurate perspective on sample differentiation, the hieratical clustering followed by heatmap served to confirm the results obtained through PCA. It presented valuable information about the importance of drift times for all injected samples in a two-dimensional graph (Eugene et al., 2018). The hieratical clustering utilized the Spearman distance function to determine the similarity between drift times and among samples for the purpose of clustering. The ordered data matrix was color-coded and illustrated as a heatmap for better visualization. Fig. 3B exhibits the heatmap and clustering of samples based on drift times, aiding in the visualizing of distinctions among the samples. Together, these two chemometric methods offer a comprehensive overview of the data and effectively distinguish between pure black tea samples and synthetic colorants with high accuracy.

Classification of pure black tea and synthetic colorants by using the PLS-DA model

PLS-DA is a widely used supervised classification method for classifying samples into known groups and predicting the class of unknown samples (Mohamad Asri et al., 2022). It has been reported to offer near-perfect performance for datasets with few classes. PLS-DA has distinct advantages over PCA and hieratical clustering (as unsupervised methods), making it a superior approach. While PCA focuses on capturing variance and grouping samples, PLS-DA goes beyond that by incorporating class labels or categorical outcomes associated with each sample, facilitating classification of sample groups. This allows for more effective discrimination between groups. The classification-centric approach of PLS-DA facilitates the identification of influential variables, contributing significantly to the separation between groups. On the other hand, PCA and hieratical clustering methods may not effectively capture the subtle differences between groups. PLS-DA offers a comprehensive interpretation of the data structure by integrating latent variable information and class discrimination, making it a more powerful tool for data analysis (Hur et al., 2010; Mohamad Asri et al., 2022; Wold et al., 2001).

To achieve precise analysis using the PLS-DA method, specific data segments of spectra were excluded, similar to the PCA and hieratical clustering analysis. The initial and final parts of the spectra and data related to reactant ions were removed to optimize the analysis by focusing solely on the most effective spectral region that acted as a unique fingerprint. After conducting the initial analysis of this optimal spectrum using the PLS-DA method, the 20 drift times with the highest variable importance projection (VIP) score were selected to accurately classify samples based on their fingerprint identifier parts.

Details about these 20 drift times chosen by the PLS-DA model for pure tea, brilliant blue, carmine, carmoisine, indigo carmine, sunset yellow, and tartrazine can be found in Table S1 in the supplementary data.

As depicted in the Venn diagram (Fig. 4), among the 20 most important drift times selected by the PLS-DA model, 15 were similar between tea and sunset yellow, and 18 were similar between carmoisine and indigo carmine. In contrast, there were no similar drift times between the other samples. The presence of similar drift times between carmoisine and indigo carmine can be attributed to the greater similarity in the chemical structure of these two artificial colorants compared to other colorants. These findings also confirm the results obtained by the PCA method, as illustrated in Fig. 3A. The clusters of indigo carmine and carmoisine appear to be closer to each other compared to the other clusters. Among the top 20 drift times, the pure tea, brilliant blue, carmine, carmoisine, indigo carmine, sunset yellow, and tartrazine samples exhibited 7 unique drift time patterns, which can be useful for their classification and discrimination.

The PLS-DA model has demonstrated remarkable accuracy by achieving a 100 % success rate in distinguishing pure tea from six synthetic food colorants using six components (Table S2 in the supplementary data). While the results obtained by the PCA and PLS-DA methods yielded similarities, the methods have some fundamental differences. The PCA and hieratical clustering methods are among unsupervised algorithms that show the differences in the intrinsic properties of the subjects and cluster them according to their similarities without any prior information about the group structure of the data. Contrary to unsupervised methods, the PLS-DA method provides an opportunity for prediction purposes. Also, this method helped in selecting discriminatory drift times which was not achievable using unsupervised algorithms. It also should be declared that the PLS method as a multivariate regression method can quantitatively determine the level of the added colorants in tea samples while this is not easily achievable using PCA and clustering methods. When the objective is not to identify particular metabolites for classification, the ionized metabolites with the most significant impact - as determined by drift times and peak intensities - are effectively employed during the modeling process.

