

Near-infrared spectroscopy for rapid classification of fruit spirits

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Revised: 14 March 2016 / Accepted: 17 May 2016 / Published online: 28 May 2016
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Abstract Multivariate analysis combined with near-infrared (NIR) spectral analysis was evaluated to classify fruit spirits. A total of 67 fruit spirits (12 apple, 18 apricot, 19 pear and 18 plum spirits) were analyzed. NIR spectra were collected in the wavenumber range of 4000–10,000 cm^{-1} . Linear discriminant analysis based on principal component analysis (PCA-LDA) and general discriminant analysis (GDA) based directly on NIR spectral data were used to classify the samples. The prediction performance of models in different wavenumber ranges was also investigated. The best PCA-LDA and GDA models gave a 100 % classification of spirits of the four fruit kinds in the wavenumber range from 5500 to 6050 cm^{-1} corresponding to either the C–H stretch of the first overtones of CH_3 and CH_2 groups, or to compounds containing O–H aromatic groups. The results demonstrated that NIR spectroscopy could be used as a rapid method for classification of fruit spirits.

Keywords Beverages · Fruit spirits · Near infrared spectroscopy · Multivariate analysis

Introduction

Fruit spirits are made of different varieties of fruits by the alcoholic fermentation and distillation of fleshy fruits or must of such fruits, with or without stones. According to EU regulation, the distillation of fruit spirit must occur at less than 86 vol%, so that the spirit retains an aroma and taste of the fruit from which it is derived [Regulation (EC) No. 110/2008; European Union (EC) 2008]. The physico-chemical and sensory qualities of fruit spirits depend on the nature and quality of the raw materials, fermentation, distillation and aging (Le Dauphin et al. 2003). The components of freshly distilled spirits, including (apart from water and ethanol) methanol, higher alcohols, aldehydes, esters, organic acids and volatile phenols, are generally similar (Buglass 2011). However, a more detailed description reveals that the internal qualities of fruit spirits are different due to different varieties of fruits (Capobiango et al. 2013; Winterová et al. 2008). Aging in wooden casks alters the chemical composition of fruit spirits, due to extraction of wood tannins, and hydrolysis of lignin followed by oxidation of benzoic and cinnamic aldehydes to aromatic acids (Rusu et al. 2011; Tešević et al. 2005). The gas chromatographic determination of volatile constituents and the determination of $^{13}\text{C}/^{12}\text{C}$ isotope ratios by isotope ratio mass spectrometry (IRMS) analysis as well as $(\text{D}/\text{H})_{\text{I}}$ and $(\text{D}/\text{H})_{\text{II}}$ ratios by site-specific natural isotope fractionation nuclear magnetic resonance (SNIF–NMR) analysis are powerful analytical tools which can be used for checking the authenticity of fruit spirits and for detecting their adulteration (Bauer-Christoph et al. 1997; Winterová et al. 2008). However, the methods are relatively expensive, time-consuming and require highly skilled operators. Therefore, it was necessary to develop a new and fast method for the variety discrimination of fruit spirits.

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Near-infrared (NIR) spectroscopy has proved to be one of the most efficient and advanced tools for monitoring of process and product quality in food industry (Alander et al. 2013; Pontes et al. 2006; Huang et al. 2008). The method was applied for the determination of the most important parameters such as alcoholic strength in wine, beer and spirits (Lachenmeier et al. 2010), total acid content and soluble salt-free solids in Chinese vinegars (Chen et al. 2012), alcoholic strength, density, and total dry extract in spirits and liqueurs (Arzberger and Lachenmeier 2008), or ethyl carbamate in stone-fruit spirits (Lachenmeier 2005). Associated with the chemometric methods, NIR has been used for discrimination of fruit vinegars (Liu et al. 2008) or Chinese liquors (Li et al. 2014). Fourier transform infrared spectroscopy was useful to distinguish spirits distilled from *Prunus avium* L. (cherry) and spirit distilled from *Prunus domestica* L., however, a differentiation between the sub-species *domestica* (plum) and *syriaca* (mirabelle) was not possible (Lachenmeier 2007).

The aim of this study was to investigate the capability of using NIR spectroscopy combined with multivariate analysis to provide a rapid screening tool for discriminating between different fruit (apple, apricot, pear and plum) spirits. Specific objectives were to discriminate the fruit spirits using the selected spectral regions, to find the spectral region that is most useful for the discrimination of the fruit spirits, and to compare the results of linear discriminant analysis (LDA) with those obtained using general discriminant analysis (GDA).

