Journal of Fluorescence (2019) 29:1103–1111
https://doi.org/10.1007/s10895-019-02421-0

ORIGINAL ARTICLE

The Parallel Factor Analysis of Beer Fluorescence

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Received: 2 April 2019 / Accepted: 29 July 2019 / Published online: 8 August 2019

Abstract

Fluorescence excitation-emission matrices were measured for 111 samples of different types of beer and studied by the parallel factor analysis (PARAFAC). The 5-component PARAFAC model was found to suitably describes the beer fluorescence, accounting for 99.4% of the fluorescence variance in the measured set of samples, and providing the completely resolved excitation and emission spectra of each component. The model was chosen based on a model's core consistency and split-half analysis. It is shown that beer fluorescence is the sum of fluorescence of aromatic amino acids (tryptophan, tyrosine, and phenylalanine), different forms of vitamin B, and phenolic compounds. Obtained PARAFAC model of beer fluorescence demonstrated the potential for the quantification and quality analysis of beer fluorophores and classification of different beer types.

Keywords Fluorescence · Beer · PARAFAC · PLS-DA · Excitation-emission matrices

Introduction

Beer is one of the most popular alcoholic beverages consumed worldwide. Its' refreshing and pleasant taste mainly comes from the water and different nutrients such as malted barley and other cereals, hops, etc. Because beer contains a variety of healthy constituents such as polyphenols, essential vitamins (particularly B vitamins), and minerals, its' consumption may provide valuable effects to healthy adults which include the reduced risk for cardiovascular diseases, diabetes and some forms of cancer [1, 2].

As is for other types of food and beverages, obtaining and circulating trustworthy data on the chemical composition, geographical origin and quality of beer products is public interest nowadays and the growing matter of study for many researches in the world. So far, many techniques were proposed for analyses of beer properties [3–5]. Phenolic compounds, which are responsible for the nutritional value of beer, and the beer's flavor stability have been analyzed by coulometric array detection [6, 7]. Several electrochemical [8, 9] as well as photodiode array analyses were suggested for the same purpose [10]. Also, phenolic profile of beer samples was analyzed using low resolution [11] and high resolution mass spectrometry [12]. However, these methods can be regarded as an expensive and time and labor demanding since they require pre-treatment of samples and operation by highly skilled personnel. Spectroscopy methods are less demanding in this respect, and many of them are successfully applied for food analyses [13, 14]. For example, nuclear magnetic resonance (NMR), near-infrared (NIR) and infrared (IR) spectroscopy are proven as exceptionally useful methods in the direct beer analysis [15–17].

Successful applications of fluorescence spectroscopy in food analyses [18, 19] have encouraged research on its use for the beer characterization. Regarding fluorescence, beer and many other food products are complex systems because they contain numerous components that either cause or influence fluorescence. Consequently, conventional emission and excitation spectra of beer are not suitable for detailed studies since they do not comprise all contributions from fluorophores, chromophores and scatters in the beer. This problem can be overcome using total fluorescence spectroscopy techniques, i.e. excitation-emission matrix (EEM; also known as fluorescence excitation-emission landscapes) and total synchronous fluorescence scanning (TSFS). EEMs are acquired by recording the sequence of emission spectra, each of which is excited with a different energy over the spectral range of interest. Synchronous fluorescence method involves simultaneously scanning both emission and excitation wavelengths while maintaining the interval constant between

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emission and excitation (constant-wavelength mode) or maintaining the frequency gap constant (constant-energy mode). TSFS is obtained as a series of synchronous spectra over the selected range of synchronous intervals [20]. In this way EEMs and TSFSs are able to record almost complete fluorescence information from the complex system under study and, thus, may be considered as the unique "fluorescence fingerprint" of the measured specimen. Recently, EEM and TSFS have been effectively utilized for the evaluation of aromatic amino acids and riboflavin contents in beer samples and for the beer quality monitoring in different storage conditions [21–24].

