Scientific Research

SENSORIAL INTERPRETATION OF MINERALITY IN WINES

Sensory basis of the mineral character in wine at olfactory and gustatory level
September, 2015

Private Research
Antonio Palacios PhD & David Molina AIWS

Very special thanks to
Elvira Zaldivar & M.P. Fernández

EXCELL IBÉRICA
Asesoría Análisis

LABORATORIOS EXCELL-IBÉRICA
Logroño - La Rioja
Spain

outlook wine

OUTLOOK WINE
The Barcelona Wine School
Spain

INDEX

Sensory basis of the mineral character in wine at olfactory and gustatory level

E. Zaldívar. [1], D. Molina[2], M.P. Fernandez[3], y A. Palacios[1y3]
(1) Laboratorios Excell Ibérica S.L. de La Rioja; (2) Outlook Wine de Barcelona;
(3) Universidad de La Rioja.

1. Summary

When speaking of minerality in wines it is common to find descriptive terms such as flint, silex, match smoke, kerosene, rubber eraser, slate, granite, limestone, earthy, tar, coal, graphite, rock dust, wet stones, salty, metal, steel, ferrous, etc. These are just a few of the descriptors that are commonly found in the tasting notes of wines that show this profile. However, not all wines show this aromatic footprint. Certain varieties of grape are more prone than others to generate this scent, for example whites Riesling, Chardonnay, Chenin blanc, Sauvignon blanc, Albariño and reds Syrah and Pinot noir, and to a lesser extent Cabernet franc, Nebbiolo and Cabernet sauvignon. Among all these wines some aspects can be found in common when they express minerality, such as the origin in cold or cool climates, early vintages or not over-matured, a high acidity and elaborations of reductive character. Generally they tend to be wines of "single vineyard" profile seeking potentially to reflect a 'terroir' expression. In many cases they tend to be dry white wines of high acidity, low fruity aromatic profile and most commonly produced in the old world, although there are obvious exceptions. In the vast majority of cases this perception is interpreted by the influential market prescriptors and by consumers as a value of intangible quality that praises the hedonistic and economic value of the wine.

There is no doubt that the concept that transmits the term minerality in wines is certainly one of the more mysterious attributes from the chemical viewpoint. Little was known to date, since there had been no studies in depth on how certain chemical compounds can affect the description of the term minerality given by the taster and the consumer.

Minerality in wines is frequently associated with the ¨terroir" concept, often with clear commercial purposes where the expression linked to the soil allows to justify or argue the authenticity of the origin of the wine. It would therefore be easy to link the term minerality to the composition and content of minerals present in a wine, even though there are no scientific studies sufficiently grounded as to establish this direct association.

This study is the natural result of the preliminary investigation already published "Chemical bases of mineral character at olfactory and gustatory level in white and red wines", and its purpose is to verify the hypothesis that certain chemicals and not essentially the content of metals in wine are responsible for the use of the attribute minerality in tasting sessions and sensory descriptions. This paper concludes by mentioning the chemical compounds associated with the term minerality identified in this research. The guideline followed in the choice of these chemical compounds subject to the judgment of two tasting panels for the sensory analysis of synthetic wines was established on the basis of the results obtained in the first part of the research study. These chemical compounds were identified in wines interpreted as mineral by the market (first part of the study) and it is mentioned in the paper which sensory descriptors were used by both panels and to which extent the induced suggestion may condition the tasters in their perception.

This report does not address some aspects that very likely influence the perception of minerality of the wine, such as geology, geo-microbiology, biology and physiology of the plant, as well as techniques and chemical treatments applied both in viticulture and enology.

2. Introduction

The chemical composition of wine is very varied and complex, having been isolated until now more than 900 different chemical elements in its global composition. Many of them are widely studied and characterized at organoleptic level since their presence brings noticeable aromatic and/or gustatory features. However other sensory descriptors as it is the case of the so-called minerality remain without a clear scientific consensus about the chemical bases on which the sensory perception of this descriptive term is founded.

It is widely known that in the wine world there is a huge list of descriptors to transmit by way of articulated language and to define the qualities, types, and styles of wines at the sensory level. Without a doubt the use of the term "mineral" is very trendy into the 21st century and it is widely used by producers, distributors, and especially by tasters and well-known gurus as a relevant differential and refinement value between wines, particularly those of high range and high price. To talk about minerality in the tasting description of a wine is to potentially add sensory and commercial value to it.

Nowadays the impact that has the interpretation of this term becomes important internationally. There is a strong need to find the possible causes and the origin of the association of the term "minerality" with the presence of odiferous volatile compounds, certain minerals or other aromatic or sapid substances that may come from the soil, from the same plant, as the result of viticulture and oenology techniques as well as treatments applied in the vineyard or oenological treatments applied in the winery.

There are many professionals, amateurs and even some consumers that use this term but there aren't that many who have a clear idea of its meaning, provenance and veracity. Thus arises the need to find pragmatic responses to determine the real meaning of this great and valuable lexicon, "minerality", which in a poetic, emotional or induced form enriches so much the product especially in its hedonistic value and probably also its price.

It is true that the physical-chemical state through which pass some wines during their different stages of production and maturation, and certain oenological and/or specific vinification techniques can show a profile associated with descriptors that tasters define as "match smoke", "flint", "lighter flint" or "silex", terms which in some cases are associated with the "mineral" concept. However, we must go beyond and verify which are the compounds and to what extent they contribute to the perception of minerality of wine at the time of consumption.

The lack of a definition truly argued about the term "mineral" or "minerality" has become in itself the Achilles heel of this powerful term. Here appears the division between those who define themselves as followers "pro-mineral" which often coincide with the profile of the "pro-terroir", against the "anti-mineral" which in turn tend also to be skeptical with the very concept of "terroir".

Therefore various authors have suggested that the term minerality cannot be attached only to the presence of mineral or metallic elements. Thus recent articles suggest the possibility of the union of this term with high levels of acidity, the presence and richness in organic acids, the absence of powerful aromatic compounds such as terpenes or fruity esters and the presence of complex sulfur compounds associated with reductive aromas.

This study aims to show the possible association of certain chemical compounds, both at emotional and sensory level, with minerality used as attribute or descriptor in wine tasting.

In the previous study conducted by this same work group were analyzed chemically 17 wines that had been defined by prescriptors internationally as mineral. Following several tasting sessions by two panels of sensory judges 500 km apart from one another, was selected a group of wines with higher scores in the descriptor minerality and a statistical study was performed through Principal Components Analysis (PCA) and linear regression in relation to their chemical composition. The chemical study consisted of the analysis using different analytical techniques of more than 100 different compounds. The statistical analysis of the results indicated that certain oenological parameters, such as the levels of free sulfur dioxide, pH and total acidity could be directly related to the use of the descriptor minerality. In the same way, other chemical compounds among which were pre-fermentative and fermentative aromatics and ageing compounds may be partly responsible for the categorization of a wine as mineral. A fairly logical hypothesis may be also considered and it is that such mineral perception is the result of the synergistic effect of various compounds acting in synergy at the same time and in different concentrations according to the chemical composition of each wine.

