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Relationship between Flavor Dilution Values and Odor Unit Values in Hydroalcoholic Solutions: Role of Volatility and a Practical Rule for Its Estimation

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The gas–liquid partition coefficients (GLPC) of a series of compounds in hydroalcoholic solutions have been determined experimentally in order to show that it is possible to establish a direct relationship between the odor unit values (actual concentration/odor threshold) and the flavor dilution values from an aroma extract dilution analysis (AEDA). GLPCs depend primarily on the chemical functionality of the compound and secondarily on its intrinsic volatility, and it is shown that GLPCs can be estimated from GC retention data. The GLPC of a compound is directly proportional to $I_{ap}^{1.32}$ and inversely proportional to $\Delta I^{4.61}$, ΔI being the difference between the retention indexes of the compound in a Carbowax 20M column and in a BP-5 column, while I_{ap} is the RI of the compound in the latter column. The function has been applied to the determination of the odor spectrum of Grenache red wine from FD values and has yielded satisfactory results.

Keywords: Gas chromatography/olfactometry; AEDA; flavor; odorant; wine

INTRODUCTION

Olfactometric techniques are at present very useful and well-established tools in flavor chemistry, particularly in its basic quantitative procedures: Charm analysis (Acree et al., 1984), aroma extract dilution analysis (Grosch, 1993; Schieberle and Grosch, 1987), and Osme (McDaniel et al., 1990; Miranda-López et al., 1992). The first two techniques allow the researcher to get an estimation of the potency of the odorants eluted from a gas chromatographic column, while the third gives an estimate of the intensity of the odorants (Acree, 1997). Both strategies offer numerous advantages, mainly due to the fact that the odorants do not need to be previously identified nor isolated or synthesized to obtain a first idea of their potential role in the flavor of a foodstuff. It is not strange, then, that these techniques should have become a common first step in flavor research and that plenty of work should be invested in getting the corresponding Charm values, flavor dilution values, or intensity values. It must be noted, however, that in most cases the relationship between these parameters and the odor unit values (ratio of the actual concentration of a flavor compound to its odor threshold), or the real intensity values of the odorants in the foodstuff, is not clear. This is due to both losses of odorants during the isolation process and the fact that in olfactometric experiments the odorants are fully volatilized while, in real situations, liquid–vapor or solid–vapor equilibria can introduce serious differences (Fischer et al., 1994; Acree, 1997; Guth, 1997; Leland, 1997).

Several attempts have been made in order to overcome these simplifications. Some authors have stressed the need to get representative extracts (Abbot et al., 1993; Moio et al., 1995; Priser et al., 1997), while others have

developed olfactometric techniques based on the analysis of the headspace (Guth and Grosh, 1993; Guth, 1997), but the question of how to relate the olfactometric results to the actual role of the odorants in the foodstuff remains unsolved. In this sense, there is a primary need to measure the effects of the gas–liquid partition equilibria in order to know what can be really expected from a list of olfactometric data and also to develop some system capable of estimating the gas–liquid partition coefficients (GLPCs) of the odorants. These are the main aims of this paper, where the relationship between flavor dilution values and odor unit values in hydroalcoholic solutions has been determined through the study of the GLPCs of 15 odorants belonging to different chemical classes. In the second part of the paper, the possibility of using gas chromatographic retention data for the estimation of those coefficients has been explored and applied to a real case, which has proved to be a useful method to solve the question raised.

EXPERIMENTAL PROCEDURES

Reagents. Hexane, dichloromethane, and diethyl ether were HPLC quality from Lab-Scan (Dublin, Ireland); freon 11 was from Merck (Darmstadt, Germany); ethanol was from Panreac (Barcelona, Spain); freon 113 was from Aldrich (Gillingham, U.K.). The pure reference compounds used in the study were purchased from Aldrich (Gillingham, U.K.), Sigma (St. Louis, MO), Fluka (Buchs, Switzerland), Poly Sciences (Niles), or Lancaster (Strasbourg, France).

