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Analysis of polyphenols in wines: Correlation between total polyphenolic content and antioxidant potential from photometric measurements Prediction of cultivars and vintage from capillary zone electrophoresis fingerprints using artificial neural network

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Abstract

The polyphenols (some of them are also called phytoalexins, flavonols, flavanons, flavanonols, flavons, flavanols, and anthocyanines) are usually marked as potent antioxidants or radical scavengers which assist the body cells against oxidation. Polyphenols in wine are also considered to explain so called French paradox (long life aging and low number of coronary diseases despite of high alcohol and fat consumption). The total polyphenolic content (TPC) and total antioxidant potential (TAP) were determined by photometry and found strongly correlated. This finding suggests that the determination of TAP can be replaced by a more simple procedure of TPC determination. Capillary zone electrophoresis (CZE) with preconcentration by solid phase extraction (SPE) was applied for some polyphenols determination and for obtaining electropherograms of the SPE extracts (fingerprints). From mathematical evaluation of the fingerprints, prediction of cultivars and vintage using artificial neural networks (ANN) was done with more than 90% correct prediction. The study was performed on a set of 47 samples of young wines (vintage 1999–2002) from south Moravia (Czech Republic) and New South Wales (Australia).
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Keywords: Wine; Total phenolic content; Total antioxidant potential; Resveratrol; Capillary zone electrophoresis; Fingerprints; Artificial neural networks

1. Introduction

Capillary electrophoresis (CE) is rapidly developing analytical tool successfully used in many areas of analytical chemistry, e.g. for analysis of biological and environmental samples. CE (including non-aqueous CE) [1–5] is the most common method for wine analyses, together with high performance liquid chromatography (HPLC) [6–15].

The use of CE typically excludes complicated sample treatment and also reduces the amount injected to less than a microliter. However, to determine low concentrated analytes presented in the sample, some preconcentration technique is still required prior to the analysis. The solid-phase extraction (SPE) is easy feasible technique combining two advantages which both contribute to a lower limit of detection: an increase in analyte concentration and the elimination of an interferring matrix. In wine analysis, the technique of SPE on C18-columns has been successfully applied [1,3,16]. Apart from liquid–liquid extraction, determination of resveratrol in grape skin with a combination of supercritical fluid extraction (SFE) and HPLC has also been reported [17].

In this work, a relationship between the total antioxidant potential (TAP) and the total polyphenolic content (TPC) of commercial wines was determined. TPC was determined by using Folin-Ciocalteu's reagent. Total antioxidant activity values were measured as stability of free radicals using 2,2′ azinobis (3-ethylbenzothiazoline 6-sulfonic) (ABTS) [18]. Gallic acid was used as a reference.

The main aim of this work was to determine *cis*- and *trans*-resveratrol in Moravian and Australian wines and to use the electropherogram of SPE extract (fingerprints) for characterization of the wines. The SPE and CZE methods for polyphenol analysis were optimized earlier [19,20].

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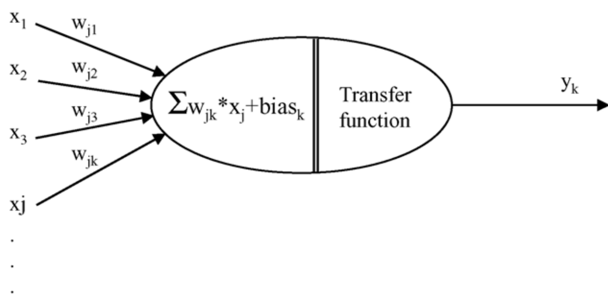

Fig. 1. Basic structure of an artificial neuron—the unit of the artificial neural network.

2. Theory of artificial neural networks

The theory of different networks has been reviewed by Zupan and Gasteiger [21]. Application of artificial neural networks for data processing is characterized by a very simplified analogy with biological neurons. Each neuron (a processing element) is linked to its neighbors with varying strengths. The strength of connection between two neurons is called *weight* and is represented by coefficients of connectivity w. In Fig. 1, the basic of an artificial neuron is shown.