Quantification of synthetic colorants in adulterated tea using the PLSR model

The PLSR method was employed to accurately determine the percentage of synthetic colorants added to pure tea. PLSR is a widely used chemometric technique known for its accurate prediction and measurement of adulteration or changes in food quality with minimal error and high precision (Garrido-Delgado et al., 2018; Zeng et al., 2023).

Fig. 5 shows the plots of the experimental amounts of colorants added to pure tea compared to those predicted using the PLSR method. To comprehensively validate the PLSR model, various performance metrics were considered, including the root mean square error of cross-validation ($RMSE_V$), coefficient of determination of cross-validation (R_V^2), root mean square error of calibration ($RMSE_C$), coefficient of determination of calibration (R_C^2), root mean square error of the test set ($RMSE_T$), and coefficient of determination of the test set (R_T^2) (Table 1). The R_C^2 and $RMSE_C$ values evaluate the model's predictive ability based on the training set. The ten-fold cross-validation approach was used for selecting the optimal number of components (ncomp) used. The R_T^2 and $RMSE_T$ values indicate the model's accuracy in predicting new data. To determine the most optimal PLSR model, it is recommended to minimize RMSE and ncomp while maximizing R^2 for the cross-validation procedure (Cozzolino et al., 2004; Qin et al., 2015).
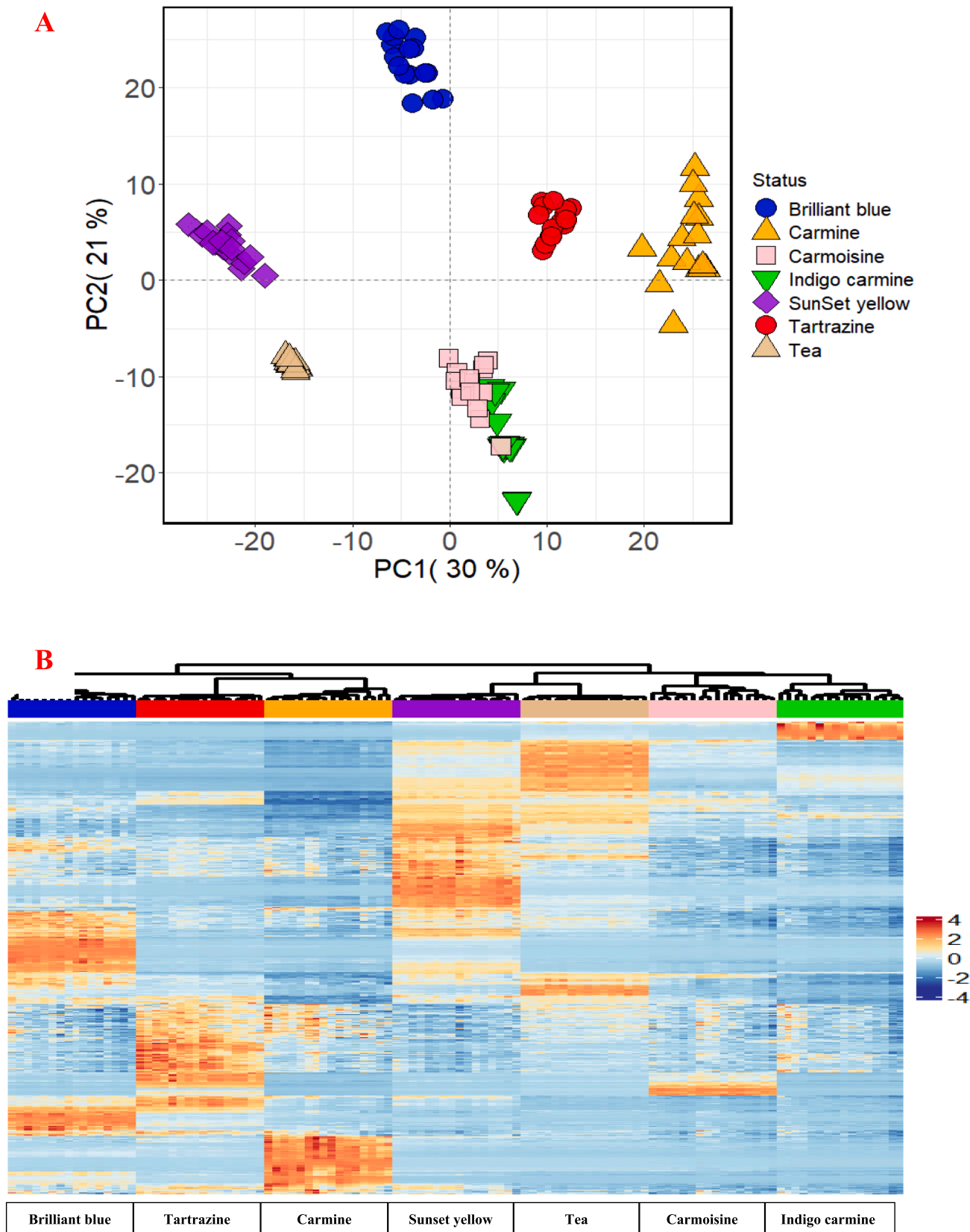
A