Measurement of Gas–Liquid Partition Coefficients (GLPCs). GLPCs were measured by analyzing between 0.1 and 5 mL of the headspace of hydroalcoholic solutions (12% v/v in ethanol, pH 3.5, 5 g/L tartaric acid plus NaOH, 0.1 N) containing variable amounts (between 0.1 and 100 mg/L) of the analytes tested: 50 mL of the solutions was placed in a 200-mL glass bottle, hermetically capped with a septum-fitted cap, and left to equilibrate at 28 °C for 40 min. After the equilibration, the headspace sample was taken with a gastight

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syringe and directly analyzed by gas chromatography. Volatility values were estimated as the slopes of the straight graphs "concentration in vapor phase vs concentration in liquid phase" built through the analysis of sets of solutions containing increasing amounts of the compounds.

Determination of the Gas Chromatographic/Olfactometric Detection Limits of the Compounds (GCO_d). A set of hexane solutions containing known amounts of the tested compounds was analyzed by a panel of four trained judges by gas chromatography/olfactometry in order to determine the concentration at which each compound becomes odorless.

Determination of the Olfactory Threshold (O_t) of the Compounds. The olfactory thresholds were determined in hydroalcoholic solutions (12% v/v in ethanol, pH 3.5, 5 g/L tartaric acid plus NaOH, 0.1 N) by a panel composed of 17 students.

Aroma Extract Dilution Analysis of a Red Wine. Volumes of 1100 mL of a red wine (Grenache wine from Cariñena, Spain, 1996 harvest) were continuously extracted with 2 × 250-mL freon 11 fractions for 24 h each. Water bath temperature was 28 °C. Coolant temperature was 2 °C. The two freon 11 fractions were collected and mixed together in a 500-mL volumetric flask and brought to volume with freon 11. Volumes of the crude extracts obtained from the wine were concentrated under a 60-cm long Vigreux column until 30 mL and then in a micro kuderna Danish concentrator fitted to a 3-ball Snyder column until a final volume of 3 mL. The different solutions were finally concentrated, when necessary, under a N₂ stream to constitute the base solutions for the AEDA study. The solutions were prepared so that 1 µL of the final solutions equaled 1, 4, 40, and 400 µL of wine. The solutions were then analyzed by HRGC-MS-olfactometry.

Quantitative Analysis of Odorants (Ferreira et al., 1996). The wine was first adjusted to 13% in ethanol (v/v), 25 µL of the internal standard solution was added, and later an organic layer was demixed by salting out 50 mL of the wine with 6.57 g of NaH₂PO₄·H₂O and 27 g of (NH₄)₂SO₄; 2 mL of this organic phase was diluted with 10 mL of a saline solution prepared by the dissolution of 47.5 g of (NH₄)₂SO₄ in 100 mL of water and extracted with 0.1 mL of freon 113. The freon extract was fractionated in a 500-mg silica cartridge Bond-Elut from Varian with 4 mL of CH₂Cl₂ and another second 4 mL of diethyl ether. Both fractions were collected separately and then analyzed. Quantitative data were obtained through the interpolation of the corresponding relative areas in the calibration graphs built by extracting and analyzing six synthetic wines containing known amounts of odorants.

Headspace Gas Chromatography. Fisons 8000 series gas chromatograph was used. Column: BP-5 column (J&W, Folsom, CA), 30-m length, 0.53-mm i.d., 3.0-µm film thickness. Temperature program, initial 30 °C held 4 min and then raised at 15 °C/min up to 200 °C. Carrier H₂ at 9 mL/min. Injection: 0.1–5 mL of gas in splitless mode, splitless time 90 s. The gas was not injected faster than 1 mL/12 s. Detector: FID.

Gas Chromatography/Olfactometry. PE 8310B gas chromatograph, fitted to a splitter at the column exit, was used. One end was directed to a sniffing port and the other one to a FID detector; 80% of the effluent was directed to the sniffing port and the rest to the FID. Column: DB-WAX (J&W), 50 m × 0.53-mm i.d., 1.0-µm film thickness. Chromatographic conditions: carrier N₂ at 6 mL/min, injected volume 1 µL, injector and detector temperatures were 220 °C. Initial column temperature: 40 °C held for 5 min and then raised to 210 °C at 2 °C/min. Detector: FID.

