Classification of wine varieties using multivariate analysis of data obtained by gas chromatography with microcolumn extraction

DÁŠA KRUŽLICOVÁ – JÁN MOCÁK – JÁN HRIVŇÁK

Summary

Seventy-two wine samples of six varieties originating from the Small Carpathian region, Slovakia and produced in Western Slovakia in 2003 were quantitatively analysed by gas chromatography (GC) using headspace solid-phase microcolumn extraction. Wine aroma compounds were extracted from the headspace into a microcolumn; the microcolumn was then transferred into a modified GC injection port for thermal desorption and the released compounds were analysed. This combination was simple, rapid and suitable for characterization of wine aroma compounds without the use of a complicated sample preparation procedure. Areas of chromatographic peaks of the same retention time corresponding to the selected 65 volatile aroma compounds were used for grouping of varietal wines. Wines were characterized by a set of identified compounds with corresponding relative abundances. The relative standard deviation of 5 peak area measurements varied between 1.0% and 8.4%, the median of all observed relative standard deviation values was 2.4%. Using a new chemometrical approach, a complete chromatographic peak assignment was not necessary and only the peak pattern was utilized. The best classification performance exhibited linear discriminant analysis, the K-th nearest neighbour method and logistic regression, by which more than 95% correct classifications were obtained. Principal component analysis, cluster analysis and artificial neural networks provided complementary information.

Keywords

wine; volatile compounds; solid-phase microcolumn extraction; thermal desorption; headspace; capillary gas chromatography

Gas chromatographic (GC) analysis of volatile compounds present in wine is a very important tool for wine classification, quality control or for understanding sensory properties of wine. A complete analysis of wine aroma is, however, complex and expensive, due to the great number of compounds present (alcohols, esters, organic acids, aldehydes, ketones and monoterpenes), which have different polarities, volatilities and are found in a wide concentration range. Therefore, sample preparation, in particular extraction and pre-concentration of aroma compounds, remains a critical step in the analysis of aroma volatiles.

Sample preparation methods are based on liquid-gas extraction, such as purge and trap (P&T), liquid-liquid extraction (LLE), solid-phase extraction (SPE), solid phase microextraction (SPME) or stir bar sorptive extraction (SBSE). At present, the systems based on liquid-gas-solid equilibrium are widely utilized [1-8].

In the recent time, several papers utilizing various chemometrical tools were published [9-12]. Chemometrical data processing was implemented also in the present work, which is based on a simple and inexpensive method for pre-concentration of the wine aroma compounds using headspace solid-phase microcolumn extraction (SPMCE) followed by desorption in the GC injection port [13]. The used variant of SPME was succesfuly applied to different analytes in four papers [14-17] where further details are described.

MATERIALS AND METHODS

Instrumentation

Analyses were carried out on a GC 8000 Top Series, CE Instruments (Rodano-Milan, Italy) equipped with a modified split-splitless inlet and flame ionization detector. The inlet was modified

Dáša Kružlicová, Institute of Analytical Chemistry, Slovak University of Technology, Radlinského 9, SK – 812 37 Bratislava, Slovakia.
Ján Mocák, Department of Chemistry, University of Ss. Cyril and Methodius, nám. J. Herdu 2, SK – 917 01 Trnava, Slovakia.
Ján Hrivňák, Research Institute of Oenology and Viticulture, Matúškova 25, SK – 831 01 Bratislava, Slovakia.

Correspondence author:
Ján Mocák, Institute of Analytical Chemistry, Slovak University of Technology, Radlinského 9, SK – 812 37 Bratislava, Slovakia.
e-mail: jan.mocak@stuba.sk

so that it was possible to insert a glass microcolumn. The microcolumn (1 mm i.d.) was packed with 5.0 mg of 60–80 mesh Tenax TA (Alltech, Deerfield, Illinois, USA). The outlet of the microcolumn afforded a tight connection with the capillary column. The fused silica capillary column Omegawax 250, 30 m × 0.25 mm × 0.25 μm film thickness (Supelco, Bellefonte, Pennsylvania, USA) was used. The GC inlet and the detector temperatures were 250 °C and the initial column temperature was maintained at 25 °C. Thermal desorption was performed at a pressure of 10 kPa for 5 min, then the pressure was increased to 50 kPa and the column temperature was programmed at a rate of 4 °C.min^{-1} up to 210 °C and maintained at 210 °C for 10 min. Helium was used as the carrier gas.