However, the proper analysis of food EEMs and TSFSs are neither easy nor straightforward. Fluorescence spectra of different specimens of the same product can differ amongst themselves, because even the slightest biochemical variation between specimens is reflected through fluorescence. Further, the fluorescence of a food product is an overlapping sum of fluorescence from each of the many fluorophores in the sample. For these reasons, proper analysis is only achieved if it is performed on a statistically significant number of samples and measurements. In addition, measurements yield large and complex datasets, so finding an appropriate method to process and extract the relevant information from measurements is of the utmost importance. In case of three- (such as EEM and TSFS) and higher-order data arrays, traditional two-way statistical methods are not optimal choice for data analyses. Instead, multi-way analyses such as parallel factor analysis (PARAFAC), PARAFAC2, Tucker3, and N-PLS (N-partial least squares regression) can be successfully employed [25]. Among these, PARAFAC is the most popular and widely used analysis technique for fluorescence data modeling [26].

For food analysis and control, PARAFAC model of EEMs offers many benefits of which three are quite valuable [27–32]. First, it provides the fluorescence model of the food system. Second, it decomposes EEMs of food samples to corresponding excitation and emission spectra of the most dominant fluorophores that food contains. Third, it provides the relative concentrations or contributions of fluorophores in each sample. Additional benefits include the possibility to calibrate relative concentrations of fluorophores by some standard methods which may facilitate the development of standardized fluorescence-based analytical methods for these fluorophores. This would provide significantly reduced number of parameters which contain majority of variation in the tested group which can be exploited for the further analysis by standard statistical techniques, for example for the determination of botanical or geographical origin of the food.

Herein, we aimed to develop the PARAFAC model of the beer fluorescence. To do so, we have collected and measured EEMs of 111 beer samples, which were of different type and from different countries worldwide. The optimal model was chosen based on its' core consistency and a split-half analysis results. We identified the most dominant components that affect beer fluorescence and determined their relative concentrations. Finally, we tested the possible application of this model for the classification of the beer type based on its fluorescence signal.

Materials and Methods

Samples and Measurements

A total of 111 beer samples (51 samples of Pale lager, 21 Wheat beer, 12 Stout, 9 Dark lager, 10 Pale Ale, and 8 India Pale Ale (IPA)) were purchased directly from the market and stored in a dark place at room temperature. Beer fluorescence excitation-emission matrices (EEMs) were measured on Fluorolog-3 Model FL3–221 spectroflurometer system (Horiba JobinYvon), utilizing 450 W Xenon lamp as an excitation source and R928 photomultiplier tube as a detector. Beer samples were pipetted into the 3 ml quartz cuvette (10 mm diameter, 1 mm thick wall) and measured in a front-face geometry. Bubbles were not removed from samples since no difference between spectra measured on the intact sample and one which was degassed was observed. EEMs were obtained by combining a series of emission scans recorded from 275 to 600 nm while exciting at wavelengths ranging between 255 to 550 nm with an interval of 2.5 nm and with emission and excitation slits set to 1 nm and 2 nm, respectively. Emission intensity was normalized to the power of excitation source using built-in reference photodetector. Contributions to measured signal intensity from the first and second order Rayleigh scattering were removed and replaced with interpolated values. The use of interpolated values to remove scattering contribution has been shown to provide better and more meaningful PARAFAC models compared to the data deletion [33].

Data Analyses

Data analyses included the decomposition of EEM data and the extraction of relevant information using PARAFAC, Analysis of variance (ANOVA) and Tukey's test for the analysis of PARAFAC scores, and Partial Least Squares Discriminant Analysis (PLS-DA) for building classification models. All the analyses were performed using the Solo Version 6.5.4 software package (Eigenvector, 108 Inc., Chelan, WA, USA) and R software package (R Foundation for Statistical Computing, Vienna, Austria).

Modelling EEM by PARAFAC

Each fluorescence EEM measurement provides an output in the form of a data matrix. When several samples are measured, each matrix is added to a three-way array. If each sample is measured at J emission wavelengths and K excitation

wavelengths, then the obtained fluorescence intensities can be gathered in a matrix of size $J \times K$. If I is the number of measured samples, then the final $I \times J \times K$ three-way array is constructed from the measurements of the I samples. This array is then used for multi-way PARAFAC modeling. The sample direction (corresponding to the matrix rows) is called the first mode; the second mode is the emission mode; and the excitations constitute the third mode. PARAFAC analysis decomposes a three-way array into a set of trilinear terms by minimizing the sum of squares of the residuals e_{ijk} that contain all unexplained variations [34]:

