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Instrumental and sensory analysis of Greek wines; implementation of principal component analysis (PCA) for classification according to geographical origin

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Abstract

Wine is one of the most important products of Greece and other Mediterranean countries. Adulteration of wines, either in terms of geographical origin or variety, has been a major topic of debate and extensive research. Various instrumental methods (gas chromatography, high pressure liquid chromatography) and sensory analysis, in conjunction with statistical analysis, were developed and applied in an attempt to provide reliable answers to this issue. This research aimed at classifying 33 greek wines from various regions by employing both instrumental and sensory analysis. Application of principal component analysis (PCA) to our experimental data resulted in satisfactory classifications of only Greek red wines in terms of their geographical origin. Greek wines were effectively distinguished in two or three groups (depending on PCA figure); wines from Aegean/Ionean islands. North Greece and South Greece. However, further work with greater numbers of samples is required in order to draw more valid conclusions and to obtain a detailed map of greek wines according to their geographical origin and variety. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Greek wines; Authentication; Chemometrics; Multivariate analysis; Principal component analysis; GC; HPLC; Sensory analysis

1. Introduction

Chemical differentiation of wines is of great importance in oenology, especially when the origin is to be verified (De la Presa-Owens, Lamuela-Raventos, Buxaderas & Dela Torre-Boronat, 1995). Wine is a complex mixture of organic as well as inorganic compounds the composition of which is influenced by many and varying factors. These begin in the vineyard and end in the fermentation cellar. They are related to the oenological environment including ground, climate and variety of starting vine, and oenological practice (Arvanitoyannis, Katsota, Psarra, Soufleros & Kallithraka, 1999).

Wine characterisation has been attempted by several authors. Day, Zhang and Martin (1995) employed trace elements for the identification of geographical origin, using step-wise discriminant analysis. Elements can be considered as good indicators of wine origin since they are neither metabolized nor modified during the vinification process. The most frequently quantified elements are: K, Na, Fe, Zn, Rb, Ca, Mg, Mn, Cu, Cr, Co, Sb, Cs, Br, Al, Ba, As, Li, Ag (Baxter, Crews, Dennis, Goodall & Anderson, 1997; Moret, Di Leo, Giromini & Scarponi, 1984; Moret, Scarponi & Cescon, 1994; Seeber, Sferlazzo & Leardi, 1991). Moreover, Mulet, Berna and Forcen (1992) managed to classify wines satisfactorily, according to their geographical and varietal origin, by employing conventional parameters treated with discriminant analysis.

Phenolics constitute another promising class of compounds widely used to categorize wines. The concentrations

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of fifteen polyphenols were determined in wines from a range of red and white cultivars grown in the region of Niagara. Several significant differences in the contents were identified and relative patterns of individual phenols were determined (Soleas, Dam, Carey & Goldberg, 1997). Caftaric and coutaric acids, as well as procyanidins were compounds that showed considerable differences between two wine varieties from Spain (Mayen, Baron, Maid & Median, 1997). Furthermore, the flavonoids, myricetin and quercitin, were successfully employed to classify red wines of various origins (McDonald, Hughes, Burns, Lean, Mathews & Crozier, 1998). For wines from the Medoc area, discrimination was achieved by two-dimensional analysis of myricetin and epicatechin levels (Manterola, 1985). Moreover, several phenolic compounds, such as epicatechin and *p*-coumaric acid, were found to be significantly different, according to variety, vintage year and winery, for white wines from the Penedes region (De La Presa-Owens et al. 1995). Some researchers also showed that certain types of anthocyanins and some flavonoids could be used to discriminate wines from different regions (Etievant, Schlich, Bertrand, Symonds & Bouvier, 1988).

Although sensory evaluation is important and until recently considered, the only valid way to classify wines according to vintage and origin, Frank and Kowalski (1984) showed that sensory data do not provide sufficient information to separate wines from various areas of France and USA. Hence, verification of wine authenticity may lay in the joint determination of two or more chemical classes of compounds and/or sensory parameters (Arvanitoyannis et al. 1999).

Multivariate analysis has traditionally been employed for food quality evaluation as well as for wines or other products. Principal component analysis (PCA) is a frequently employed statistical analysis and has been successfully applied to analytical results, both for individual compounds and component combination (Arvanitoyannis et al. 1999). For example, PCA in conjunction with discriminant analysis was applied to anthocyanins, flavonoids and colour parameters determined in Spanish red wines, and aided distinction of origin (Gomez-Cordoves, Gonzalez-San Jose, Junquera & Estrella, 1995).

In this study, 33 wines from different varieties and vintage areas were differentiated and classified in an attempt to determine which instrumental and/or sensory descriptors are most important for greek wine authentication. All grapes were grown in Greece (North, Central, South and Islands). The following parameters were determined: minerals, total phenols, polyphenols and anthocyanins. determined by HPLC, and sensory data. The results obtained were analysed using multivariate analysis of PCA.

2. Materials and methods

2.1. Wine samples

All wines used in this study were commercial samples from the 1998 vintage. The wine varieties and production areas are presented in Table 1. When required, samples were kept at 4°C in an amber vial filled to completion under nitrogen. All analyses were completed within three days.

2.2. Total phenols

The total phenols were determined according to the procedure described by Singleton and Rossi (1965) and were expressed as mg/l of gallic acid.

2.3. Non-coloured phenolic compounds

The polyphenolic fraction was analysed according to the HPLC method described by Kallithraka, Bakker and Clifford (1997). A Hewlett-Packard 1090M Series II with an auto injector (25 μl injection volume) and a diode array detector, recording at 280, 320, 365 and 265 nm, was used to detect the phenolic compounds. A reversed phase ODS Hypersil column (250×4 mm id, particle size 5 μm) at 40°C was used with a flow rate of 1 ml/min. Using 0.6% aqueous perchloric acid and methanol as eluants, the following linear gradient was used: in 55 mm from 5 to 80% methanol, hold for 15 min at 80% methanol to wash the column and then return to the initial conditions to re-equilibrate for 10 min.

Peaks were identified by comparison of retention times and ultraviolet (UV) spectra with commercial standards: gallic acid, protocatechuic acid, vanillic acid, caffeic acid. syringic acid, *p*-coumaric acid. *o*-coumaric acid, ferulic acid, (+)- catechin, (−)-epicatechin, tryptophol, myricetin, quercetin, kaempherol (all from Sigma) procyanidin B1 and procyanidin C1 (Gift from Dr. A.G.H. Lea, Reading, UK). The concentration of phenolic acids are expressed as mg/l gallic acid, (+)-catechin, tryptophol, and procyanidins B1 and C1 are expressed as mg/l (−)-epicatechin and quercetin and kaempherol are expressed as mg/l myricetin. Gallic acid, (−)-epicatechin and myricetin are expressed against their own calibration curves. All analyses were performed in duplicate.