Analytical procedure

A volume of 500 ml of the wine sample was transferred into a 1000 ml volumetric flask and the flask was vigorously shaken for 5 min at ambient temperature. Immediately after shaking, an appropriate volume of headspace was taken through the microcolumn using a glass syringe with a glass plunger lauer (Poulten and Graf, Wertheim, Germany). The distance between the microcolumn and the surface of the liquid was about 1 cm. The loaded microcolumn, with the volatile compounds sorbed, was transferred into the GC inlet at 10 kPa carrier gas pressure and the compounds desorbed were analysed as described earlier. Analysis of each wine sample was repeated twice. A computer program Class-VP 7.2, SP1 (Shimadzu, Columbia, Maryland, USA) was used for data acquisition.

Chemometrical processing

Seventy-two wine samples from the Small Carpathian region, Slovakia produced in 2003 by known producers in Western Slovakia were quantitatively analysed by gas chromatography. Six wine varieties, namely Frankovka Blue (11 samples, code FM), Chardonnay (12 samples, code Ch), Müller Thurgau (16 samples, code MT), Welsch Riesling (9 samples, code RV), Sauvignon (7 samples, code Sv) and Grüner Veltliner (17 samples, code VZ) were studied. The sample numbering was made in the mentioned order so that the samples No. 1–11 denote FM, No. 12–23 denote Ch, No. 24–39 denote MT, No. 40–48 denote RV, No. 49–55 denote Sv, and No. 56–72 denote VZ. For instance, the third Chardonnay sample is No. 14. The same chromatographic peaks of 65 aroma compounds, characterized by the same retention time under identical separation conditions, were evaluated for all wine samples.

Quantitative analysis was made according to the integrated peak area determined for all 65 selected values of retention time in the time range 3.2–42.0 min. It is important to note that the retention time order for the selected compounds was the same in all samples and the way of chromatographic signal evaluation was identical. The obtained final data matrix contained 72 rows and 65 columns (4 680 data altogether).

Even though assignment of some chromatographic peaks was made, it should be stressed that identification of the compounds corresponding to the peaks was not needed for chemometric analysis of the final data matrix, which made the experimental work as well as its assessment more simple.
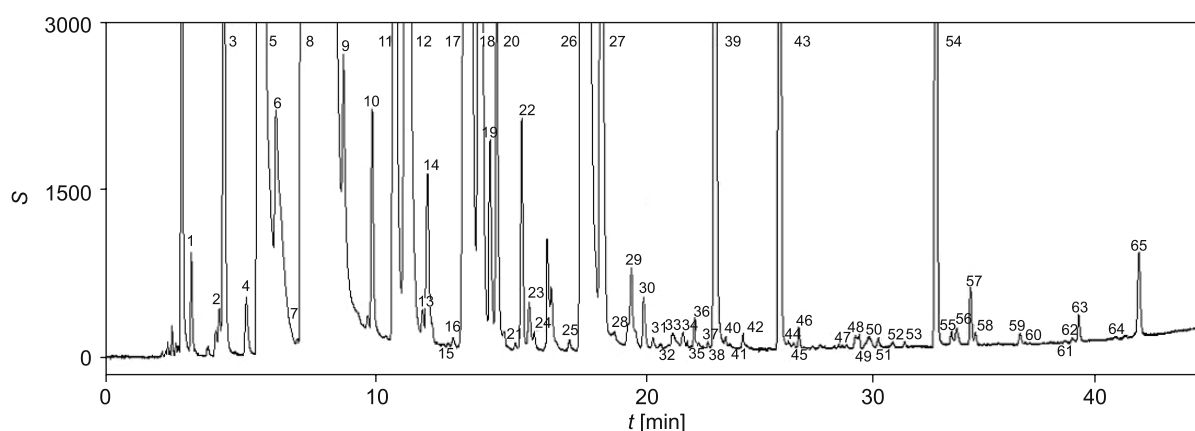

Fig. 1. Chromatogram of wine aroma compounds.
Red wine Frankovka Blue. 4.0 ml headspace on 5.0 mg Tenax TA. Selected 65 peaks, observed at the same retention time for all wine samples and indicated in the picture, were used for chemometrical processing.

It is worth mentioning that the peak selection was made in the way to respect at maximum the purity of the peaks even though some eventual co-elution might happen; the results described in further text testify legitimacy of the used approach.