$$x_{ijk} = \sum_{r=0}^{R} a_{ir} b_{jr} c_{kr} + e_{ijk} \quad (1)$$

where $i = 1, ..., I$; $j = 1, ..., J$; $K = 1, ..., K$; $r = 1, ..., R$. The PARAFAC model is defined by the three loading matrices **A**, **B**, and **C** with elements a_{ir}, b_{jr}, and c_{kr}, respectively. In Eq. (1), x_{ijk} corresponds to one data point in the three-way array for the i^{th} sample, with the j^{th} and k^{th} variables on modes 2 and 3, respectively. In the case of fluorescence EEM data this means that the terms represent the fluorescence intensity at the j^{th} emission and k^{th} excitation wavelength for the i^{th} sample. The term mode corresponds to each way (dimension) of a data set. R is the number of PARAFAC components used in the model. Each component in the model is defined by its corresponding a, b, and c values. The PARAFAC model components correspond to fluorophores present in the complex system being analyzed. Thus, parameter a contains information about the relative concentration (scores) of each fluorophore in every sample, and parameters b and c (loadings) represent the pure emission and excitation spectra of the modeled fluorophores, respectively. Estimation of the number of components in the PARAFAC model of beer's EEMs and the assurance that appropriate assessment is made is achieved by the model validation through the Core consistency diagnostics [35] and the split-half analysis. Considering that PARAFAC model must be unique for the given set of specimens, two models obtained with original data set split in halves must possess the same excitation and emission loadings [36].

PLS-DA

Partial least squares discriminant analysis (PLS-DA) is a chemometric classification method used for the separation of different classes of samples. This technique is based on PLS2 algorithm which builds classification models with multiple different groups of samples [37, 38]. The method uses the partial least squares regression algorithm for the transformation of the initial dataset into a smaller set of latent variables. Calculated latent variables are used for the classification of unknown samples (prediction of class variable of each sample) [30]. The class variable (dummy variable) indicates if analyzed sample belongs to a particular class. Each classification model must be validated (different approaches can be used) in order to determine the correct number of linear latent variables used in the model [39]. Here, we used Venetian blind cross-validation technique, which comprises of selecting every s^{th} sample from the data set, in such a way that s data splits are made and each sample is left out only once ($s = 3$).

Results and Discussion

EEM Spectra

Figure 1 shows EEM contour maps of six different groups of beers (pale lager, dark lager, pale ale, dark ale, India pale ale, stout and wheat beer). In EEMs, Rayleigh's first and second order reflections are replaced with interpolated values. EEMs clearly show two distinct spectral regions, the one covering excitation range from 255 nm to 300 nm and emissions from 300 nm to 475 nm, and the second spanning excitations from 310 nm to 500 nm and emissions from 350 nm to 600 nm. Even though EEMs of different type beers look similar, differences in shapes, band positions and emission intensities are evidently visible. It is noticeable that India pale ale shows lowest emission intensity in the first spectral region, while for second spectral region weaker emission intensity than average is evident for pale ale. Generally, the intrinsic fluorescence of beers comes from fluorophores they contain. The aromatic amino acids, such as tryptophan (excitation/emission at 280/350 nm), tyrosine (275/300 nm) and phenylalanine (260/280 nm) are responsible for the beer fluorescence in ultraviolet (UV) spectral region [21, 24, 40]. In visible spectral region, beer fluorescence occurs from different forms of vitamin B, such as vitamin B_3 (excitation/emission at 260, 340/470), vitamin B_6, vitamin B_{12}, vitamin B_2 (riboflavin) and various phenolic compounds [21, 23, 24, 40].

PARAFAC Model

PARAFAC analysis was carried out on the 111 × 131 × 107 three-way data array obtained by combining EEM's of 111 beer samples. To identify the appropriate number of components for the model, 10 PARAFAC models with varying number of components (1 to 10) were built. Based on the core consistency diagnostic of models and values of the explained variance (see Table 1) [35], the 5-component PARAFAC model seemed the appropriate one (the value of core consistency sharply declined for models having more than 5 components and the explained variance by 5 component model is sufficiently high, Table 1). Decomposition of beer EEMs into excitation and emission spectra by the 5-component model is shown in Fig. 2a and b, respectively. The model is validated using the split-half analysis, i.e. by modeling beer EEMs with