Table 1 shows the summary of the chemical compounds found in significant statistical relation through the study PCA type.

Chemical classification	White wines	Red wines
Routine parameters	**Free sulfur dioxide**	**Free sulfur dioxide**
	Total acidity and pH	**Total acidity and pH**
	Succinic acid	**Succinic acid**
Pre-fermentative aromas	**β−Phenylethanol**	**β−Phenylethanol**
	Diethyl succinate	**m-Cresol**
	Ethyl decanoate	**γ−Butyrolactone**
Ageing aromas	**γ−Decalactone**	**γ−Decalactone**
	4-Ethylphenol	**4-Ethyphenol**
	4-Ethylguaiacol	**4-Ethylguaiacol**
	Furfural/ 5-Methylfurfural	**Furfural/ 5-Methylfurfural**

Table 1. Overview of the chemical compounds selected by their relevance in white and red wines defined as mineral and selected through Principal Components Analysis (PCA).

Tables 2 and 3 show the results previously found in red and white wines respectively by statistical analysis of linear regression, taking the average results of the tasting sessions performed by the two panels in comparison with the analytical results from more than 100 different chemical compounds.

Analytical group	Descriptor minerality	Chemical parameters	% Probability
Enological	Gustatory	**pH**	82.88
Enological	Gustatory	Tartaric acid	86.06
Enological	Gustatory	IPT	93.54
Pre-fermentative aromatics	Aromatic	m-Cresol	82.10
Fermentative aromatics	Aromatic	**Butyric acid**	88.51
Fermentative aromatics	Aromatic	**Hexanoic acid**	90.292
Fermentative aromatics	Aromatic	Ethyl isovalerate	80.333
Fermentative aromatics	Aromatic	Ethyl butyrate	84.67
Fermentative aromatics	Aromatic	Ethyl decanoate	92.94
Fermentative aromatics	Aromatic	Isobutanol	81.00
Fermentative aromatics	Aromatic	**Ethyl hexanoate**	92.84
Ageing aromatics	Aromatic	4-Ethylguaiacol	91.77
Ageing aromatics	Aromatic	***cis*-Whisky-lactone**	96.70
Ageing aromatics	Aromatic	Eugenol	92.03
Ageing aromatics	Aromatic	δ-Octalactone	81.88
Ageing aromatics	Aromatic	2,6-Dimethoxiphenol	89.55
Ageing aromatics	Aromatic	**4-Alyl-2,6-dimethoxiphenol**	88.58
Ageing aromatics	Aromatic	**Methyl vanillate**	94.70
Defects	Aromatic	4-Ethylguaiacol	89.80
Sulfur defects	Aromatic	Ethyl thioacetate	97.59
Thiols	Aromatic	2-Methyl-3-furanthiol	99.15
Thiols	Aromatic	2-Furfurylthiol	91.07
Thiols	Aromatic	**4-Mercapto-4-4-methyl-2-2-pentanone**	94.62
Thiols	Aromatic	**3-Mercaptohexanol**	95.39
Metals	Gustatory	Boron	80.01

Table 2. In bold overview of minerality-related chemical compounds obtained from the results in statistical analysis of linear regression on red wines.

Analytical group	Descriptor minerality	Chemical parameters	% Probability
Enological	Gustatory	Alcoholic strength	80.99
Enological	Gustatory	**pH**	88.36
Enological	Gustatory	Glucose + Fructose	86.44
Enological	Gustatory	Total sulfur dioxide	95.50
Enological	Aromatics	Total sulfur dioxide	80.28
Enological	Gustatory	Acetaldehyde	95.54
Varietal aromatics	Aromatics	β-Citronellol	91.71
Varietal aromatics	Aromatics	α-Ionone	91.64
Varietal aromatics	Aromatics	β-Ionone	85.90
Varietal aromatics	Aromatics	Linalool acetate	89.77
Fermentative aromatics	Aromatics	**Butyric acid**	97.969
Fermentative aromatics	Aromatics	Isobutyric acid	98.81
Fermentative aromatics	Aromatics	**Hexanoic acid**	94.67
Fermentative aromatics	Aromatics	β-Phenylethanol	94.70
Fermentative aromatics	Aromatics	Benzylic alcohol	96.05
Fermentative aromatics	Aromatics	Isoamyl acetate	89.88
Fermentative aromatics	Aromatics	Ethyl butyrate	85.80
Fermentative aromatics	Aromatics	Ethyl acetate	92.37
Fermentative aromatics	Aromatics	Isoamylic alcohol	99.03
Fermentative aromatics	Aromatics	**Ethyl hexanoate**	85.72
Fermentative aromatics	Aromatics	Acetic acid	96.52
Fermentative aromatics	Aromatics	Decanoic acid	91.82
Fermentative aromatics	Aromatics	Iso valerianic	98.44
Fermentative aromatics	Aromatics	Ethyl isobutyrate	94.07
Fermentative aromatics	Aromatics	Isobutyl acetate	95.97
Ageing aromatics	Aromatics	*trans*-Whisky-lactone	86.90
Ageing aromatics	Aromatics	***cis*-Whisky-lactone**	87.98
Ageing aromatics	Aromatics	Eugenol	95.53
Ageing aromatics	Aromatics	o-Cresol	90.94
Ageing aromatics	Aromatics	4-Vinylguaiacol	87.12
Ageing aromatics	Aromatics	**2,6-Dimethoxifenol**	89.17
Ageing aromatics	Aromatics	**Methyl vanillate**	98.60
Ageing aromatics	Aromatics	Ethyl vanillate	86.32
Defects	Aromatics	4-Vinylguaiacol	94.79
Thiols	Aromatics	**4-Mercapto-4-4-methyl-2-2-pentanone**	90.10
Thiols	Aromatics	3-mercapto hexyl acetate	89.21
Thiols	Aromatics	**3-Mercaptohexanol**	91.62
Thiols	Aromatics	Benzyl mercaptan	97.56
Metals	Gustatory	Magnesium	84.79

Table 3. In bold overview of minerality-related chemical compounds obtained from the results in statistical analysis of linear regression on white wines.

To study how some of these chemical compounds play a role in the perception of the term minerality, both at gustatory and olfactory level, two panels of tasters were recruited. Following the guidelines set out in the previous study, tasting panels were constituted one in Rioja (producers) and one in Barcelona (non producers) made up of 20 and 23 judges trained in sensory analysis respectively. The first one was constituted by winemakers producers and the second by wine sector professionals non producers. Samples consisted of a hydro alcoholic neutral base distributed along 16 tasting positions. The test was the triangular type (3 glasses/two wines). Three glasses were presented in each position and one of the two wines had been modified chemically by the addition of a certain chemical compound to assess its impact against the witness.

