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## Multivariate data analysis as a discriminating method of the origin of wines

by

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### Multivariable Datenanalyse zur Sortenklassifizierung von Weinen

**Zusammenfassung:** Die Analysendaten von 178 Weinen aus Piemont, die drei verschiedenen Rebsorten angehörten (Barbera, Grignolino, Barolo), wurden mit Hilfe der multivariablen Datenanalyse ausgewertet, um Modelle der Sortencharakteristik zu erstellen und untypische Proben auszuwählen. Durch Auswahl der Merkmale („Fisher-Gewichte“) blieben von den ursprünglich 28 chemischen und physikalisch-chemischen Variablen aufgrund ihrer hohen eindimensionalen Unterscheidbarkeit 8 Variable übrig. Auf den achtdimensionalen Datensatz wurden verschiedene Klassifizierungsmethoden (KNN, LDA, PCA) und Techniken statistischer Modelle (Bayes-Statistik, SIMCA) angewandt; die Klassifizierbarkeit lag bei 98 %.

**Key words:** wine, analysis, characteristic, variety of vine, statistics, Italy

### Introduction

All the factors helping in the production of certified-origin wines must comply with several laws and regulations which impose various limitations. These limitations do not apply to the final product, they are concerned with the vine-growing soil, the grape yield per hectare, the harvest time, and so on. They are in fact control procedures from vine growing to wine making which aim at assuring the production of wines showing constantly the distinctive features which give them the V.Q.P.R.D. appellation (vins de qualité produits dans des régions déterminées). Beside the above, other laws command the wine ready to be sold to conform to fixed standards. According to the item 14 of EEC Act 338/79, for instance, the appellation of origin of a wine cannot fit wines not conforming to the same chemical and sensorial characteristics.

Wine tasters may sometimes reach surprising results by sensorial analysis; it is obvious, however, that the only use of sensorial analysis cannot be accepted as a universally valid criterion and accordingly it cannot be taken for the only discriminant factor, even though it gives useful and often basic contributions.

Chemical and physico-chemical analyses, on the other hand, give accurate and precise results, the only contribution of which is, still, quite often inadequate to fully describe the typical characteristics of a wine.

According to the EEC Act quoted above, only a few parameters must be checked (density, alcoholic degree, total acidity, fixed and volatile acidity, extracts, sugars, sulphur dioxide) which are not strictly linked to the geographic origin of the considered wine. It is obvious that the characterization of typical wines based on chemical analysis

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Inorganic constituents have been largely used; they are, to some extent, relatable to the soil composition and then could be a means of classifying wines on the basis of vine-root selective absorption. Several and differently grouped elements were considered: the basic groups ranged from a minimum of 5—6 elements (18, 26, 29), chosen among the more abundant and easily detectable to a maximum of 15—16 (2, 14, 28), europium, thallium, hafnium and rubidium included. The use of trace elements as variables may lead to interesting results even though the instruments and experience requested are not easily available, while minimal and occasional pollution with trace elements might occur, thus biasing the results.

Proteins (6), amino acids (20) and enzymes (34) are highly selective variables themselves. The use of enzymes as discriminating factors between different cultivars is questionable, owing to the enzyme instability in alcoholic media. Yeast activity on amino acids and enzymatic hydrolysis or precipitation of proteins, on the other hand, are factors strongly limiting the use of those parameters as variables.

Data and variables · a) Categories and number of samples, b) Variables  
Daten und Variable · a) Kategorien und ihre Stichprobenzahl, b) Variable

a)	Cat.index	Cat.name	Samples per year										Total
			'70	'71	'72	'73	'74	'75	'76	'77	'78	'79	
	1	Barolo		19		20	20						59
	2	Grignolino	9	9	7	9	16	9	12				71
	3	Barbera					9		5		29	5	48
b)	1	Alcohol					15	Sulphate					
	2	Sugar-free extract					16	Total phenols					
	3	Fixed acidity					17	Flavanoids					
	4	Tartaric acid					18	Nonflavanoid phenols					
	5	Malic acid (total, see 'Literature' (20))					19	Proanthocyanins					
	6	Uronic acids					20	Color intensity					
	7	pH					21	Hue					
	8	Ash					22	OD <sub>280</sub> /OD <sub>315</sub> of diluted wines					
	9	Alcalinity of ash					23	OD <sub>280</sub> /OD <sub>315</sub> of flavanoids					
	10	Potassium					24	Glycerol					
	11	Calcium					25	2,3-butanediol					
	12	Magnesium					26	Total nitrogen					
	13	Phosphate					27	Proline					
	14	Chloride					28	Methanol					