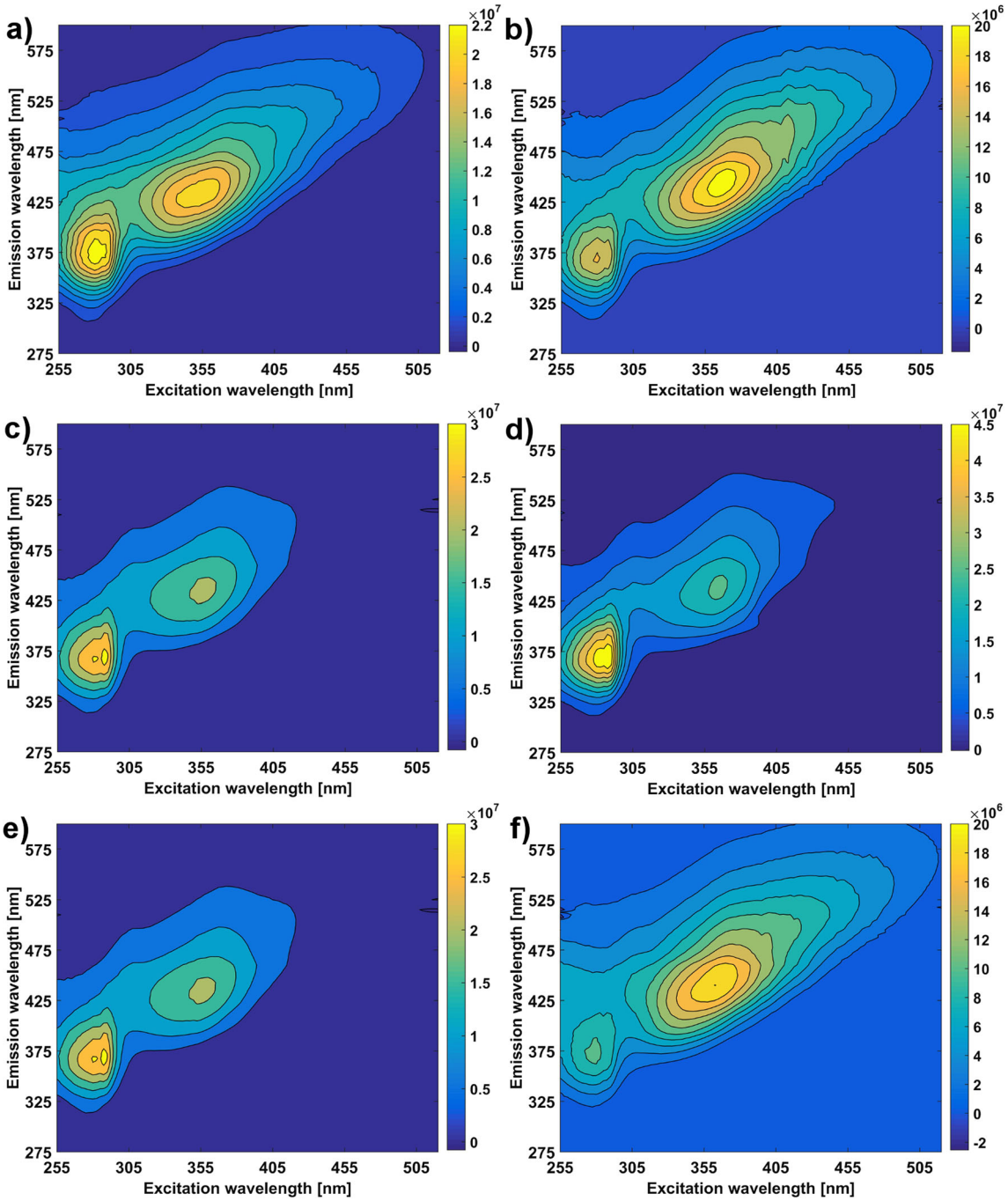

Fig. 1 EEM contour plots of different types of beer: **a**) pale lager **b**) dark lager **c**) pale ale **d**) India pale ale **e**) wheat and **f**) stout

two models generated with two sets of data each containing EEMs from the half of samples. Two models produced similar results (see Fig. 2c and d) which is a proof that 5-component model is an optimal one for the analysis of beer EEMs, as the uniqueness of a solution is one of a PARAFAC model characteristics. Please note that non-negativity constraint in all modes was applied for all constructed models.