3. Materials and methods used in the experiment

The two tasting sessions performed by the panel of selected judges were designed following the triangular test methodology. The feature of this test lies in 3 coded samples presented to the panel member; two of them are identical and the judge must indicate which sample is different. The hypothesis posed for this test also called the null hypothesis is to establish that the samples are identical.

In addition to the above, a validation study of one of the two participating tasting panels (group of winemakers) was performed by means of the application of "Panel Check" software developed by the University of Denmark, for the evaluation of the reliability and quality of sensory judges panels.

Figure 1 shows several graphs with results of statistical analysis type Anova in second grade and Fisher F values. From left to right are shown possible interactions between products (with significant differences), between tasters (no significant differences), as well as the interaction between judges and products (no significant differences), which validates the expertise of the tasters, and also validating the panel for the attributes examined at gustatory level.

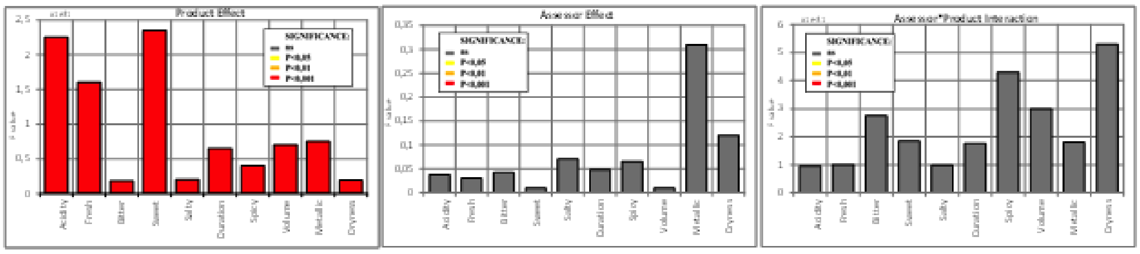

Figure 1. Validation results from the sensory panel of the University of La Rioja using Panel Check software.

The hydro alcoholic neutral base, which formed the basis of the samples of synthetic wines evaluated by the sensory judges, was prepared seeking the greatest similarity to a wine. To do so it was added up to 12% ethanol on a watery base with an addition of 4.5 g/l of tartaric acid and acidity levels adjusted to a pH of 3.75. For the chemical modification of this hydro alcoholic base, was used a collection of patterns of commercial pure volatile compounds with a minimum of 95% purity. The closest to a real wine profile was obtained with this combination.

4. Results and discussion

4.1 Design of the tasting panels

16 positions for triangular tasting were designed, each with a different sample to be evaluated on a sensory level by each panel of judges, as it is detailed in Table 4. The compounds used were those most relevant obtained in the previous study on the chemical basis of the perception of minerality.

Position	Compound/s added	Position	Compound/s added
1	Compounds mix	9	Dimethyl sulfur
2	Metals	10	Low pH and high SO_2
3	Ethylphenols	11	High total acidity
4	Succinic acid	12	Sulfur compounds
5	Isoamyl acetate	13	Pyrazines
6	Ethyl butirate	14	Geosmin
7	Ethyl decanoate	15	Thiols
8	Ethyl succinate	16	m-Cresol

Table 4. Detail of tasting positions and chemical compounds added to a hydro alcoholic base presented to the two collaborating tasting panels.

The choice of concentrations which were added for each chemical compound to the hydro alcoholic base was carried out taking into consideration the average concentration found in the chemical characterization performed in a previous study on 17 wines with "mineral" connotations. This experimental design based on synthetic wines was meant to avoid making the tasting on real wines blended with the chemical compounds studied, since the wine by its chemical matrix complexity could mask the detection by the tasters of some of the compounds selected.

The relationship of each tasting position and its chemical composition is as follows:

- Position No. 1: It contained a mixture of all the chemical compounds added in positions from number 2 to 16 at the average concentrations found previously.
- Position No. 2: It contained a mixture of iron and copper salt added at double concentration of the average levels in metal content found previously.

- Position No. 3: A mixture of compounds 4-Ethylphenol and 4-Ethylguaiacol was added at double of the average concentrations.
- Positions No. 4 to 9: They contained at least one sample of each of the compounds described in Table 4 at double the average concentration found in the previous study.
- Position No. 10: The acidity was modified to a pH of 3.0 and Potassium metabisulfite was added to obtain a level of 30 mg/l free sulfur dioxide.
- Position No. 11: Tartaric acid was added until a total acidity equal to 7.3 g/l was obtained.
- Position No. 12: It contained a mixture of three compounds responsible for sulfur aromas in wine, Ethanethiol, Dimethyl sulfide and Mercaptoethanol; the added concentrations are detailed in Table 5.
- Position No. 13: A sample was presented containing a mixture of compounds known as Pyrazines: -2-Isobutyl-3-methoxypyrazine (IBMP) and 2-Isopropyl-3-Methoxypyrazine (PMP).
- Position No. 14: It contained a modification of the hydro alcoholic base with the compound Geosmin.
- Position No. 15: It contained a mixture of three of the compounds called Thiols: 4-Mercapto-4-4-Methyl-2-2-pentanone, 3-Mercapto hexyl acetate and 3-Mercaptohexanol, with boxwood, passion fruit and grapefruit aromas respectively.
- Position No. 16: It contained an addition of double of the average concentration of compound m-Cresol, of pepper and leather aroma.

Table 5 shows the chemical compounds and the concentrations added in each tasting position presented to both panels.

Compound	Concentration	Compound	Concentration
Geraniol	100 ng/l	Dimethyl sulfur	193 μg/l
4-Mercapto-4-4-methyl-2-2 pentanone	16 ng/l	β-methyl Octalactone *cis*	552,56 μg/l
3-mercaptohexyl acetate	24 ng/l	β-methyl Octalactone *trans*	387,76 μg/l
3-Mercaptohexanol	2,4 ng/l	Ethanethiol	3,8 μg/l
Isoamyl acetate	10,0 μg/l	Mercaptoethanol	104 μg/l
4-Ethyl-phenol	100 μg/l	Furfural	514,8 μg/l
4-Ethyl-guaiacol	50 μg/l	Ethyl butirate	410 μg/l
Ethyl succinate	4,1 g/l	β-Ionone	242 ng/l
m-Cresol	4,0 μg/l	α-Ionone	320 ng/l
Copper salts	450 μg/l	Ethyl decanoate	120 μg/l
Iron salts	320 μg/l	β-methyl Octalactone *trans*	387,76 μg/l
IBMP-2-Isobutyl-3-Methoxipyrazine	24 ng/l	Ethanethiol	3,8 μg/l
IPMP-2-Isopropyl-3-Methoxipyrazine	24 ng/l	Geosmin	41,2 ng/l

Table 5. Detail of added concentrations of chemical compounds to the hydro alcoholic base in the 16 tasting positions.