Materials and methods

Samples

A total of 67 (Slovak, Czech, Polish, Hungarian and French) fruit spirits produced during 2011–2013, representing four different fruits (apple, apricot, pear and plum) were analyzed. 8 authentic Slovak fruit spirits (two samples of each type of fruit spirit) were included in the study. The company that supplied the samples provided the water, ethanol and methanol content of each sample and an indication of the authenticity of the samples. Other fruit spirits were commercially obtainable in local markets. 44 samples (8 apple, 12 apricot, 12 pear and 12 plum spirits) were selected randomly for the calibration set, and 23 samples (4 apple, 6 apricot, 7 pear and 6 plum spirits) for the prediction set. The alcoholic degree ranged within 35–42 % ethanol. The samples were stored in the dark at room temperature.

NIR spectroscopy

NIR absorption measurements were carried out using a spectrophotometer (NICOLET 8700™, Thermo Scientific, USA) equipped with a quartz cell with an optical path of 1 mm. NIR spectra were collected by data acquisition software (OMNIC 8.1., Thermo Electron Corp., Madison, WI, USA) and saved in absorbance format. NIR spectra were obtained between 4000 and 10,000 cm^{-1} with a 4- cm^{-1} resolution. The spectrum of each sample was the average of 50 successive scans. The spectral range between 4000 and 7500 cm^{-1} was used to create the multivariate models. Standard normal variate (SNV) and smoothing were used as spectral data preprocessing methods (Xu et al. 2008).

Multivariate analysis

Data were processed with the Microsoft Office Excel 2010 software, STATISTICA version 7.0 (StatSoft, USA, 2004) and MATLAB Version 7.0 (The MathWorks, Inc., USA, 2005). Whole spectrum (4000–7500 cm^{-1}) and also four spectral intervals (7500–6050, 6050–5500, 5500–4500 and 4500–4000 cm^{-1}) were used in the multivariate analysis.

To achieve a reliable differentiation between different fruit spirit types, unsupervised and supervised pattern recognition procedures were applied to the data sets. Principal component analysis (PCA) was used as unsupervised method to visualize the data trends. LDA and GDA were applied as supervised learning method to find classification rules.

PCA is a method that aims to recognize patterns in multivariate data sets or to reduce the dimensionality of a data set by forming linear combinations of original variables called principal components (PCs). Classification of objects using PCA is done by constructing two- or three-dimensional plots, using PCs chosen by the researcher. The number of principal components was based on the eigenvalue criterion and the total variance explained (Kozak and Scaman 2008).

LDA is concerned with determining the so-called discriminant functions as linear combinations of the descriptors which best separate the classes according to minimization of the ratio of within class and between-class sum of squares. Although LDA usually gives a good discrimination performance, it suffers from some deficiencies if variables are highly correlated or class boundaries are complex or non-linear. To avoid such deficiencies, variables are often transformed by correlation-reducing methods such as PCA (Li and Yang 2012). In this study, the first few PCs were used by LDA, for developing discrimination models.

GDA applies a general multivariate linear model to the discriminant function analysis problem. The discrimination is determined not only by the most significant wavenumbers but also by all the spectra. A selection of the discriminant bands was performed using the forward stepwise method (P inclusion 0.05 and P exclusion 0.05). This selection procedure is based on the evaluation of equal mean values between the sets hypothesis for each variable candidate to be discriminatory. The selected variables were those with a significant ($P < 0.05$) F value (Longobardi et al. 2012).

Results and discussion

NIR spectra

Figure 1 shows the representative NIR spectra of apple, apricot, pear, and plum spirit samples. All samples had similar spectra; however, there were differences in the intensity of some peaks depending on the sample. These differences were observed mainly for peaks around 6877, 4339 and 4413 cm^{-1} . The spirits with different water content had different absorption values around 6877 cm^{-1} . Absorption band around 6877 cm^{-1} is related to the first overtone of the OH stretch and a combination of stretch and deformation of the OH group (especially water) (Chen et al. 2012; Pontes et al. 2006; Shen et al. 2012; Yu et al. 2007). The sequence for the absorbance intensity in the range from 4310 to 4440 cm^{-1} was in accordance with that of alcohol content (Shen et al. 2012). The absorption band around 4413 cm^{-1} is related to CH combinations and OH stretch overtones (Shen et al. 2012; Yu et al. 2007), and that around 4339 cm^{-1} is related to CH overtones of ethanol and sugars (Büning-Pfaue 2003; Damberg et al.