The first component (red lines in Fig. 2) of PARAFAC model has maximum values excitation and emission modes at 280 nm and 365 nm, respectively. Such spectroscopic properties show aromatic amino acids such as tryptophan and tyrosine [21, 24]. The second (cyan lines), fourth (green lines) and fifth (violet lines) component have excitation maximums at 335, 405 and 445 nm, and emission maximums at 415, 460 and 525 nm, respectively. These spectral characteristics resemble those of different forms of the vitamin B. Fluorescence of a pyridoxic acid (the form of vitamin B_6) has excitation/emission maxima at 315/425 nm, while niacin

Table 1 The core consistency diagnostics and the percent of explained variance for calculated PARAFAC models

Number of components	The explained variance [%]	The core consistency
1	70.29	100.00
2	91.26	98.63
3	97.85	95.80
4	99.08	78.94
5	99.44	64.59
6	99.48	12.74
7	99.69	1.56
8	99.74	1.45
9	99.81	−0.07
10	99.86	−0.22

(the form of vitamin B_3) exhibits excitation/emission maxima at 260,340/470 nm [21, 24, 40]. Riboflavin (vitamin B_2) emits in the range 500–600 nm and has excitation band maximum at 450 nm [21]. Finally, the third component (blue) shows the excitation maximum at 370 nm and the emission maximum at 440 nm, so it can be related to iso-α-acids and phenolic compounds [23]. The presence of these compounds in beer has been also confirmed by non-fluorescence techniques [41, 42].

Applications of PARAFAC Model

The obtained PARAFAC model is employed for calculations of the relative concentrations of 5 dominant fluorescent components in beer samples. These data were subjected to Tukey's test to examine if there are significant differences in component concentrations between different beer types. Calculated *p*-values, showing how significant is the difference between