HRGC-MS-Olfactometry. A Star 3400CX (Varian) gas chromatograph fitted with a Saturn 4 electronic impact MS detector and equipped with a sniffing port (open split interface, makeup flow 4 mL/min He) was used. Columns: Carbowax 20M (J&W), 60 m × 0.32-mm i.d., 0.5-µm film thickness; BP-5 column (J&W), 50-m length, 0.32-mm i.d., 1.0-µm film thickness. Chromatographic conditions: carrier He at 1.2 mL min⁻¹, 1 µL of sample was injected into a 1093

Table 1. Gas-Liquid Partition Coefficients, Gas Chromatographic Retention Data, Gas Chromatographic/Olfactometric Detection Limits, and Flavor Thresholds of a Series of Compounds

compound	GLPC, ng/mL ^a	I _{pol} ^b	I _{ap} ^c	ΔI ^d	GCO detection limit, ng	O _t , ng/mL
ethyl isovalerate	0.977 ± 0.07	1075	864	211	0.84	3
ethyl hexanoate	1.17 ± 0.08	1238	1004	234	4.85	14
ethyl heptanoate	1.40 ± 0.09	1338	1103	235	3.9	18
ethyl octanoate	1.19 ± 0.08	1439	1201	238	2.2	5
ethyl decanoate	1.03 ± 0.07	1634	1399	235	53	200
α-terpinol	0.043 ± 0.005	1684	1199	485	2.08	250
linalool	0.089 ± 0.006	1551	1106	445	0.44	30
nerol	0.032 ± 0.003	1809	1234	575	4.90	700
β-citronellol	0.018 ± 0.002	1773	1231	542	4.65	700
isoamyl alcohol	0.026 ± 0.004	1219	753	466	280	40000
hexanol	0.027 ± 0.003	1359	888	471	74	8000
β-phenylethanol	0.003 ± 0.003	1931	1118	813	16	14000
guaiacol	0.003 ± 0.002	1882	1103	779	0.040	30
eugenol	0.012 ± 0.002	2140	1369	771	0.061	10
octanoic acid	0.008 ± 0.003	2050	1214	836	50	10000

^a The figures are ng of compound present in 1 mL of headspace equilibrated with a 1 mg/L hydroalcoholic solution. ^b Retention indexes on a Carbowax 20M column. ^c Retention indexes on a BP-5 column. ^d I_{pol} - I_{ap}.

septum-equipped programmable injector held for 6 s at 20 °C and then raised to 190 °C at 200 °C/min. Initial column temperature: 40 °C held for 5 min and then raised to 190 °C at 2 °C/min. Quantitative HRGC-MS was performed with the same equipment, column (Carbowax 20M), and conditions but with the column exit directly connected to the MS.

RESULTS AND DISCUSSION

Gas-Liquid Partition Coefficients. The GLPCs of a selected series of flavor compounds were measured by analyzing the equilibrated headspace of hydroalcoholic solutions containing small amounts of the test compounds. The results, expressed as ng of compound present in 1 mL of headspace equilibrated with a 1 mg/L solution, can be seen in Table 1. The most volatile compounds in this particular system are the ethyl esters, whose headspaces contain more than 1 molecule per each thousand present in the hydroalcoholic solution. On the other hand, β-phenylethanol, octanoic acid, and guaiacol are the least volatile compounds, and their headspaces contain less than 10 molecules per each million originally present in the system, which is almost 3 orders of magnitude less than the figures observed in the case of the esters. It can be observed, just by comparing the cases of ethyl octanoate (bp 208 °C), linalool (bp 199 °C), and guaiacol (bp 205 °C), that the boiling point of the compound only plays a secondary role in its gas-liquid distribution, while its chemical nature seems to play a major role: the more polar the chemical compound, the lower its GLPC. Still more shocking is the relationship between boiling points and GLPCs in the case of the ethyl esters, which show a maximum GLPC for ethyl heptanoate.