4.2 Statistical analysis of the triangular test

The methodology used in sensory analysis was the triangular tasting type, which is a discriminatory test. Discriminatory tests represent one of the most useful analytical tools for sensory analysis, allowing finding significant differences between two or more samples and a certain pattern used as a control element. All methods or descriptive tests aim to answer the same question: are these products different between each other?

At the time of the evaluation of the samples, two triangular blind tastings of the same synthetic wines synthetic were carried out in two distinct sessions (tasting A and B). The first tasting (A) without indication of any objective and the second tasting (B) with same samples but inducing the tasters to find and define the term "mineral" in the samples. Thus it could be evaluated objectively if the tasters found minerality in the samples without having to indicate it, and also take into account the psycho-sensorial part when inviting them to find the term as induced.

The first session (Tasting A) was designed following the methodology of triangular blind tasting requesting two answers from the sensory judges. First they were asked to identify the different samples and second to indicate a preference for any of the two samples present at each tasting position.

In the second session (Tasting B) were presented the same 16 synthetic wines and exactly in the same position, but this time the sensory judges were instructed to find the mineral attribute in the submitted samples. Two additional questions were also asked: first, to again identify the different sample following the methodology of triangular tasting; and second to indicate the sample presenting a greater mineral character in the opinion of the taster.

All tasting positions were evaluated by panelists at olfactory level, however tasters were also requested to evaluate at gustatory level those posts containing Metals (position 2), Succinic acid (position 4), modified pH and Sulfur dioxide (position 10), modified total acidity (position 11) and Geosmin (position 14). Also, positions containing compounds Isoamyl acetate (position 5), Ethyl butyrate (position 6), Ethyl decanoate (position 7), Ethyl succinate (position 8) and Thiols (position 15) were used as negative controls looking for the definition of "anti-mineral" wine or completely opposite to the term mineral.

Once data were collected from both tasting sessions a test of contrast of hypothesis using a binomial test was performed to see if there were significant differences.

ISO standard 4120:2004 (Table 6) specifies the number of judges necessary to carry out the test and the minimum number of correct answers, distinguishing correctly the different sample between the three glasses thus affirming that there are significant differences. According to the mentioned standard the number of responses needed to conclude that there is a significant difference depends on the number *n*, which is defined as the number of judges involved in the test or the number of total responses.

n	*α*					*n*	*α*				
	0,20	**0,10**	**0,05**	**0,01**	**0,001**		**0,20**	**0,10**	**0,05**	**0,01**	**0,001**
6	4	5	5	6	–	27	12	13	14	16	18
7	4	5	5	6	7	28	12	14	15	16	18
8	5	5	6	7	8	29	13	14	15	17	19
9	5	6	6	7	8	30	13	14	15	17	19
10	6	6	7	8	9						
						31	14	15	16	18	20
11	6	7	7	8	10	32	14	15	16	18	20
12	6	7	8	9	10	33	14	15	17	18	21
13	7	8	8	9	11	34	15	16	17	19	21
14	7	8	9	10	11	35	15	16	17	19	22
15	8	8	9	10	12						
						36	15	17	18	20	22
16	8	9	9	11	12	42	18	19	20	22	25
17	8	9	10	11	13	48	20	21	22	25	27
18	9	10	10	12	13	54	22	23	25	27	30
19	9	10	11	12	14	60	24	26	27	30	33
20	9	10	11	13	14	66	26	28	29	32	35
21	10	11	12	13	15	72	28	30	32	34	38
22	10	11	12	14	15	78	30	32	34	37	40
23	11	12	12	14	16	84	33	35	36	39	43
24	11	12	13	15	16	90	35	37	38	42	45
25	11	12	13	15	17	96	37	39	41	44	48
26	12	13	14	15	17	102	39	41	43	46	50

Table 6. Minimum number of correct answers necessary to conclude that there are detectable differences in a triangular test.

In this case, for the first panel of winemakers constituted with 20 judges, according to standard ISO 4120:2004 the minimum number of successful answers to determine that there are significant differences is 11, 13 and 14 for levels of significance α of 0.05, 0.01, and 0.001 respectively; therefore with a confidence level of 95, 99 and 99.9%. In the case of the second tasting panel consisting of 23 judges, the minimum number of successful answers to determine significant differences is 12, 14 and 15 for the same levels of significance α above mentioned. In short, the statistical results of the tastings provide confidence for accuracy of 95, 99 and 99.99% depending on compounds.

The panel formed by winemakers obtained 62% of hits in the first part of the tasting sessions and 67% in the second phase of guided tasting, as shown in Figure 2. In the second phase of the tasting the judges from the same panel were able to define as mineral 67% of samples modified with the tested chemical compounds. Only those positions where a 95% significance level was at least obtained were taken into account, in which panelists were able to find significant differences among the samples submitted at that level of trust. By way of example Figure 2 represents the global results of both tastings.

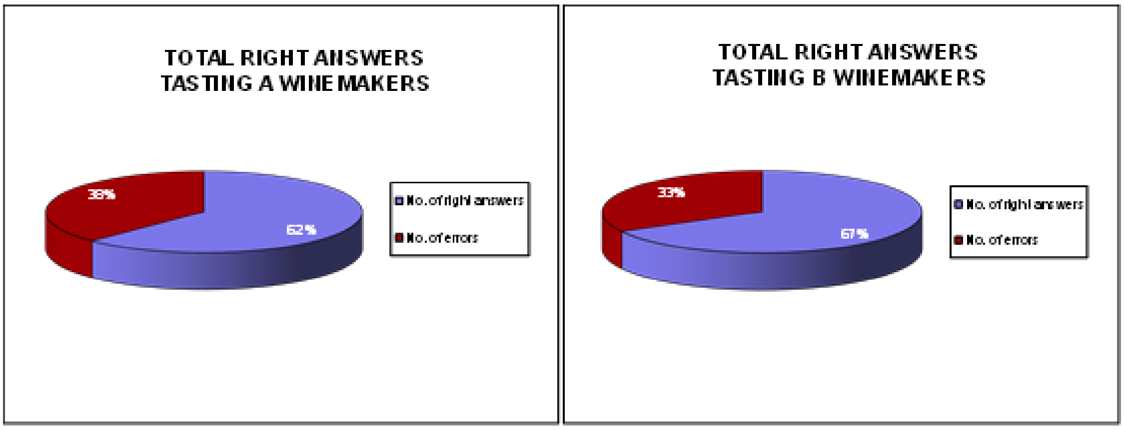

Figure 2 Percentage of success for the two triangular tasting sessions carried out by the panel of winemakers.

For the second panel formed by professionals non producers from the wine sector, 65% of hits were obtained in the first part and 69% in the second directed phase. In the second phase the same criteria were followed as with the first panel and the judges rightly defined as mineral those samples modified by 60%.