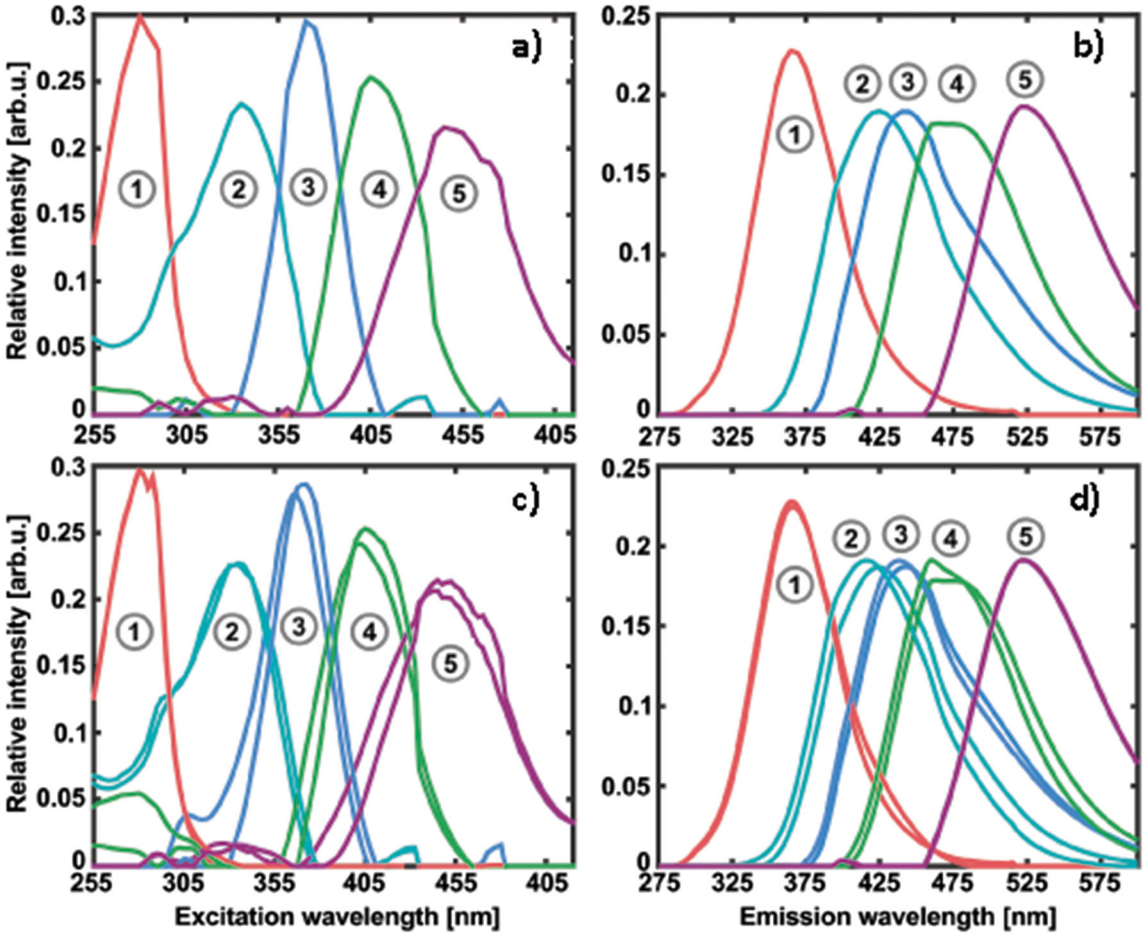

Fig. 2 Decomposition of beer EEM by the 5-component PARAFAC model into: (**a**) excitation mode and (**b**) emission mode. The split half analysis results: (**c**) excitation modes and (**d**) emission modes

Table 2 Multiple comparisons of different types of beer based on the calculated *p* values (p values smaller than 0.05 are bolded)

		1st Component	2nd Component	3rd Component	4th Component	5th Component
Pale Lager	Wheat	**0.00002**	0.09143	**0.00035**	**0.00030**	**0.00021**
	Stout	**0.04305**	**0.00158**	0.11124	0.42711	0.99793
	Dark Lager	0.43236	0.63179	0.66361	0.98761	**0.01038**
	Pale Ale	0.93502	0.99695	0.81585	**0.00200**	**0.0000005**
	IPA	0.97248	0.14076	0.99978	**0.0000001**	**0.00000002**
Wheat	Stout	**0.0000001**	**0.000005**	**0.000005**	**0.00006**	**0.05438**
	Dark Lager	**0.00003**	**0.02586**	**0.00068**	0.19738	0.99998
	Pale Ale	**0.00058**	0.74422	**0.00114**	0.99424	0.19360
	IPA	0.14125	0.99055	**0.03778**	**0.04193**	**0.00015**
Stout	Dark Lager	0.98871	0.57298	0.98715	0.41706	0.13150
	Pale Ale	0.69164	**0.01255**	0.93742	**0.00018**	**0.00024**
	IPA	0.08003	**0.00006**	0.61012	**0.0000001**	**0.0000001**
Dark Lager	Pale Ale	0.97412	0.61476	0.99987	0.14545	0.47070
	IPA	0.35836	**0.02977**	0.94500	**0.00032**	**0.00302**
Pale Ale	IPA	0.78426	0.57468	0.98334	0.26503	0.26014

two group means, are presented in Table 2. Regarding fluorescence, the main difference between different beer types comes from different concentration levels of 2nd, 4th and 5th component, which all correspond to vitamin B complexes. Also, it is evident that wheat beers have significantly different concentration levels of the first component (aromatic amino acids) compared to other groups. It can be observed in Table 3 that wheat beer has the highest concentration level of aromatic amino acids compared to other types of beer. Stout beer stands out from other types of beer because of the lowest concentration levels of vitamin B complexes (Table 3). In addition to the comparison, it is possible to calibrate relative concentrations of fluorescent beer components to absolute values using standard analytical methods (the so-called second order calibration). This is the subject of further work.

As discussed in the Introduction, PARAFAC model reduces the large number of measured data for each sample to the much lower value, in this case to 5, which accounts 99.44% of the total fluorescence variance in samples (see Table 1). To investigate separation between different types of beer we used the score plot with values of PARAFAC scores of 2nd and 5th components (see Fig. 3). Good discrimination is evident between pale lager, stout and India pale ale. For other groups, there are some data overlapping, but, still, data exhibit rather good clustering of samples from the same group. One should note that this discrimination is done only accounting two fluorescent beer components due to the limitation of presentation by 2-dimensional graph. Much better discrimination between beer types groups is achieved when using all 5 components. Then, it is possible to use some of standard tools of chemometry for additional analyses. PLS-DA model classification errors (see Table 4) were calculated to quantify the differences between different beer types. Obtained errors indicate that the best separation is achieved for pale lager, wheat, stout and India pale ale, where calibrated errors are between 12.1 and 16.2%. Classification success rate was over 78% for dark lager and pale ale. Even though this first results present relatively high errors, they indicate that the PARAFAC model of beer fluorescence can be effectively used for beer characterization, testing and control.

