Talanta 90 (2012) 46–50

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Statistical analysis of wines using a robust compositional biplot

K. Hron[a,*], M. Jelínková[b], P. Filzmoser[c], R. Kreuziger[d], P. Bednář[b], P. Barták[b]

[a] Department of Mathematical Analysis and Applications of Mathematics, Faculty of Science, Palacký University, 17. listopadu 12, CZ-77146 Olomouc, Czech Republic
[b] Regional Centre of Advanced Technologies and Materials, Department of Analytical Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, CZ-77146 Olomouc, Czech Republic
[c] Department of Statistics and Probability Theory, Vienna University of Technology, Wiedner Hauptstrasse 8-10, A-1040 Vienna, Austria
[d] Department of Analytical Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, CZ-77146 Olomouc, Czech Republic

ARTICLE INFO

Article history:
Received 23 September 2011
Received in revised form
19 December 2011
Accepted 22 December 2011
Available online 2 January 2012

Keywords:
Phenolic acids
Compositional data
Principal component analysis
Robust compositional biplot
Centered log-ratio transformation
Gas chromatography–mass spectrometry

ABSTRACT

Eight phenolic acids (vanillic, gentisic, protocatechuic, syringic, gallic, coumaric, ferulic and caffeic) were quantitatively determined in 30 commercially available wines from South Moravia by gas chromatography–mass spectrometry. Raw (untransformed) and centered log-ratio transformed data were evaluated by classical and robust version of principal component analysis (PCA). A robust compositional biplot of the centered log-ratio transformed data gives the best resolution of particular categories of wines. Vanillic, syringic and gallic acids were identified as presumed markers occurring in relatively higher concentrations in red wines. Gentisic and caffeic acid were tentatively suggested as prospective technological markers, reflecting presumably some kinds of technological aspects of wine making.

1. Introduction

When quantifying chemical data, the results are frequently expressed in concentrations, like in mg L^{-1}, or directly in percentages to see the proportions of various chemical compounds on the whole solid/sample. This implies that not the absolute values, but the ratios are of interest. Such data (called in the following compositional data or only compositions for short) are in fact quantitative descriptions of the compounds (parts) of some whole, conveying exclusively relative information. From a mathematical point of view, the compositional data have another sample space, the simplex, which is in fact only a subset of the Euclidean real space, the domain of the standard multivariate observations. This induces singularity of compositions that make the use of standard statistical methods not possible. Besides a different sample space, compositional data also have a specific geometrical behavior, corresponding to the so-called relative scale. In terms of this relative scale, 5% is considered half of 10%, while 45% forms a fraction of 0.9 of 50%. If we would treat these numbers as absolute values, the difference between 5% and 10% appears to be the same as that between 45% and 50%, but obviously this result does not account for the real information behind the data. Statistical methods directly applied to the original data, where the information contained is absolute and not relative, can lead to completely useless results. This was already seen more than 100 years ago in the context of correlation analysis for this kind of multivariate observations [1], and recent work confirms the problems and provides new approaches [2,3].

The new conceptual approach to deal with compositional data was introduced in the early 1980s, when John Aitchison proposed the use of log-ratios [4]. It is based on the idea that the simplex as sample space of compositions induces a natural geometry (nowadays usually called the Aitchison geometry [5]) that is coherent with the intuitive concept of difference associated to the relative scale of compositions. A statistical approach has to account for the natural scale of the data, and this is possible for compositional data using the log-ratio approach [6]. It includes a family of log-ratio transformations from the simplex to the real space with the standard Euclidean geometry, namely the additive, centered and isometric log-ratio transformation [4,7]. These transformations allow for the use of standard statistical methods for the transformed data, although with some limitations or modifications [2,4,6,8–10]. Nowadays only the latter two mentioned log-ratio transformations seem to be fully reasonable according to adequate theoretical properties.

---

[*] Corresponding author. Tel.: +420 585634605, fax: +420 585634002.
E-mail addresses: hronk@seznam.cz (K. Hron), korhonovam@seznam.cz (M. Jelínková), P.Filzmoser@tuwien.ac.at (P. Filzmoser), kreuzi9f@seznam.cz (R. Kreuziger), bednarp@prfnw.upol.cz (P. Bednář), petr.bartak@seznam.cz (P. Barták).