2.4. Anthocyanins

Anthocyanins were extracted by solid phase extraction, according to the method described by Bridle and Garcia-Viguera (1996). The detection and quantification was performed by HPLC. A Hewlett-Packard 1090M Series II with an auto injector (20 μl injection volume) and a diode array detector, recording at 520 and 280

Table 1
Codes, grape varieties and geographical origin of the greek wines

Code No.	Type	Variety	Area of production
1	Red	Xinomauro, Krasato&Stavroto	North Greece (Rapsani)
2	Red	Xinomauro	North Greece (Chalkidiki)
3	Red	Cabernet Sauvignon	North Greece (Porto Carras)
4	Red	Limnio	North Greece (Porto Carras)
5	White	Asirtiko	North Greece (Porto Carras)
6	Red	Roditis & Xinomauro	North Greece (Goumenissa)
7	Red	Syrah	North Greece (Porto Carras)
8	Red	Limnio & Cabernet Sauvignon	North Greece (Porto Carras)
9	White	Roditis	North Greece (Porto Carras)
10	Red	Xinomauro Krasato & Stavroto	North Greece (Rapsani)
11	Red	Xinomauro Krasato & Stavroto	North Greece (Rapsani)
12	Red	Xinomauro & Negoska	North Greece (Goumenissa)
13	White	Moschoflero	South Greece (Mantinia)
14	White	Asirtiko	Islands (Santorini)
15	White	Asirtiko	Islands (Santorini)
16	White	Moschofilero	South Greece (Mantinia)
17	White	Moschoflero	South Greece (Mantinia)
18	White	Robola	Islands (Kefalinia)
19	White	Robola	Islands (Kefalinia)
20	White	Robola	Islands (Kefalinia)
21	White	Robola	Islands (Kefalinia)
22	White	Athiri	Islands (Rodes)
23	Red	Mandilaria	Islands (Rodes)
24	Red	Agiorgitiko	South Greece (Nemea)
25	Red	Agiorgitiko	South Greece (Nemea)
26	Red	Xinomauro & Negoska	North Greece (Goumenissa)
27	Red	Xinomauro & Negoska	North Greece (Aminteo)
28	Red	Agiorgitiko	South Greece (Nemea)
29	Red	Liatiko	Islands (Crete/Sitia)
30	Red	Monemvasia & Mandilaria	Islands (Paros)
31	Red	Liatiko	Islannds(Crete/Dafnes)
32	Red	Kotsifali & Mandilaria	Islands (Crete/Peza)
33	Red	Kotsifali & Mandilaria	Islands (Crete/Archanes)

nm, was used to detect anthocyanins. A reversed phase ODS Hypersil column (250×4 mm id, particle size 5 μm) at 40°C was used with a flow rate of 0.5 ml/min. Using 0.6% aqueous perchloric acid and methanol as eluants, the following linear gradient was used: in 30 min from 15 to 80% methanol, hold for 15 min at 80% methanol to wash the column and then return to the initial conditions to re-equilibrate for 10 min.

Peaks were identified by comparison of retention times and UV spectra with commercial standards: delphinidin 3-glucoside, cyanidin 3-glucoside, petunidin 3-glucoside, peonidin 3-glucoside and malvidin 3-glucoside (all from polyphenol co, Finland). The concentration of anthocyanins is expressed as mg/l malvidin 3-glucoside.

2.5. Minerals

Wine samples were diluted 1:100 with sample diluent (2% nitric acid) and analysed by an inductively coupled plasma apparatus (LEMAN, INC Model PS-100080), according to the method of Baxter et al. (1997).

2.6. Sensory analysis

Ten healthy subjects were selected to evaluate the samples. All of them were fully trained with more that five years experience in evaluating all types of wine. Tests were conducted from 10:00 to 12:00 pm in individual booths. To balance out any order effects that might occur, the order of presentation was randomized for each subject for the three replications. The 33 samples were assessed in groups of six. A 4-mm break was taken between samples, during which the panellists were required to eat a cracker and rinse the mouth thoroughly with spring water. Judges were presented with 15 ml samples and they were asked to swirl them in their mouths for about 15 s and to start immediately rating the intensity of all attributes on a scale anchored to the left, with “none” of the attribute, and on the right with “extreme”. The attributes they had to evaluate were the following: astringency, sweetness, acidity, body, flavour (a combination of olfactory-gustatory-tactile and kinesthetic sensations), after-taste and overall acceptability.

2.7. Statistical analysis

PCA attempts to identify underlying variables or factors that explain the pattern of correlations within a set of observed variables. PCA is often used in data reduction to identify a small number of factors that explain most of the variance observed in a much larger number of manifest variables. The PCA procedure is characterised by a high degree of flexibility: seven methods of factor extraction, five methods of rotation and three methods of computing factor scores.

The PCA was carried out with SPSS base 9.0 (SPSS Inc., 1999). Varimax was applied in order to ensure that the resulting factors were uncorrelated.

3. Results and discussion

3.1. Comparison of greek wines with wines from other countries

3.1.1. Phenolic compounds

All the results related to determination of minerals, phenolic compounds. anthocyanins and sensory analysis, obtained from greek red and white wines are summarised as mean values and standard deviations in Tables 2, 3, 4 and 5, respectively.

Phenolic compounds contribute to colour, taste, mouthfeel oxidation/antioxidant properties and related characteristics of juices and wines (Blanco, Auw, Sims & O’Keefe, 1998; Wulf & Nagel, 1976). The main sources of phenolic compounds are grape skin and seeds. The major classes of phenolics, identified in grapes and wines, include flavonoids (catechin, flavonols, anthocyanins and polymers), as well as non-flavonoid compounds. Due to the heterogeneity of phenolics in wines,

Table 2
Mineral (ions) concentrations (mg/l mean value±standard deviation) of Greek red and white wines

Wine codes	K^+	Na^+	Ca^{2+}	Mg^{2+}	Fe^{3+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	P^{5+}
1	919±15.3	65.8±0.7	275±1.5	109±1.0	10.8±1.6	0.9±0.2	1.1±0.3	1.9±0.3	197±3.3
2	667±2.7	24.7±0.3	336±0.7	126±0.5	13.5±0.5	0.7±0.2	0.8±0.1	1.4±0.2	89.4±2.3
3	761±4.5	42.7±0.2	320±1.7	139±3.3	5.3±0.7	1.0±0.1	1.0±0.2	1.6±0.1	124±5.1
4	756±3.6	37.7±0.2	285±0.6	126±2.2	2.9±0.2	0.6±0.3	0.8±0.3	0.7±0.4	112±6.1
5	554±1.3	30.9±0.1	292±0.2	108±3.3	1.9±0.3	0.8±1.0	0.5±0.2	0.7±0.2	88.7±4.4
6	756±2.1	20.7±0.3	375±0.5	145±6.6	3.3±0.1	0.7±0.3	1.2±0.3	1.0±0.3	153±3.2
7	767±1.3	37.7±0.3	352±0.6	143±2.1	5.0±0.4	0.8±0.3	0.9±0.1	0.9±0.3	109±5.2
8	661±7.2	25.3±0.2	97.4±0.2	96.4±5.1	1.5±0.2	0.7±0.2	0.4±0.1	0.6±0.1	72.7±3.7
9	565±4.1	19.5±0.2	139±0.1	120±4.2	1.9±0.1	0.9±0.3	0.7±0.2	1.0±0.1	83.1±2.6
10	1267±10.0	8.5±0.2	123±1.3	121±3.1	8.1±0.5	0.7±0.1	1.3±0.2	1.1±0.2	196±4.2
11	980±4.5	10.3±0.2	260±3.3	125±0.5	14.5±0.1	1.0±0.3	2.0±0.9	2.4±0.2	224±4.2
12	1176±6.6	20.5±0.1	150±0.4	108±2.3	3.2±0.1	0.4±0.2	0.8±0.2	0.5±0.1	83.8±0.5
13	672±3.1	51.3±0.3	165±0.2	109±0.5	6.4±0.3	0.7±0.1	5.1±0.4	1.2±0.1	109.5±4.0
14	651±6.8	87.5±1.4	167±2.6	94.4±2.9	1.1±0.1	0.7±0.3	0.8±0.5	1.1±0.1	125±2.3
15	708±3.1	98.4±0.4	219±1.5	96.5±6.7	4.0±0.4	0.9±0.1	1.0±0.2	2.0±0.3	130±5.5
16	487±1.2	27.1±0.2	101±0.3	81.3±0.2	2.0±0.2	0.3±0.1	1.5±1.1	2.7±0.1	44.9±1.0
17	504±7.7	19.6±0.1	141±0.5	83.7±1.6	3.3±0.2	0.4±0.2	1.0±0.2	1.0±0.2	64.0±0.8
18	359±3.5	10.4±0.1	176±2.6	96.2±0.2	6.1±0.1	0.7±0.1	0.7±0.1	0.6±0.2	93.9±1.0
19	501±6.3	38.0±0.3	166±0.4	106±0.2	17.1±1.5	1.0±0.1	1.0±0.2	0.5±0.1	113.5±2.2
20	505±2.8	11.1±0.2	435±0.4	118±0.2	9.8±0.2	0.3±0.1	5.2±0.3	3.3±0.2	268±5.5
21	321±2.1	8.8±0.2	144±0.2	98.4±0.6	2.4±0.4	0.4±0.3	0.6±0.2	0.5±0.2	88.5±2.6
22	794±7.9	55.5±0.1	159±0.3	87.6±0.4	4.0±0.3	0.8±0.3	0.8±0.3	2.8±0.4	131±1.2
23	1023±12.8	55.2±0.2	539±0.4	195±3.7	22.0±0.1	1.0±0.3	6.9±0.4	7.8±0.9	221±4.4
24	1074±2.4	38.5±0.7	390±8.8	166±1.4	11.2±1.5	1.3±0.4	2.2±0.2	4.9±0.2	255±5.0
25	1020±2.5	5.3±0.3	97.4±0.3	114±0.3	5.6±0.8	0.3±0.2	1.5±0.5	0.5±0.1	94.9±0.2
26	683±3.6	8.0±0.1	82.2±1.5	134±0.2	2.9±0.4	0.3±0.1	1.4±0.4	0.5±0.1	147±0.9
27	601±3.1	20.3±0.1	146±0.5	99.7±0.3	1.6±0.3	0.9±0.5	0.2±0.1	0.3±0.1	22.3±1.1
28	921±2.9	14.0±0.3	113±0.3	112±0.3	8.7±0.7	1.0±0.3	1.7±0.1	1.1±0.2	106±0.9
29	1097±2.5	51.2±0.1	225±2.5	164±2.2	9.7±0.1	1.2±0.2	1.5±0.1	2.1±0.3	136±1.5
30	1093±10.7	187±0.4	291±6.4	102±1.4	7.4±2.1	1.0±0.1	4.2±0.1	2.0±0.4	498±3.4
31	784±3.7	18.3±0.9	153±0.1	107±0.3	4.4±0.6	0.5±0.3	0.4±0.1	0.5±0.2	79.2±0.4
32	646±6.5	21.6±0.1	131±0.1	113±0.2	6.1±0.1	0.8±0.3	0.9±0.2	0.5±0.1	82.3±0.6
33	838±0.2	2.7±0.3	54.1±0.2	159±0.5	11.3±8.1	6.3±0.2	0.8±0.2	1.3±0.1	111±0.1