Discriminant analyses were successfully based on volatile components of wines easily detectable by gas chromatography (21, 22, 24, 25). Owing to the presence of typical terpenes (5, 23, 27), wines from aromatic grapes, Muscat in particular, can be easily recognized. Given that the majority of the volatile compounds comes from the yeast activity, the occurrence of these compounds, at least from a qualitative point of view, is quite the same even in different wines. Differences in wine origin seem to be yet responsible for the different extent to which these components occur, and it is proved true for both 2,3-butendiol (4) and propanol-1 (3). Similarly, a good discrimination was obtained, both for white and red wines, but taking into account a few volatile components simultaneously (16, 17, 19). KWAN and KOWALSKI (13) obtained good results by multivariate analysis of inorganic and volatile components in wines.

We carried out the multivariate analysis of 28 variables listed in Table 1, using the package PARVUS (7) which provides for classification, clustering and modelling. 178 wine samples subdivided into vintages and including Barolos, Barberas and Grignolino (32, 33, 34) were used. All wines were from Piedmont, each of them deriving from a single cultivar, while the production areas overlap, at least in part.

### Feature selection

Fisher weights (interclass variance/intraclass variance ratio) were calculated for each category pair and for all the data (Table 2). 9 variables showed high univariate

Table 2

Fisher weights of the variables · a) Total, b) between categories 1 and 2, c) between categories 1 and 3, d) between categories 2 and 3

Fisher-Gewichte der Variablen · a) Insgesamt, b) zwischen den Kategorien 1 und 2, c) zwischen den Kategorien 1 und 3, d) zwischen den Kategorien 2 und 3

Variable index	a	b	c	d
17	8.13	1.3	20.2	2.9
22	5.07	0.4	11.0	3.8
23	3.05	0.0	6.4	2.8
27	3.03	4.9	3.9	0.3
15	2.89	3.9	4.7	0.1
21	2.70	0.0	5.5	2.6
16	2.44	0.8	5.7	0.8
1	2.14	4.3	0.7	1.4
20	2.04	2.5	0.5	3.1
3	0.97	0.0	2.0	0.9
6	0.82	0.0	1.3	1.2
9	0.79	0.6	1.7	0.1
4	0.78	0.2	1.4	0.7
19	0.75	0.1	1.7	0.4
5	0.66	0.0	1.1	0.9
24	0.62	1.3	0.3	0.3
18	0.58	0.3	1.2	0.2
13	0.50	0.8	0.6	0.0

discriminant ability. 8 of them (alcohol, total phenols, flavanoids, colour intensity, hue,  $OD_{280}/OD_{315}$  of diluted wines,  $OD_{280}/OD_{315}$  of flavanoids, proline) were used for classification and modelling analysis. Sulphates were eliminated since they can partly come from chemically treated cooperage. Among the discarded variables only the net extract (the Fisher weight of which is 1 in the discrimination between Barolo and Grignolino) as well as uronic acids (the Fisher weight of which is 1.2 in the discrimination between Barbera and Grignolino) showed some discriminant ability. The other variables showed discriminant ability between Barolo and Barbera; for these two classes of wines some out of the 8 selected variables (flavanoids,  $OD_{280}/OD_{315}$  of diluted wines) have so high Fisher weights as to give a perfect classification.

Feature selection by univariate criteria (Fisher weights) is highly criticizable. We used this method simply as a preselective technique in order to make the subsequent methods applicable and faster, otherwise the number of objects should have been drastically reduced in order to use all the variables in SIMCA, due to the limited capacity of PARVUS. We also used multivariate criteria of feature selection. The best results were obtained with a recently introduced method, the stepwise Bayesian analysis (9); the results are going to be published.