All these data can be easily explained, at least from a semiquantitative point of view, in terms of solubility and intrinsic volatility. Polar molecules are fairly soluble in hydroalcoholic solutions, and the gas-liquid equilibrium is strongly displaced to the liquid side. On the other hand, small organic molecules are more soluble than the higher and more hydrophobic members of a homologous series, but the higher the number of carbons, the smaller the differences in solubility between consecutive members of the same homologous series. Thereby, the GLPC of ethyl heptanoate is higher

than that of ethyl hexanoate, because the former is less soluble, although it is less volatile. However, the GLPC of ethyl heptanoate is higher than that of ethyl octanoate because the difference in solubility between the two molecules is too small to account for the difference in volatility.

Relationship between FD and Odor Unit Values.

An AEDA (aroma extract dilution analysis) experiment was carried out in order to determine the minimum amount of material that must be introduced into the chromatographic system to perceive an olfactory stimulus. These GCO detection limits are shown in Table 1, which clearly shows that the most powerful odorants are guaiacol and eugenol, whereas the weakest are isoamyl alcohol, octanoic acid, and hexanol. Differences between odorants are still bigger than those observed before, since the values range from 0.04 ng (guaiacol) to 280 ng (isoamyl alcohol). If we correct these data by the GLPCs estimated before, we should get a new set of values closely related to the olfactory thresholds of the compounds in the hydroalcoholic solution, which is clearly confirmed by the linear relationship shown in Figure 1a. The fact that the slope of the straight line is so close to 1 (in fact, it does not differ significantly from 1) demonstrates that the olfactory threshold of each compound in a given solution is directly proportional to its olfactory threshold in the GCO system and inversely proportional to its GLPC, as the following algebraic equation clearly shows:

$$\log(O_t) = 0.592 + 0.960 \log\left(\frac{GCO_t}{K}\right)$$

$$O_t = 3.91 \left(\frac{GCO_t}{K}\right)^{0.96} \approx 3.91 \frac{GCO_t}{K} \quad (1)$$

where O_t is the olfactory threshold in hydroalcoholic solutions expressed in ng/mL; GCO_t is the gas chromatographic/olfactometric detection limit determined in the AEDA experiment, expressed in ng of compound injected in the column; K is the gas-liquid partition coefficient expressed as ng of compound per mL of headspace equilibrated with a 1 ppm hydroalcoholic solution (12% in alcohol).

This relationship should be found in all the systems and indicates that, provided that the GLPCs of the odorants in the matrix are known, it is possible to determine the odor unit values of the odorants (concentration of odorant/olfactory threshold) from an AEDA experiment, as can be easily demonstrated from an algebraic point of view:

$$OUV = \frac{C_x}{O_t} = \frac{C_x K}{GCO_t 3.91} = ct(FD) \frac{K}{3.91} \quad (2)$$

where C_x is the concentration of the odorant in the matrix and ct is a constant.

The value of the new constant can be known if the flavor dilution values from the AEDA experiment are properly defined and the olfactory system has been previously calibrated. These observations should make it possible to extract very useful information from the different olfactometric techniques and would eventually justify the use of more sophisticated and refined gas chromatographic olfactometric techniques. Unfortunately, the estimation of GLPCs requires the chemical standard or, at least, to know the identity of the com-