Table 3
Phenol concentrations (mg/l; mean value±standard deviation) of Greek red and white wines

Wine codes	Total phenols	Gallic acid	Procyanidin Bi	Catechin	Vanillic acid	Caffeic acid	Procyanidin Cl	Epicatechin	Syringic acid
1	1650±42	116±25	128±49	19.2±08	3.1±0.1	118±16	13.2±12	10.4±12	0.6±0.1
2	1500±10.6	74.2±1.4	123±6.9	75.6±2.5	0.0±0.0	5.0±1.8	60.2±1.6	90.1±1.7	0.0±0.0
3	1510±5.5	158±5.2	72.1±1.2	97.0±0.9	33.5±2.0	66.2±2.3	7.8±0.6	45.0±0.3	13.2±0.5
4	1910±5.7	174±11.6	162.5±4.1	76.3±1.0	42.7±5.5	81.6±2.2	4.1±0.1	46.2±1.7	14.4±0.2
5	270±2.4	16.2±1.2	104±3.5	100±4.5	17.8±1.1	49.6±2.2	32.4±0.6	61.3±1.3	0.0±0.0
6	2040±13.5	226±5.7	74.3±3.3	111±4.3	54.2±1.2	172±2.1	84.5±3.5	67.2± 3.3	11.3±1.7
7	1990±4.6	130±16.8	65.9±1.8	82.0±3.2	28.0±0.5	49.0±0.8	12.8±1.1	38.2±1.3	10.5±0.8
8	600±6.0	22.2±0.6	135±7.3	39.8±0.9	0.0±0.0	78.2±0.4	10.6±1.0	12.8±1.2	3.4±0.4
9	590±4.1	23.1±2.4	60.1±1.4	41.9±0.8	42.8±7.6	143 ±2.8	9.6± 0.1	11.0±0.2	0.0±0.0
10	1860±35.8	172±10.5	31.5±4.4	76.3±2.2	0.0±0.0	185±4.4	0.0±0.0	59.4±4.4	8.5±1.5
11	1820±5.8	197±12.1	63.1±2.9	116±9.1	11.8±1.4	66.5±5.9	0.0±0.0	76.4±2.4	11.0±2.9
12	1460±3.9	113±4.9	39.1±0.2	70.3±1.2	15.5±1.3	0.0±0.0	29.6±1.0	75.5±2.5	37.5±6.7
13	240±1.6	16.0±1.5	82.2±1.1	1.0±0.1	1.6±0.6	11.5±0.9	1.0± 0.1	3.5±0.5	2.7±0.5
14	440±1.1	6.1±0.3	170±4.0	0.0±0.0	0.0±0.0	89.2±0.6	12.3±0.2	4.2±0.4	0.0±0.0
15	520±8.7	10.2±0.8	53.7±4.0	16.3±0.6	14.6±1.7	50.0±3.8	13.2±0.3	0.0±0.0	0.0±0.0
16	260±6.1	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	189±8.9	0.0±0.0	0.0±0.0	4.4±0.3
17	210±5.5	0.5±0.2	67.1±0.6	0.0±0.0	15.6±0.9	15.6±0.1	2.2±0.0	0.0±0.0	0.0±0.0
18	290±4.9	0.0±0.0	173±3.0	10.0±1.8	8.8±1.4	37.6±1.0	11.7±0.9	0.0±0.0	0.0±0.0
19	300±3.3	0.0±0.0	110±6.0	5.1±0.6	11.1±1.5	43.1±0.8	5.8± 0.2	0.0±0.0	0.0±0.0
20	350± 2.6	0.3±0.1	29.4±2.7	3.1±0.2	13.9±1.5	48.9±0.9	0.0±0.0	0.0±0.0	0.0±0.0
21	330±7.1	0.0±0.0	14.4±0.9	0.0±0.0	11.2±0.7	37.1±2.9	0.0±0.0	0.0±0.0	0.0±0.0
22	200±8.6	0.8±0.1	19.9±1.3	0.0±0.0	3.5±0.6	12.2±1.2	0.0±0.0	0.0±0.0	0.0±0.0
23	1970±13.3	163±10.0	115±5.1	61.6±6.1	0.0±0.0	64.1±1.1	4.0±0.6	22.1±1.5	14.8±2.0
24	1770±18.3	110±2.0	43.0±4.8	62.6±7.8	20.4±2.5	29.4±2.4	3.0±0.3	28.4±4.3	17.1±1.8
25	1650±19.4	157±2.3	72.1±2.8	62.7±2.3	18.6±0.9	113±4.3	1.9±0.1	32.1±0.5	16.6±1.8
26	1850±13.6	157±5.2	53.3±3.0	63.0±1.0	0.0±0.0	119±6.3	5.8±0.6	37.3±5.2	12.4±1.3
27	1430±10.4	64.7±2.9	67.8±1.1	56.0±3.2	15.3±1.7	18.1±1.5	3.8±0.2	37.4±4.4	8.2± 1.0
28	1280±5.0	60.2± 1.9	44.4±1.5	47.4±2.5	13.9±0.7	1.0±0.1	27.4±0.9	56.2±3.1	0.0±0.0
29	1700±12.2	283±9.8	72.0±2.8	39.2±1.5	50.2±1.9	65.8±1.8	2.8±0.3	28.9±4.9	7.5±2.4
30	1190±3.1	151±8.3	49.2±2.9	35.8±1.4	36.5±1.0	85.4±4.4	3.3±0.3	20.1±0.9	13.4±1.2
31	1070±3.8	92.9±5.2	77.1±3.8	58.7±4.6	43.7±1.1	32.7±2.4	0.0±0.0	32.9±2.8	3.2±0.2
32	1170±1.2	107±7.5	110±7.1	71.6±3.0	70.9±3.0	116±4.6	12.3±1.3	30.6±0.2	13.2±1.3
33	1638±1.6	16.4±1.0	3.2±0.2	59.6±4.3	83.9±2.5	28.8±3.1	46.5±6.2	10.2±0.6	27.0±3.7