Primary data processing included data transformation, descriptive and robust statistical treatment as well as correlation analysis, performed mainly by MS Excel (Microsoft Corporation, Redmond, Washington, USA). Multivariate data analysis, namely analysis of principal components (PCA), cluster analysis (CA), linear and quadratic discriminant analysis (LDA/QDA), K-th nearest neighbour method (KNN), logistic regression (LR) and artificial neural networks (ANN), were carried out using commercial software packages SPSS ver. 15 (SPSS, Chicago, Illinois, USA), SAS ver. 9.1.3 and SAS JMP ver. 6.0.2 (SAS Institute, Cary, North Carolina, USA), and Statgraphics Plus, ver. 5.1. (StatPoint, Herndon, Virginia, USA).

RESULTS AND DISCUSSION

Chromatographic analysis of wine samples

Fig. 1 shows a typical chromatogram of wine aroma compounds (red wine Frankovka Blue of Slovak origin) with 4.0 ml of headspace used. Sixty-five chromatographic peaks observed at the same retention time for all wine samples were utilized for chemometrical processing. Nineteen of these peaks were identified by mass spectra using Shimadzu GC-MS QP 2010 and using the software library provided with the instrument. Some of the peaks were also identified by analysing mixtures of pure compounds. Even though the assignment of nineteen peaks was completed, it was not needed for chemometrical data processing, in which only the constant peak order was important for recognizing the chromatographic pattern of individual varietal wine samples.

Repeatability of the area measurement of the mentioned nineteen peaks for Müller Thurgau wine samples, expressed by the corresponding relative standard deviation (RSD), are shown in Tab. 1. The RSD values of five repetitive measurements of the peak area varied between 1.0% and 8.4%, the median of all observed RSD values was 2.4%.

Wine characterization
by principal component analysis

Natural grouping of varietal wines in the space of the most important principal components (PC) can be illustrated by PCA. Data of all selected 65 peak areas as well as the areas of the optimized

Tab. 1. Repeatability of the measured peak area using SPMCE-GC technique for Müller Thurgau wine samples expressed as the relative standard deviation (RSD).

Peak	Identified compound	Mean	RSD [%]
1	acetaldehyde	69	7.03
2	acetone	330	3.31
3	methylacetate	1 104	5.04
5	ethylacetate	172 526	1.48
10	*i*-buthylacetate	826	1.62
11	2-butanol	2 473	1.39
12	propanol	7 011	1.25
14	buthylacetate	215	3.03
17	*i*-butanol	39 473	2.02
20	*i*-amylacetate	11 953	2.41
21	butanol	504	1.04
22	amylacetate	2 303	2.40
26	*i*-pentanol	219 472	2.01
27	ethylhexanoate	8 616	1.77
39	hexanol	1 985	4.35
43	ethyloctanoate	16 847	3.56
50	linalool	744	3.14
54	ethyldecanoate	3 226	6.74
65	2-phenylethanol	201	8.42

Mean values represent five times repeated measurements of the peak area of 19 identified chromatographic peaks. Only three figures are significant with regard to the measurement error.

30 best peaks were used for this purpose. The choice of the best peaks was made by the stepwise selection method applicable under discriminant analysis and, in this way, two series of the PCA results were obtained. Thus, a large number of original chromatographic peaks could be reduced to a small number of PC, which, in contrast to the original variables, were independent and uncorrelated.

Total information contents of the given number of PC is expressed by cumulative percent (cum. %) value of the total variance. For instance, when using all 65 variables, the first two PC represented 39.9 cum. %, whereas five and eight PC represented 61 and 72 cum. %, respectively. The eigenvalues of the first 13 PC (82.1 cum. %) were larger than 1, which indicated their significance.