An artificial neural network is composed of a large number of simple, highly interconnected neurons working in parallel. The neurons in a network are sorted in (i) an input layer, (ii) hidden layer(s) (one or more) and (iii) an output layer. Input neurons accept the input data characterizing a given observation (experiment), output neurons yield the predicted (expected) value. A neuron sums the product of each connection weight (w_{jk}) from a neuron j to the neuron k and input (x_j) and the additional weight called the bias to get the value sum for the neuron k:

$$\mathrm{sum}_k = \sum w_{jk} x_j + \mathrm{bias}_k \quad (1)$$

The sum of the weighted inputs is further transformed with a *transfer function* to get the output value. There are several transfer functions; the most common is the sigmoidal function [21].

To find suitable w's and biases for each neuron, a process of training is essential; it is the first step of building an ANN. Training means that the weights are corrected to produce prespecified (“correct”, known from experiments) target values. The training requires sets of pairs (X_S, Y_S) for input: the actual input into the network is a vector X_S, and the corresponding target is labelled Y_S. After successful training when correct values Y_S for each vector X_S from the training set are obtained, it is hoped that the network will give correct predictions Y for any new object X.

The most utilized training method for multilayered neural network is called *back propagation*. Information about errors (differences between target and predicted values) is filtered back through the system and is used to adjust the connections between the layers, thus improving performance.

3. Experimental

3.1. Chemicals and reagents

Methanol (99.8%), ethanol (>99%), sodium tetraborate $Na_2B_4O_7·10\ H_2O$ were purchased from Lachema (Brno, Czech Republic). Sodium carbonate $Na_2CO_3·10H_2O$, potassium peroxodisulfate $K_2S_2O_8$, Folin-Ciocalteu's phenol reagent and mesityloxide for EOF measurement were from Fluka (Buchs, Switzerland). Sodium tartrate $Na_2C_4H_4O_6·2\ H_2O$ and gallic acid $C_7H_6O_5·H_2O$ were from Riedel de Haën (Seelze, Germany). Sodium hydroxide was from Merci (Brno, Czech Republic). [(2,2′ azinobis (3-ethylbenzothiazoline 6-sulfonic)], ABTS, and *trans*-resveratrol were purchased from Sigma (St. Louis, Mo, USA). Water was double distilled in Heraeus apparatus (Hanau, Germany). The standard solution of resveratrol (concentration 0.1 mM) was prepared in 12% ethanolic solution.

3.1.1. Photometry

UV–VIS photometer UV2 Unicam (Cambridge, UK) was used with 1 cm quartz cells. The measurements were done at ambient temperature.

3.1.2. SPE

The extraction columns endcapped BakerBond SPE octadecyl (C_{18}) reversed phase by J.T. Baker (Phillipsburg, NJ, USA) with 100 mg of octadecyl and 1 ml column size were used (product number 7020–01). The dosing vessel, the column and the detector were connected with tubes I.D. 0.32 mm from Gilson (OH, USA).

The solutions were dosed by peristaltic pump Labeco PCR 01 (Spišská Nová Ves, Slovakia) on the column. Electrophoretic measurements were made on HP 3DCE Agilent Technologies equipment (Agilent Technologies, Germany).

The following procedure has been used for wine sample preconcentration. The C18 column was treated by 2 ml of methanol and by 2 ml of distilled water. Later, 2 ml of wine sample was dosed on the column and the matrix was flushed by 4 ml of distilled water. Analytes were eluted by 3 ml of methanol, but only first 0.2 ml of extract was collected and used for CZE (preconcentration factor of 10). The flow rate of solvents was 1 ml min^{-1}. The recovery of resveratrol was 90%.

3.1.3. Capillary electrophoresis

All measurements were done with fused-silica capillary (Composite Metal Services, The Chase, Hallow, UK), total length 38.5 cm (effective length 30.0 cm) × 75 μm I.D. 25 mM borate (pH 9.38) as the running buffer was used. The sample was injected hydrodynamically for 4 s (50 mbar) and the positive separation voltage +20 kV was applied. 0.1% mesityloxide was measured every day before analyses as the EOF marker. All the measurements were measured at 25 °C and electropherograms were collected at 305 nm.