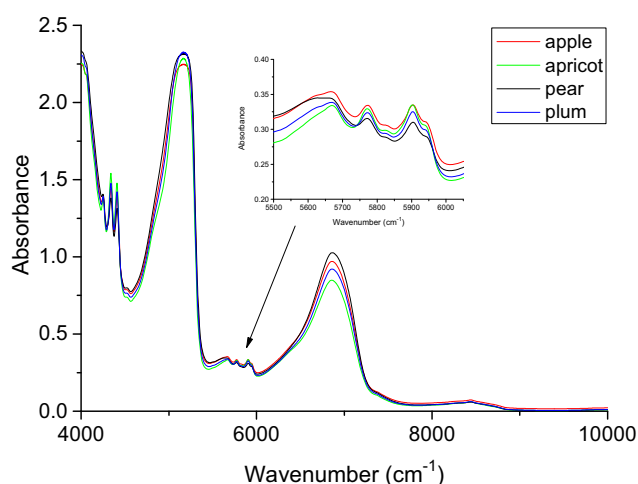


Fig. 1 Representative near-infrared spectra of fruit spirits

2002; Niu et al. 2008; Wang et al. 2012). Absorption band around 4248 cm^{-1} may be caused by the CH group of ethanol (Yano et al. 1997), and that around 4523 cm^{-1} is related to aromatic CH and $-\text{C}=\text{CH}$ (Cen and He 2007). Strong absorption band observed around 5171 cm^{-1} is related to a combination of stretch and deformation of the OH group in water and ethanol (Chen et al. 2012; Shen et al. 2012; Yu et al. 2007). The region from 5600 to 5950 cm^{-1} may correspond to either the CH stretch of the first overtones of CH_3 and CH_2 groups (Cozzolino et al. 2004; Li et al. 2014), or to compounds containing OH aromatic groups (Cen and He 2007). The region from 8300 to 8600 cm^{-1} corresponds to the third overtone band of the bond CH (Gaydou et al. 2011). In the vicinity of 8620 cm^{-1} , carbonilic and aromatic compounds usually exhibits its second overtone absorption (Pontes et al. 2006).

PCA

PCA was applied separately to the whole spectra (4000–7500 cm^{-1}) and four spectral intervals (7500–6050, 6050–5500, 5500–4500 and 4500–4000 cm^{-1}). The loadings for the first three PCs are shown in Table 1. Figure 2 shows the score plots of the first three PCs. Each plot describes the 99.8, 99.8, 99.8, 99.8 and 99.6 %, respectively, of the total variance of the 7500–4000, 7500–6050, 6050–5500, 5500–4500 and 4500–4000 cm^{-1} spectral intervals of the fruit spirits analyzed. In general, the PCA score plots indicate that it was not possible to discriminate between the different fruit spirits regardless of spectral interval used. The best classification was achieved using spectral interval 5500–6050 cm^{-1} . The highest loadings in PC1 were observed around 5672 and 5771 cm^{-1} related to CO stretch associated with aldehydes, carboxylic acids and esters (Bevin et al. 2008). Additional loading observed around 5903 cm^{-1} can be attributed to the methyl group. It is probably the first overtone of the asymmetric stretch of the methyl group (Workman and Weyer 2012). The highest loading in PC2 was observed around 5585 cm^{-1} , associated with sucrose, fructose, and glucose (Yu et al. 2007). The highest loadings in PC3 were observed around 5690, 5917 and 5958 cm^{-1} , related to CH_2 , CH stretch first overtones in glucose (Martelo-Vidal et al. 2013), the second CH stretching overtone and combination bands of CH from aromatic groups (Pontes et al. 2006) and carbonyl group in aromatic aldehydes (Powers et al. 1960), respectively.