0039-9140/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2011.12.060

In many practical approaches, compositional data are simply log-transformed in order to bring the distributions of the single variables closer to symmetry. However, this transformation does not move the compositions out from the simplex, but in fact it only converts the natural constraint of the data to a more complicated one. In addition, the log-transformation does not preserve the singularity of compositions, what in practice destroys the correlation structure of the transformed data and makes a meaningful interpretation impossible.

A further problem in practical data sets is the presence of outlying observations (outliers), i.e. observations that do not follow the main data structure. Outliers can have a severe influence to results of the standard statistical methods, and thus lead to wrong conclusions. The main reason is that both the arithmetic mean and the sample covariance matrix, that occur as estimators of location and covariance in most multivariate statistical procedures, are very sensitive to deviations from the main data structure. This holds also for the well known principal component analysis (PCA), used for dimension reduction of the multivariate observations. PCA tries to explain as much of the overall variability as possible with the first few principal components. Outliers can artificially increase this variability, thus change the directions of principal components and, consequently, also values of the resulting loadings and scores. A solution is to downweight the influence of outlying observations. In case of PCA, robustness against outliers can be achieved by replacing the arithmetic mean and the sample covariance matrix by their robust counterparts. A frequently used robust estimator of location and covariance is the minimum covariance determinant (MCD) estimator, but also several other proposals were made in the literature [11]. Finally, note that although PCA by definition maximizes data variance, the main variance cannot be associated with the studied effect (like class membership). PCA thus can be used for exploration, compression and visualization of data trends, but it cannot be used for classification purposes.

Results of PCA are often presented in a biplot [12]. A biplot is a planar graph, where both loadings (representing information of variables) and scores (representing information of observations) are displayed. In order to distinguish between both sources of information, the loadings are represented by arrows from the origin and the scores by points in the plot. The biplot is usually constructed on the basis of the first two principal components, forming a rank-two approximation of the multivariate data, see, e.g., [13,14] for details. A robust biplot displays loadings and scores from a robust PCA.

The aim of the study is to compare different statistical procedures for the evaluation of eight phenolic acids contained in Moravian wines. Phenolic acids (and other phenolic compounds) belong to a group of important secondary plant metabolites widely spread throughout the plant kingdom [15]. Phenolic acids are located in several parts of grape berries, primarily in the skin. Their content in wines depends on grape variety, maturity degree, technology of wine making process and chemical reactions occurring during wine fermentation and ageing [16–18].

2. Robust compositional biplot

PCA as a statistical method and as a basis for constructing the biplot is designed for data following the standard Euclidean geometry. Thus, applying the method directly to compositions usually gives misleading results [9]. On the other hand, the data can be transformed with the centered log-ratio (clr) transformation, defined for a D-part composition $\mathbf{x} = [x_1, \ldots, x_D]$ as

$$\mathbf{y} = [y_1, y_2, \ldots, y_D] = \left[\ln \frac{x_1}{\sqrt[D]{\prod_{i=1}^{D} x_i}}, \ldots, \ln \frac{x_D}{\sqrt[D]{\prod_{i=1}^{D} x_i}} \right].$$

Besides the theoretical correctness of PCA for clr transformed data, also an easier interpretation of the resulting PCA loadings and scores is usually possible [19].

Since the denominator of the log-ratios in the clr transformation is the geometric mean of the transformed composition, the origin of the biplot corresponds to the geometric mean of the data set. The PCA scores have an analogous meaning as in the standard case, i.e. they picture the multivariate data structure of compositions. Due to the clr transformation, the data structure is already represented in the usual sense of Euclidean distances. On the other hand, the interpretation of loadings is different. The squared distance between two vertices (vectors) approximates the variance of the log-ratios of the compositional parts. If the vertices, corresponding to y_i and y_j, $i, j = 1, \ldots, D, i \neq j$ nearly coincide, the variance of the log-ratio of x_i and x_j, $\mathrm{var}(\ln(x_i/x_j))$, is nearly zero and hence the ratio x_i/x_j is almost a constant.

The advantages of using the compositional biplot are reflected in the literature by many applications, like from the fields of geochemistry and analytical chemistry [2,3,9,20,21]. Moreover, in Ref. [3] a detailed description is provided, how to apply the classical compositional biplot to a concrete chemical data set.