At the beginning, the capillary was conditioned with 1 M sodium hydroxide for 30 min at 40 °C, 10 min with distilled water and 10 min with the 25 mM borate buffer at 25 °C. Between analyses, the capillary was flushed 1 min with distilled water, 1 min with 0.1 M sodium hydroxide and 2 min with the running buffer. The EOF for optimized conditions measured using mesityloxide was $+57.6 \times 10^9\ m^2\ V^{-1}\ s^{-1}$. Thus, the separation process is a cathodically driven electrophoresis of anions.

The concentration of *trans*-resveratrol was determined from the calibration curve of *trans*-resveratrol, concentration of *cis*-resveratrol was calculated knowing the ratio 2.69 of molar absorptive coefficients of *trans*- and *cis*-form, respectively at 305 nm. The molar absorptive coefficients of both forms of resveratrol were determined experimentally by photometry [19]. Limit of detection of the method (including the preconcentration step) was 0.03 mg/l.

3.2. Wine samples

The complete list of the samples is in Table 1. There is 47 wine samples, 10 from New South Wales and 37 from Moravia; 24 of them were white, 23 of them red wines.

3.3. Data processing

The data were processed using Trajan 3.0 software package Trajan Neural Network Simulator, Release 3.0 D (Copyright Trajan Software Ltd, 1996–1998) and Matlab (The MathWorks, Inc., Novi, USA).

4. Results and discussion

4.1. Spectrophotometric determination

Spectrophotometry was used for measuring polyphenolic content in wine samples.

4.1.1. Total polyphenolic content (TPC)

The total polyphenolic content was determined according to the Folin-Ciocalteu method, expressed as gallic acid equivalents (GAE) [22]. The Folin-Ciocalteau reagent is a solution of complex polymeric ions formed from phosphomolybdic and phosphotungstic heteropoly acids. It oxidises phenolates, reducing the heteropoly acids to a blue Mo–W complex.

The method was adopted for wine analysis according to [18] as follows: Adequately diluted sample of wine 1 ml was mixed with 250 μl carbonate tartrate solution (200 g of sodium carbonate and 12 g of sodium tartrate in 1 l of distilled water) and 50 μl of Folin-Ciocalteu were added. The absorbance of sample was measured at 700 nm after 30 min of reaction.

Our results show a variation in total phenolic contents of tested wine samples. The values of TPC were ranged from 1687 to 4102 mg GAE/l in red wine samples and 292 to 858 mg GAE/l in white wine studied (see Table 1).

4.1.2. Total antioxidant potential (TAP)

The total antioxidant potential of wine samples was determined by bleaching of ABTS radical cations. The preformed radical monocation of ABTS is generated by reaction of ABTS with potassium persulfate. Its blue–green colour can be detected at 660 nm. Antioxidants in the sample cause the suppression of this colour production to a degree that is proportional to their concentration. As an equivalent standard, gallic acid was used. Generally, red wine contains higher concentrations of gallic acid than white wine. The method was adopted for wine analysis according to [18] and optimized as follows:

ABTS radical cations were prepared by incubation of 5 ml (concentration was 1.8 mM) with 1.25 ml 2 mM potassium persulphate for 2 h at 50 °C. It was diluted five times with phosphate buffer, pH 7.0 (0.02 M). To 996 μl of the ABTS radical cation, 4 μl of wine sample were added. The absorbance of each sample was measured after 15 min at 734 nm. The amount of total antioxidants in red wine samples ranged from 593 to 1929 mg GAE/l, in white wines from 111 to 269 mg GAE/l (see Table 1).