Fig. 2 shows the most important PCA graph, PC2 vs. PC1, where the natural grouping of the studied 72 wine samples is demonstrated. Wine varieties Frankovka Blue and Sauvignon are separated from other varieties and are characterized by large PC1 values. Chardonnay sample No. 14, localized at large PC1 value (approximately +1.6), is an outlier. Some Müller Thurgau samples had different PC2 values compared to other samples of this variety. Compared to other varieties, large
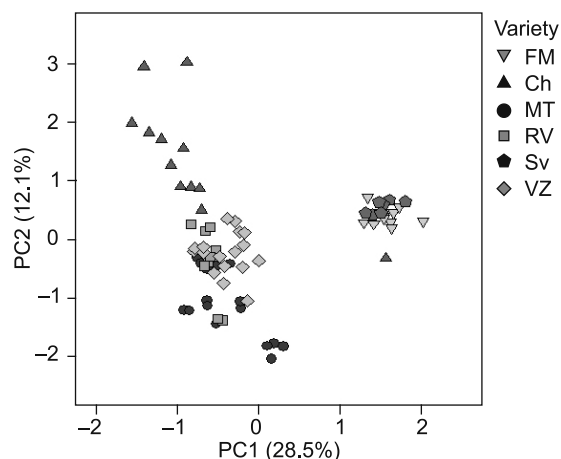
Fig. 2. Principal component analysis of 72 varietal wines of the Small Carpathian origin, scatterplot of PC2 vs. PC1 dependence. Chardonnay sample No. 14, localized at large PC1 value (approximately +1.6), is an outlier. All 65 original variables were used.
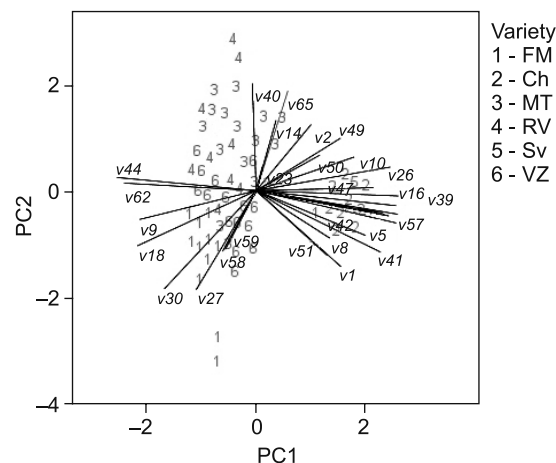

Fig. 3. The PCA biplot for 72 wine samples of six varieties of the Small Carpathian origin and the selected 30 best variables, selected using a stepwise method applicable in LDA, denoted by the variable symbol *v* and the corresponding number.

PC3 values were characteristic for the Chardonnay samples whilst for the Müller Thurgau samples, relatively low PC3 values were typical. Two wine varieties could be separated by the PC4 values, since Sauvignon wines were localized at lower and Frankovka Blue wines at higher PC4 values.

Fig. 3 shows a PCA biplot where the objects, varietal wines as well as the variables, chromatographic peak areas (ordered in the increasing retention time), are simultaneously depicted. It is apparent that the Chardonnay samples (2) and the Sauvignon samples (5) were characterized by large values of the variables *v*39 (area of peak 39), *v*16, *v*57, *v*5, *v*26, *v*56, *v*12, *v*41, *v*47, and *v*42, oriented towards positive PC1 values. In contrast, large values of the variables *v*44, *v*62, *v*18, and *v*9

were typical for other varieties, localized at negative PC1 values. With regard to PC2, the variables *v*40, *v*65, *v*14, *v*2, *v*49 and *v*41 as well as the Welsch Riesling and Müller Thurgau varietal wines were at more positive values whilst more negative PC2 values were typical for the variables *v*27, *v*30, *v*1 and *v*51 as well as Frankovka Blue (1) and Grüner Veltliner (6) varietal wines. These observations express the most important correlation of the individual peaks and the wine varieties. Due to a better recognition, the best 30 peaks were used instead of the complete 65-peak set.

Qualitative wine classification by cluster analysis

Natural grouping of varietal wine samples (the objects, in general) or the chromatographic peak
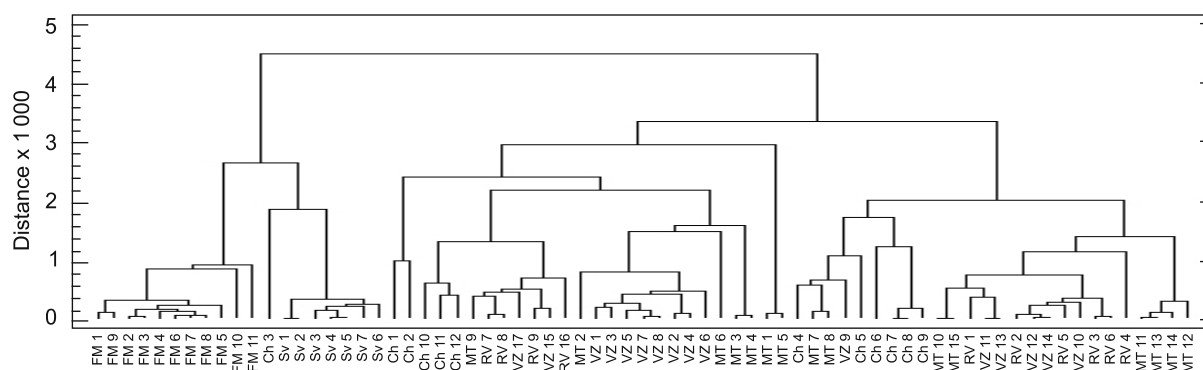