Table 4
Anthocyanin concentrations (mg/l; mean value±standard deviation) of Greek red wines

Wine codes	Delphinidin-3-glucoside	Cyanidin-3-glucoside	Petunidin–glucoside	Peonidin-3-glucoside	Malvidin-3-glucoside	Acylated malvidin-3-glucoside
1	0.00±0.00	0.00±0.00	0.00±0.00	12.1±0.00	76.0±0.00	63.8±0.00
2	0.00±0.00	0.00±0.00	0.00±0.00	8.62±1.18	119.4±7.67	142±2.95
3	0.00±0.00	0.00±0.00	0.00±0.00	19.0±5.54	20.5±0.87	182±4.06
6	0.00±0.00	0.04±0.06	33.2±0.65	61.3±2.04	703± 6.37	144±7.41
7	21.5±1.44	9.92±1.29	30.8±6.19	64.3±6.03	482± 9.06	437±12.38
10	30.8±8.49	21.1±3.28	42.4±1.17	38.5±8.45	555±9.11	25.8±3.82
11	27.3±2.29	2.97±0.62	28.8±5.19	39.7±2.75	405±5.11	6.41±0.89
12	19.5±3.13	0.00±0.00	0.00±0.00	1.74±0.12	91.2±2.90	105±0.02
23	4.10±5.80	0.00±0.00	5.52±0.80	31.5±6.60	173±4.08	370±14.00
24	24.6±2.10	0.00±0.00	85.0±9.47	126±3.28	857±9.67	2232±1.94
25	70.8±4.51	0.00±0.00	56.7±6.27	78.4±7.98	638±3.30	87.0±8.86
26	0.82±1.16	0.00±0.00	5.64±0.11	12.7±2.17	187±6.96	5.76±0.89
27	5.31±0.63	0.00±0.00	3.51±0.96	7.85±0.25	152±6.27	77.7±0.69
28	65.7±4.65	0.00±0.00	51.2±5.65	75.4±7.95	701±5.68	85.6±5.42
29	0.00±0.00	0.00±0.00	0.00±0.00	3.95±0.70	18.3±4.95	65.5±5.62
30	0.00±0.00	0.00±0.00	0.00±0.00	22.3±4.19	10.2±4.48	483± 7.55
31	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	42.5±2.08
32	0.58±0.57	3.56±0.78	0.00±0.00	37.8±3.78	45.4± 4.09	84.9±4.31
33	0.00±0.00	0.00±0.00	0.00±0.00	5.38±2.09	15.7±0.61	61.7±5.43

Table 5
Sensory evaluation (mean value) of Greek red and white wines

Wine code	Astringency	Sweetness	Acidity	Body	Flavour	Aftertaste	Overall acceptance
1	2.5	2	2.28	2.25	2.91	2.2	2.125
2	3	1.55	4.2	3	3.1	2.6	2.51
3	3.2	1.9	2.4	2.83	3.1	3	3.36
4	3.2	1.9	2.4	2.83	3.1	3	2.61
5	1.75	1.7	2.45	2.45	2.5	2.38	2.45
6	3.5	2	2.9	3	3.33	2.9	3.27
7	3.23	3	1.75	3	3.25	2	3.1
8	1.6	1.62	2	2.5	2	2.83	2.27
9	2	2	2.16	2.5	2.6	2.65	2.7
10	4.1	1.9	3	2.3	2.9	3.1	2.05
11	3	1	1.7	2	2.3	2.25	2.5
12	2.95	1.8	2.6	1.8	2.5	1.8	2.6
13	1.5	1.9	3.5	3.36	3.82	3.2	3.58
14	1.7	1.5	3	2.8	2.7	2.25	2.9
15	1.7	2.1	3.3	3	2.95	3.9	2.93
16	1.9	2	1.7	3.85	3	4	5.025
17	1	1.6	3	2.75	2.88	3.3	3.68
18	1.9	1.9	1.87	3	3.1	3	3.125
19	3.9	1.4	4.9	3	3.9	2.5	1.78
20	2.4	1.8	2.5	3	3.3	2.3	2.25
21	1.45	1.75	4.8	3.85	3.75	3	2
22	1.9	1.67	1.87	1.75	2.38	2.4	2.6
23	3.74	1.5	3	2.7	3.22	3.1	3.07
24	3.4	1	1.87	2.75	2	3	3.025
25	3	1.5	2.7	3.2	3.6	4	3.17
26	3.1	1.8	3.7	2.3	3	3	2.25
27	2	1.2	3.42	2.33	3	3	2.05
28	3	2.5	2.7	3	3.75	3	3.125
29	3	2.5	3	3	3.4	2.7	2.93
30	2.5	1.5	4	2.75	3	2	3.43
31	2.8	1.5	2.5	3.4	3.4	3.8	2.87
32	2.8	3	2.75	2	2.17	2.3	2.25
33	2.9	1.5	4	2.7	3.6	3.6	2.67

phenolics are commonly reported as gallic acid equivalents.

Tables 3 and 4 show that the determined total phenolic content of Greek red wines (1514 ppm) was in satisfactory agreement with the values reported for other countries (925 and 2430 for Portugal and Italy, respectively). The values found for Greek white wines (354 ppm) fell in line with values reported elsewhere; 160 and 721 for Spanish and Portuguese wines, respectively. In fact, the reported values in Tables 6 and 7 are in satisfactory agreement with those reported by Fischer and Noble (1994) and Shahidi and Naczk (1995) for white and red wines (100–250 and 1000–4000 ppm, respectively).

The values of phenolic compounds of Greek red wines were among the highest, if not the highest compared to other countries (Table 6). Only in certain categories, i.e. catechin, yugoslavian and USA and canadian wines score higher (95, 152 and 240 ppm) than Greek wines (60.4 ppm). Similarly, yugoslavian and canadian wines had higher values for (−)-epicatechin (53.2 and 82.0 ppm, respectively) than the mean value of 40.7 for greek wines. It is interesting to note that an Italian wine (Pinot Nero, North Italy) showed extremely high phenolic values but this could possibly be attributed to the particularity of the method employed (Liquid chromatography–MS using a capillary-scale particle beam interface; Cappiello & Famiglini, 1999). There are many factors (grape cultivar, employed method, climatic conditions and soil composition) that affect the composition and content of phenolic compounds in wines. Another important variable contributing to flavonol concentrations in wines from different regions might be the contact duration between the skins and the juice prior to fermentation. This time can vary between zero and four or even more hours and constitutes an important part of the traditional winemaking style practised in specific regions. The use of different clones of the same cultivar and length of barrel ageing may be two equally important factors (Goldberg & Soleas, 1999). The colour, stability, possible nutritive benefits and sensory characteristics of the wine will be strongly affected by these changes (Blanco et al. 1998).