B

Fig. 3. A) PCA score plot of the first two principal components (PCs) for ion mobility spectra of pure tea and six synthetic colorants. B) Heatmap dendrogram for ion mobility spectra of pure tea and six synthetic colorants.
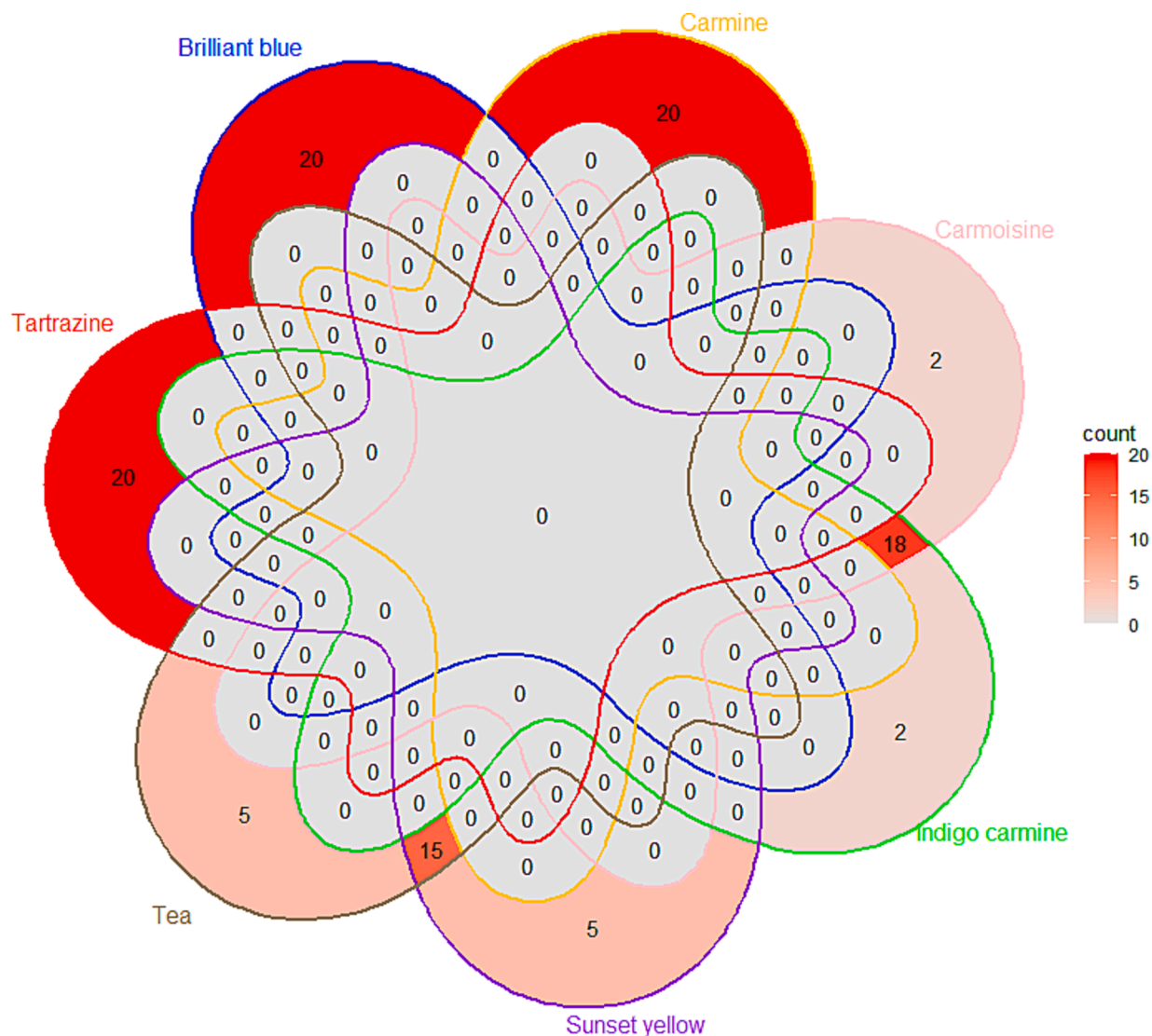
Fig. 4. Interactive Venn diagram of 20 selected drift times for pure tea and 6 synthetic colorants.