Fig. 4. Cluster analysis of 72 varietal wine samples by Ward clustering technique using squared Euclidean distances.
Samples are denoted by the variety symbol and the corresponding number.

areas (generally the utilized variables) may be visualized also by cluster analysis. Fig. 4 shows a dendrogram using the squared Euclidean distance and Ward clustering technique. Wine samples form the clusters following more or less the separation by wine varieties. Almost unambiguously separated are the red wine samples (Frankovka Blue) and the Sauvignon samples. Remaining four varieties are rather mixed up. Anyway, it should be stressed that neither cluster analysis nor the principal component analysis are used as the tools for the object or variables discrimination. Discrimination among the object categories is the aim of classification techniques discussed in further text.

Quantitative wine classification by linear discriminant analysis

The goal of the group of the discriminant analysis techniques, mainly the linear discriminant analysis (LDA) and quadratic discriminant analysis (QDA), is to achieve maximal discrimination among the object categories. Their first task is to create a discriminant model, which is formed by an appropriate combination of original variables. Then an object, e.g. a wine sample, is categorized either to the original category or, if needed, it is relocated into another, more appropriate category. The classification performance of the discriminant analysis is evaluated by comparing the number of correctly categorized objects to the number of all objects, usually in percents.
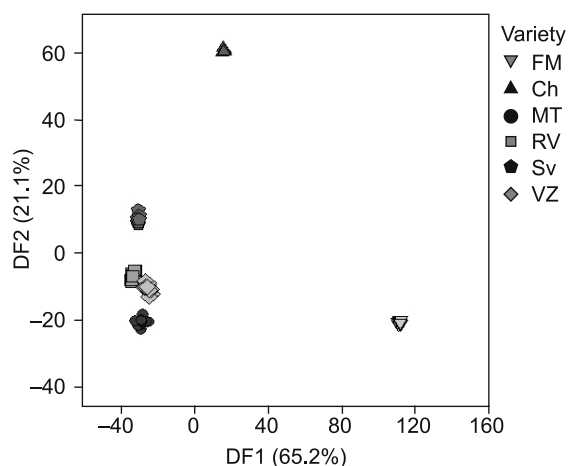

Fig. 5. Discriminant analysis of 72 Small Carpathian wine samples of 6 varieties in the plane DF2 vs. DF1. All 65 variables were employed, which were chromatographic peak areas at the selected retention time. DF1 separates clearly the Frankovka Blue samples with high positive values, and Chardonnay with positive values, from remaining samples with negative values. DF2 distinctively separates the Chardonnay samples with high positive values from other wines.

The most important feature of discriminant analysis is its prediction capability, by which it is possible to classify the objects, not used in the calculation of the discriminant model. It can be used for predicting the categorization of unknown objects and also for validation of the discrimination model by comparing the predicted object categorization with that which is known but unused in the modelling step. The categorization performance in the validation step is usually lower than in modelling. If the number of objects is not sufficiently high for validation, then the leave-one-out method is mostly recommended and applied according to the chemometrical literature. The method uses all objects but one in the modelling step and the remaining object is used for validation. In a stepwise mode, each object is once omitted in modelling and used for validation so that the modelling as well as prediction is evaluated as many times as the number of objects used. Similarly, two objects can be alternately omitted in modelling instead of one in a leave-two-out method or even three objects can be left out in a leave-three-out method, using the same calculation procedure. Since in these cases, the number of calculations increases considerably, not all combinations but just a reasonable number is used.

Fig. 5 illustrates very well separated narrow clusters of the studied six varietal wines in the plane of the first discriminant functions, DF2 vs. DF1. Performance of the LDA classification of 72 wine samples into 6 categories by variety was 100% since all samples were categorized into the supposed classes. The use of further discriminant functions, DF3 and DF4, contributed to additional separation of the wine categories and testified that the wine samples were excellently separated by variety in the four-dimensional hyperspace of the discriminant functions. Utilization of DF5 was not needed since it represented only a very small fraction of the total information (0.2%).

