

Reliability of the Spanish Official Method for Colour of Red Wines in Comparison with the CIE 1931-(x, y)Method*

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ABSTRACT

The Spanish official method for determining the colour of a wine is based on a simplified adaptation of the selected ordinate method from CIE. Forty-seven samples of Spanish red wines from twelve 'origin appellations' have been tested by both methods. Differences between the chromatic variables calculated by both methods have been obtained for determining the reliability of the Spanish method. An interval of chromatic variables in which differences oscillated within a narrow range and another interval with a linear increase of differences were found. Some chromatic parameters show cutpoints between the two sets of samples. A discriminant analysis for classifying wines in the two sets has been carried out.

INTRODUCTION

Spanish regulations (Presidencia del Gobierno, 1981) have adopted the OIV Recommendations (OIV, 1969) and the so-called Rapid Method (Sudraud, 1958) for the chromatic characterization of red wines. This approach is a simplified version of a more rigorous procedure (Berg *et al.*, 1964) based on the CIE 1931-(x, y) selected ordinate method.

Some authors (Negueruela & Echavarri, 1983) have observed that, for some 'Rioja' wines, significant differences were found when the above chromatic methods were applied to the same wine samples. In this study the reliability of the OIV method, in comparison with the CIE method, is

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discussed. This reliability is dependent on some chromatic parameters inherent in the analyzed red wines.

MATERIALS AND METHODS

Materials

Samples

Forty-seven representative samples of Spanish red wines from twelve 'origin appellations' (*Alicante, Ampurdán-Costa Brava, Campo de Borja, Cariñena, Jumilla, La Mancha, Navarra, Ribeiro, Rioja, Valdepeñas, Valencia, Yecla*) have been considered in this study. The samples were selected at random, following the criterion of an adequate representativity, according to their production and consumption. All the wines were bottled and commercialized samples. The samples studied showed no turbidity, so previous centrifugation or filtration process was not necessary.

Apparatus

Experimental absorbances were measured in a Bausch & Lomb 'Spectronic 2000' spectrophotometer provided with a continuous X-Y recorder 333508. 'Hellma' precision glass cells with 1, 2, 5, 10 mm pathlengths were used.

Methods

The methods proposed for computing chromatic parameters were the following: the Reference Method and the Rapid Method (Sudraud, 1958; OIV, 1969), in force in Spanish Regulations (Presidencia del Gobierno, 1981); the CIE 1931-(x, y) Colorimetric System (Hardy, 1936); CIELUV and CIELAB Uniform Color Spaces (CIE, 1978). Absorbence measurements were carried out within a time interval of an hour after the bottles were opened; this action avoids the effect of colour instability with time elapsed (Heredia & Guzmán, 1988).

Data were processed using a Digital VAX-11/785 computer. Statistical analyses were performed using the BMDP software (BMDP, 1981).

RESULTS AND DISCUSSION

The differences (δ) between the respective chromatic parameters obtained by both methods have been chosen as objective indices of reliability of the OIV method. In Table 1 chromatic parameters for the wine samples, such as chromaticity coordinates (x, y), luminance (Y), lightness (L^*) , purity (P),



Fig. 1. Section of the chromatic diagram showing displacements of chromaticity (δ_c) by both methods (\blacktriangle , OIV method; \bigcirc , CIE method) for four cases: (a) Valdepeñas; (b) Rioja; (c) La Mancha; (d) Ribeiro.

saturation (s_{uv}^*) , dominant wavelength (λ_d) , chroma (C_{uv}^*, C_{ab}^*) , hue angle (h_{uv}, h_{ab}) , tint (Tn) and colour intensity (CI) are offered.

Displacements between the significant parameters from CIE 1931-(x, y)and OIV methods for all the samples were calculated. Chromaticity (x, y) is a bidimensional variable whose displacements (δ_c) were computed too. For a given sample, δ_c corresponds to the length of the segment formed between the colour points (x, y) calculated by CIE and OIV methods, respectively (Fig. 1). By plotting each δ value versus each of the values for the chromatic



Fig. 2. δ_c values versus s_{uv}^* .

