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**Flavour  
Science**

*Proceedings from XIII Weurman  
Flavour Research Symposium*

Edited by Vicente Ferreira  
and Ricardo Lopez



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# FLAVOUR SCIENCE

## Proceedings from XIII Weurman Flavour Research Symposium

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# Improvement of Partition Coefficients Determination of Aroma Compounds in Food Matrices by the Phase Ratio Variation Method

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## 75.1 INTRODUCTION

Before its perception, aroma compounds must move from the liquid phase towards the vapor phase, and aroma release from food matrices constitutes a determinant step for its perception. In previous works, we used the Quantitative Structure-Property Relationships (QSPR) approach to identify the nature of interactions involved between constituents of food matrix and aroma compounds [1]. In this way, a study of  $K = C_{\text{vap}}/C_{\text{liq}}$  at equilibrium is the usual method to account for the balance between liquid phase and vapor phase. Because QSPR methodology is based on statistical regression tools, a limitation of the QSPR approach is the size of the dataset. Indeed, good applicability conditions require a sufficiently large training set, constituted by at least 10 compounds belonging to the same chemical space [2]. However, partition coefficient determinations are based on headspace methods and are time-consuming because the quantification of aroma compounds in vapor phase by chromatographic experiment requires substance-response factor detector calibration.

The Phase Ratio Variation (PRV) method [3] allows one to overcome the calibration step. Ette et al. [3,4] established the following Eq. 1, based on the influence of the volume of the sample on the concentration of volatiles in the headspace:

$$\frac{1}{A} = \frac{1}{f_i \times C_{\text{liq}}} \times K + \frac{1}{f_i \times C_{\text{liq}}} \times \beta \quad [75.1]$$

where  $A$  is the chromatographic peak area at equilibrium,  $f_i$  the proportional factor,  $C_{\text{liq}}$  is the sample concentration, considered close to the initial concentration  $C_0$  in the liquid phase,  $\beta$  the ratio  $V_{\text{vapor}}/V_{\text{liquid}}$  and  $K = [\text{volatile compound}]_{\text{liquid phase}}/[\text{volatile compound}]_{\text{vapor phase}}$  the partition coefficient between vapor phase and liquid phase. On the basis of the PRV equation,  $K$  is also equal to the ratio of slope and intercept of the linear regression  $1/A$  vs.  $b$ .

Nevertheless, there are some limitations to this method, particularly when compounds are strongly retained by food matrices [5], but also in case of very volatile molecules. However, as the PRV approach is a very valuable method for partition coefficients data acquisition, we have carefully examined its principle in order to improve the reliability of results.

## 75.2 MATERIALS AND METHODS

We consider that volumes remain constant:  $V_t = V_{\text{liq}} + V_{\text{vap}}$ , and  $V_{\text{liq}(t_0)} = V_{\text{liq}(t_{\text{eq}})}$  (volume variation due to vaporization in vapor phase is negligible in comparison with  $V_{\text{liq}}$ ).

Our calculations are based on:

the law of conservation of mass ( $n_0 = n_{\text{vap}} + n_{\text{liq}}$ ) which states that the mass of a closed system remains constant over time [6];

the partition coefficient value  $K = C_{\text{vap}}/C_{\text{liq}}$ .

We have chosen two  $K$  values:  $K_1 = 10^{-3}$  and  $K_2 = 5.10^{-2}$  in the range of partition coefficient already known for aroma compounds [7,8], and performed the calculations for 12  $V_{\text{liq}}$  values: 0.15; 0.2; 0.3; 0.4; 0.5; 0.75; 1; 1.25; 1.5; 2; 3; and 5 mL. Initial liquid phase concentration was set to  $C_0 = 10^{-4}$  mol/L. Total volume was set to 21 mL.

For each  $V_{\text{liq}}$ , we calculated:

$$n_0 = C_0 \times V_{\text{liq}}$$

$$n_{\text{vap}} = C_{\text{vap}} \times V_{\text{vap}} = K \times C_{\text{liq}} \times V_{\text{vap}} = \left( K \times (V_t - V_{\text{liq}}) \times n_0 \right) / \left( V_{\text{liq}} + K \times (V_t - V_{\text{liq}}) \right) \text{ and } n_{\text{liq}} = n_0 - n_{\text{vap}}$$

$$C_{\text{vap}} = n_{\text{vap}}/V_{\text{vap}} \text{ and } C_{\text{liq}} = n_{\text{liq}}/V_{\text{liq}}$$