Since classical compositional biplots are sensitive to outliers, for many practical situations a robustification is necessary. This step is not straightforward because the clr transformation results in singular data (the sum of $y_1, \ldots, y_D$ equals zero), and robust estimators of location and covariance cannot cope with data singularity. This problem can be overcome with isometric log-ratio (ilr) transformations that form the family of mutually orthogonal transformations in the $(D-1)$-dimensional Euclidean real space. Taking one of them [7], it moves the composition $\mathbf{x}$ to

$$\mathbf{z} = [z_1, z_2, \ldots, z_{D-1}],\ z_i = \sqrt{\frac{i}{i+1}} \ln \frac{\sqrt[i]{\prod_{j=1}^{i} x_j}}{x_{i+1}} \quad \text{for} \quad i = 1, \ldots, D-1. \tag{1}$$

Moreover, there exist linear transformations between various ilr transformations and the clr transformation [7]. Thus, now one can compute the robust estimators and, consequently, the robust PCA loadings and scores. Unfortunately, the new variables z_i are not straightforward to interpret in sense of the compositional biplot. Thus, we use the linear relationship between the ilr and clr transformations and back-transform the loadings and scores to the clr space. Finally, they can be used to construct the robust compositional biplot with the interpretation as described above.

3. Materials and methods

3.1. Chemicals and materials

Vanillic, syringic, caffeic, p-coumaric, ferulic, 4-cyclohexylbutanoic acid, bis(trimethylsilyl)-trifluoracetamid (BSTFA), methanol and pyridine of p.a. purity were purchased from Fluka (Buchs, Switzerland). Protocatechuic acid of p.a. purity was purchased from Dr. Theodor Schuschardt (Munich, Germany). Gallic acid, ethyl acetate, hexane, hydrochloric acid and sodium chloride of p.a. purity were from Lachema (Brno, Czech Republic). Commercially available wines of Czech production were purchased in local supermarkets and wine shops.

3.2. Sample preparation

Five mililiter of wine sample was adjusted by 100 μL of 2 M HCl to pH 2 then 1 mL of saturated solution of NaCl, 100 μL of methanolic stock solution of an internal standard (4-cyclohexylbutanoic acid, 50 mg L^{-1}, final concentration in the sample 1 mg L^{-1}) and

Table 1
Representation of phenolic acids in Czech wine samples (mg L^{-1}).

Wine samples		Phenolic acids							
	No.	Vanilic (1)	Gentisic (2)	Protocatechuic (3)	Syringic (4)	Gallic (5)	Coumaric (6)	Ferulic (7)	Caffeic (8)
White	1	0.853	6.409	12.499	0.575	6.234	3.578	0.933	5.740
	2	0.524	4.401	5.427	0.296	1.803	2.902	0.563	4.573
	3	0.099	6.565	8.099	0.352	3.693	4.875	0.727	6.965
	4	0.535	2.111	8.151	0.225	2.314	1.053	0.259	4.434
	5	0.413	2.125	5.603	0.189	8.039	2.473	0.905	6.662
	6	0.281	7.992	6.613	0.141	2.272	27.905	1.330	2.861
	7	0.412	3.589	8.403	0.230	4.445	2.810	0.671	2.015
	8	0.734	7.688	5.352	0.539	41.237	1.679	1.418	10.353
	9	1.911	14.489	16.057	1.256	21.223	9.350	3.725	34.206
Rosé	10	0.972	2.970	5.628	0.832	4.65	1.9036	0.558	3.220
Red	11	10.734	4.192	23.347	9.900	109.666	6.019	0.544	13.337
	12	11.217	5.991	25.484	10.240	95.896	14.304	1.001	26.742
	13	4.608	2.915	35.097	3.473	72.259	7.496	0.757	14.032
	14	6.869	4.832	20.662	7.049	92.833	7.529	0.579	13.268
	15	2.156	3.975	4.313	2.954	1.657	1.965	0.301	6.043
	16	17.364	2.985	4.110	23.845	16.562	16.011	1.001	12.275
	17	8.510	1.537	18.977	12.033	88.096	6.685	0.933	52.378
	18	6.163	2.051	9.362	6.114	53.155	4.892	0.350	1.552
	19	4.614	3.978	10.778	4.590	60.919	5.139	0.286	4.605
	20	3.831	2.043	7.219	5.792	68.390	2.281	0.305	7.045
	21	4.528	4.264	22.749	5.992	51.992	10.880	0.328	14.758
	22	3.836	1.325	5.457	6.654	66.746	2.929	0.292	8.180
	23	5.486	10.034	15.856	5.526	69.166	10.669	0.505	16.980
	24	4.746	8.429	3.053	5.199	14.415	16.843	1.658	43.295
	25	6.044	1.863	8.508	9.940	57.440	4.028	0.310	9.235
	26	6.731	2.972	7.047	8.316	61.711	1.807	0.700	9.511
	27	8.040	2.950	1.555	12.440	47.864	10.472	0.563	5.430
	28	7.625	1.708	19.518	8.413	38.448	3.607	0.409	7.617
	29	5.484	4.965	5.666	4.293	22.586	11.780	1.806	25.474
	30	5.187	1.822	10.123	4.434	68.869	15.590	1.649	63.768