### Correlation analysis — Typical correlations

The correlation coefficients of the 8 variables let us single out the following highly meaningful correlations for all the wine samples:

a)	$OD_{280}/OD_{315}$ of diluted wines and $OD_{280}/OD_{315}$ of flavanoids	$r = 0.91$
b)	Total phenols and flavanoids	$r = 0.86$
c)	Flavanoids and $OD_{280}/OD_{315}$ of diluted wines	$r = 0.78$
d)	Color intensity and $OD_{280}/OD_{315}$ of flavonoids	$r = 0.72$
e)	Color intensity and $OD_{280}/OD_{315}$ of diluted wines	$r = 0.71$
f)	Total phenols and $OD_{280}/OD_{315}$ of diluted wines	$r = 0.70$

In each wine class we can single out the correlations (or the lack of correlation) typical of each category. For the class Barolo correlations c and f disappear, while they diminish only slightly for the class Grignolino. The class Barbera has also correlation b. The class Barolo shows high correlation between flavanoids and color intensity, which is not meaningful when all the data are considered.

Very high correlations show that the real dimension of the system is lower than the variable number.

### Principal component analysis

Raw data have been autoscaled (11) and the eigenvectors of the covariance generalized matrix computed.

The eigenvectors form a new system of Cartesian coordinates, obtained by orthogonal rotation. Rotation is characterized by direction cosines (loadings) among eigenvectors and original variables. The greater the absolute value of a loading, the greater is the contribution of the corresponding variable to that eigenvector.

The sample (object) coordinates are named scores in the new eigenvector system. The significance analysis of eigenvectors has been carried out by the methods of aver-

age variance criterion, inbedded function criterion and screen test (15). The first two criteria show two significative eigenvectors, while the graphic evaluation of screen test is doubtful for two or three components. The first two eigenvectors alone contain almost 80 % of the information. They are the axes of the plot of scores in Fig. 1 and of the plot of loadings in Fig. 2. The plot of scores shows that the used variables contain enough information to allow a good graphic separation of the categories. In the tridimensional plot of Fig. 3 (10), the separation is even clearer. The plot of loadings shows the contribution of the variables to the more significant eigenvectors; it displays the same variables as regards the data fundamental structure and it gives information already obtained in part from correlation study.

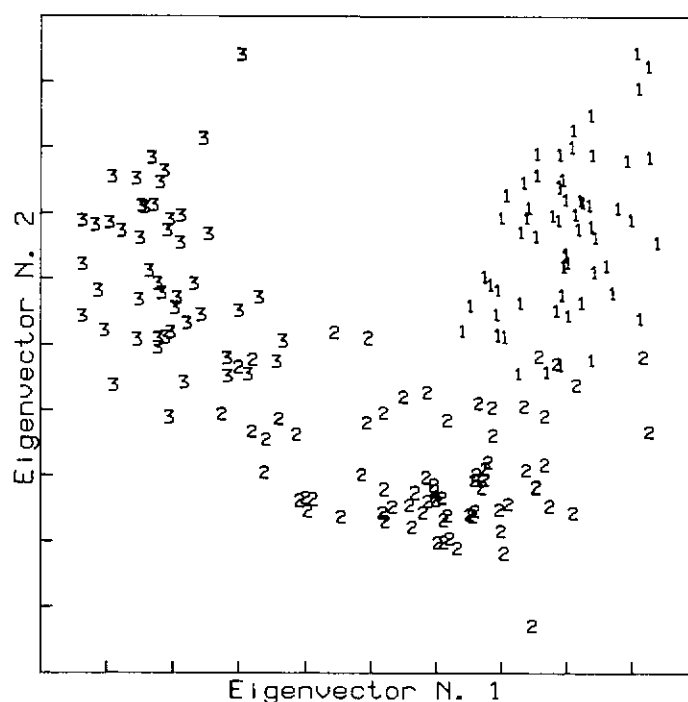


Fig. 1: Eigenvector projection of the samples. — 1: Barolo, 2: Grignolino, 3: Barbera.