	Origin appellation ^a							
	(1)	(2)	(3)	(4)	(5)	(6)		
Âmax	506·667 ± 5·081 ^b	490·783 ± 39·558	510.600	514.600	509·800 ± 4·214	524·200		
$A_{\rm max}$	2·079 <u>+</u> 0·407	2.225 ± 0.528	1.359	2.010	2·458 ± 0·310	5.330		
CI	3·957 <u>+</u> 0·722	4·140 <u>+</u> 0·897	2.557	3.620	4.555 ± 0.399	8.620		
Tn	7.435 ± 9.002	1·433 <u>+</u> 13·116	7.842	21.306	$16 \cdot 982 \pm 12 \cdot 809$	62.731		
OIV								
N	0.613 ± 0.026	0.616 ± 0.029	0.521	0.607	0.640 ± 0.014	0.675		
r	0·336 ± 0·009	0.339 ± 0.001	0.331	0.317	0·328 ± 0·006	0.321		
Y(%)	9·958 ± 2·896	10·155 ± 3·370	16.459	10.791	8·403 ± 0·768	2.638		
ż,	608·735 ± 3·492	607·677 ± 3·769	607.898	616-312	611·729 <u>+</u> 2·243	614.472		
P(%)	$86 \cdot 137 \pm 6 \cdot 210$	87.877 ± 6.803	60.502	79.545	91·294 <u>+</u> 2·231	99 ·190		
CIE 1931	(x,y)							
X	0.613 ± 0.031	0.615 ± 0.034	0.520	0.602	0.641 ± 0.017	0.710		
y.	0.335 ± 0.013	0.339 ± 0.016	0.335	0.319	0.325 ± 0.010	0.287		
Y(%)	9·793 <u>+</u> 3·029	10·037 <u>+</u> 3·593	16.759	10.376	7·894 <u>+</u> 1·021	2.482		
i.	609·142 ± 4·832	607·992 <u>+</u> 5·889	606-141	615.075	613·005 <u>+</u> 4·200	634·453		
P(%)	85·896±6·304	87·679 <u>+</u> 6·765	61.069	78.881	90·921 <u>+</u> 1·993	99 ·197		
CIELUV								
u*	$105 \cdot 234 \pm 2 \cdot 886$	104·162 ± 4·496	91.454	113.732	111·796 ± 3·920	84.748		
v*	28·363 <u>+</u> 4·913	29·710±6·246	26.873	24.813	26·145 ± 2:378	12.289		
L*	36·956±5·770	37·137 ± 6·795	47.955	38.509	33·697 <u>+</u> 2·190	17.839		
C^*_{uv}	109·070 ± 3·361	108·448 ± 5·300	95·321	116-407	114·840 ± 3·406	85.635		
huv	15.055 ± 2.413	15·846 ± 2·962	16.375	12.307	13·189 ± 1·521	8.251		
s#	$3 \cdot 008 \pm 0 \cdot 437$	3.004 ± 0.511	1.988	3.023	3·421 ± 0·315	4.801		
CIELAB								
a*	52.248 ± 2.157	51.328 ± 2.508	45.566	57.278	56.155 ± 2.733	52.855		
b*	53·707 ± 15·568	60·500 ± 15·349	31.274	38.178	74·683 ± 0·579	58.000		
L*	36·956 <u>+</u> 5·770	37·137 ± 6·795	47·955	38.509	33·697 ± 2·190	17.839		
C_{ab}^*	75·507 <u>+</u> 11·939	79·886 ± 12·127	55·266	68·835	93·459 ± 1·503	78·4 7 0		
h_{ab}	$44{\cdot}850\pm7{\cdot}611$	48·744 ± 7·147	34.464	33.685	$53{\cdot}074 \pm 1{\cdot}439$	47.657		

 TABLE 1

 Chromatic Parameters of the Wine Samples

parameters listed in Table 1, it was inferred that in some instances (such as Y_{CIE} , L^* , P_{CIE} , s_{uv}^* , h_{uv}) samples behave according to two distinguishable patterns, as follows: an interval (set I) of chromatic parameter values in which δ oscillates within a narrow range, and another interval (set II) in which a linear increase of δ values was observed (Fig. 2). A cutpoint was found between the two sets. Table 2 lists the values for δ , together with their statistics, for the two mentioned sets.