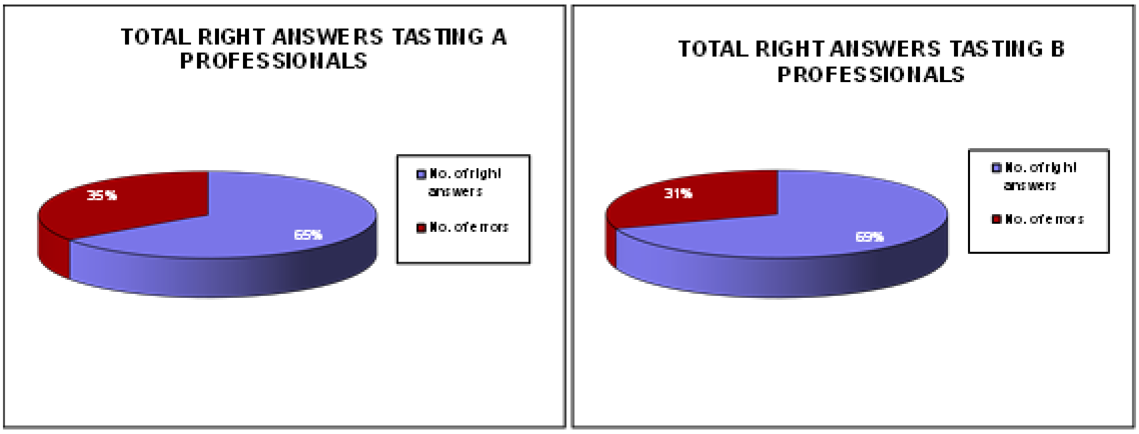

Figure 3 Percentage of success for the two triangular tasting sessions carried out by the panel of professionals non producers.

Table 7 (p. 18) shows the statistical results of the panel of winemakers. In the first three columns the x mark indicates tasting positions where significant differences with levels of 0.5, 0.01, and 0.001 were found in tasting phases A and B. The last three columns indicate the positions found with significant differences for the same levels in relation to the question addressed to the tasters in which they were asked to identify the most mineral sample. In bold have been identified compounds used as negative or anti-mineral controls.

According to the results found in the tasting of the first panel, the presence of Succinic acid and a low pH combined with high levels of free sulfur dioxide are directly related to the use of the term minerality with a probability of 95%. The presence of Ethylphenols, m-Cresol and metals obtained a significance of 99% to relate as minerality in wine. Finally, with the same probability appears the compound Geosmin. Also the presence of Isoamyl acetate and Thiols is directly related in 99.9% with the emergence of the term minerality for the panel of producers winemakers; however the effect is somewhat ambiguous in this regard since the tasting panel of professionals non producers did not relate Isoamyl acetate with minerality but it did relate it to a lesser extent with Thiols.

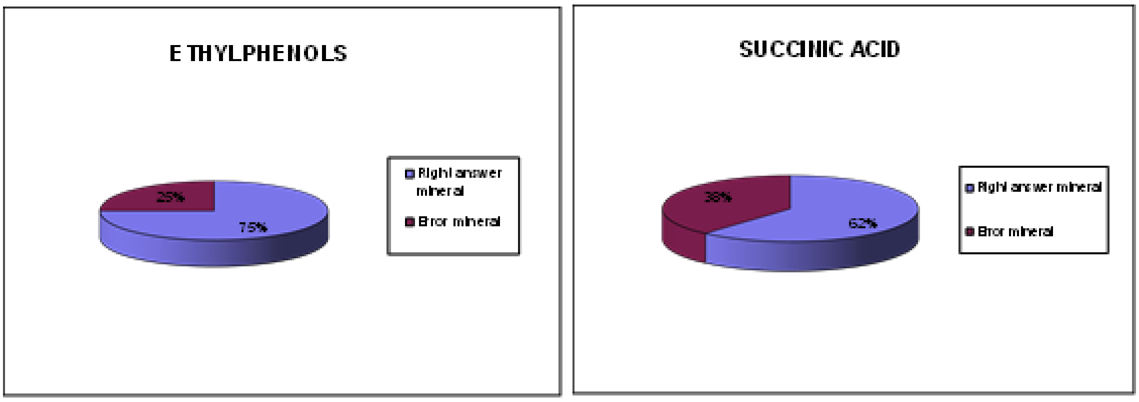

Figure 4 Percentage of success of phase B from the tasting session carried out by the panel of winemakers for the compounds 4-Ethylphenol and 4-Ethylguaiacol (left graph) and Succinic acid (right graph).

Table 8 (p. 19) shows the statistical results from the panel of professionals non producers. On this occasion the so-called sulfur compounds: Ethanethiol, Dimethyl sulfide and Mercaptoethanol showed to be linked with a 95% probability to the term minerality. Similar results for the compounds 4-Ethylphenol and 4-Ethylguaiacol of leather aromas, although this compound is only related to minerality during the induced tasting (B) and not during the spontaneous tasting (A). The same situation happens with synthetic wines modified with low pH and high sulfur.

Position	Compound	Session A			Session B			MINERALITY		
		α 0.05	α 0.01	α 0.001	α 0.05	α 0.01	α 0.001	α 0.05	α 0.01	α 0.001
Position 1	Compounds mix	x	x	x	x	x	x			
Position 2	Metals	x	x	x				x	x	
Position 3	Ethylphenols				x	x	x	x	x	
Position 4	Succinic acid	x						x		
Position 5	**Isoamyl acetate**	x	x	x	x	x	x	x	x	x
Position 6	**Ethyl butirate**	x	x	x	x	x	x			
Position 7	**Ethyl decanoate**				x					
Position 8	**Ethyl succinate**									
Position 9	Dimethyl sulfur									
Position 10	Modified pH and SO_2				x	x		x		
Position 11	Modified total acidity									
Position 12	Sulfur compounds									
Position 13	Pyrazines	x			x					
Position 14	Geosmin	x	x	x	x	x	x	x	x	x
Position 15	**Thiols**	x	x	x	x	x	x	x	x	x
Position 16	m-Cresol	x	x	x	x	x	x	x	x	

Table 7. Results obtained by the panel of winemakers producers. In the column on the left and in bold are designated compounds evaluated with a completely inverse relationship with minerality, as totally opposite to the term minerality. In the next column marked with an x are designated tasting positions found as significant for levels of 0.5, 0.01, and 0.001 in tasting session A. The third column marked with an x indicates tasting positions found as significant for levels of 0.5, 0.01, and 0.001 in tasting session B. The fourth column indicates positions found with significant differences against the modified sample as the most mineral.