Eigenvektor-Projektionen der Stichproben.

By further axis clockwise rotation of about  $90^\circ$  in the plane of the principal components of Fig. 2, two new directions are located: the one seems principally formed by chromatic variables, while the other one is principally formed by chemical variables.

Ideally overlapping the loading plot to the score plot, we can see that the chromatic factor is important in Grignolino and Barbera discrimination; on the other hand, the chemical factor discriminates between Barolo and Grignolino.

### Linear discriminant analysis

Linear discriminant analysis, LDA (30), is based on amplified statistical model, where categories are supposed to have equal covariance matrices; the differences among categories are supposed to derive from the different position of category barycenters (centroids) only in the variable hyperspace. The pooled covariance matrix is calculated as the mean of the covariance matrices of the categories.

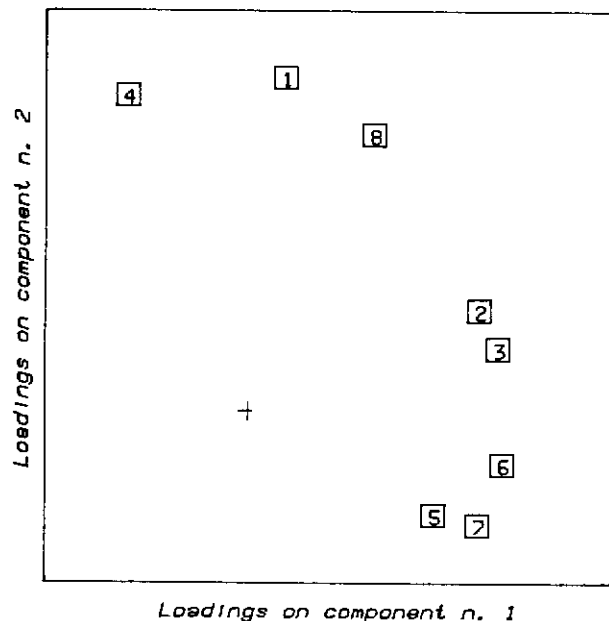


Fig. 2: Loadings on the first components of the generalized covariance matrix (indices of variables of Table 1).

Ladungen auf den ersten Komponenten der verallgemeinerten Kovarianzmatrix (Indizes der Variablen von Tab. 1).

The study of typical correlation showed a wide difference in the correlation among the three categories. In spite of that, as many other cases showed, the very simplified model of LDA produced good results.

The results of LDA were displayed using, as plot axes, the eigenvectors (canonical variables) of the asymmetrical matrix obtained premultiplying the centroid dispersion matrix by the inverted pooled covariance matrix (12).

Fig. 4 shows the discrimination in the plane of the two canonical variables: excluding one sample of Grignolino, the three categories may be linearly separated. The LDA ability was proved by a random subdivision of the data into two subsets (training and evaluation set). In the first set, the statistical parameters were calculated (centroid axes, pooled covariance matrix). Then the classification of objects was carried out by computing, for each object, the Mahalanobis distance (31) from the three centroids and classifying it as belonging to the category of the nearest centroid.