2 mL of ethylacetate were added. Each sample was extracted in a 10 mL centrifugal plastic tube and an incurred emulsion was separated out by centrifuge (30 s, 3000 rpm). The organic phase was removed into glass vial, evaporated to dryness in thermo block (35 °C) in a steam of nitrogen. Afterwards, 100 μL of pyridine and 100 μL of BSTFA were added, sealed vial was heated up to 70 °C (30 min). Cooled samples were filled in 1 mL with hexane and analyzed by GC–MS.

3.3. GC/MS analyses

Analyses of wine samples were performed on a HP 6890 Series GC system with an Agilent 5973 N Mass Selective Detector (Agilent, Palo Alto, CA, USA), equipped with NIST mass spectra library. A ZB-5MS capillary column (5% phenyl, 95% dimethyl polysiloxane) (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used. The GC temperature was programmed as follows: start temperature 50°C (2 min hold), increase to 300 °C at 10 °C min^{-1}, hold for 10 min; pulsed splitless injection (1 μL, 140 kPa, 24 s) was used. The carrier gas helium (99.998%; SIAD, Bergamo, Italy) was maintained at a constant flow of 0.9 mL min^{-1}. MS scans were recorded within the range 29–520 *m*/*z* using EI mode (energy 70 eV). Phenolic acids were identified by comparison of retention times with those of particular standards and by comparison of mass spectra with those from MS library NIST 08. Phenolic acids were quantified by an internal standard method.

3.4. Data processing

All the calculations were performed using the statistical software R [22]. R is nowadays one of the most used tools for statistical computing and provides a huge variety of functions from basic descriptive statistics to advanced statistical methods and graphical procedures. Specialized functions are associated to libraries. Two libraries are available for compositional data analysis: “compositions” and “robCompositions”. The latter contains a function to obtain robust PCA for constructing the robust compositional biplot in the clr space as described above.

4. Results and discussion

Hydroxybenzoic acids as vanillic acid (1), gentisic acid (2), protocatechuic acid (3), syringic acid (4), gallic acid (5), and hydroxycinnamic acids as coumaric acid (6), ferulic acid (7), caffeic acid (8) were identified and quantitatively determined in 30 wine samples by the GC–MS technique (Table 1). Although the sum of the compositional parts for each wine is rather small (and far away from 100%), the data are of compositional nature, because an increase of one part could automatically imply a decrease of other parts. Therefore, only the ratio between the parts include the relevant information, but not the raw numbers.

In the following we demonstrate the results arising from the two different approaches: analyzing the raw data set, and treating the data as compositional data set. In both cases we use a classical and a robust approach for constructing the biplot. Due to the nature of the data set, we would expect a grouping of the white and of the red wines. The rosé wine (no. 8) could possibly form an own group.