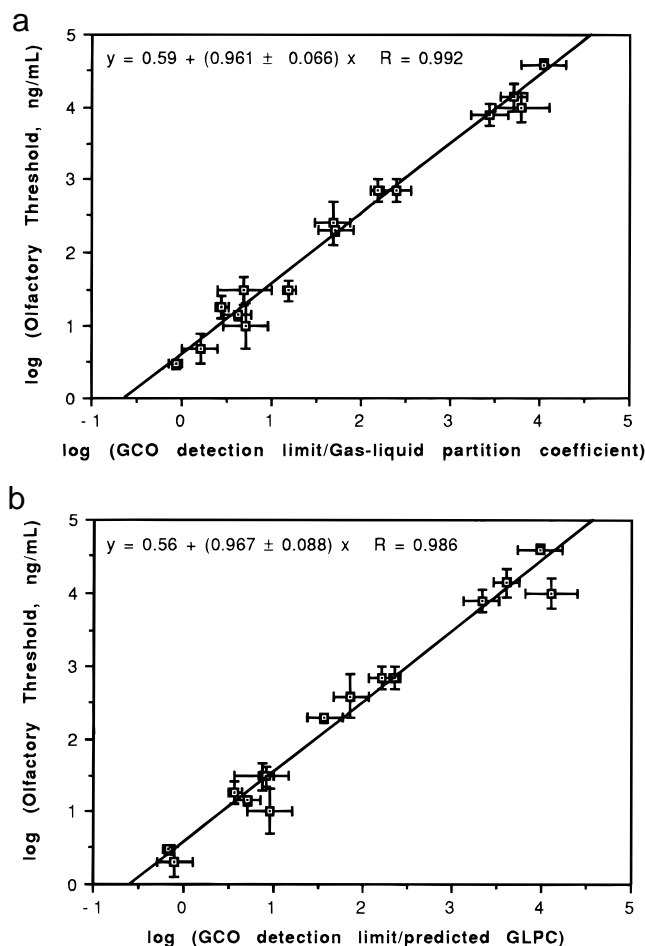


Figure 1. Relationship between the olfactory thresholds of odorants and their corresponding GC olfactometric detection limits, corrected by the experimental values of GLPCs (a) or by the predicted GLPCs (b); log scale.

pound when, most frequently, the olfactometric experience is carried out as a first step in flavor research for the establishment of a hierarchy of unknown odorants that will be subsequently identified. Things would change, however, if we could get an estimation of GLPCs from easily available data, which constitutes the second main concern of this article.

Estimation of Gas-Liquid Partition Coefficients. As was previously stated, the GLPC of a compound in a solution must be the result of, at least, two opposing parameters: (a) the intrinsic volatility of a molecule and (b) its solubility in the matrix media. The intrinsic volatility of a molecule can be somehow measured through its boiling point, or through the vapor pressure of the pure compound, but a far better measure is its retention index on an apolar column (Ferreira et al., 1998) since, in this kind of column, polar interactions responsible for unideal behavior can hardly take place. Furthermore, retention indexes can be easily determined in a simple olfactometric experiment that does not need the previous identification of the odorant. With regard to the solubility of organics in aqueous or hydroalcoholic media, this is directly related to the polarity of their functional group and to the overall hydrophobicity of the molecule. The polarity of a molecule can be satisfactorily measured through the differences between its retention indexes on Carbowax and apolar phases (let us denominate it ΔI), while the

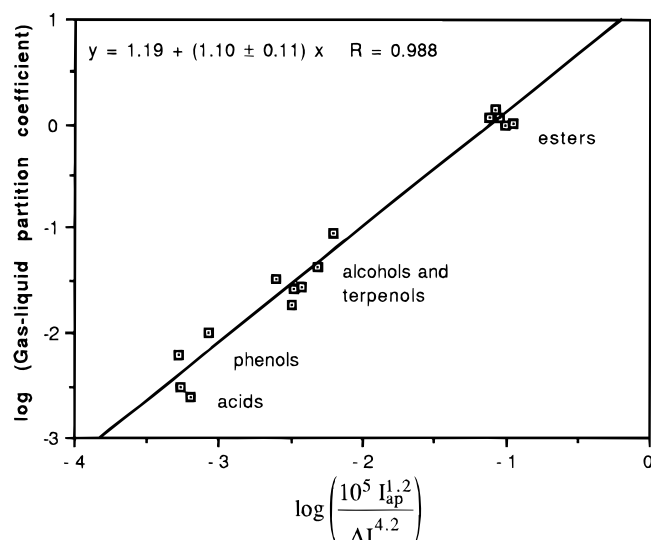


Figure 2. Predictive function of GLPC; log scale.