Optimal selection of the best variables

Selection of the best variables in discriminant analysis is based on the F-test and can be performed by three different ways: (1) backward selection, (2) forward selection, and (3) stepwise selection, which is a combination of the previous two ways. Using the third way, 30 variables were chosen, which facilitated the best discrimination among the six considered wine varieties. The classification performance for the samples used in the discriminant model as well as for the leave-one-out validation is illustrated in Fig. 6.

Important LDA characteristics of 72 wine samples of 6 varieties using 30 optimally selected
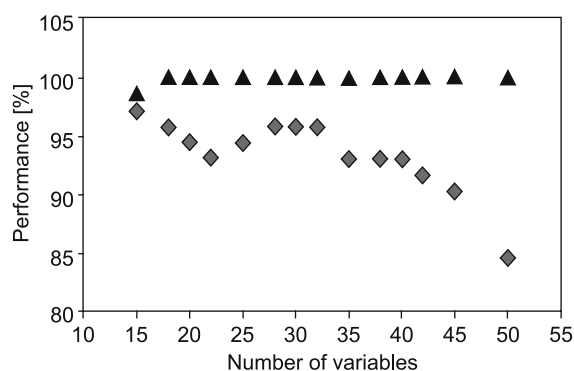
Fig. 6. Optimization of the number of variables with regard to the classification performance when creating the discriminant model (triangles) and using leave-one-out crossvalidation (diamonds).
Thirty best variables are selected as a compromise considering the results of leave-one-out validation, the number of variables and the results of modelling.

variables are summarized in Tab. 2. The p-value, indicating the significance of the discriminant function, was rounded to 3 decimal places; due to very low values (less than 0.0005) they were rounded to zero, which indicates a very high significance.

Considering the categorization by variety and selection of 30 best peaks, the classification performance was evaluated using software packages JMP 6.0.2, SAS 9.1.3 and SPSS 15.0. The results obtained for the classification of the samples used in the discriminant model calculation as well as for the model validation were very similar but not identical. In the model validation, either leave-one-out validation or leave-three-out validation were used. Thus, instead of 72 wine samples, the discriminant model was calculated from 71 or 69 samples, respectively.

When the discriminant model in LDA was calculated by variety, the classification performance using all three mentioned software packages was 100%. In the leave-one-out vali-

dation with JMP 6.0.2 and SPSS 15.0, four samples were incorrectly classified, which made $4/(3 \times 24) \times 100\% = 5.6\%$ and 68 objects (wine samples) were classified correctly, which represented $(72 - 4)/(3 \times 24) \times 100\% = 94.4\%$. Incorrect classification was observed three times when the Müller Thurgau samples were categorized as Welsch Riesling and once when the Welsch Riesling sample was classified as Grüner Veltliner. When using SAS 9.1.3, only three wine samples were misclassified, two times Müller Thurgau as Welsch Riesling and once Welsch Riesling as Grüner Veltliner. So, 69 samples were correctly classifed, which made $(72 - 3)/(3 \times 24) \times 100\% = 95.8\%$. The mentioned results are summarized together with the results of other multidimensional techniques in Tab. 3. When all 65 chromatographic peaks were used (all variables), a very good classification performance was observed in leave-one-out validation by KNN and QDA (100% and 88.9%, respectively) and by ANN in leave-three-out validation (93.1%). On the other hand, other classification results were much worse compared to those with the optimally selected 30 variables.

Application of further classification multivariate techniques

QDA, LR and KNN were also used in this work. Unlike in LDA, an independent covariance matrix is utilized in QDA for each category of objects (e.g. varietal wines). Variety was used as the target categorical variable.

LR is nowadays also considered as a variant of discriminant analysis [18], in which logit is used as the dependent variable. It is expressed by the logarithm of the probabilities ratio where the numerator corresponds to the selected category and the denominator to the complementary category. Since six wine varieties were used as the categories, multinomial variant of logistic regression was utilized with Müller Thurgau variety as the referential category.

Tab. 2. LDA characteristics of 72 Small Carpathian wines of 6 varieties using 30 best variables.