The values of TPC and TAP, respectively, confirmed that red wines exhibit higher both the values and the values of TPC are approximately twice higher than TAP. A correlation between these values for all the data set ($N = 47$) yields a value of slope = 0.42735 ($R = 0.95215$). Comparison of the value with the values of regression lines for eight individual vintage groups (ryzlink vlašský, veltlínské zelené, sauvignon, chardonnay, cabernet, andré, frankovka, svatovavřinecké) and evaluation of distribution around the individual regression lines revealed seven outliers, namely the samples b01, b03, b02, b06, b24, c02, c23. These were excluded and from the rest two graphs were plotted: for Australian and Moravian wines, respectively (Fig. 2). Slopes obtained, namely 0.407 and 0.502, respectively suggest that Australian wines exhibit higher amount of antioxidants than Moravian wines though values of TPC were on similar level (compare Fig. 2a and b).

In Fig. 3 there is an analogous graph of the outliers only with the slope as low as 0.285. Because these samples were specially treated (the producer of b01, b02, b03, b06, c02 and also other two producers of b24 and c23, respectively, reports controlled fermentation in their certificates), our findings suggest that an extra treatment of the fermentation process (controlled fermentation, special material of barrels) can decrease the value of TAP probably due to chemical changes (oxidation of catechin). These finding are in agreement with Burns et al. [23] conclusions that catechin-derived compounds are more strongly related to the antioxidant potential and account for a greater proportion of this potential in contrast to quercetin and myricetin.

Table 1
List of the wine samples and concentrations of TAP, TPC, *trans*-resveratrol and *cis*-resveratrol, respectively obtained, abbreviations used: qw = quality wines, qwsa = quality wines with special attributes

White wines		Vintage	TPC (mg/l)	TAC (mg/l)	*trans*-Resveratrol (mg/l)	*cis*-Resveratrol (mg/l)	Red wines		Vintage	TPC (mg/l)	TAC (mg/l)	*trans*- Resveratrol (mg/l)	*cis*- Resveratrol (mg/l)
b01	Ryzlink vlašský, qwsa kabinett	2002	474	140	0.36	0.93	c01	Cabernet mor., qwsa	2002	2214	601	2.99	7.67
b03	Ryzlink vlašský, qwsa kabinett	2002	589	178	0.43	–	c02	Cabernet mor., qwsa barrique	2002	1687	593	2.34	7.82
b09	Ryzlink vlašský, qwsa late harvest	2002	299	146	0.41	1.99	c17	Cabernet sauvignon, qwsa	2001	4029	1929	1.03	2.11
b02	Veltlínské zelené, qwsa kabinett	2001	646	169	0.53	–	c18	Cabernet sauvignon, qwsa	2001	3522	1754	1.32	2.98
b06	Veltlínské zelené, qwsa kabinett	2002	292	111	–	–	c15	Cabernet Merlot, qwsa	2001	2699	1366	1.62	3.71
b07	Veltlínské zelené, qwsa late harvest	2001	414	192	1.10	2.06	c20	Merlot, qwsa	2002	2873	1443	1.80	7.80
b10	Veltlínské zelené, qwsa late harvest	2002	421	183	0.55	2.84	c16	Shiraz Cabernet, qwsa	2001	2352	1305	1.81	4.46
b14	Veltlínské zelené, qw	2002	360	149	0.36	–	c19	Shiraz, qwsa	2001	2853	1488	1.31	2.92
b17	Veltlínské zelené, qwsa selection	2000	773	257	2.28	1.46	c04	Modrý Portugal, qwsa	2002	2073	614	0.59	2.38
b23	Veltlínské zelené, qwsa	2001	385	233	0.75	1.10	c05	Modrý Portugal, qwsa barrique	2002	1878	892	1.30	3.09
b24	Veltlínské zelené, qwsa kabinett	2002	858	201	1.96	3.55	c08	Svatovavřinecké, qwsa late harvest	2002	1704	897	1.25	4.88
b04	Sauvignon, qwsa barrique	2001	602	252	3.36	–	c10	Svatovavřinecké, qw	2001	2316	940	2.02	8.41
b05	Sauvignon, qwsa	2001	553	211	0.53	0.81	c14	Svatovavřinecké, qw	2002	2735	1227	3.46	5.30
b08	Tramín červený, qwsa selection	1999	529	207	0.94	0.96	c09	Frankovka, qw	2000	2367	1179	2.55	7.41
b11	Rulandské šedé, qwsa selection	2002	651	249	0.37	3.32	c 11	Frankovka, qw	2002	2854	1149	2.31	7.13
b15	Rulandské bílé, qwsa late harvest	2000	612	201	3.10	1.68	c21	Frankovka, qwsa late harvest	2000	1907	977	2.20	7.03
b12	Müller Thurgau, qw kabinett	2002	437	226	–	–	013	Rulandské modré, qw	2001	3037	1253	2.56	6.14
b16	Müller Thurgau, qw	2001	403	144	0.67	1.72	c12	André, qw	2002	4102	1437	1.78	7.37
b13	Chardonnay, qw selection	2002	410	158	0.48	1.58	c07	André, qwsa late harvest	2002	2613	1328	1.67	4.69
b22	Chardonnay, qwsa	20002	408	269	0.67	–	c22	André, qwsa	2000	2393	1237	3.67	7.31
b19	Chardonnay, qwsa	2001	421	179	0.76	1.07	c03	Zweigeltrebe, qwsa late harvest	2002	3700	1368	2.02	3.60
b20	Chardonnay, qwsa	2001	473	205	0.36	1.98	c06	Zweigeltrebe, qwsa late harvest	2002	2977	1028	1.61	5.42
b18	Semillon Chardonay, qwsa	2002	364	162	–	–							
b21	Semillon Sauvignon Blanc, qwsa	2002	353	162	–	–							