Table 2. Flavor Dilution Values, Concentrations, and Odor Unit Values of a Series of Compounds Detected in an AEDA Experiment Performed on a Grenache Red Wine

compound	I_{pol}^a	FD	concn, ng/mL	OUV	
				determined	predicted
isoamyl alcohol	1219	400	217000	5.4	12
β -phenylethanol	1931	400	58000	4.1	1.6
ethyl isobutyrate	955	100	27.8	3.6	117
ethyl butyrate	1043	100	292	15	64
ethyl hexanoate	1238	100	440	31	95
ethyl octanoate	1439	100	543	109	111
ethyl 2-methylbutyrate	1061	10	1.92	2.4	12
ethyl isovalerate	1075	10	7.8	2.6	12
isoamyl acetate	1128	10	1330	30	6.1
hexanol	1359	10	3120	0.39	0.34
<i>cis</i> -3-hexenol	1389	10	100	0.25	0.19
linalool	1551	10	10.9	0.36	0.59
guaiacol	1882	10	0.99	0.033	0.048
ethyl cinnamate	2122	10	1.05	0.52	0.14
eugenol	2140	10	1.52	0.15	0.067
phenylethyl acetate	1851	10	59	0.24	0.24
geraniol	1869	10	10.1	0.30	0.18
β -ionone	1952	10	0.72	0.55	0.72
γ -nonalactone	2038	10	26	0.60	0.13
4-vinylguaiacol	2173	10	4.1	0.09	0.04
ethyl decanoate	1634	1	179	0.89	1.4
α -terpinol	1684	1	3.3	0.014	0.045
ethyl benzoate	1662	1	0.48	0.06	0.045
α -ionone	1879	1	0.05	0.03	0.084
furfural	1475	1	14	0.01	0.009

^a Retention indexes on a Carbowax 20M column.

overall hydrophobicity of the molecule can be related to the quotient between ΔI and, again, its retention index on apolar phases. In algebraic notation:

$$K \equiv I_{ap}^{a'} \Delta I^{b'} \left(\frac{\Delta I}{I_{ap}} \right)^c = I_{ap}^a \Delta I^b \quad (3)$$

where K is the gas-liquid partition coefficient, I_{ap} is the retention index in the BP-5 column, ΔI is the difference between the Kovat index in Carbowax columns and apolar columns, and a' , b' , c , a , and b are real numbers (a' , b' , $c < 0$).

The optimization of these mathematical equations through iterative procedures reveals that an optimal linear relationship can be found for $a > 0$ and $b \approx -3a$, and a plot of the logarithm of the GLPCs versus an optimal function of this kind can be found in Figure 2,

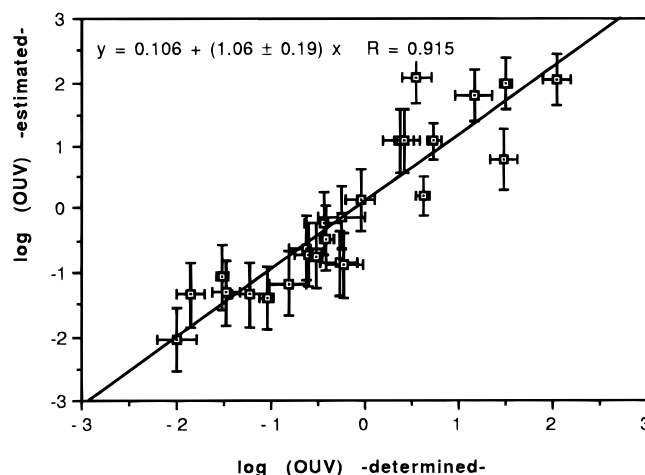


Figure 3. Relationship between the experimental odor unit values and the predicted odor unit values of the odorants of a red wine from Grenache; log scale.