Fig. 1 shows the biplots for the raw data set where the fact of dealing with compositional data is ignored. Data groups are visible in the classical (left) as well as in the robust (right) biplot. However, these groups do not correspond to our suspicion: a red wine (no. 15) falls into the cluster of white wines, a white wine (no. 6) is far away from the white wine cluster but closer to the red wine group, and the rosé wine (no. 10) is in the center of the white wine group. An apparent outlier seems to be white wine no. 9. Robustness leads to a slightly different configuration of the observations and variables

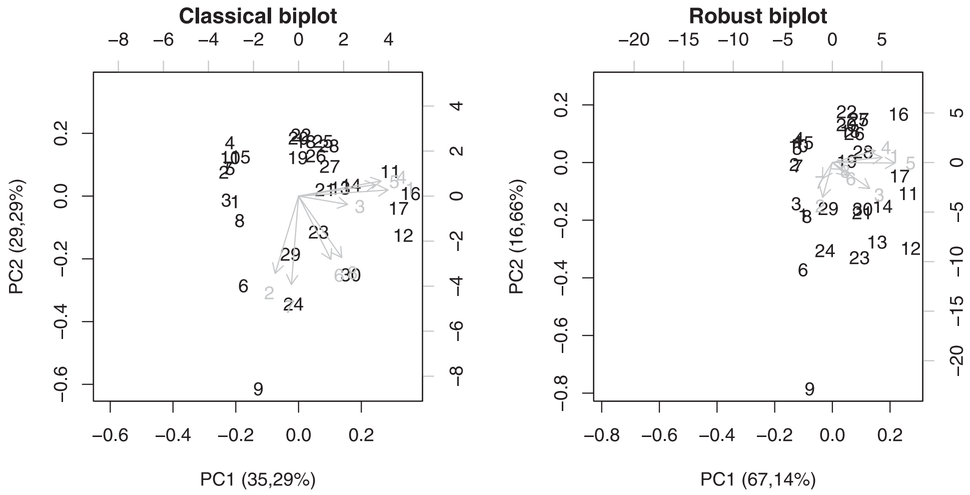

Fig. 1. Classical (left) and robust (right) biplot for the raw data.

in the biplot, but it does not reveal the potential groups in the data. It is of course possible that either the presumed grouping structure is not present, or that it is only visible in higher-order principal components.

Fig. 2, on the other hand, confirms what has been expected. In the classical compositional biplot (left), the white wine samples form a clear group, and the rosé wine sample 8 is located in between the white and red wine sample. Now also the real relations between the compounds are identifiable. There are two groups of compositional parts (2, 6, 7, 8 and 1, 4) with mutually quite stable ratios, and two other compounds (3, 5) with different behavior. The robust compositional biplot (right) gives less weight to outlying samples, and the resulting plot corresponds even more to our intuition, with two data groups consisting of white and red wines, respectively, and the rosé wine in between. A natural exception forms the white wine sample no. 8. The reason is quite nicely visible by looking at Table 1. Comparing mean log-ratios between the original compounds (elements of the so-called variation array, see Ref. [4] for details) of the white and red wine groups, respectively, with the corresponding log-ratios of sample 8 reveals that in some aspects this sample behaves as a red wine rather than a white one. For example, the mean log-ratio between caffeic and gallic acids equals 0, 23 for the white wine group (without 8) and −1, 30 for the red wine group, while the same log-ratio for sample 8 equals −1, 38. Consequently, the ratio between caffeic and gallic acids in 8 is more than 5 times less than the corresponding average ratio in the white wine group. An analogous behavior is visible also for some of the other (log-)ratios between coumpounds, like between protocatechuic and gallic acids (even approximately a 15 times smaller ratio than the white wine average) or for protocatechuic and caffeic acids, respectively. Conversely, looking at the corresponding log-ratios helps to explain why red wine no. 15 tends to enter the white wine group. The main responsible (log-) ratios seem again to be connected with the gallic acid – its ratios to gentisic (more than 40 times smaller ratio than the red wine average), protocatechuic and ferulic acids, respectively, indicate a clear deviation of 15 to the white wines behavior. However, these outliers are still associated with the correct groups in Fig. 2 (right), although at the boundary on these groups. Finally, the role of white wine no. 9 has changed from the previous case, where the statistical analysis of raw compositional data (where the ratios are informative) was strongly influenced by absolute values of the compounds. None of log-ratios in this sample justifies its outlying behavior comparing to the other samples, in fact, it quite nicely follows the white wine group properties.