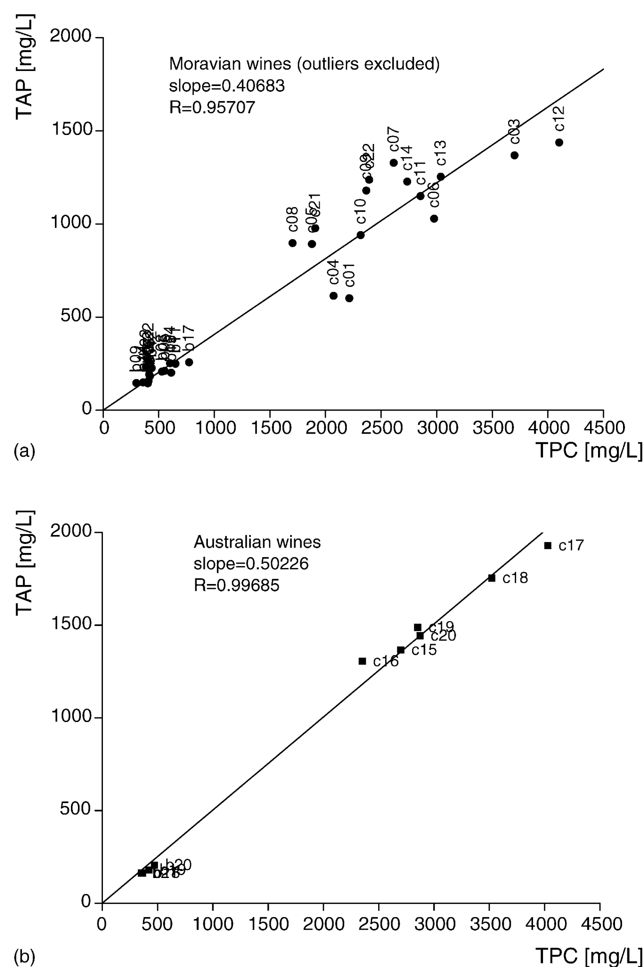

Fig. 2. Correlation between TAC and TPC. Full circles and squares, respectively with codes represent all the samples tested except outliers (see text). R is correlation coefficient. For Moravian wines the number of samples was 30 (15× white + 15× red), for Australian wines the number was 10 (4× white, 6× red).