The results presented in Table 1 demonstrate a strong correlation between the actual and predicted percentages of synthetic colorants added to pure tea in both test and train data sets. The PLSR model proved to be highly efficient in predicting all six synthetic colorants. Among the colorants, when predicting tartrazine percentages, the model with ncomp = 10 had the highest $RMSE_T$ (0.133) and the lowest R^2_T (0.986). On the other hand, the model developed to predict carmoisine percentages was found to be the most reliable, accurately predicting the percentages of carmoisine added to pure tea with the lowest $RMSE_T$ (0.059) and the highest $R2_T$ (0.997) using 8 components. These research findings align with two previous studies conducted on identifying and measuring artificial colorants in saffron and tea (Fattahi et al., 2023; Wei et al., 2020). However, the accuracy of the results obtained in this research surpassed those of two previous studies. In Fattahi's report (Fattahi et al., 2023), the PLSR method was found to be capable of detecting the amount of four artificial colorants in saffron at concentrations of 10 %, 20 %, and 30 %. The R^2 and RMSE values obtained from analyzing the IMS-CDI⁻ data ranged between 0.880 and 0.954 and 2.39–3.53, respectively. Wei et al. (2020) obtained an R^2 value of 0.972 and a mean relative difference of −2.11 when detecting carmine in black tea through the analysis of HPLC data using the MLP method.

The accuracy of the research can be attributed to the careful consideration of the set of peaks obtained from the IMS device. These peaks serve as distinct identifiers for each sample. Rather than focusing on a specific type of metabolite, our study concentrated on a group of effective metabolites that acted as a unique fingerprint for each sample. For example, if only a single metabolite's peak was analyzed, it would have been difficult to detect small instances of fraud, as tea and sunset yellow have similar peaks in the 8.4–9.0 ms time range. However, by analyzing the pattern of the peak set, the research was able to detect even the most subtle cases of fraud.