The displacements of the chromaticity points (δ_c) in OIV against CIE 1931 plots are shown in Table 3. This table offers, for each of the chromatic parameters shown, the cutpoint delimiting the two sets, and the number of

			Origin ap	pellation ^a		
	(7)	(8)	(9)	(10)	(11)	(12)
Amax	509·267 ± 1·890	468·800 ± 54·144	517.000	502.500	513·857 ± 4·192	507·867 ± 3·445
Amax	2.822 ± 1.341	2.212 ± 1.202	15.100	3.360	2.802 ± 0.851	1.496 ± 0.427
CI	5.270 ± 2.314	3.712 ± 1.099	25.400	6.170	5·133 ± 1·633	2.838 ± 0.843
Tn	15.406 ± 18.278	-5.803 ± 11.935	78·232	17.745	22.255 ± 12.105	5·999±7·191
oiv						
X	0.638 ± 0.032	0·594 ± 0·039	0.677	0.666	0.639 <u>+</u> 0.044	0.550 ± 0.053
y	0·331 ± 0·007	0.348 ± 0.011	0.323	0.328	0.321 ± 0.007	0.335 ± 0.008
Y(%)	7·576±4·163	12·763 ± 5·010	0.005	4.920	6.684 ± 4.205	16·669 ± 5·072
1.	610.715 ± 2.806	$604 \cdot 485 \pm 4 \cdot 019$	614.067	611.901	614.775 ± 3.120	$607 \cdot 210 \pm 4 \cdot 022$
P(%)	91·562 <u>+</u> 6·838	84·379 ± 8·652	100.00	98 ·577	89·239 ± 12·646	69·035 ± 13·930
CIE 1931	(x, y)					
X	0.648 ± 0.049	0.594 ± 0.040	0.731	0.679	0.650 ± 0.054	0·547 ± 0·053
r	0.320 ± 0.024	0.348 ± 0.014	0.269	0.316	0.308 ± 0.010	0.337 ± 0.008
Y(%)	7.359 ± 4.091	12.863 ± 5.348	0.200	4.609	6.324 ± 4.320	16.835 ± 5.395
À.	615.765 ± 11.428	$604 \cdot 268 \pm 4 \cdot 673$	663-188	616-819	621.063 ± 6.152	606.086 ± 4.272
P(%)	91·435 ± 6·959	84·549 ± 8·438	100.000	98·447	88.691 ± 12.878	69.073 ± 13.571
CIELUV						
u*	102.346 ± 14.144	102.951 ± 2.815	9.666	99.431	99·059 ± 13·174	99·876 ± 11·288
v^*	23·921 ± 8·966	33·518±6·527	1.106	20.668	18.977 ± 3.901	29.682 ± 2.889
L_{uv}^*	31·122 ± 10·633	41·618 ± 8·293	1.806	25.589	28.536 ± 9.290	47.398 ± 7.124
C*	$105 \cdot 211 \pm 15 \cdot 712$	108.425 ± 2.883	9.729	101.557	100.890 ± 13.485	104.288 ± 10.593
h	12.828 ± 3.314	18.010 ± 3.416	6.526	11.742	10.795 ± 1.495	16.736 ± 2.778
S [*] uv	3.583 ± 0.893	2.686 ± 0.512	5.389	3.969	3.735 ± 0.729	$2 \cdot 273 \pm 0 \cdot 584$
CIELAB						
a*	53.609 ± 1.322	49·179 <u>+</u> 3·114	13.755	53·621	54·163 ± 4·050	48·648 ± 5·939
b*	51.083 ± 7.955	52.966 ± 14.821	3.113	70.589	56.263 + 16.937	42.296 + 18.739
L*	31.122 + 10.633	41.618 ± 8.293	1.806	25.589	28.536 + 9.290	47.398 + 7.124
C*	74.226 ± 5.091	72.770 ± 11.828	14.103	88.645	79.064 + 11.227	65.205 + 16.466
hab	43.408 ± 4.760	46.335 ± 7.028	12.752	52·779	44.961 ± 10.276	39.540 ± 8.360

TABLE 1-contd.

^a The origin appellations, together with the sample size (n), are as follows: (1) Navarra (n = 6); (2) Rioja (n = 12); (3) Campo de Borja (n = 1); (4) Cariñena (n = 1); (5) Ampurdán-Costa Brava (n = 3); (6) Ribeiro (n = 1); (7) Alicante (n = 3); (8) Jumilla (n = 5); (9) Valencia (n = 1); (10) Yecla (n = 1); (11) La Mancha (n = 7); (12) Valdepeñas (n = 6).