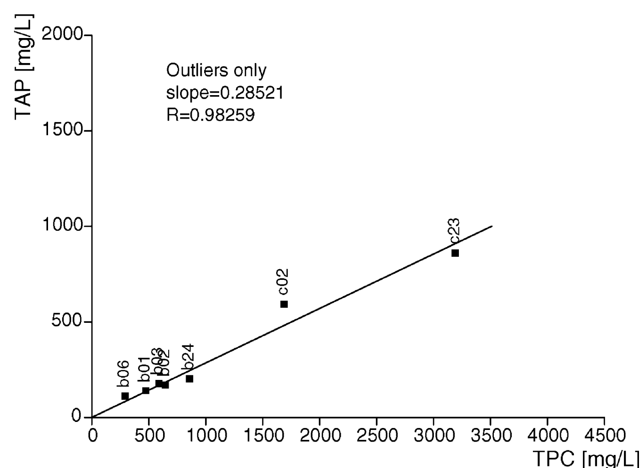

Fig. 3. Graph of correlation between TAP and TPC for seven wine samples marked as outliers. In all cases, the fermentation was controlled (modified), see text.

4.2. Capillary electrophoresis and artificial neural networks—prediction of cultivars and vintage

The content of resveratrol determined in the wine samples was below 10 mg/l (see Table 1), higher for red wines than white wines, which agrees with commonly quoted values [24].

Because capillary electrophoresis exhibits high separation efficiency and wine is a complex mixture of compounds, electropherograms of methanolic eluates from C-18 SPE column of wine samples still contain many compounds (peaks). Although identification of some of them is feasible by, e.g. spiking [4], for our purpose it was not necessary—principally the peaks did not even need to be spectrally pure (correspond to a pure compound), they must be only obtained under the same conditions. We utilize the fact that the electropherograms of methanolic eluates were characteristic by a peak pattern (fingerprint). The evaluation procedure of an electropherogram is illustrated in Fig. 4 and explained as follows.

It is well known that in capillary electrophoresis the uncontrolled electroosmotic flow (capillary inner surface) causes migration times to be not constant—therefore instead of migration times, peaks are better identified by spiking, spectral analysis or other means. For our purposes, relative migration times (RMT) of the most intensive peaks were selected: the first two peaks of *trans*- and *cis*-resveratrol, respectively (which were identified by spiking and quantified for each sample), and other five peak from the rest of electrophoreograms.

The first two input values for ANN, concentrations of *cis*- and *trans*-resveratrol, respectively, were obtained from calibration curves (if the concentration were not of interest for us, just peak heights could have been used). Other five inputs were heights in mAU of the five most intensive peaks from the rest of the electropherogram starting from the most intensive peak with migration time 2.9–3.5 min and ending with the last intensive peak in the electropherogram (migration time 5.3–7.5 min). In order to simplify the identifica-

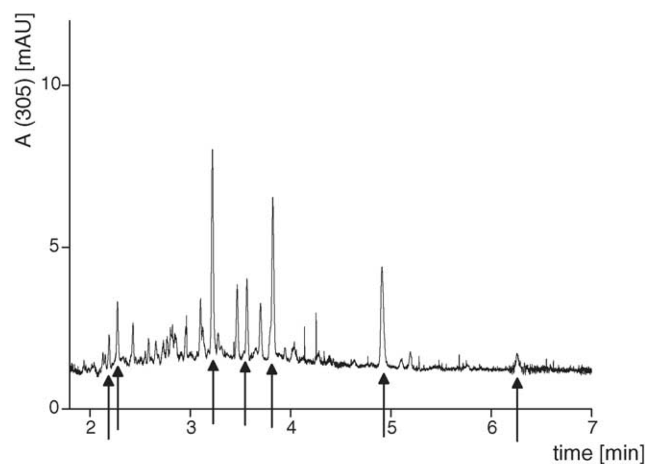

Fig. 4. Evaluation of electropherograms after SPE (fingerprints). The arrows point to the peaks which were used as input values for ANN.