whose algebraic form is as follows:

$$\log(\tilde{K}) = 1.196 + 1.098 \log \left(\frac{10^5 I_{ap}^{1.2}}{\Delta I^{4.2}} \right)$$

$$\tilde{K} = 15.7 \left(\frac{10^5 I_{ap}^{1.2}}{\Delta I^{4.2}} \right)^{1.098} = 4.85 \times 10^6 \frac{I_{ap}^{1.32}}{\Delta I^{4.61}} \quad (4)$$

As the high linear regression coefficient shows, the function is quite satisfactory and allows to get an approximate value of the GLPC of a compound only from its retention data on two chromatographic phases. It should be noted, however, that the function is only an approximation and that it cannot accurately reflect the small variations found in a chemical family, as is the case with esters. It is possible to build more complicated functions capable of reflecting these minor variations, but those functions have to be restricted to narrower segments of volatility, thus losing general applicability. Despite this limitation, the proposed function makes it possible to simulate eq 1 by replacing the experimental GLPCs by the ones estimated through eq 4. This result can be seen in Figure 1b and in the following algebraic expressions which, not surprisingly, are completely equivalent to eqs 1 and 2:

$$\log(O_t) = 0.565 + 0.967 \log \left(\frac{GCO_t \Delta I^{4.2}}{10^5 I_{ap}^{1.2}} \right)$$

$$O_t = 3.67 \left(\frac{GCO_t}{\tilde{K}} \right)^{0.97} \approx 3.67 \frac{GCO_t}{\tilde{K}} \quad (5)$$

$$OUV = \frac{C_x}{O_t} \left(\frac{C_x(\tilde{K})}{GCO_t 3.67} \right) = ct(FD) \frac{(\tilde{K})}{3.67} \quad (6)$$

where O_t is the olfactory threshold in hydroalcoholic solutions expressed in ng/mL, GCO_t is the olfactory threshold determined in the AEDA experiment, expressed in ng, and \tilde{K} is the estimated gas-liquid partition coefficient through eq 4.

Practical Application: Odor Spectrum of Grenache Red Wine. To check the applicability of eq 6 to a real situation, an AEDA experiment has been carried out on an extract from a Grenache red wine. The data