In this biplot, also the configuration of the variables has a very intuitive interpretation: two markedly distinguished groups of phenolic acids (1, 4, 5 and 3, 6, 7) of supposedly opposite behavior are evidently responsible for the resolution of the samples in the horizontal direction, largely consistent with the resolution of

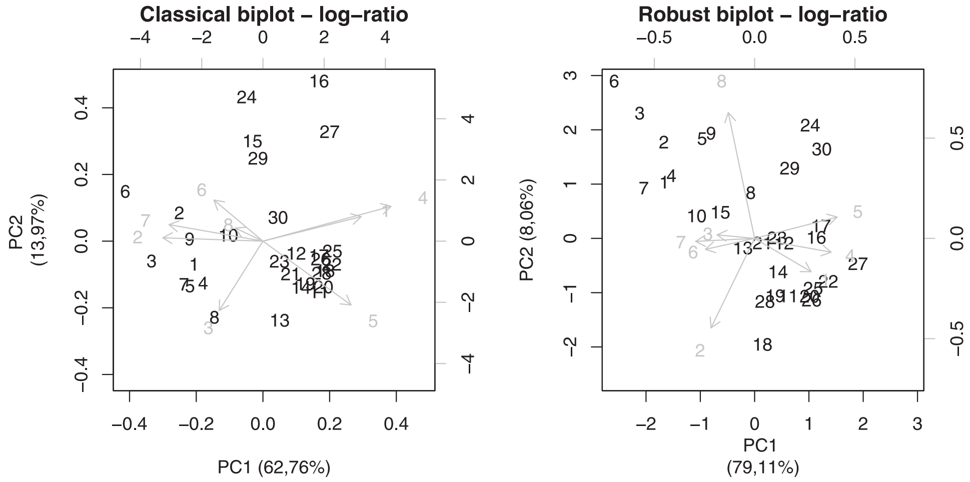

Fig. 2. Classical (left) and robust (right) compositional biplot for the clr transformed data.

red and white wines. Phenolic acids of both groups, i.e. vanillic (1), syringic (4) and gallic acid (5) as well as protocatechuic (3), coumaric (6) and ferulic acid (7) are frequently detected in red and white wines. However acids from the first group are typically presented in red wines in much higher concentrations in comparison to the white wines, while concentrations of the acids from the second group are more or less equal in red and white wines. In this sense, vanillic, syringic and gallic acid could be regarded as the true markers of red wines. The results are in good agreement with other related studies concerning the determination of phenolic acids in wines [23]. Note that these three variables also allow for a separation of white and red wines in Fig. 1, but the resulting grouping is much more vague.

In the robust compositional biplot, two other phenolic acids, gentisic (2) and caffeic (8), are located in orthogonal direction to the main (horizontal) distribution. Some kind of orthogonal behavior of gentisic and gallic acid was observed in a study aimed at investigating phenolic acids during the fermentation of different types of wines [24]. When the concentration of gentisic acid increases during the fermentation, the concentration of gallic acid goes down and vice versa. In a similar way, the caffeic acid exhibits an opposite behavior to ferrulic acid and both couples often act somewhat complementary. The findings could be further supported considering the general biochemical pathways for phenolic acid biosynthesis. Gentisic and gallic acids are two products of different synthetic pathways from the same precursor (3-dehydroshikimate). The complementarity could be due to the preference of one of the possible pathways according to particular conditions during the fermentation and maturation [25]. Caffeic and ferrulic acid is a pair of biosynthetic precursor and product of enzymatic reaction, and the preference is given by activities of enzymes in subsequent reactions [26]. Some kind of competition takes place in both cases, and particular conditions determine the mutual ratio of synthesized phenolic acids in both couples. The content of gentisic and caffeic acid and their ratio to other phenolic acids depends not only on the variety of the grapes, but probably also on the process of wine making.

5. Conclusions

Classical and robust versions of principal component analysis were applied on raw (untransformed) and centered log-ratio transformed data concerning the content of eight phenolic acids in a set of 30 red, rosé and white Czech wines. The robust compositional biplot of centered log-ratio transformed data gives the best resolution of the particular categories of wines, allowing straightforward interpretation and explanation. Vanillic, syringic and gallic acids were identified as supposed markers of red wines, while gentisic and caffeic acids were tentatively suggested as prospective markers reflecting to some extent also the technological aspect of wine making.