In Table 7 (white wines), the already observed trend for Greek red wines became more evident, since Greek wines continued to score higher on most individual categories of phenolics than wines from other countries,

Table 6
Comparison of the phenolic contents of Greek white wines with wines from other countries

	Phenols	Gallic acid	Procyanidin B1	Catechin	Vanillic acid	Caffeic acid	Procyanidin C1	(−)-Epicatechin	Ferrulic acid	Quercetin	*p*-Coumaric	References
Greece	4	7.33	78.4	16.7	39.3	61.9	7.59	7.14			24.3	Current study
Italy												Moret et al., 1994
Canada		2.5		11.5	2.45	4.9		3.75			2.4	Soleas et al, 1997
Spain	160	1.03		2.71				4.04				De La Presa-Owens & Noble, 1995
Yugoslavia			94.7	93.1			15.9	48.9				Kovac, Alonso, Bourzeix & Revilla, 1992
France	357											Sato, Ramarathnam, Suzuki, Ohkubo, Takeuchi & Ochi, 1996
Hungary	342.3											
Italy		3.8										
Japan	425.1											
Portugal	721											McDonald et al., 1998
Russia												
Spain	259.4											
USA				5.3				0.9			1.7	
Italy				3.1				0.4			0.7	
France				4.5				4.3			1.9	
Iberia				4.2				1.3			2.0	Goldberg et al., 1996
Central Europe				1.3				1.1			1.1	
North America				4.1				1.1			1.5	
Canada	200			45				34.0			1.6	Goldberg and Soleas, 1999
South Africa				7.8				3.1			1.8	
Australia and New Zealand				6.1				2.5 1.2			1.7	Goldberg et al., 1996
Canada				4.7							1.3	
Germany				3.7				1.4			2.3	
South America				5.2				2.3			1	
Greece									3.40	5.47		current Study
Italy												Moret at al., 1994
Canada									1.6	0.08		Soleas et al., 1997
Spain									0.13			Dela Presa-Owens, & Noble 1995

except for quercetin and (−)epicatechin for which higher values were reported for canadian wines (5.47 ppm quercetin for greek vs. 11.4 ppm for canadian; 7.14 ppm epicatechin vs. 34 ppm for canadian wines).

However, as regards total phenols, the countries in ascending order (increasing phenol content) were as follows:

$$\text{Spain(1)} < \text{Canada} < \text{Spain(2)} < \text{Hungary} < \text{Greece} < \text{France} < \text{Japan} < \text{Portugal}$$

The highest value of total phenols was reported for portuguese white wines while it is noteworthy that the corresponding value for red wines was the lowest. Another factor that should be taken into account as a possible source of error is in the stability of wine phenolics once the bottle has been opened. This factor is often not properly evaluated and it has been recently shown that, for resveratrol, a drop in concentration of ~16% occurs (Goldberg, Tsang, Karumanchiri, Diamandis & Soleas, 1996).

3.1.2. Anthocyanins

The mean value of our results amounts to 270 ppm which, though a little lower, is in rather good agreement with elsewhere reported values (330 and 377 for port wine and californian wines, respectively (Bakker & Timberlake, 1985; Niketic-Aleksic & Hrazdina, 1972).

3.1.3. Minerals

A comparison of levels of K (ppm) among wines from Greece, Spain and France showed that Greek and Spanish wines had almost similar levels of potassium (variation range ~4%) whereas the French wines contained substantially greater amounts of K^+ (20–100% greater values). It is noteworthy that the highest K^+ values were obtained when measurements were taken on the pressed grapes (Day, Zhang & Martin, 1994). Since K^+

Table 7
Comparison of the phenolic contents of Greek red wines with wines from other countries

	Phenols	Gallic acid	Myricetin	Quercetin	Catechin	Vanillic acid	Caffeic acid	Epicatechin	*p*-Coumaric	Ferulic acid	References
Greece	1514	128	6.15	25.7	60.4	26.4	62.8	40.7	21.0	3.94	Current study
Italy											Moret et al., 1994
Canada		20.33		1.95	72.17	2.70	5.50	38.8		1.71	Soleas et al., 1997
Spain							0.38	1.22	3.36	0.12	De La Presa-Owens, & Noble 1995
Yugoslavia					94.78			53.2			Kovac et al., 1992
Spain											Bonilla, Mayen, Merida & Medina 1999
Spain											Almella, Lazaro, Lopez-Roca & Fernandez-Lopez, 1993
Australia	2138										Sato et al., 1996
Chile	2875										
France	2099										
Hungary	1225										
Italy	2430										
Japan	2011										
Portugal	926										
Russia	2170										
Spain	1802										
USA	2727										
Italy			2.26	2.26							McDonald et al., 1988
France			4.00	6.53							
Chile			12.8	14.0							
USA			7.87	10.9							
Australia			2.70	10.6							
Romania			1.90	5.90							
Bulgaria			3.05	2.30							
Brazil			4.50	9.30							
Spain			11.4	4.20							
New Zealand			6.80	10.0							
Morocco			6.00	28.3							
Hungary			2.00	3.60							
Canada	1200			18.5	240			82.0	3.80		Goldberg & Soleas, 1999
USA				2.20	80			31.0			Goldberg et al., 1996
Italy				8.00	37			23.0			Goldberg et al., 1996
France				3.40	67.3			31.3			Goldberg et al., 1996
Australia				8.20	39.8			34.1			Goldberg et al., 1996
Italy			3763			160	2267		217	38	Goldberg et al., 1996
USA			59	7.30	152						Waterhouse and Teissedre, 1999

levels greatly depend on anthropological activity, the latter were found to gradually decrease, as already shown by other researchers (Table 8), whereas the levels for other minerals may increase or decrease depending on the particular kind of treatment and equipment employed (Day, Zhang & Martin, 1994; Latorre, Garcia-Jares, Medina & Herrero. 1994). The Na^+ content of greek wines was twice as high the levels of spanish and french wines. This characteristic of Greek wines is advantageous in terms of their physiological action since it is well known that the most widely distributed active-transport system in higher animals, the human organism included, is the Na^+ K^+–ATPase of the plasma membrane which extrudes Na^+ from cells and allows K^+ to enter. High internal K^+ content is required for ribosome function, glycolysis, and many other functions. Furthermore, the active-transport systems for glucose and aminoacids usually require an inward gradient of Na^+ as the energy source to transport amino acids into the cell (Lehninger, 1975). Therefore, our findings K^+/Na^+ (839/62.3)~13.5 are in agreement with the range of 12–16 (K^+/Na^+) for most animal cells as reported by Lehninger (1975). However, for the remaining wines (spanish and french) this ratio moved to substantially higher values (27.5 and 61.1).

The determined values for greek wines were found to be very high (almost 20 times higher) than the Ca^{2+} levels reported for the respective hungarian, french and spanish wines. Although the levels of Na^+, K^+, and Ca^{2+} (and occasionally Fe^{3+}) in wines can be greatly influenced by regional variations in soil fertilization practices and wine processing (Latorre et al. 1994), they can most probably be effectively employed to characterise wines according to geographical origin (provided they are

Table 8
Comparison of Greek wines with other wines regarding mineral levels

	K	Na	Ca	Mg	Fe	Cu	Mn	Zn	P	References
Red wines										
Greece	838	63	1487	174	16.4	1.01	1.76	1.82	190	current study
Hungary			61.9		10.4	0.36	1.20	0.64		Muranyl & Papp, 1998
France	1253	20.5	76.7	53.3			0.62			Etiévant, Schlich & Bonvier, 1988; Etiévant, Schich, Bertrand et al. 1988
France	1000									Tapias, Callao & Larrechi 1987
Spain						0.16		0.27		Acros, Anain, Echeverria, Gonzalez & Garrido 1993
France	1532		65.2	63.3	1.60	1.06	0.44	0.77		Day et al., 1994
Spain	799	29.0	86.8		5.55		2.05			Latorre et al., 1994
France					4.75	0.32	0.86	0.43		Baxter et al., 1997
White wines										
Greece	560	37.2	185	99.6	4.73	0.66	1.48	1.38	109	current study
Italy	674	21.4	96.8	74.6						Moret et al., 1994
Hungary			63.5		20.5	0.35	2.30	1.45		Muranyl and Papp, 1998
France					5.31	0.27	0.95	0.35		Baxter et al., 1997

excluded from the remaining parameters which increase the noise). Similarly to Maarse, Slump, Tas and Schaefer (1987), who managed to distinguish wines from the Rhein-Pflatz and Mosel regions, Etievant, Schlich and Bouvier (1988) effectively classified french wines by Li^+ and Rb^+ levels. The Mg^{2+} level of greek wines was also found to be three times higher than that for French wines and can be successfully employed as another promising feature for differentiation. In the case of Fe^{3+}, the greek wines also showed greater levels than the other wines but this can hardly be considered an advantage since it is well known that high levels of Fe^{3+} and Cu^{2+} can result in iron and copper casse (hazy and cloudy wines).