Table 3 Mean values of relative concentrations of PARAFAC components ($\times 10^8$) for different types of beer

	1st Component	2nd Component	3rd Component	4th Component	5th Component
Pale Lager	3.87	3.76	3.40	2.03	0.94
Wheat	5.88	4.65	5.14	3.11	1.55
Stout	2.43	2.10	2.14	1.47	1.01
Dark Lager	2.85	3.03	2.57	2.25	1.58
Pale Ale	3.38	3.97	2.74	3.31	2.01
IPA	4.32	4.98	3.24	4.27	2.54

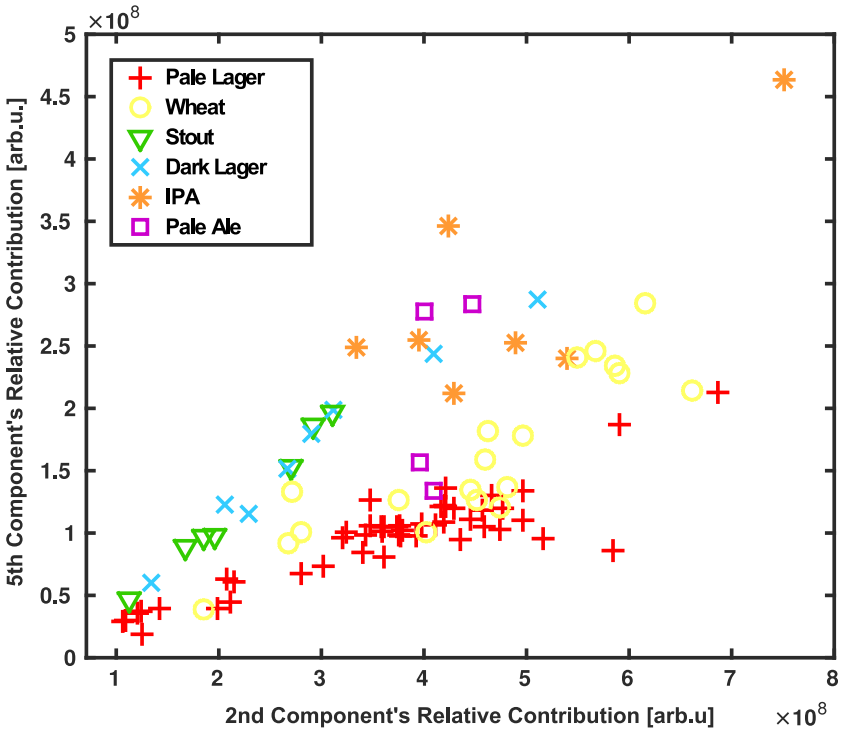

Fig. 3 PARAFAC score plot

Summary and Conclusion

Fluorescence of beer mainly comes from aromatic amino acids (tryptophan, tyrosine, and phenylalanine), different forms of vitamin B, and phenolic compounds. Emissions are notable in two spectral regions: from 300 nm to 475 nm (when beer is with 255–300 nm radiation) and from 350 nm to 600 nm (for 300–475 nm excitations). Excitation-emission spectra of beer are well-described by the 5-component PARAFAC model which accounts for 99.44% variance in fluorescence of 111 beer samples from this study samples (51 samples of Pale lager, 21 Wheat beer, 12 Stout, 9 Dark lager, 10 Pale Ale, and 8 India Pale Ale (IPA)). Using this model, it is possible to completely decompose beer EEMs into well-resolved excitation and emission spectra of dominant fluorescent components in beer, as well as to calculate and compare their relative concentrations. Finally, this model provides the reduced data suitable for further characterization of beer samples using standard tools of chemometry. Future work may be focused on the applications of beer fluorescence, alone or in combination with standard analytical methods, for the authenticity of beer production origin, control of the beer characteristics, or the like.

Table 4 Calibrated and cross-validated classification errors of the PLS-DA model

	Calibrated Error [%]	Cross-validated Error [%]
Pale Lager	12.1	12.1
Wheat	14.01	16.2
Stout	12.7	12.7
Dark Lager	20.7	21.3
Pale Ale	22	22
IPA	12.1	12.1

Acknowledgments Authors acknowledge the financial support of the Ministry of Education, Science and Technological Development of the Republic of Serbia (Project No: 45020).

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