Conclusions

In conclusion, our study highlights the successful utilization of IMS and chemometric methods including PCA, hieratical clustering analysis, PLS-DA, and PLSR analysis, to effectively differentiate and determine the concentrations of six synthetic colorants in pure tea without the necessity of precise metabolite identification. This method offers numerous advantages, including cost-effectiveness, efficiency, user-friendliness, and environmentally sustainability, making it highly applicable in identifying and quantifying adulterants in beverages, food, and agricultural products.
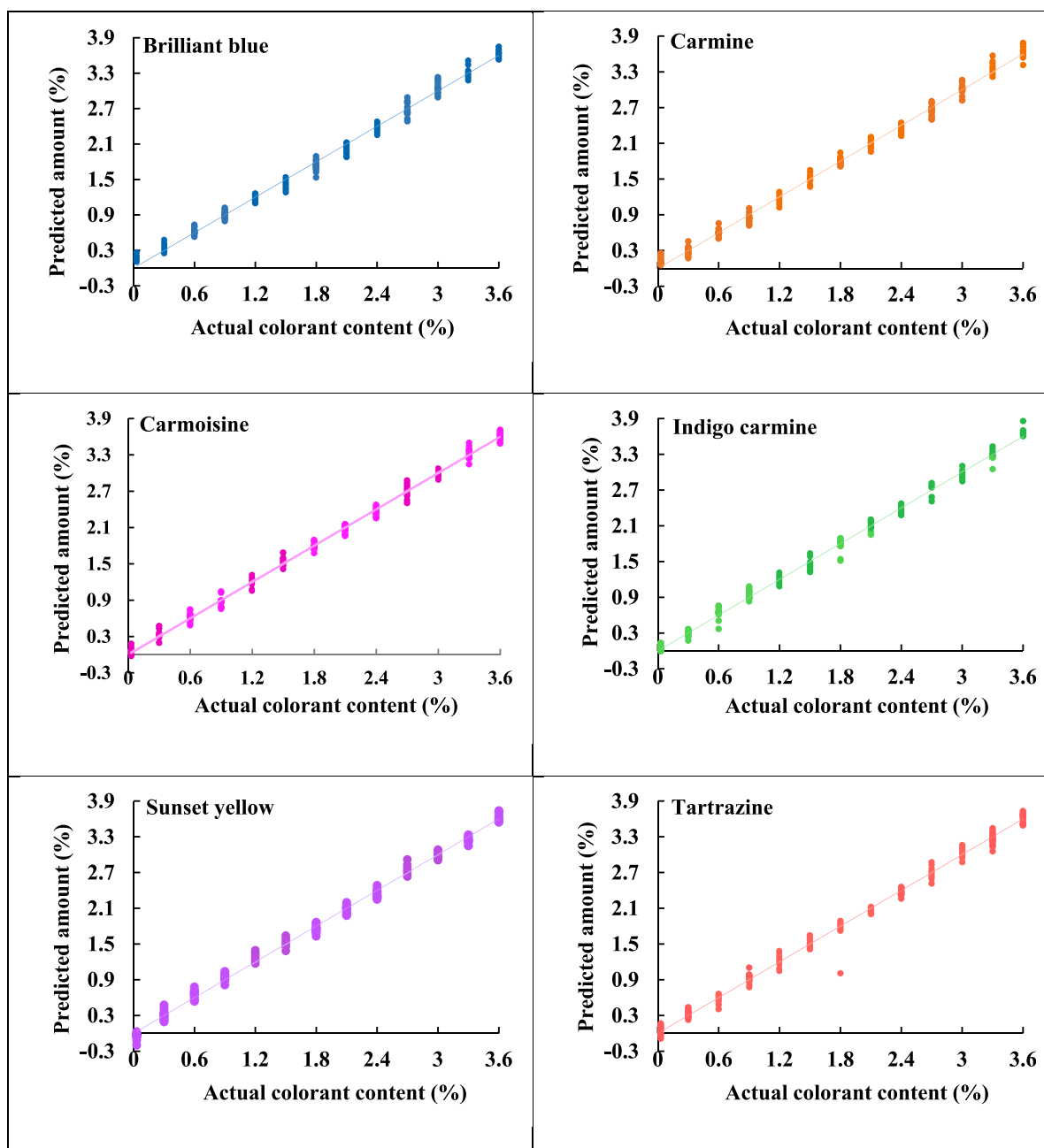
Fig. 5. Comparison of actual percentages of colorants (X) vs. the percentages predicted by the PLSR model (Y) for six synthetic colorants added to pure tea.