According to the responses obtained from the tasting panel of professionals non producers the presence of the Thiols: 4-Mercapto-4-4-methyl-2-2-Pentanone, 3-Mercaptohexyl acetate and 3-Mercaptohexanol is inversely related in 99% with the emergence of the term minerality and could be defined as non-mineral. Finally, as in the results obtained by the panel of producers a low pH combined with high levels of free sulfur dioxide free and compound Geosmin are directly related to the use of the term minerality with a 99.9% probability.

Position	Compound	Session A			Session B			MINERALITY		
		α 0.05	α 0.01	α 0.001	α 0.05	α 0.01	α 0.001	α 0.05	α 0.01	α 0.001
Position 1	Compounds mix	x	x	x	x	x	x			
Position 2	Metals									
Position 3	Ethylphenols	x	x	x	x	x	x	x		
Position 4	Succinic acid									
Position 5	**Isoamyl acetate**	x	x		x	x	x			
Position 6	**Ethyl butyrate**	x	x		x	x	x			
Position 7	**Ethyl decanoate**				x			x		
Position 8	**Ethyl succinate**									
Position 9	Dimethyl sulfur									
Position 10	Modified pH and SO_2	x			x	x		x	x	x
Position 11	Modified total acidity	x						x	x	x
Position 12	Sulfur compounds	x	x	x	x			x		
Position 13	Pyrazines	x	x	x	x	x	x			
Position 14	Geosmin	x	x	x	x	x	x	x	x	x
Position 15	**Thiols**	x	x	x	x	x	x	x	x	
Position 16	m-Cresol	x	x	x	x	x	x			

Table 8. Results obtained by the panel of professionals non producers. In the column on the left and in bold are designated compounds evaluated with a completely inverse relationship with minerality, as totally opposite to the term minerality. In the next column marked with an x are designated tasting positions found as significant for levels of 0.5, 0.01, and 0.001 in tasting session A. The third column marked with an x points tasting positions found as significant for levels of 0.5, 0.01, and 0.001 in tasting session B. The fourth column indicates positions found with significant differences against the modified sample as the most mineral.

Surprisingly and contrary to the results from the tasting panel made up of producers, this panel does not relate the Isoamyl acetate with the term minerality though they do coincide about the Thiols.

Just as it happened in the tasting session of modified synthetic wines with the panel of winemakers producers with the Ethylphenols, the modified pH with lower levels and the sulfur in high ranks, these only reached sufficient significance levels in the induced tasting (B). This tasting panel shows the same effect for Ethyl decanoate.

4.3 Analysis of the enumerative test

Finally, a compilation was carried out of the linguistic terms used by tasters from both panels and obtained during the two tasting sessions.

During the first phase which was not directed toward the term minerality, judges were requested to describe with a couple of attributes the olfactory and taste sensations. A similar request was asked for the second phase of the tasting, which was directed toward the elements related with minerality.

When comparing the type of attributes named in both tasting sessions it was observed that some judges had included the term mineral in the first phase of the study, increasing the use of that term in the second phase induced on purpose. Also, the term minerality was used on one occasion by one of the tasting panels for the sample modified with Geosmin. In addition, in both panels were found descriptors that usually accompany the term minerality such as "soil" used in several occasions, "limestone", "plaster", "tar", "saline" or "dusty".

By way of illustration, Figure 5 shows a comparison between tasting phase A and B for Succinic acid. It can be observed how during the phase not directed towards the concept minerality none of the sensory judges used a single linguistic term that could be related to the concept of mineral, rock, clay or silex. However, in phase B the judges agreed indicating the same sample as mineral with a 60% frequency, and the most common response was the word rock.

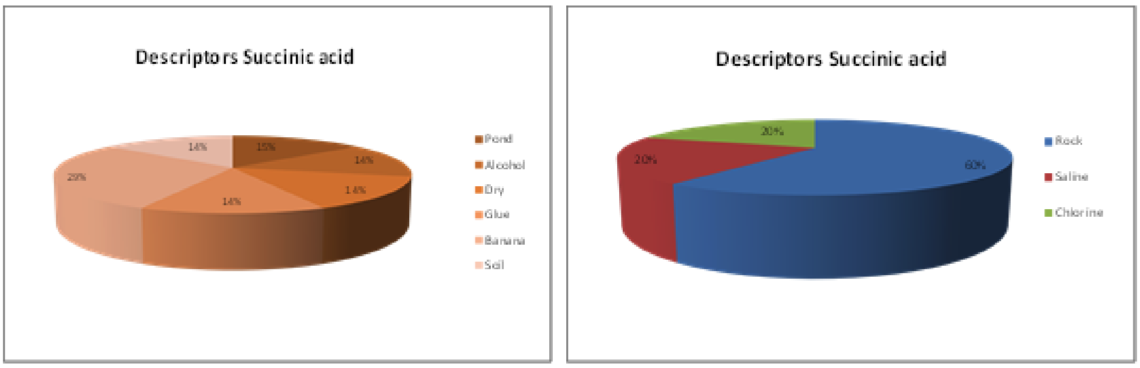

Figure 5. Descriptors named for the compound Succinic acid by the winemakers tasting panel during session A (not directed) and B (directed to the term mineral).

5. Conclusions

In the present study a high percentage of right answers by both tasting panels in sessions A and B of triangular tasting was observed. It should be noted the great similarity of the percentage of success obtained in both phases (A and B) between both panels, which gives the tasters considerable credibility; thus for session A the producers panel was 62% right in their replies and 65% the panel of professionals non producers. The same situation occurs in tasting sessions B directed towards the descriptor minerality. Both panels showed even a higher percentage of success than at session A and with great similarity between the two, achieving a 67% and 69% for winemakers and professionals non producers respectively. It seems risky to allocate to fate such similarities of success on both panels given the high percentage of hits found. However, even though these similarities are noticeable only some compounds, those with significant differences, affect the perception of the term minerality either at gustatory or olfactory level.

- In relation to the aromatic phase of minerality: The statistical analysis of the results of both tasting panels revealed that both groups of tasters agreed in selecting in a statistically significant way with a confidence level of at least 95% or higher the phenolic compounds 4-Ethylphenol and 4-Ethylguaiacol, the sulfur compounds Ethanethiol, Dimethyl sulfide and Mercaptoethanol and the compound Geosmin responsible for memories of wet soil, with a direct relationship between their presence and the use of the term mineral. The same situation occurred when the pH levels were decreased to a value of 3 and the concentration of free sulfur dioxide was increased to 30 mg/l.

Certain compounds showed a profile that moves completely away from the interpretation of minerality. Both tasting panels were also coincident in pointing out a relationship but in this case inverted or completely opposite to the mineral descriptor in the presence of Thiol compounds: 4-Mercapto-4-4-methyl-2-2-Pentanone, 3-Mercaptohexyl acetate and 3-Mercaptohexanol.