WINE SAMPLES IN SPACE OF FIRST THREE PRINCIPAL COMPONENTS  
 CUBES= BAROLO PYRAMIDS=GRIGNOLINO INVERT PYR= BARBERA

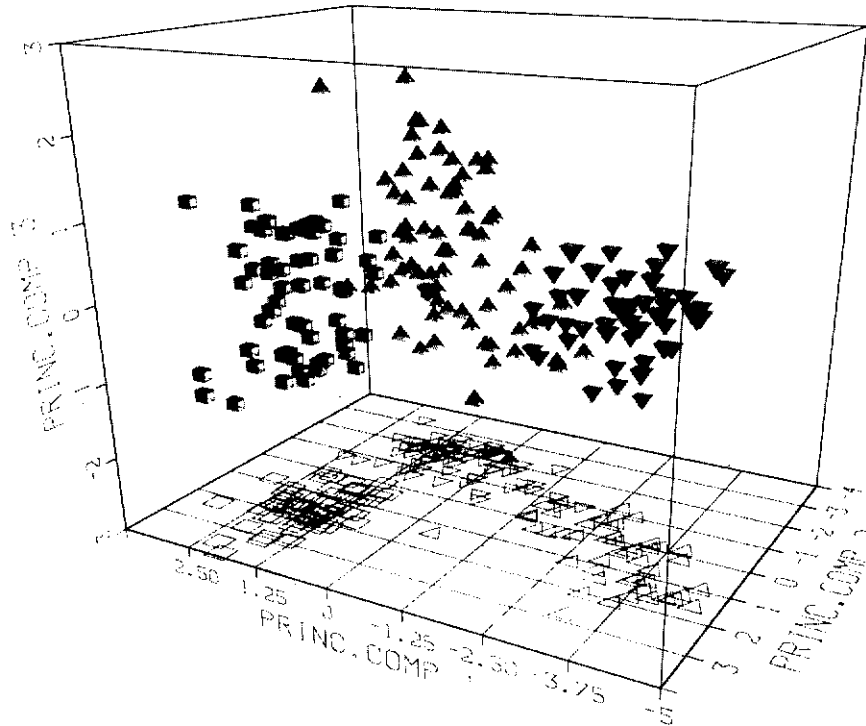


Fig. 3: Tridimensional plot of the first three eigenvectors.

Dreidimensionale Darstellung der ersten drei Eigenvektoren.

### Modelling analysis

The classification method of the first level of pattern recognition (1), as LDA, KNN, Learning Machine, do not single out anomalous samples. In fact, these samples are always classified in one of the categories of the problem even if the measured variables are very different from those typical of the categories.

Recognition ability is the percentage of training set objects correctly classified; predictive ability is the percentage of evaluation set objects correctly classified; the objects in the evaluation set were not used to compute statistical parameters and they were used by statistical method as unknown category objects.

On a sequence of 10 random subdivisions between training and evaluation set with 40–60 objects (22–34 %) in evaluation set, both the recognition and predictive ability were found to be 97–98 % and 95–99 %, respectively. The errors were always caused by the same samples (two of Barolo and three of Grignolino) every time differently distributed between training and evaluation set.



By modelling methods, Bayesian analysis and SIMCA, it is possible to select anomalous samples and evaluate how well each object fits into the category model. It is also possible to obtain a measure of the peculiarities of the object. Obviously the meaning of these peculiarities is limited by the variables used for the model.

For each modelling method, in each category, the borders of the part of the hyper-space of the variables in which the category samples are contained were computed. Each object occurring within this space was considered as belonging to the category. All the objects occurring outside the category space and used to compute the category model itself are considered outliers. In this case the model was recomputed without their contribution.

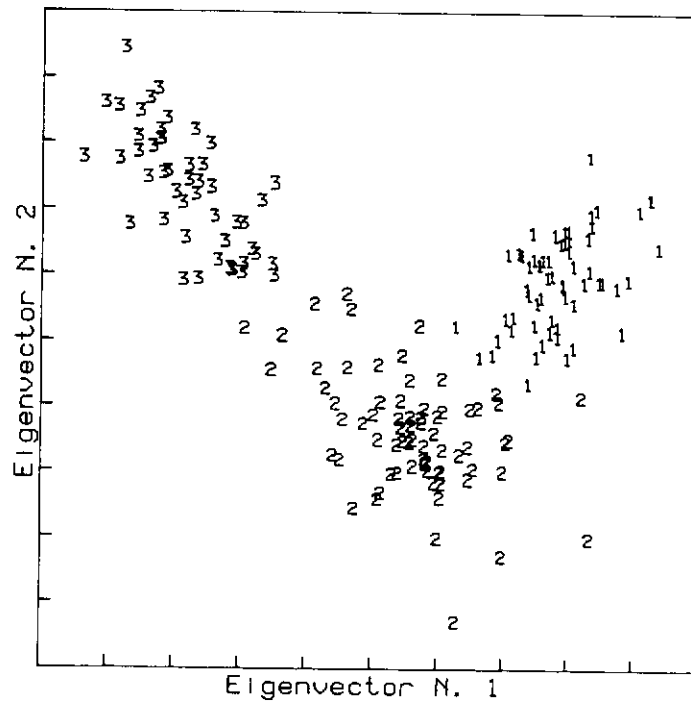


Fig. 4: LDA: discrimination in the plane of the two canonical variables.