Table 1

The number of components (ncomp), root mean square errors (RMSE), and the coefficient of determination (R^2) for validation, calibration, and test set obtained through PLSR modeling for the quantification of synthetic colorants added to tea.

Sample	ncomp	R^2_V	$RMSE_V$	R^2_C	$RMSE_C$	R^2_T	$RMSE_T$
Brilliant Blue	8	0.992	0.107	0.993	0.093	0.996	0.075
Carmine	8	0.994	0.097	0.994	0.085	0.993	0.095
Carmoisine	8	0.995	0.086	0.995	0.074	0.997	0.059
Indigo Carmine	9	0.993	0.086	0.994	0.079	0.993	0.089
Sunset Yellow	10	0.994	0.087	0.995	0.077	0.995	0.079
Tartrazine	10	0.993	0.094	0.995	0.075	0.986	0.133

CRediT authorship contribution statement

Mina Sobhaninia: Data curation, Formal analysis, Investigation, Methodology, Software. **Ahmad Mani-Varnosfaderani:** Data curation, Methodology, Software, Validation, Writing – review & editing. **Mohsen Barzegar:** Conceptualization, Funding acquisition, Supervision, Writing – review & editing. **Mohammad Ali Sahari:** Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2024.101213.

References

Ali, H. (2010). Biodegradation of synthetic dyes- A review. *Water, Air, and Soil Pollution, 213*, 251–273. https://doi.org/10.1007/s11270-010-0382-4

Alves, S. P., Brum, D. M., Branco de Andrade, É. C., & Pereira Netto, A. D. (2008). Determination of synthetic dyes in selected foodstuffs by high performance liquid chromatography with UV-DAD detection. *Food Chemistry, 107*, 489–496. https://doi.org/10.1016/j.foodchem.2007.07.054

Amchova, P., Kotolova, H., & Ruda-Kucerova, J. (2015). Health safety issues of synthetic food colorants. *Regulatory Toxicology and Pharmacology, 73*, 914–922. https://doi.org/10.1016/j.yrtph.2015.09.026

Basu, A., & Suresh Kumar, G. (2015). Thermodynamics of the interaction of the food additive tartrazine with serum albumins: A microcalorimetric investigation. *Food Chemistry, 175*, 137–142. https://doi.org/10.1016/j.foodchem.2014.11.141

Bonan, S., Fedrizzi, G., Menotta, S., & Elisabeta, C. (2013). Simultaneous determination of synthetic dyes in foodstuffs and beverages by high-performance liquid chromatography coupled with diode-array detector. *Dyes and Pigments, 99*, 36–40. https://doi.org/10.1016/j.dyepig.2013.03.029

Cozzolino, D., Kwiatkowski, M. J., Parker, M., Cynkar, W. U., Dambergs, R. G., Gishen, M., & Herderich, M. J. (2004). Prediction of phenolic compounds in red wine fermentations by visible and near infrared spectroscopy. *Analytica Chimica Acta, 513*, 73–80. https://doi.org/10.1016/j.aca.2003.08.066

Deb Pal, A., & Das, T. (2018). Analysis of adulteration in black tea. *International Journal of Biological Research, 3*, 253–257.

Eiceman, G.A., Karpas, Z., & Hill Jr., H.H., 2013. Ion Mobility Spectrometry, 3rd Ed. CRC Press, Boca Raton, Florida, United States. https://doi.org/10.1201/b16109.