On the other hand, analyzing the results of each panel independently the panel of winemakers located a significantly larger number of compounds that were related to the term minerality. So in addition to the previously mentioned significance of at least 95% confidence, the position with added Succinic acid, the position modified with the ageing aromatic compound m-Cresol were identified and the positions modified with metal salts of copper and iron were added. At the same time the professionals non producers panel also noted a relationship between the emergence of the term minerality and high total acidity.

This concordance of hits between both panels points out the compounds previously mentioned as being responsible for drawing the mineral footprint of a wine.

Perception of aromatic minerality
m-Cresol
Ethylphenols: 4-Ethylphenol and 4-Ethylguaiacol
Sulfur compounds (reductions): Ethanethiol, Dimethylsulfur, Mercaptoethanol
low pH and free SO_2 (30 mg/l)
Geosmin
Isoamyl acetate (Only true for the tasting panel of winemakers producers since the panel of professionals non producers identified it as anti-mineral)

Table 9. Compounds related to the perception of minerality at aromatic level.

Perception of aromatic antiminerality
Ethyl butyrate
Ethyl decanoate
Ethyl succinate
Isoamyl acetate (Only true for the tasting panel of professionals non producers since the panel of winemakers producers identified it as mineral)
Thiols: Mercapto-4-4-methyl-2-2-Pentanone, 3-Mercaptohexyl acetate, 3-Mercaptohexanol

Table 10. Compounds related to the perception opposite to minerality at aromatic level.

- In relation to the gustatory phase of minerality: If we look at the results obtained it can be observed that there are certain compounds with significant relevance in any of the two panels such as Succinic acid, the presence of metals and changes in pH and free sulphur dioxide that were evaluated as mineral according to the gustatory tasting.

Perception of gustatory minerality
Succinic acid
Modified pH
Sulfur dioxide
Metals (copper and iron)
High total acidity

Table 11. Compounds related to the perception of minerality at gustatory level.

It should then be noted that both the olfactory and the gustatory component contribute to the use of the term minerality and very probably under an effect of synergy between compounds and the sensory cognitive interpretation.

It is worth mentioning the fact that these results open a stimulating way for new studies to pursue further in depth the two aspects of the mineral footprint; on the one hand a contribution on the olfactory level, on the other at gustatory level and the interference between both phases at the level of translating the sensory stimuli in the interpretations.

The preliminary results seem to indicate that the relationship of the ¨terroir¨ and the mineral concept in wines is not closely related with levels of mineral materials present in the chemical composition of wine at least as the only relevant factor directly linked; there exist other compounds also linked to this term with a relevant effect. This statement challenges the popular belief that it is the characteristics of the soil where the vines and grapes grow that provide a higher concentration of minerals in its metallic form or forming part of other organic compounds, these being responsible for the minerality of wine.

The results of the sensory analysis through blind tasting, directed and non-directed towards the perception of this term, show that part of its use is due to situations of subjectivity once this is clearly induced since there were obvious changes in the type of descriptors that tasters used in both tasting sessions, appearing in the directed phase terms such as smell of rock, stone boulders or flint which had not previously been mentioned.

The two panels included spontaneously in certain samples linguistic terms that could relate to the descriptor minerality in the blind tasting phase not directed toward minerality (phase A), such as soil, earthy, plaster, lime, saline, dust and tar. Although it is true that the emergence of more defined terms such as rock, slate or stone boulder only appeared in the second session induced to detect the minerality in the tasting (phase B). This may be due as the results of this study seem already to suggest that the minerality descriptor is not linked to the presence of one or two chemical compounds and is rather the result of a mixture of compounds which provide sometimes a gustatory component, sometimes an olfactory one, or both at the same time in relation to the minerality.

It is important to note the relevance that takes on the subjective power of induction to perceive minerality, direct or indirectly, since it seems clear the fact that the subjective component plays a major role in the use of the term minerality. Thus the tasters appear to have learned over the years in which this term has now settled in the sector that the language descriptors to be used are those related with stones, soil or even with the brackish sea water sensation. The trademark itself and its weight on the market may already be linked to the term thanks to the media.

However, the final conclusions of this study accept that molecules can exist in the volatile chemical composition and in solution of wine, that in one way or another remind cognitive olfactory and gustatory associations related with the world of minerals although the soil does not have to be necessarily the only source of the minerals.

These findings open the door to future research that will contribute in the coming years to more accurately determine the chemical composition that is responsible for the term mineral in wines from the gustatory and olfactory perception.

With this second part of global research on the chemistry of wine and its link with the perception of minerality, Excell-Ibérica and Outlook Wine put an end to the conclusions of this study. After considerable economic investment and two long years of work and conclusive analysis, we want to thank the invaluable collaboration of M.P. Fernández of the University of La Rioja and very especially of Elvira Zaldívar of Laboratorios Excell-Ibérica, who have developed a great task of incalculable value. We sincerely hope that these two reports will provide some contribution to the huge spectrum of data that relate wine chemistry to the sensory stimulation of the taster, and even in a much more complex form with the cognitive interpretation.

6. Bibliographic references

1. Abdil, H. 2007. RV coefficient and congruence coefficient. In Encyclopedia of Measurement and Statistics (N. Salkind, ed.)

2. Araujo, Ivan E. de, Rolls, Edmund T. Velazco, Maria Inés, Margot, Christian, Cayeux Isabelle, (2005) Cognitive Modulation of Olfactory Processing, Neuron Vol 25, p 671-679, http://www.oxcns.org/papers/381_DeAraujo+Rolls+++05.pdf, (Accessed 15 April, 2012)

3. Arikawa Y., Kuroyanagi T., Shimosaka M., Muratsubaki H., Enomoto K., Kodaira R., Okazaki M. (1999): Effect of gene disruptions of the TCA cycle on production of succinic acid in *Saccharomyces cerevisiae*. Journal of Bioscience and Bioengineering, 87:28-36

4. Ashley, Rachel, Grapevine Nutrition – an Australian perspective, Fosters Wine Estates, http://ucanr.org/sites/nm/files/76731.pdf, (Accessed 18 May, 2012)

5. Ballester, J., Mihnea, M., Peyron, D. and Valentin, D. 2013. Exploring minerality of Burgundy Chardonnay wines: A sensory approach with wine experts and trained panelists. Aust. J. Grape Wine Res. 19, 140–152

6. Bamforth, C.W. 2006. Scientific Principles of Malting and Brewing, American Society of Brewing Chemists, St Paul, MN

7. Baron, Mojmir, Fiala, Jaromir, (2012) Chasing after Minerality, Relationship to Yeast Nutritional Stress and Succinic Acid Production, Czech Journal of Food Science, Vol. 30 2012, No.2 pp188-193, Prague, Czech Republic

8. Bird, David, (2005) Understanding Wine Technology, DBQA Publishing, Newark, Nottinghamshire, UK

9. Bryant, Jason, (2012) Can you taste minerals in wine? Unscrewed – The Independent New Zealand Wine Review, http://www.unscrewed.co.nz/can-you-taste-minerals-in-wine/, (Accessed 1 May 2012)

10. Campbell, Neil; Reece, Jane, (2004) Biology, 7th Edition, Pearson Education Publishing, Essex, UK

11. Campo, E., B., Ferreira, V. and Valentin, D. 2008. Projective mapping in sensory analysis of ewe's milk cheeses: A study on consumers and trained panel performance. Food Res. Intern. 37, 723–729

12. Cox, J. 2008. In: The Wine News, October/November Wine News, Coral Gables, FL

13. Cox, Jeff, (2008) The Minerality in Wines. Decanter.com, http://www.decanter.com/people-and-places/wine-articles/485746/the-Minerality-in-wines, (Accessed 16 March, 2012)

14. Dawson, e. 2009. Taking our vitamins and minerality. Palate press 2009, Oct. de Cassagnac, P. and Knowles, G.1930. French Wines, Chatto and Windus, London, U.K.