LDA: Diskriminanzfunktion in der Ebene der zwei kanonischen Variablen.

We singled out the discarded objects and so we recomputed the model by a procedure (8) which involves the evaluation of the scores on the principal components of the category, the estimation of the significance level and the evaluation of their histogram.

In modelling methods, the confidence level which fixes the borders of the category space may be modified by increasing or reducing the category space according to the particular demands of the problem and/or knowledge of the sample. In Bayesian method, the category model is a point, the category centroid, and the category space is given by a confidence hyperellipsoid at a predetermined confidence level.

Table 3 shows some of the results obtained by this method. They refer to a model computed after the elimination of some non-typical objects (sample too different from the mean composition of the class). Fig. 5 shows, in the plane of the two principal eigenvectors (eigenvectors of the generalized covariance matrix, computed on all the 178 objects), the category spaces computed by the Bayesian technique, before and after having discarded the outliers.

Table 3  
Results of the second cycle of Bayesian analysis  
Ergebnisse des zweiten Durchgangs der Bayes-Statistik

Category	Discarded	Outliers		Accepted (95 % conf.lev.) by cat.		
		95 %	98 %	1	2	3
1	8	8	2	—	1	0
2	4	7	4	4	—	3
3	4	6	5	0	3	—
Total	16	21	11		11	

General classification matrix				
True category	Computed category			% of correct classifications
	1	2	3	
1	59	0	0	100
2	0	68	3	95.8
3	0	1	47	97.9

Total classification errors: 4  
Total of correct classifications: 97.8 %

In SIMCA method the model is a segment, or a part of a plane, or a part of a hyper-plane; the axes are given respectively by one, two or more significant components of the category of the objects (eigenvectors of the covariance matrix of the category). By means of a computation based upon the distance of the objects from the model, the category space, called SIMCA box, is built around the model. The borders of the model are computed assuming the range of the scores on the components (raw model) as a basis and then extending (1) or reducing (8) the model, considering the number of the objects and their distribution. The results are listed in Table 4 and displayed in Fig. 6; they refer to a reduced model, formed by two components, computed after the elimination of some non-typical objects, as Bayesian technique does.

Beside box shapes, the main difference between SIMCA and Bayesian methods lies in the fact that in SIMCA an object very close to the model plane and within its limits has a high fiducial level (and then a high fitting to the category model), though comparatively far from the category centroid; on the contrary, in Bayesian technique the high distance from the centroid gives the object a poor fitting into the category model.

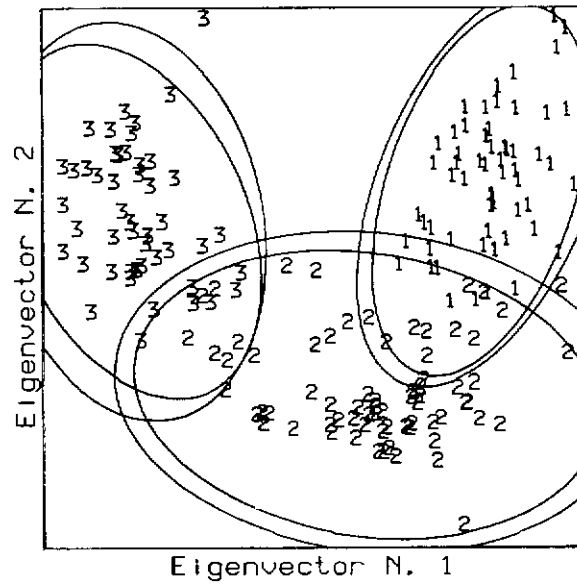


Fig. 5: Bayesian analysis: first (wider) and second cycle confidence hyperellipsoids (95 % confidence level) of the categories, projected on the plane of the first two eigenvectors.