Esteban, M., Ariño-Blasco, M.C., Díaz-Cruz, J.M., 2020. Chemometrics in Electrochemistry, in: Brown, S., Tauler, R., Walczak, B. (Ed.), Comprehensive Chemometrics (Second Edition). Elsevier, Oxford, pp. 1-31. https://doi.org/10.1016/B978-0-12-409547-2.14622-0.

Esteki, M., Simal-Gandara, J., Shahsavari, Z., Zandbaaf, S., Dashtaki, E., & Vander Heyden, Y. (2018). A review on the application of chromatographic methods, coupled to chemometrics, for food authentication. *Food Control, 93*, 165–182. https://doi.org/10.1016/j.foodcont.2018.06.015

Eugene, A., Masiak, J., & Eugene, B. (2018). Predicting lithium treatment response in bipolar patients using gender-specific gene expression biomarkers and machine learning. *F1000Research, 7*, 474. https://doi.org/10.12688/f1000research.14451.3

Fattahi, R., Mani-Varnosfaderani, A., Barzegar, M., & Sahari, M. A. (2023). An ion mobility spectrometry-chemometrics combination approach for assessing adulteration in saffron (Crocus sativus L.) with synthetic colorants. *Industrial Crops and Products, 193*, Article 116161. https://doi.org/10.1016/j.indcrop.2022.116161

Feng, J., Cerniglia, C. E., & Chen, H. (2012). Toxicological significance of azo dye metabolism by human intestinal microbiota. *Frontiers in Bioscience (Elite Edition), 4*, 568–586. https://doi.org/10.2741/e400

Frost, T., 2017. Quantitative Analysis, in: Lindon, J.C., Tranter, G.E., Koppenaal, D.W. (Ed.), Encyclopedia of Spectroscopy and Spectrometry (3th Ed.). Academic Press, Oxford, pp. 811-815. https://doi.org/10.1016/B978-0-12-803224-4.00263-6.

Garkani Nejad, F., Sheikhshoaie, I., & Beitollahi, H. (2022). Simultaneous detection of carmoisine and tartrazine in food samples using GO-Fe$_3$O$_4$-PAMAM and ionic liquid based electrochemical sensor. *Food and Chemical Toxicology, 162*, Article 112864. https://doi.org/10.1016/j.fct.2022.112864

Garrido-Delgado, R., Eugenia Muñoz-Pérez, M., & Arce, L. (2018). Detection of adulteration in extra virgin olive oils by using UV-IMS and chemometric analysis. *Food Control, 85*, 292–299. https://doi.org/10.1016/j.foodcont.2017.10.012

Huang, F.-F., Yang, P.-D., Bai, S.-L., Liu, Z.-H., Li, J., Huang, J.-A., & Xiong, L.-G. (2024). Lipids: A noteworthy role in better tea quality. *Food Chemistry, 431*, Article 137071. https://doi.org/10.1016/j.foodchem.2023.137071

Jafari, M. T., Torki, F., & Saraji, M. (2012). Simultaneous determination of nitrite and nitrate in potato and water samples using negative electrospray ionization ion mobility Spectrometry. *Analytical Sciences, 28*, 391–395. https://doi.org/10.2116/analsci.28.391

Martin, F., Oberson, J.-M., Meschiari, M., & Munari, C. (2016). Determination of 18 water-soluble artificial dyes by LC–MS in selected matrices. *Food Chemistry, 197*, 1249–1255. https://doi.org/10.1016/j.foodchem.2015.11.067

Masone, D., & Chanforan, C. (2015). Study on the interaction of artificial and natural food colorants with human serum albumin: A computational point of view. *Computational Biology and Chemistry, 56*, 152–158. https://doi.org/10.1016/j.compbiolchem.2015.04.006

Mohamad Asri, M. N., Verma, R., Mahat, N. A., Nor, N. A. M., Mat Desa, W. N. S., & Ismail, D. (2022). Discrimination and source correspondence of black gel inks using Raman spectroscopy and chemometric analysis with UMAP and PLS-DA. *Chemometrics and Intelligent Laboratory Systems, 225*, Article 104557. https://doi.org/10.1016/j.chemolab.2022.104557

Munim Khan, M. R., Islam, M. A., Uddin, R., Kalam, M. A., Baishakh, N. N., Barua, P., Rahman Talukder, M. H., & Ahmad, I. (2023). Biochemical investigation of Bangladeshi black tea and their correlation to organoleptic quality evaluation. *Heliyon, 9*, e16802.