As regards copper ion levels, some french wines scored higher (1.16 ppm) than greek wines (1.01), whereas hungarian and spanish wines had considerably lower values (0.36 and 0.16/0.41 ppm, respectively; Day, et al. 1994). In fact, the latter fell in satisfactory agreement with a second group of french wines (0.25 ppm) analysed by Baxter et al. (1997). A reasonable explanation that one group of french wines had such a high copper ion content (Day et al. 1994), is wine enrichment by trace elements from spray treatments (e.g. copper in Bordeaux mixture; Baxter, et al. 1997).

The manganese ion levels were rather low for the french wines (0.44, 0.62 and 0.864 ppm; Baxter, et al. 1997; Day et al. 1994; Etievant, Schlich & Bouvier, 1988) whereas the highest values were reported for Hungarian, Greek and Spanish wines in ascending order (1.20. 1.76 and 2.05 ppm, respectively).

The greek wines appeared to have substantially higher levels of Zn^{2+} than hungarian, spanish and french wines (0.64, 0.27 and 0.77 ppm, respectively). However, it is well known that wines can easily be enriched in zinc ion, both by water treatment (even tap water) and/or contact with the appropriate equipment.

As regards to white wines, comparison of greek to italian wines proved to be very interesting, since the Na^+ levels of italian wines were as much as five times higher than K^+ ($Na^+/K^+ \sim 4.55$), whereas exactly the opposite trend occurred for Greek wines ($K/Na \sim 15.14$).

The Greek wines had higher Ca^{2+} and Mn^{2+} values; the former may be dependent on several of the previously mentioned parameters, whereas the latter is more closely linked to the soil (Baxter et al. 1997; Lattore et al. 1994). Another interesting finding was the high values of Fe for the hungarian wines, five times higher than those for the greek and french wines. However, such variations in Fe can be attributed to soil variation, fertilizing practices, wine processing and anthropological activity (Day et al. 1994; Lattore et al. 1994). Cu^{2+}, Mn^{2+} and Zn^{2+} values varied within an acceptable range for greek, hungarian and french wines, The latter showed the lowest values, while greek and hungarian wines scored the top values (current study, Muranyl & Papp, 1998).

3.2. PCA analysis of anthocyanins, and sensory properties of red wines

Two groups A and B are clearly distinguished for north greek and south greek wines, respectively (Fig. 1, PC1 vs. PC2). Although north greek wines are characterised by descriptors such as peonidin and acetyl malvidin (anthocyanins, colour-related parameters), wines from south Greece and the Aegean islands displayed satisfactory sensory properties such as flavour intensity, body, and high general acceptance. Therefore, the wines originating from the south part of Greece and the islands are described as milder, more flavoured and of greater acceptability, most probably due to climate conditions, than wines from northern Greece.

3.3. PCA of anthocyanins of red wines

Three wine groups (A, B and C), two belonging to north Greece (A and B) and one to south Greece, (C), can be clearly identified (Fig. 2, PC 1 vs. PC2). PC2 primarily describes north greek wines (apart from W25, a wine from south Greece). The descriptor for PC2 is acetyl malvidin whereas the descriptors for PC1, standing for wines from Crete and Aegean sea, are malvidin-3-glucoside, delphinidin-3-glucoside and cyanidin-3-glucoside. However, group B, the descriptors of which are peonidin-3-glucoside and petunidin-3-glucoside, seems to be located rather closer to PC1 (group C) thus implying that, at least in terms of colorants, this group of north greek wines (B) more closely resembles the characteristics of south greek wines.

Both PC1 vs. PC3 and PC2 vs. PC3 failed to discriminate the wines (irrespective of their origin) since all

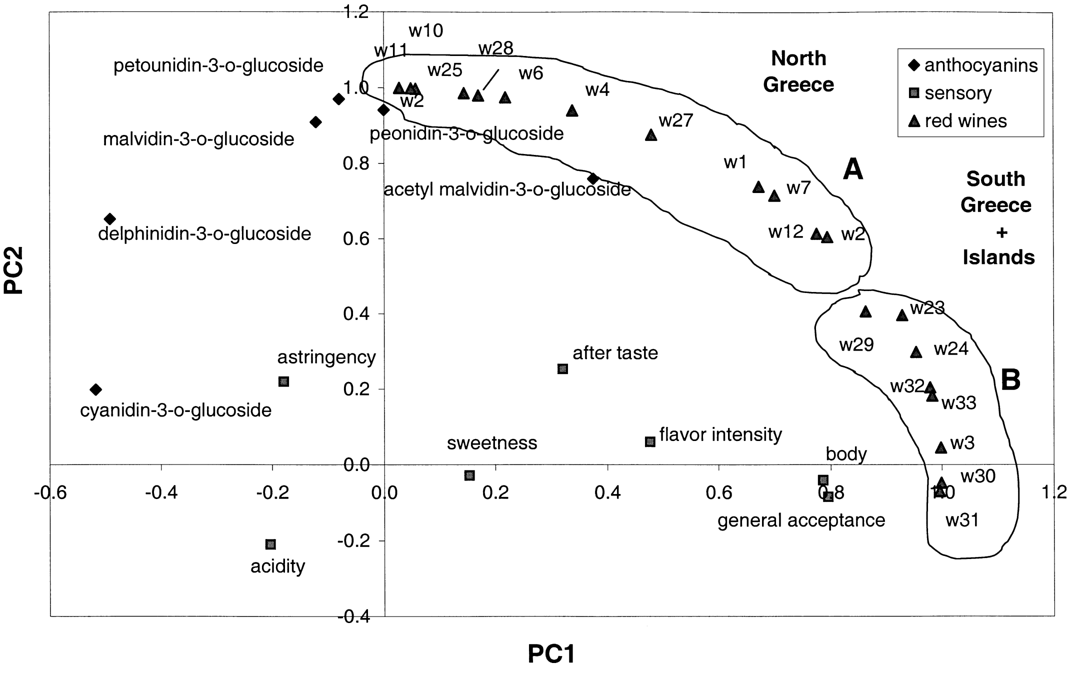

Fig. 1. Principal component analysis of anthocyanins, and sensory analysis of red wines (PC1 vs. PC2).