LDA

LDA of the PC scores was used to improve discrimination between groups that were difficult to separate using PCA. LDA was carried out using the score values of the first PCs

Table 1 The highest loadings for the first three PCs using different spectral ranges

PC	Wavenumber range (cm^{-1})				
	7500–4000	7500–6050	6050–5500	5500–4500	4500–4000
1	4253, 4338, 4408, 5172	6808	5672, 5771, 5903	5168	4288, 4374
2	4975, 5281, 6900	7027	5585	4985, 5281	4187
3	5056, 5252	6771	5690, 5917, 5958	5042, 5252	4294, 4378

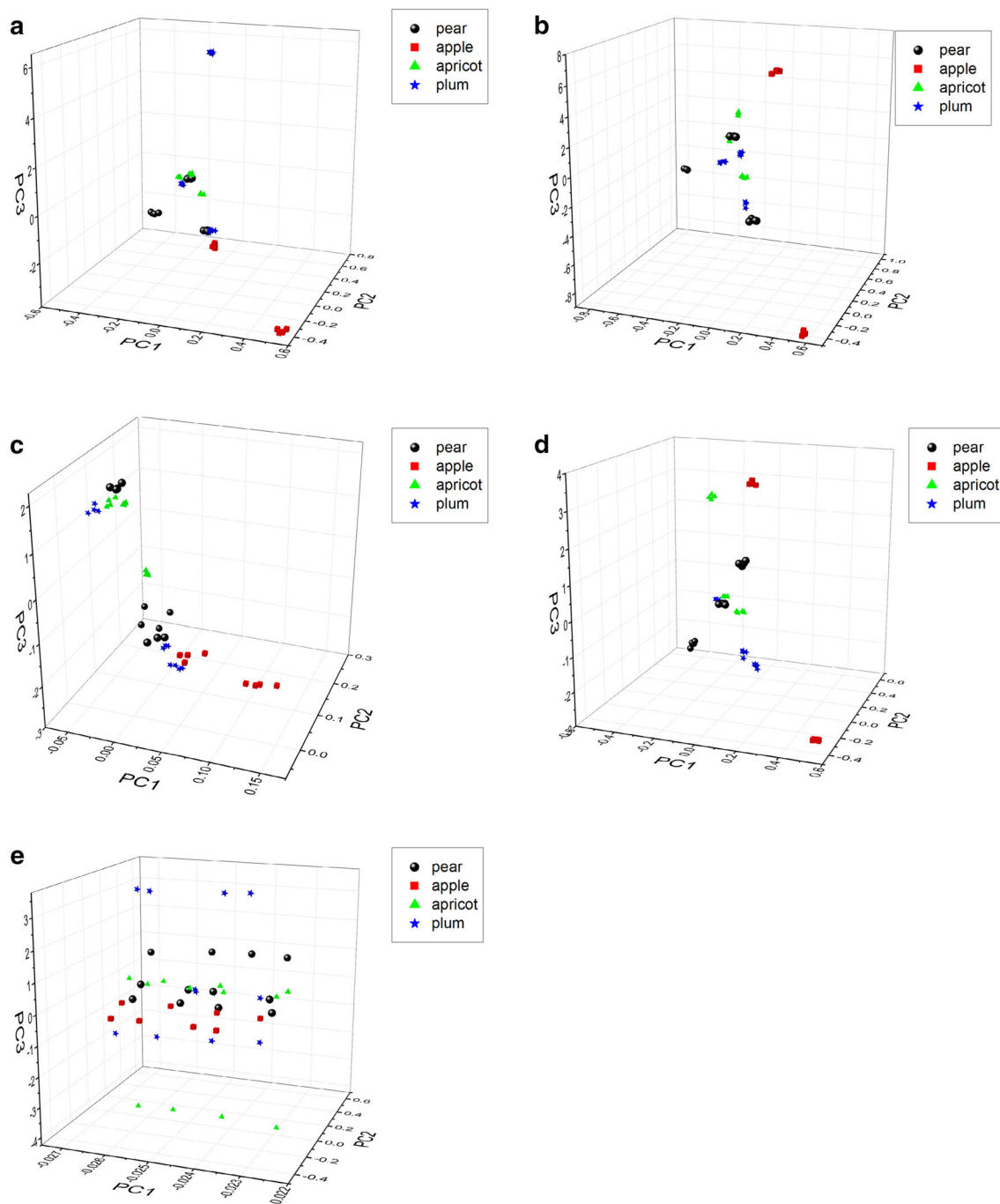
**Fig. 2** Principal component analysis score plot for spectral intervals: 7500–4000 cm^{-1} (a), 7500–6050 cm^{-1} (b), 6050–5500 cm^{-1} (c), 5500–4500 cm^{-1} (d) and 4500–4000 cm^{-1} (e)