Acknowledgments

The financial support by project No. P206/10/0625 of Grant Agency of Czech Republic, grant no. MSM 6198959214 of Council of Czech Government and project No. CZ.1.05/2.1.00/03.0058 of the Ministry of Education, Youth and Sports of the Czech Republic, Operational Program Research Development for Innovations – European Regional Development Fund is gratefully acknowledged.

References

[1] K. Pearson, Proc. R. Soc. Lond. 60 (1897) 489–502.
[2] P. Filzmoser, K. Hron, C. Reimann, Sci. Total Environ. 408 (2010) 4230–4238.
[3] M. Korhoňová, K. Hron, D. Klimčíková, L. Müller, P. Bednář, P. Barták, Talanta 80 (2009) 710–715.
[4] J. Aitchison, The Statistical Analysis of Compositional Data, Chapman & Hall, London, 1986, Reprinted 2003 with additional material by The Blackburn Press.
[5] J.J. Egozcue, V. Pawlowsky-Glahn, in: A. Buccianti, G. Mateu-Figueras, V. Pawlowsky-Glahn (Eds.), Compositional Data Analysis in the Geosciences: From Theory to Practice, Geological Society, Special Publications 264, London, 2006, pp. 145–160.
[6] A. Buccianti, G. Mateu-Figueras, V. Pawlowsky-Glahn (Eds.), Compositional Data Analysis in the Geosciences: From Theory to Practice, Geological Society, Special Publications 264, London, 2006.
[7] J.J. Egozcue, V. Pawlowsky-Glahn, G. Mateu-Figueras, C. Barceló Vidal, Math. Geol. 35 (2003) 279–300.
[8] P. Filzmoser, K. Hron, Math. Geosci. 40 (2008) 233–248.
[9] P. Filzmoser, K. Hron, C. Reimann, Environmetrics 20 (2009) 621–632.
[10] P. Filzmoser, K. Hron, C. Reimann, Sci. Total Environ. 407 (2009) 6100–6108.
[11] R. Maronna, R.D. Martin, V.J. Yohai, Robust statistics: Theory and Methods, John Wiley, New York, 2006.
[12] K.R. Gabriel, Biometrika 58 (1971) 453–467.
[13] R. Johnson, D. Wichern, Applied Multivariate Statistical Analysis, sixth ed., Prentice-Hall, London, 2007.
[14] K. Varmuza, P. Filzmoser, Introduction to Multivariate Statistical Analysis in Chemometrics, CRC Press, Boca Raton, 2009.
[15] K. Herrmann, Crit. Rev. Food Sci. Nutr. 28 (1989) 315–347.
[16] R. Ramos, P.B. Andrade, S.M. Seabra, C. Pereira, M.A. Ferreira, M.A. Faia, Food Chem. 67 (1999) 39–44.
[17] F. Fang, J.M. Li, Q.H. Pan, W.D. Huang, Food Chem. 101 (2007) 428–433.
[18] I. Budić-Leto, T. Lovrić, Food Technol. Biotechnol. 40 (2002) 221–225.
[19] J. Aitchison, M. Greenacre, Appl. Stat. 51 (2002) 375–392.
[20] A. Buccianti, V. Pawlowsky-Glahn, Math. Geol. 37 (2005) 703–727.
[21] B. Papoušková, P. Bednář, K. Hron, J. Stávek, J. Balík, R. Myjavcová, P. Barták, E. Tománková, K. Lemr, J. Chromatogr. A 1218 (2011) 7581–7591.
[22] R development core team, Vienna, 2011 http://www.r-project.org/ (September 2011).
[23] M.Á. Pozo-Bayón, M.T. Hernández, P.J. Martín-Álvarez, M.C. Polo, J. Agric. Food Chem. 51 (2003) 2089–2095.
[24] R.R. Tian, Q.H. Pan, J.C. Zhan, J.M. Li, S.B. Wan, Q.H. Zhang, W.D. Huang, Molecules 14 (2009) 827–838.
[25] N.R. Mustafa, R. Verpoorte, Planta 222 (2005) 1–5.
[26] C.J. Douglas, Trends Plant Sci. 1 (1996) 171–178.