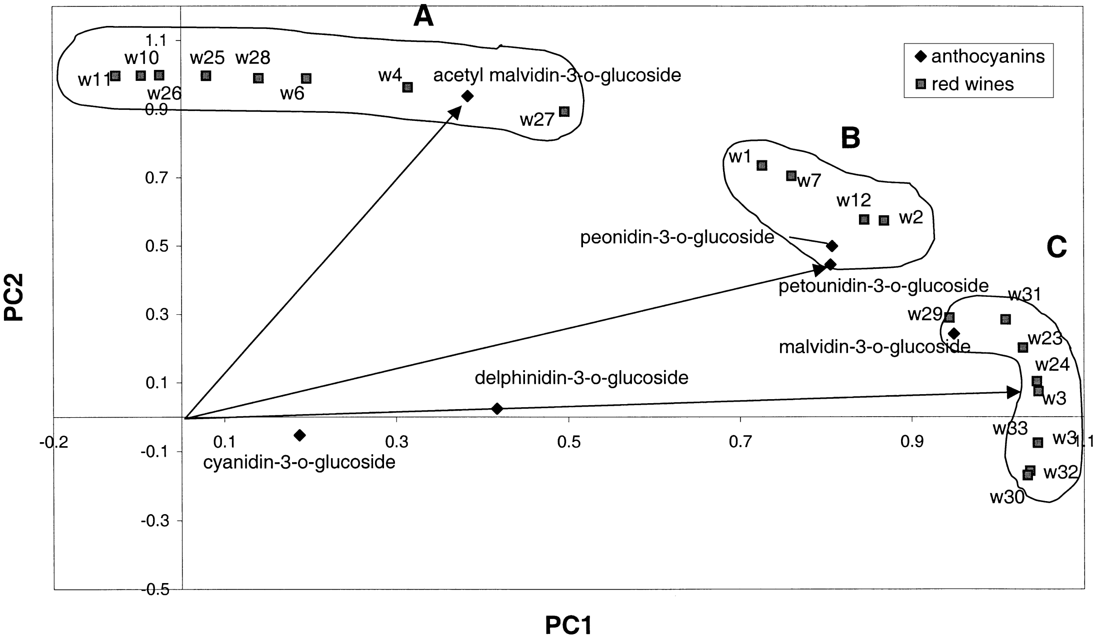

Fig. 2. Principal component analysis of anthocyannins of red wines (PC1 vs. PC2).

of them were located, as two or three groupings, along the PC1 or PC2 axes, respectively.

3.4. *PCA of Phenols and minerals of red/white wines*

The PCA analysis of red wines (Fig. 3), with both instrumental and sensory analysis, resulted in grouping all (group A) but two of them (W30 and W33). The parameters which described this grouping were primarily phenols (o-coumaric acid, vanillic acid, ferulic acid, protocatechuic acid, myricetin and kaempferol) and minerals (Fe^{2+}, Cu^{2+}, Na^{+}). In general, the observations for white wines were quite similar to the ones for red wines.

3.4.1. *PCA of minerals of red wines*

Fig. 4 shows that all (but one) red wines are located around PC1 and are characterised by high Fe^{3+}, Cu^{2+} and Na^{+} and rather low Zn^{2+} content. Although no classification or grouping of red wines according to geographical origin is feasible, the W30 (from Paros) seems to be the only one which is very well described by PC2, the descriptors of which are Ca^{2+} and Mg^{2+}.

PC1 vs. PC3 displays the presence of all red wines along the first axis (PC 1). The descriptors of PC1 are Fe^{3+}, Cu^{2+} and Na^{+} whereas the W30 (from Paros) is located at the very beginning of PC1, almost at the intersection of the two axes. The descriptors of the latter are Ca^{2+} and Mg^{2+}, similar to our results obtained from PC vs. PC2, PC2 vs. PC3 gave similar results in terms of grouping along the PC2 axis. However, it should be noted that a clear classification of wines according to their geographical origin was not feasible as elsewhere reported by Baxter et al. (1997); Day, et al. (1994) and Lattore et al. (1994). Implementation of PC analysis to minerals and white wines resulted in conclusions similar to the ones drawn from the corresponding PCA for minerals of red wines; no classification of white wines in terms of their geographical origin was possible.

3.5. *PCA of phenols, minerals and sensory properties of red/white wines*

In Fig. 5 all red wines fell into the same area, since it appeared as if there were no major differences among the red wines, despite their different geographical origin. The main parameters expressing this grouping of red wines were: Fe (minerals) and *o*-coumaric acid, *p*-coumaric acid, vanillic acid, kaempherol and procyanidinCl (phenols), and, to a comparatively lesser degree, Na^{+} and Cu^{+} (minerals) and protocatechuic acid, myricetin and syringic acid (phenols). Therefore, one can conclude that phenols appeared to be much more effective than minerals in describing the white wines, since in Fig. 5 (PC1 vs. PC2) eight parameters (variables) appeared to be very closely placed for the wine samples.

Similar conclusions were derived for white wines which could not be classified in different groups in terms

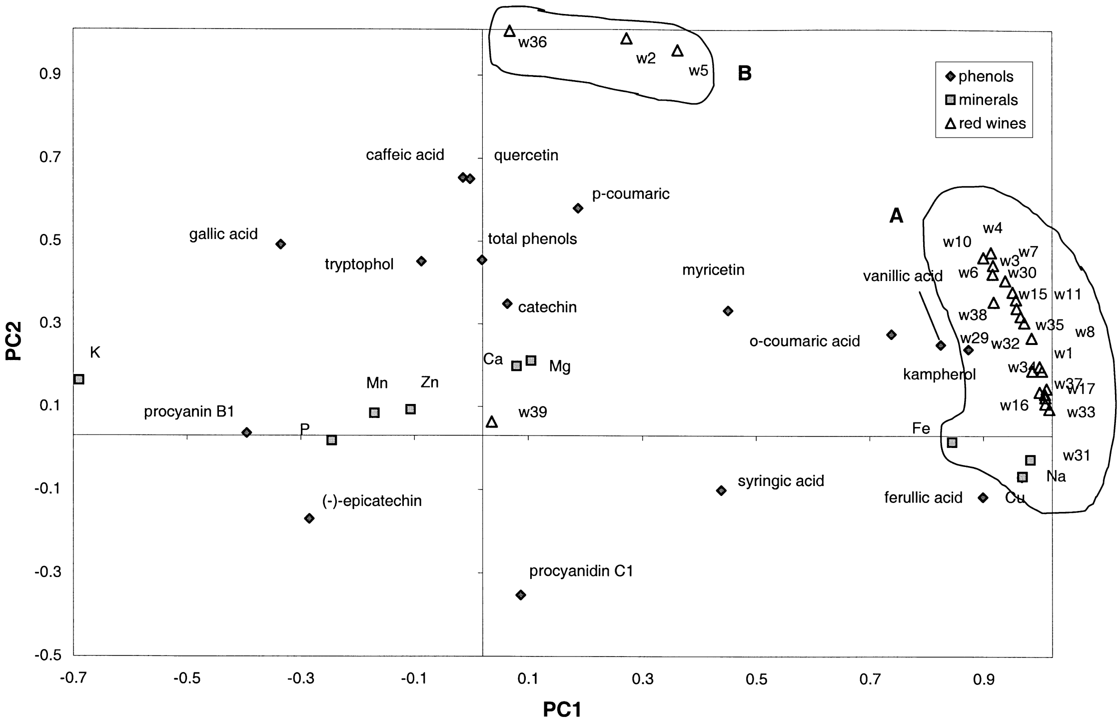

Fig. 3. Principal component analysis of phenols, minerals of red wines (PC1 vs. PC2).