DF	λ	% Variance	Cumul. %	Wilks λ	χ^2	df	p
1	249.4	63.6	63.6	0.000	919.145	150	0.000
2	99.1	25.3	88.8	0.000	626.418	116	0.000
3	30.7	7.8	96.6	0.001	382.267	84	0.000
4	10.4	2.7	99.3	0.023	199.111	54	0.000
5	2.7	0.7	100.0	0.267	69.952	26	0.000

DF - discriminant function, λ - eigenvalue, *df* - the number of degrees of freedom, *p* - probability of rejecting the hypothesis claiming insignificance of the *DF* (rounded to three decimal figures). Cumul. % is obtained by stepwise addition of percents corresponding to the given *DF* to the previous cumulative % value. Wilks λ and χ^2 are statistical quantities characterizing the importance of the calculated new variables; the most important ones have a low Wilks λ value and a high χ^2 value.

Tab. 3. Results of classification using various multivariate methods and 30 optimally selected chromatographic peaks, classification by six varieties.

Method	Classification performance	Leave-one-out validation			Leave-three-out validation		
		SPSS	SAS	JMP	SPSS	SAS	JMP
ANN	Correct/total	–	–	–	–	–	68/72
	% of correct classifications	–	–	–	–	–	94.4
KNN	Correct/total	–	72/72	–	–	67/72	–
	% of correct classifications	–	100.0	–	–	93.1	–
LDA	Correct/total	69/72	69/72	–	68/72	69/72	68/72
	% of correct classifications	95.8	95.8	–	94.4	95.8	94.4
QDA	Correct/total	–	66/72	–	66/72	65/72	–
	% of correct classifications	–	91.7	–	91.7	90.3	–
LR	Correct/total	–	–	–	69/72	–	–
	% of correct classifications	–	–	–	95.8	–	–

A 100% classification performance was achieved for the samples included in the model computation irrespective of the used technique.

KNN is a classical pattern recognition technique, which is regarded to be a robust variant of discriminant analysis [18] since it is independent from any assumption about the error distribution. In this case, 3, 5 or 7 nearest neighbours were used with similar results concerning classification's efficiency.

ANN, a mimic of the human neuron system, is a branched structure used as the modelling tool possessing an ability to store knowledge obtained in the learning (training) process and make use of them in calculations. Classification results were obtained by using a three-layer perceptron ANN variant with 65 or 30 input neurons, 3 hidden neurons and one six-level output neuron.

The classification models calculated by all the mentioned techniques and using different software are summarized in Tab. 3. All wine samples (100%) were correctly classified into six classes by variety in the multidimensional model calculation regardless of using all variables or only 30 selected best ones for the classification. However, the leave-one-out validation was less successful as usually and depended considerably on the applied multivariate technique and partly also on the implemented software. The leave-three-out manual technique was used instead of the leave-one-out validation in the case when the latter could not be performed automatically by the given software.

When individual misclassification events were inspected in detail, similar problems as described in LDA were observed. In some cases, an incorrect discrimination took place among the white varieties Müller Thurgau, Welsch Riesling, Grüner Veltliner and partly also Chardonnay.

CONCLUSIONS

Quantitative results of classification of 72 wine samples of the Small Carpathian origin by multidimensional chemometrical techniques were obtained. Six wine varieties were studied: Frankovka Blue (11 samples), Chardonnay (12 samples), Müller Thurgau (16 samples), Welsch Riesling (9 samples), Sauvignon (7 samples) and Grüner Veltliner (17 samples). Chromatographic peak areas were used as the analytical signals with the same retention time corresponding to the selected 65 volatile aroma compounds in all samples. According to the validation results, the best performing classification techniques were the linear discriminant analysis, the K-th nearest neighbour method and logistic regression, providing a better than 95% performance (correct classifications / total) but in all studied cases, the calculated classification performance was higher than 90%. In general, a higher classification performance was achieved when instead of all peaks, 30 optimally selected peaks were used in the training set. The most innovative feature of the described chemometrical data processing is that there is no need for a detailed assignment of the used chromatographic peaks, which saves costs for standards and time. Therefore, this approach represents a suitable alternative for processing of huge quanta of analytical data, in particular in conditions when a complete compound indentification is not possible due to a complexity of analytical signal or when it is cumbersome or economically not favourable.