15. Department of Health, Canada (1979) Taste, in the assessment of drinking water quality, http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/taste-gout/index-eng.php, (Accessed 29 April, 2012)

16. EcoChem Inc, (2012) Plant Micronutritional functions, http://www.ecochem.com/t_micronutrients.html, (Accessed 3 March 2012)

17. Gadd, Geoffrey M., (2009) Metals, minerals and microbes: geomicrobiology and microremediation; http://mic.sgmjournals.org/content/156/3/609.full, (Accessed 18 March 2012)

18. Gilbert, Karen, (2006) The smell of metal can be deceiving, Virginia Tech, http://phys.org/news82229855.html, (Accessed 23 May 2012)

19. Goode, J. 2009. Clangers and Clang: Minerality in wine. The World of Fine Wine 2009, 24. GRAHAM, R. Personal communication, 2010

20. Goode, Jamie, (2009) Clangers and Clang: Minerality in Wine, The World of Fine Wine, Issue 24 2009, WFW, London, UK

21. Goode, Jamie, (2005), The Science of Wine, From Vine to Glass, The Octopus Publishing Group Ltd., London, UK

22. Goode, J. 2005. The Science of Wine: From Vine to Glass, University of California Press, Berkeley, CA

23. Felipe Laurie, Marcos A Hortellan. Analysis of major metallic elements in Chilean wines by atomic absorption spectroscopy. V Ciencia e investigación agraria 2010

24. Friendly, M. 2007. HE plots for multivariate general linear models. J. Comput. Graph. Stat. 16, 421–444

25. Friendly, M. and FOX, J. 2010. Candisc: Generalized canonical discriminant analysis. R. Package. http://cran.r-project.org/package=candisc (accessed November 18, 2013)

26. Hudelson, John, (2011), Wine Faults, Causes, Cures, Effects, The Wine Appreciation Guild, San Francisco, CA

27. IMA (Industrial Minerals Association of North America (2012), What is Feldspar, http://www.ima-na.org/feldspar, (Accessed 1 May 2012)

28. Jonh D. Greeenough and Brian J Flier. Regional trace element fingerprint of Canadian wines. Geoscience Canada 2005

29. Kamzolova S.V., Yusupova A.I., Vinokurova N.G., Fedotcheva N.I, Kindrashova M.N., Finogenova T.V., Morgunov I.G. (2009a): Chemically assisted microbial production of succinic acid by the yeast Yarrowia lipolýtica grown on ethanol. Applied Microbiology and Biotechnology, 83: 1027-1034

30. Karakasis, Ioannis, (2012) Minerality in wine: taken for granite? http://palatepress.com/2012/03/wine/Minerality-in-wine-taken-for-granite/ (Accessed 29 April, 2012)

31. Konhauser, Kurt (2007) Introduction to Geomicrobiology, Blackwell Publishing, Oxford, UK

32. Lawless, H.T., Schlake, S., Smythe, J., Lim, J.Y., Yang, H.D., Chapman, K. and Bolton, B. 2004. Metallic taste and retronasal smell. Chem. Senses 29, 25–33

33. Lewin, Benjamin MW, (2010), Wine Myths and Reality, Vendange Press, Dover, UK

34. Lopez, R., Aznar, M., Cacho, J., & Ferreira, V. (2002). Determination of minor and trace volatile compounds in wine by solid-phase extraction and gas chromatography with mass spectrometric detection. Journal of Chromatography A, 966(1–2), 167–177

35. Maltman, Alex, (2008) The Role of Vineyard Geology in Wine Typicity, Journal of Wine Research, 2008, Volume 19, Pages 1-17, Abstract, http://www.tandfonline.com/doi/abs/10.1080/09571260802163998, (Accessed 18 March 2012)

36. Nickel, Ernest H. (1995), The definition of a mineral, The Canadian Mineralogist, Vol. 33 pp689-690 http://canmin.geoscienceworld.org/; (Accessed 29 April, 2012)

37. Nicolini G., Larcher R., Pangrazzi P. and Bontempo L., (2004). Changes in the contents of micro and trace elements in wine due to winemaking treatments, Vitis, Volume 43, Pages 41-45, http://www.vitis-vea.de/admin/volltext/e040707.pdf (Accessed 12 March, 2012)

38. Nunez, M., Pena, R.M., Herrero, C., and Garcia-Martin S. (2000), Analysis of some metals in wine by means of electrophoresis. Application to the differentiation of Ribeira Sacra Spanish red wines, Facultad de Ciencias, Universidad de Santiago de Compostela, Lugo, Spain

39. Ortega, C., Lopez, R., Cacho, J., & Ferreira, V. (2001). Fast analysis of important wine volatile compounds. Development and validation of a new method based on gas chromatographic-flame ionisation detection analysis of dichloromethanemicroextracts. Journal of Chromatography A, 923(1–2), 205–214

40. Peynaud, E. 1987. The Taste of Wine: The Art and Science of Wine Appreciation. The Wine Appreciation Guild, San Francisco, CA

41. Riéreau-Gayon P., Dubourdieu D., Doneche B., Lonvaud A. (2006). Handbook of enology. Volume II: The chemistry of wine and stabilization treatments. John Wiley & Sons, Ltd., Chichester, UK

42. Sage Publications, Thousand Oaks, Ca. Amerine, M.A., Roessler, E.B. and Ough, C.S. 1965. Acids and their taste. I. The effect of pH and titratable acidity. Am. J. Enol. Vitic. 16, 29–37

43. Vidal, S., Courcoux, P., Francis, L., Kwiatkowski, M., Gawel, R., Williams, P.,Waters, E. and Cheynier, V. 2004. Use of an experimental design approach for evaluation of key wine components on mouth-feel perception. Food Qual. Prefer. 15, 209–217

44. Thesis abstract for the WSET Diploma Unit 7. Minerality in Wine: Fact, Fun or Fiction? By Graham T. Reddel