Bayes-Statistik: Konfidenz-Hyperellipsoide der Kategorien im ersten (weiten) und im zweiten Durchgang (95 %-Niveau): Projektion auf die Ebene der beiden ersten Eigenvektoren.

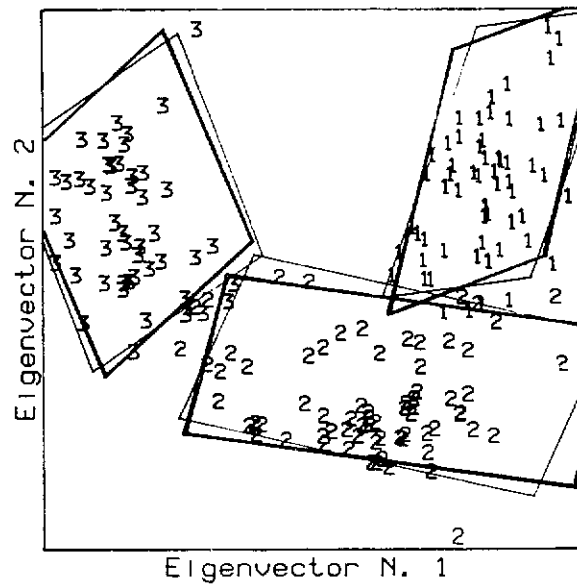


Fig. 6: SIMCA analysis: models of the categories before and after (marked) the elimination of the outliers.

SIMCA-Analyse: Modelle der Kategorien vor und nach (s. Zeichen) Entfernung der Außenseiter.

The model will be more significant when, in addition to the suitable chemical variables, the sensorial variables for quality and typical character evaluation will be available. Then, the basic correlation between the sensorial variables with the principal components of the categories will show which model is preferable. In spite of the lack of these elements, the data listed in Table 4 show that among the 178 samples only 8 (4.5 %) do not fall into their category model at the 98 % confidence level. 8 other samples, on the other hand, are accepted at 95 % confidence level by categories different from their proper one. Therefore, only 1 sample of Grignolino may be assigned to Barolo category, while using SIMCA as a pure classification method, 2 samples fall into the Barolo class.

Table 4

Results of modelling analysis by SIMCA, two-component category models, second cycle  
 Ergebnisse der Modellanalyse mittels SIMCA, Modelle für zwei Komponenten umfassende Kategorien, zweiter Durchgang

Category	Discarded samples	Outliers		Accepted (95 % conf.lev.) by cat.		
		95 %	98 %	1	2	3
1	3	4	2	—	2	0
2	2	4	2	1	—	3
3	4	4	4	0	2	—
Total	9	12	8		8	

General classification matrix				
True category	Computed category			% of correct classifications
	1	2	3	
1	59	0	0	100
2	2	68	1	95.8
3	0	1	47	97.9
Total classification errors:		4		
Total of correct classifications:		97.75 %		

### Conclusive remarks

The previous discussion emphasizes a situation which leads to some important considerations: First, it is noticeable that few, incidentally easily determinable variables, providing a sharp separation between wines from the same vineyard area, have been selected. Among these, phenolic compounds are widely represented.

It is important to remark, however, that the appropriateness of our choice depends on the nature of the wines we are trying to separate. As a matter of fact, each of the tested wines is produced from different and typical vine cultivars.

### Summary

A data set of 178 wines from Piedmont (Barbera, Grignolino, Barolo) was evaluated by multivariate data analysis in order to both build the category models and single out anomalous samples. By feature selection (Fisher weights) only 8 variables, out of the 28 chemical and physico-chemical original variables of the data set, were selected on account of their high univariate discriminant ability. Classification methods (KNN, LDA, PCA) and modelling techniques (Bayesian analysis, SIMCA) were applied to the 8-dimension data set; classification ability was about 98 %.

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