Nath, D., Sarkar, K., Tarafder, P., & Paul, G. (2013). Development of a visible spectrophotometric method for the quantitative determination of metanil yellow in different food samples. *International Journal of Pharma and Bio Sciences, 4*, 685–692.

Qin, J., Xie, L., & Ying, Y. (2015). Determination of tetracycline hydrochloride by terahertz spectroscopy with PLSR model. *Food Chemistry, 170*, 415–422. https://doi.org/10.1016/j.foodchem.2014.08.050

Qin, X., Zhou, J., He, C., Qiu, L., Zhang, D., Yu, Z., Wang, Y., Ni, D., & Chen, Y. (2023). Non-targeted metabolomics characterization of flavor formation of Lichuan black tea processed from different cultivars in Enshi. *Food Chemistry, X 19*, Article 100809. https://doi.org/10.1016/j.fochx.2023.100809

Rovina, K., Acung, L. A., Siddiquee, S., Akanda, J. H., & Shaarani, S. M. (2017). Extraction and Analytical Methods for Determination of Sunset Yellow (E110)- a Review. *Food Analytical Methods, 10*, 773–787. https://doi.org/10.1007/s12161-016-0645-9

Sarker, S. D., & Nahar, L. (2015). Applications of High Performance Liquid Chromatography in the Analysis of Herbal Products. In P. K. Mukherjee (Ed.), *Evidence-Based Validation of Herbal Medicine* (pp. 405–425). Boston: Elsevier. https://doi.org/10.1016/B978-0-12-800874-4.00019-2.

Sha, O., Zhu, X., Feng, Y., & Ma, W. (2015). Aqueous two-phase based on ionic liquid liquid-liquid microextraction for simultaneous determination of five synthetic food colourants in different food samples by high-performance liquid chromatography. *Food Chemistry, 174*, 380–386. https://doi.org/10.1016/j.foodchem.2014.11.068

Sharma, P. K., Ali, M., & Yadav, D. (2011). Physicochemical and phytochemical evaluation of different black tea brands. *J. Appl. Pharm. Sci., 1*, 121–124.

Tabrizchi, M., Khayamian, T., & Taj, N. (2000). Design and optimization of a corona discharge ionization source for ion mobility spectrometry. *The Review of Scientific Instruments, 71*, 2321–2328. https://doi.org/10.1063/1.1150618

Wei, L., Yang, Y., & Sun, D. (2020). Rapid detection of carmine in black tea with spectrophotometry coupled predictive modelling. *Food Chemistry, 329*, Article 127177. https://doi.org/10.1016/j.foodchem.2020.127177

Yamjala, K., Nainar, M. S., & Ramisetti, N. R. (2016). Methods for the analysis of azo dyes employed in food industry- A review. *Food Chemistry, 192*, 813–824. https://doi.org/10.1016/j.foodchem.2015.07.085

Zeng, S., Zhang, Z., Cheng, X., Cai, X., Cao, M., & Guo, W. (2023). Prediction of soluble solids content using near-infrared spectra and optical properties of intact apple and pulp applying PLSR and CNN. *Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy, 123402*. https://doi.org/10.1016/j.saa.2023.123402

Zhang, L., Shuai, Q., Li, P., Zhang, Q., Ma, F., Zhang, W., & Ding, X. (2016). Ion mobility spectrometry fingerprints: A rapid detection technology for adulteration of sesame oil. *Food Chemistry, 192*, 60–66. https://doi.org/10.1016/j.foodchem.2015.06.096