^b Data are the mean \pm SD of *n* samples.

samples classified in each set, according to the cutpoint of the chromatic parameter in question. For set I the mean values together with the range of chromatic parameters are shown. For set II, given that a linear distribution was obtained, the regression line and correlation coefficient (r^*) are offered. Although most of the samples were placed within set I, where the simplified method (OIV) might be applied with enough reliability, a considerable

Differences (δ)	Mean	Standard deviation	Standard error	Coefficient of variation	
Set I					
δ_x	0.003	0.002	0-000 3	0.65510	
δ_{y}	0.003	0.002	0.0004	0.76617	
$\delta_{\mathbf{Y}}$	0.282	0.215	0.034 9	0.752 58	
δ_{λ_d}	1.485	1.722	0.2793	1.15968	
δ_P	0.366	0.362	0.0587	0-98716	
$\delta_{\mathfrak{c}}$	0.002	0.003	0.000 2	0.647 92	
Set II					
δ_x	0.025	0.013	0.004 5	0.543 40	
δ_{y}	0.025	0.013	0.0044	0.523 57	
δ_{Y}	0.281	0.165	0.0550	0.58674	
δ_{λ_d}	14.586	9.364	3.1214	0.641 97	
δ_{P}	0.107	0.116	0.0388	1.092.23	
δ_{c}	0.035	0.019	0.006 3	0.533 22	

 TABLE 2

 Differences for Several Representative Parameters in the Two Sets

percentage of the samples (set II) were affected by an appreciable error. It was noted (Table 3) that this error was present as a linear function of the value of the chromatic parameter that was being considered.

A Stepwise Discriminant Analysis (SDA) was carried out between set I and set II. The twenty-five variables used to perform the SDA were chosen in a stepwise manner: at each step an F statistic was computed from a one-way analysis of variance on each remaining variable for the two sets. The variable that added the most to the separation of the sets (largest value of F) was entered into the discriminant function. Each case was classified into a group according to the classification functions. For the samples under study, classification functions were as follows:

$$z_1 = 15.898 \cdot Y_{CIE} - 126.348 \cdot s_{uv}^* - 271.895$$

 $z_{II} = 17.469 \cdot Y_{CIE} - 143.333 \cdot s_{uv}^* - 345.067$

At step zero the variable saturation, s_{uv}^* (from CIELUV system), was chosen. This means that this is the best discrimination parameter between the two sets.

The classification functions (z_i, z_{ii}) can be used to classify new samples into the sets; depending on whether $(z_i > z_{ii} \text{ or } z_{ii} > z_i)$ the sample is located within set I or set II, respectively. If a wine is located in set I we can use (with sufficient reliability) the OIV method, but if the wine is located in set II we must use the CIE 1931-(x, y) method.

		* x	-0.980	0-732	0-926	-0-974	0-991	-0-905	0-833	0-804
	Set II	Regression line	$y = 7.49.10^{-2} - 1.19.10^{-2}.x$	$y = -6.26 \cdot 10^{-1} + 6.73 \cdot 10^{-3} \cdot x$	$y = -1.11 + 1.83 \cdot 10^{-2} \cdot x$	$y = 8.23 \cdot 10^{-2} - 2.35 \cdot 10^{-3} \cdot x$	$y = -1.26 \cdot 10^{-1} + 3.68 \cdot 10^{-2} \cdot x$	$y = 1.24 \cdot 10^{-1} - 9.42 \cdot 10^{-3} \cdot x$	$y = 3.60.10^{-3} + 3.09.10^{-3}.x$	$y = -3.42.10^{-3} + 8.78.10^{-4}.x$
or δ_{ϵ} Values		Na	96	13^{b}	176	9د	12^{b}	17^{c}	12^{b}	176
of Wine Samples f		Range $\times 10^3$	13.35	13-16	9-04	13-35	10-51	9.04 40.6	13-11	09.6
Distribution 6	Set I	Mean value × 10 ³	4.56	4-40	3.61	4-56	3-97	3-61	4-44	3-90
		Na	386	34°	30 ^c	38,	35°	30 ⁶	35°	30°
	Cutpoint		5-0	39-0	612-0	28-0	3.6	13-1	5-0	12-0
	Chromatic	parameter	Ycie	Scie	idere	L*	S#	h	5ª	Тп

^a Number of samples. ^b Samples with a chromatic parameter value > cutpoint. ^c Samples with a chromatic parameter value \leq cutpoint.

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