REFERENCES

1. Arthur, C. C. - Pawliszyn, J.: Solid-phase microextraction with thermal-desorption using fused-silica optical fibers. Analytical Chemistry, *62*, 1990, pp. 2145-2148.
2. Bicchi, C. - Cordero, Ch. - Liberto, E. - Rubiolo, P. - Sgorbini, B.: Automated headspace solid-phase dynamic extraction to analyse the volatile fraction of food matrices. Journal of Chromatography A, *1024*, 2004, pp. 217-226.
3. Garcia, D. D. - Magnaghi, S. - Reichenbächer, M. - Danzer, K.: Systematic optimization of the analysis of wine bouquet components by solid-phase microextraction. Journal of High Resolution Chromatography, *19*, 1996, pp. 257-262.
4. López, R. - Aznar, M. - Cacho, J. - Ferreira, V.: Determination of minor and trace volatile compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric detection. Journal of Chromatography A, *966*, 2002, pp. 167-177.
5. Rodríguez-Bencomo, J. J. - Conde, J. E. - Rodriguez-Delgado, M. A. - Garcia-Montelongo, F. - Perez-Trujillo, J. P.: Determination of esters in dry and sweet white wines by headspace solid-phase microextraction and gas chromatography. Journal of Chromatography A, *963*, 2002, pp. 213-223.
6. Rodríguez-Bencomo, J. J. - Conde, J. E. - Garca-Montelongo, F. - Perez-Trujillo, J. P.: Determination of major compounds in sweet wines by headspace solid-phase microextraction and gas chromatography. Journal of Chromatography A, *991*, 2003, pp. 13-22.
7. Salinas, M. R. - Alonso, G. L. - Esteban-Infantes, F. J.: Adsorption-thermal desorption-gas chromatography applied to the determination of wine aromas. Journal of Agricultural and Food Chemistry, *42*, 1994, pp. 1328-1331.
8. Vas, G. - Kőteleky, K. - Farkas, M. - Dobó, A. -

Vékey, K.: Fast screening method for wine headspace compounds using solid-phase microextraction (SPME) and capillary GC technique. American Journal of Enology and Viticulture, *49*, 1998, pp. 100-104.
9. Lozano, J. - Fernández, M. J. - Fontecha, J. L. - Aleixandre, M. - Santos J. P. - Sayago, I. - Arroyo, T. - Cabellos, J. M. - Gutiérrez, F. J - Horrillo, M. C.: Wine classification with a zinc oxide SAW sensor array. Sensors and Actuators B, *120*, 2006, pp. 166-171.
10. Santos, J. P. - Fernández, M. J. - Fontecha, J. L. - Lozano, J. - Aleixandre, M. - García, M. - Gutiérrez, J. - Horrillo, M. C.: SAW sensor array for wine discrimination. Sensors and Actuators B, *107*, 2005, pp. 291-295. 11. Capron, X. - Smeyers-Verbeke, J. - Massart, D. L.: Multivariate determination of the geographical origin of wines from four different countries. Food Chemistry, *101*, 2007, pp. 1585-1597.
12. Penza, M. - Cassano, G.: Recognition of adulteration of Italian wines by thin-film multisensor array and artificial neural networks. Analytica Chimica Acta, *509*, 2004, pp. 159-177.
13. Peter Hrivňák. Sorpčný prostriedok dávkovacieho priestoru chromatografickej kolóny. (Microcolumn for thermal desorption in gas chromatographic inlet). Inventor: Hrivňák, P. Int. Cl. B01D 15/08. Slovak Republic, Utility model, 3183. 11.2.2002. (in Slovak)
14. Tölgyessy, P. - Hrivňák, J. - Šilhárová, K.: Determination of chlorinated ethenes in water using headspace solid-phase microcolumn adsorption combined with thermal desorption in GC injection port. Petroleum and Coal, *46*, 2004, pp. 88-94.
15. Kráľovičová, E. - Hrivňák, J. - Tölgyessy, P.: Determination of benzene in air by microcolumn adsorption and thermal desorption in GC inlet. Petroleum & Coal, *48*, 2006, pp. 61-65.
16. Tölgyessy, P. - Hrivňák, J.: Analysis of volatiles in water using headspace solid-phase microcolumn extraction. Journal of Chromatography A, *1127*, 2006, pp. 295-297.
17. Tölgyessy, P. - Vrana, B. - Hrivňák, J.: Large volume headspace analysis using solid-phase microcolumn extraction. Chromatographia, *66*, 2007, pp. 815-817.
18. Khattree, R. - Naik, D. N.: Multivariate data reduction and discrimination. Cary, North Carolina : SAS Institute, 2000. 558 pp. ISBN 1-58025-696-1.