Table 2 Percentage of correct LDA classification using different spectral ranges

Sample	Set	Number of samples	Wavenumber range (cm ⁻¹)				
			7500–4000	7500–6050	6050–5500	5500–4500	4500–4000
Apple	c	8	100	100	100	100	100
	p	4	100	100	100	100	100
Apricot	c	12	100	100	100	100	66
	p	6	83	100	100	83	66
Pear	c	12	100	66	100	100	100
	p	7	100	71	100	100	100
Plum	c	12	100	100	100	100	66
	p	6	100	100	100	100	50
Total	c	44	100	91	100	100	82
	p	23	96	91	100	96	78

c calibration set, *p* prediction set

Table 3 Percentage of correct GDA classification using different spectral zones

Sample	Set	Number of samples	Wavenumber range (cm ⁻¹)				
			7500–4000	7500–6050	6050–5500	5500–4500	4500–4000
Apple	c	8	100	100	100	100	100
	p	4	100	100	100	100	100
Apricot	c	12	100	100	100	100	75
	p	6	100	100	100	83	66
Pear	c	12	100	83	100	100	100
	p	7	100	86	100	100	100
Plum	c	12	100	100	100	100	66
	p	6	100	100	100	100	50
Total	c	44	100	95	100	100	84
	p	23	100	96	100	96	78

c calibration set, *p* prediction set

that gave more than 99.9 % explained variation and the highest level of classification in the LDA. The inclusion of more PCs (from three up to seven) when LDA models were developed improved the classification results. Regarding the whole spectra (4000–7500 cm⁻¹), the discrimination of the fruit spirits required seven PCs to achieve 100 % of correct classification (Table 2) in the calibration set. In the prediction step, only one apricot spirit sample was classified as plum spirit. Thus total 96 % of correct classification was achieved. Performing LDA on six PCs of spectral interval 7500–6050 cm⁻¹ the results become worst. Some of the pear spirits were classified as belonging to apricot group and total 91 % of correct classification was obtained. Regarding spectral interval 6050–5500 cm⁻¹ and seven PCs, 100 % correct classification was observed for apple, apricot, pear and plum spirit samples in both the calibration and prediction sets. Regarding spectral interval 5500–4500 cm⁻¹ and seven PCs, 100 % correct classification was observed for apple, apricot, pear and plum spirit

samples in the calibration set. In the prediction step, one apricot spirit sample was classified as plum spirit and total 96 % of correct classification was obtained using seven PCs. Considering the LDA applied to the first six PCs of the PCA performed on the spectral interval 4500–4000 cm⁻¹, apple, apricot, pear and plum spirit samples achieved 100, 66, 100 and 50 % of correct classification in the prediction step.

GDA

As the LDA classification based on PCs was unsatisfactory, with exception of PCs of the PCA performed on the spectral interval 6050–5500 cm⁻¹, we chose to discriminate the samples using GDA based directly on five NIR spectral intervals indicated above. In this case 100 % correct classification was observed for apple, apricot, pear and plum spirit samples using spectral intervals 7500–4000 and 6050–5500 cm⁻¹ (Table 3). In general, GDA gave a

better predictive performance compared to LDA in all spectral intervals, with the exception of 5500–4500 cm^{-1} .

Conclusion

Visual inspection of NIR spectra of fruit spirits did not show that they fall naturally into a number of groups. In order to extract information from the data set and to assess the potential of NIR to classify fruit spirit according to type, firstly, PCA was applied to the five data sets corresponding to the five spectral regions (7500–4000, 7500–6050, 6050–5500, 5500–4500 and 4500–4000 cm^{-1}). The plots of the scores for PC1 versus PC2 versus PC3 did not reveal any obvious spatial pattern in the sample score distribution. Next, LDA was applied to the PCs of PCA performed on the five data sets mentioned above to improve discrimination between groups that were difficult to separate using PCA. The best PCA-LDA model giving a 100 % classification of spirits of the four fruit kinds was based on seven PCs of spectral interval of 6050–5500 cm^{-1} . The prediction performance of GDA models in five spectral regions (7500–4000, 7500–6050, 6050–5500, 5500–4500 and 4500–4000 cm^{-1}) was also investigated and similarly to PCA-LDA, the best GDA model leading to a 100 % classification of spirits was based on wavenumber range of 6050–5500 cm^{-1} . This study proved that the combination of NIR spectroscopy with multivariate statistical methods can be applied as a rapid, inexpensive, and reliable tool to classify commercially apple, apricot, pear, and plum spirits.

Acknowledgments This research was supported by the Scientific Grant Agency of the Ministry of Education of Slovak Republic and the Slovak Academy of Sciences VEGA No 1/0499/14.

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