Table 2
Prediction of cultivar and vintage from fingerprint data using ANN

White wines						Red wines					
Code	Prediction		Reality		Response	Code	Prediction		Reality		Response
	Cultivar	Year	Cultivar	Year			Cultivar	Year	Cultivar	Year	
b01	?		rv	2002	?	c01	?		ca	2002	?
b02	vz	2001	vz	2001	Right	c02	ca	2002	ca	2002	Right
b03	?		rv	2002	?	c07	an	2002	an	2002	Right
b04	sa	2001	sa	2001	Right	c08	sv	2002	sv	2002	Right
b05	sa	2001	sa	2001	Right	c09	fr	2000	fr	2000	Right
b06	vz	2002	vz	2002	Right	c10	sv	2001	sv	2001	Right
b07	vz	2001	vz	2001	Right	c11	fr	2002	fr	2002	Right
b09	rv	2002	rv	2002	Right	c12	an	2002	an	2002	Right
b10	vz	2002	vz	2002	Right	c14	sv	2002	sv	2002	Right
b13	ch	2002	ch	2002	Right	c15	ca	2001	ca	2001	Right
b14	vz	2002	vz	2002	Right	c16	ca	2001	ca	2001	Right
b17	vz	2000	vz	2000	Right	c17	ca	2001	ca	2001	Right
b18	ch	2002	ch	2002	Right	c18	ca	2001	ca	2001	Right
b19	ch	2001	ch	2001	Right	c21	fr	2000	fr	2000	Right
b20	ch	2001	ch	2001	Right	c22	an	2000	an	2000	Right
b21	sa	2002	sa	2002	Right	c23	fr	2002	fr	2002	Right
b22	ch	2002	ch	2002	Right						
b23	vz	2001	vz	2001	Right						
b24	vz	2002	vz	2002	Right						

Abbreviation used for groups: rv: ryzlink vlašský; vz: veltlínské zelené; sa: sauvignon; ch: chardonnay; ca: cabernet; an: andré; fr: frankovka; sv: svatovavřinecké; right: correct prediction, ?: impossible to predict.

tion of the peaks, their migration times were normalized: the first peak from this set was denoted by zero relative migration time, RMT = 0, the last one by RMT = 1. Thus the following five peaks were evaluated for white wines: RMT = 0, 0.07, 0.15, 0.55, 1.00, respectively, for red wines RMT = 0, 0.31, 0.44, 0.66, 1.0, respectively. Relative standard deviations of RMT was better than 6% after this correction. Nineteen white wines and 16 red wines were evaluated by the procedure.

Multilayered feed-forward artificial neural networks were used. As the training scheme, the algorithm of back-propagation in combination with quick propagation, which attempts to use a simple quadratic model of the error surface (calculated independently along each weight) for speeding convergence, was applied. The training procedure was terminated when verification and target values were acceptably close. The training "correct" values (outputs) were names of eight cultivares, namely ryzlink vlašský (rv), veltlínské zelené (vz), sauvignon (sa), chardonnay (ch), cabernet (ca), andré (an), frankovka (fr), svatovavřinecké (sv) (there were three to seven samples of each kind), and three vintages, namely 2000, 2001, 2002 (there were 4, 12, and 19, respectively samples of each kind). Samples not included in any of these groups were omitted (b08, b11, b12, b15, b16, c03, c04, c05, c06, c13, c19, c20).

As clear from Table 2, the prediction rate was very high (32 correct of 35 totals). It failed only for three samples, namely b01, b03 and c03, which all come from one producer from Moravia and were also excluded from the correlation analysis between TAP and TPC (controlled fermentation, see above) and therefore can be considered as extraordinary samples.

5. Conclusions

The ratio TAP/TPC can be used as a marker of controlled (modified) fermentation of wines (the lower value, the higher probability of a special treatment). The characteristic value of this ratio also suggests that TAP can be estimated from the value of TPC for a given set of similar wines, using a conversion factor valid for the set, e.g. 0.40 (TAP = 0.40*TPC) for Moravian quality wines (for the Australian wines the factor would be 0.50). Therefore, the method for determination of TPC can advantageously substitute the method for determination of TAP, since analytical methods with radicals requires skillfull operators (preparation of solutions, obtaining acceptable reproducibility, etc.).

SPE electropherograms of the wine sample extracts (fingerprints) can be evaluated by ANN and used for very reliable prediction of wine vintage and cultivar.

Our finding on the characteristic values of TPC and TAP, respectively, and prediction efficiency from SPE fingerprints evaluated by ANN will be further verified on a larger sample set of wines.

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