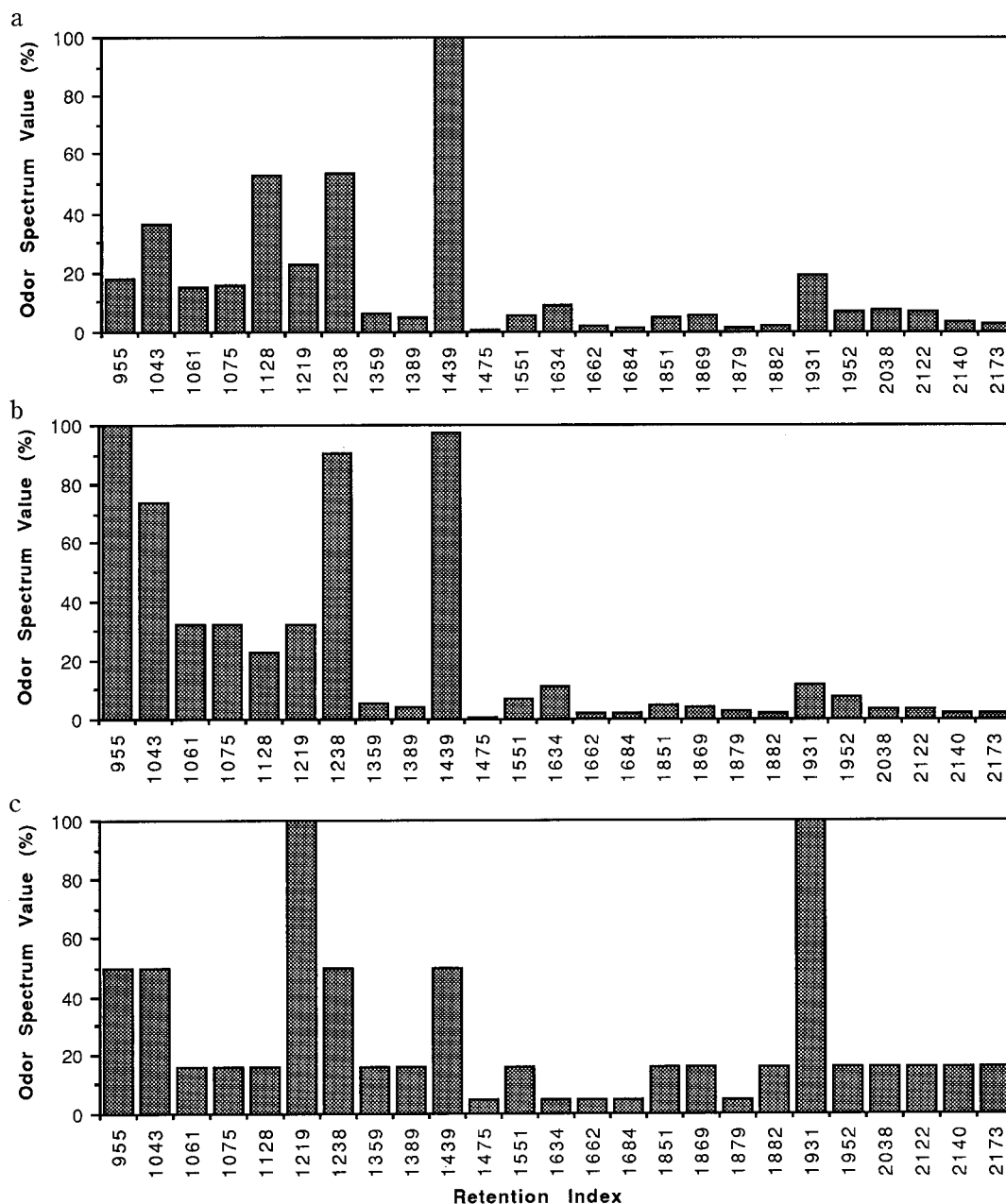


Figure 4. Odor spectra of a Grenache red wine: (a) determined, (b) estimated from FD and eq 6, (c) directly from FD.

from the experiment, together with chemical concentration data and experimental and predicted odor unit values, can be seen in Table 2. Figure 3 is a plot of the logarithm of the predicted values versus the experimental values and shows a high degree of correlation between the two sets of data, despite the low precision of the AEDA experiment (a 4-point scale has been used). Figure 4 compares the odor spectra (square roots of the normalized odor unit values) obtained from the Grenache red wine through: (1) direct experimental determination (Figure 4a), (2) estimation from FD values using eq 6 (Figure 4b), and (3) directly from the FD values (Figure 4c). As can be seen in the figure, the odor spectrum directly obtained from the FD values (Figure 4c) is completely distorted with respect to the real one (Figure 4a). The two most active odorants in Figure 4c only show moderate potency in Figure 4a, while some of the most active odorants shown in Figure 4a are classified as having low potency in Figure 4c and, in general, the odor spectrum from FD values tends to

overemphasize the role of the least volatile compounds. Some of these problems are corrected with the use of eq 6, as can be seen by comparing Figure 4a and 4b, whose central and right parts are fairly similar. The equation fails to assign the odor spectrum values to the most volatile compounds, which is due to its aforementioned inability to reflect correctly the variations of GLPC of the different members of the ethyl ester group. In particular, the major error corresponds to the odor spectrum value of ethyl isobutyrate, whose predicted GLPC is strongly overestimated, partly because its retention index is out of the range considered in the development of the model. Leaving this case aside, it must be noted that the conclusions reached from Figure 4b are almost the same as those extracted from Figure 4a and, in any case, far more accurate than those from Figure 4c.

In short, it has been demonstrated that it is possible to estimate the GLPC of the odorants through their chromatographic retention index data and that this

estimation makes it possible to get quite a correct value of the real potency of the odorant in the hydroalcoholic matrix. This system can help to establish the priorities of further research on the isolation, identification, and chemical synthesis of unknown odorants.

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