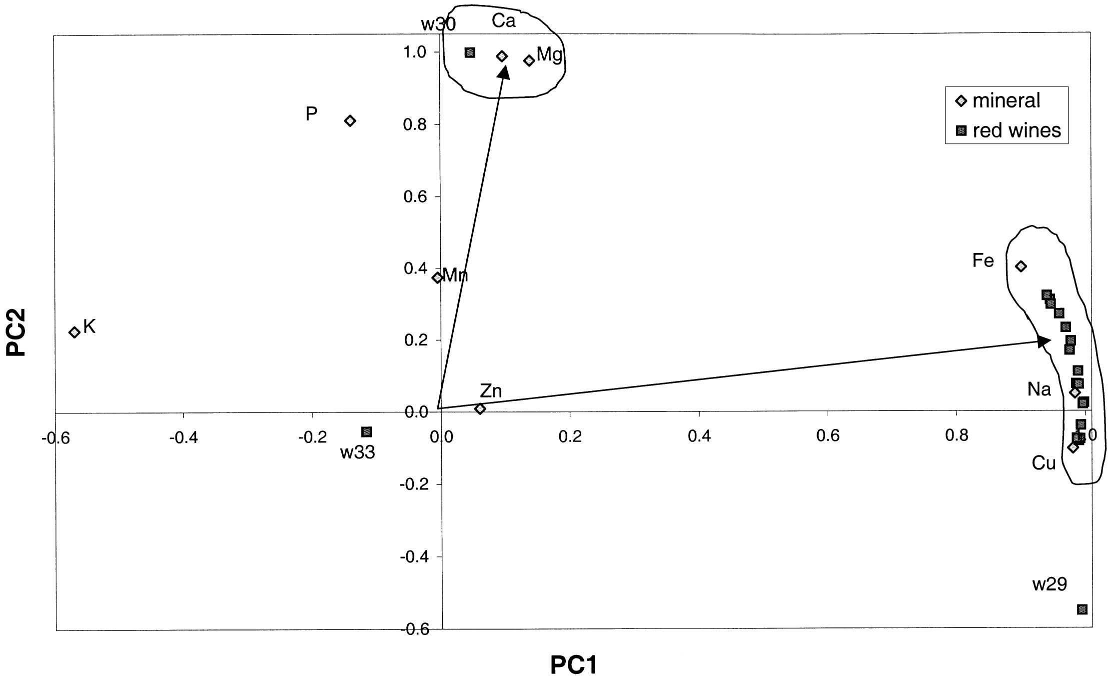

Fig. 4. Principal component analysis of minerals of red wines (PC1 vs. PC2).

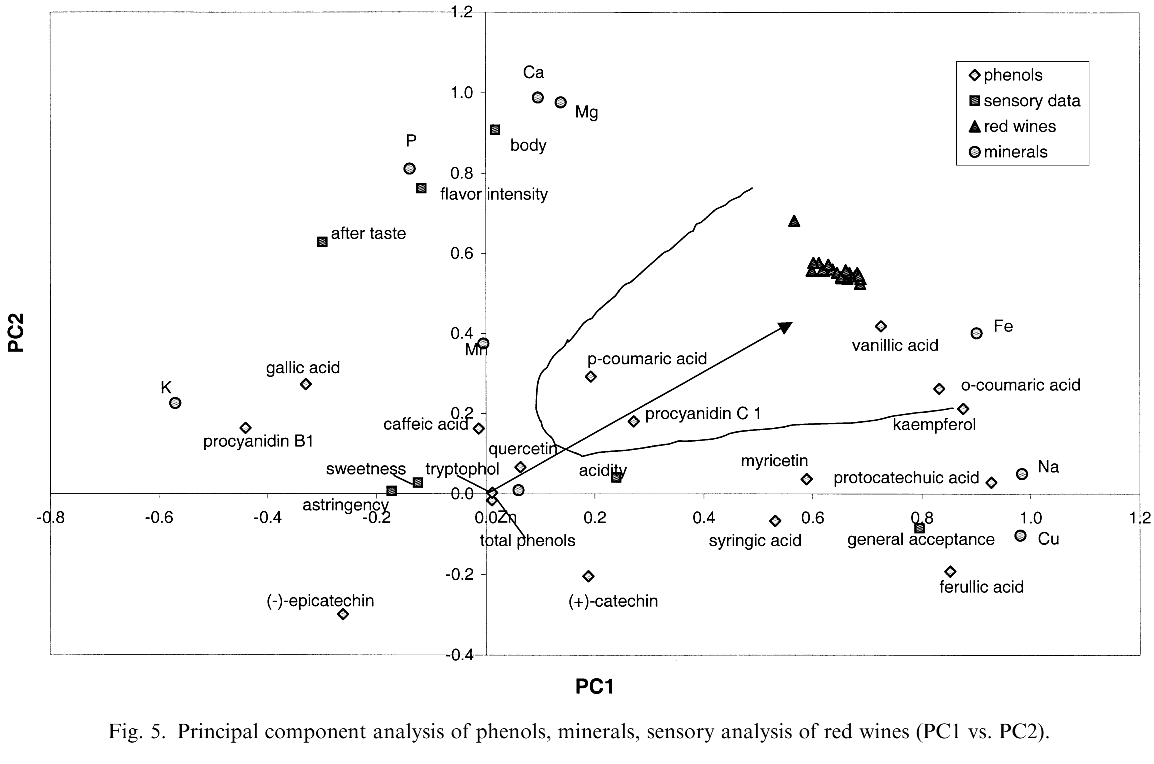

Fig. 5. Principal component analysis of phenols, minerals, sensory analysis of red wines (PC1 vs. PC2).

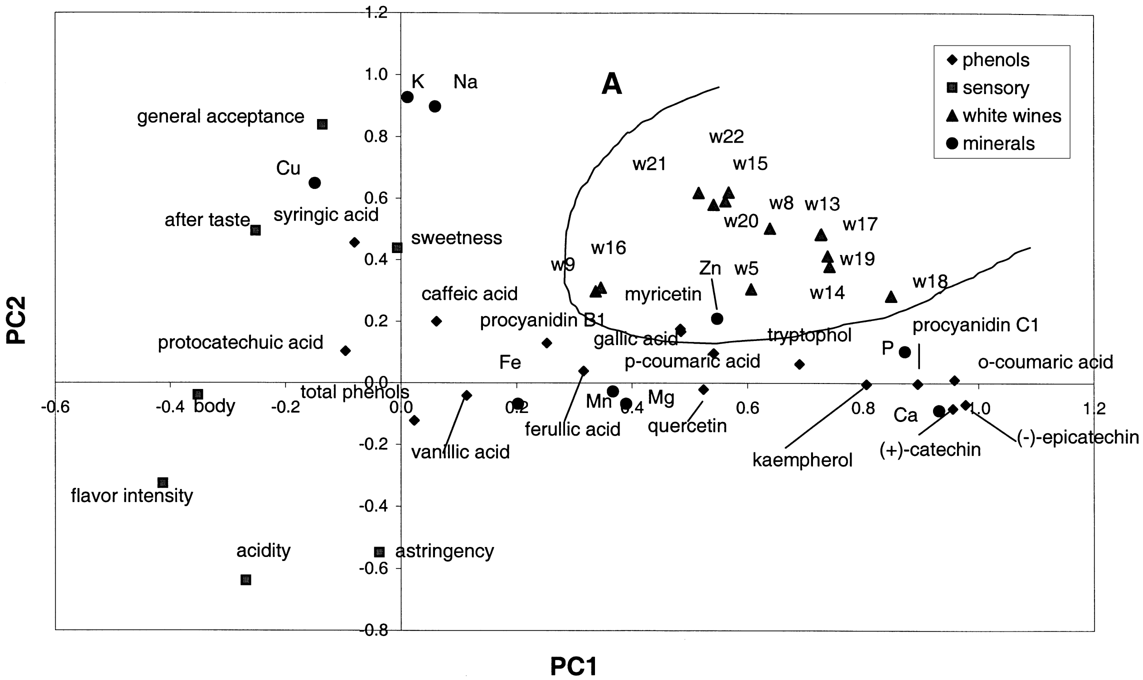

Fig. 6. Principal component analysis of phenols, minerals, sensory analysis of white wines (PC1 vs. PC2).

of their geographical origin (Fig. 6). The variables describing this grouping of white wines were; myricetin, gallic acid and *p*-coumaric acid (phenols) and Zn^{2+} (minerals). However, it is noteworthy that neither the sensory evaluation parameters nor the minerals (apart from Zn^{2+} which is hardly a representative ion) could be correlated to individual white wines. Another PCA, based on phenols, and sensory analysis of white wines, leaving out the minerals, did not result in any better classification of white wines.

4. Conclusions

PCA implementation for all instrumental and sensory data of wines did not show any major differences among either red or white wine categories, despite their different geographical origins. On the other hand, the PCA of anthocyanins and sensory analysis resulted in effective classification of red wines into two groups: north greek and south greek (Peloponese and islands) wines. Therefore, anthocyanins emerged as a crucial factor in terms of red wine classification, whereas minerals (ions) and phenols did not allow any valid clustering of wines.

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