### 75.3 RESULTS

According to Ettre et al. [3], the classical PRV equation writes:

$$\begin{aligned} 1/A &= (1/f_1 C_{\text{liq}}) \times C_{\text{liq}}/C_{\text{vap}} + (1/f_1 C_{\text{li}}) \times \beta \\ \text{with } \beta &= V_{\text{vap}}/V_{\text{liq}} \end{aligned} \quad [75.1]$$

PRV equation applicability is based on the assumption that the concentration of solute in liquid phase remains almost constant, thus close to the initial concentration  $C_0$  ( $C_{\text{liq}} \approx C_0$ ). Indeed, considering a vapor phase sampling of 1 mL and expressing concentrations in mmol/mL and volume in mL, the PRV equation becomes:

$$1/A = 1/f_1 C_{\text{vap}} \times 1 = (1/f_1 C_{\text{liq}}) \times C_{\text{liq}}/C_{\text{vap}} + (1/f_1 C_{\text{li}}) \times V_{\text{vap}}/V_{\text{liq}} \quad [75.2]$$

$$1/C_{\text{vap}} = (1/C_{\text{liq}}) \times C_{\text{liq}}/C_{\text{vap}} + (1/C_{\text{liq}}) \times V_{\text{vap}}/V_{\text{liq}} \quad [75.3]$$

so that:

$$1/C_{\text{vap}} = 1/C_{\text{vap}} + V_{\text{vap}}/(C_{\text{liq}} V_{\text{liq}}) \quad [75.4]$$

What is meant by the term  $V_{\text{vap}}/(C_{\text{liq}} V_{\text{liq}})$ ?

$$1/C_{\text{vap}} + V_{\text{vap}}/(C_{\text{liq}} V_{\text{liq}}) = V_{\text{vap}}/n_{\text{vap}} + (V_{\text{liq}}/n_{\text{liq}}) \times (V_{\text{vap}}/V_{\text{liq}}) \quad [75.5]$$

and

$$V_{\text{vap}}/n_{\text{vap}} + (V_{\text{liq}}/n_{\text{liq}}) \times (V_{\text{vap}}/V_{\text{liq}}) = V_{\text{vap}}/n_{\text{vap}} + (V_{\text{liq}} V_{\text{vap}})/(n_{\text{liq}} \cdot V_{\text{liq}}) \quad [75.6]$$

Hence

$$1/C_{\text{vap}} + V_{\text{vap}}/(C_{\text{liq}} V_{\text{liq}}) = V_{\text{vap}}/n_{\text{vap}} \times \left( (n_{\text{liq}} + n_{\text{vap}})/n_{\text{liq}} \right) \quad [75.7]$$

so leads to  $1/C_{\text{vap}} + V_{\text{vap}}/(C_{\text{liq}} V_{\text{liq}}) = 1/C_{\text{vap}} \times (n_0/n_{\text{liq}})$  and if  $n_{\text{liq}} \approx n_0, n_0/n_{\text{liq}} \approx 1$ .

In this way, the term  $V_{\text{vap}}/C_{\text{liq}} V_{\text{liq}}$  appears as an “excess” term which becomes negligible if  $n_{\text{liq}} \approx n_0$  and calculated  $C_{\text{vap}}$  from  $K$  and  $n_0$  values appears as an ideal value, whereas the “real”  $C_{\text{vap}}$  value is equal to

$C_{\text{vap}} \times (n_{\text{liq}}/n_0)$ . “Ideal” and “real”  $C_{\text{vap}}$  values are respectively called  $C_{\text{vap-ideal}}$  and  $C_{\text{vap-real}}$  in the following text, and we can write:

$$1/C_{\text{vap-real}} = (n_0/n_{\text{liq}}) \times 1/C_{\text{vap-ideal}} = (n_0/n_{\text{liq}}) \times (1/KC_0 + (1/C_0)\beta)$$

Graphs of  $1/C_{\text{vap}}$  vs.  $\beta$  are reported in Figures 75.1(a) and (b), respectively.

For both  $K_1$  and  $K_2$ , linear regression calculation  $1/C_{\text{vap-ideal}}$  vs.  $\beta$  leads to obtain an ideal regression line, which slope and intercept are equal respectively to  $1/C_0$  and  $1/C_0 \times C_{\text{liq}}/C_{\text{vap}}$ . Conversely,  $C_{\text{vap-real}}$  seems to be a regression line for the less volatile compound ( $K_1 = 0.001$ ), but there is no rigorous linear correlation between  $1/C_{\text{vap-real}}$  and  $\beta$  as appears in Figure 75.1b for the most volatile compound ( $K_2 = 0.05$ ).

The inserts displayed in Figure 75.1(a) and (b) show the variation of concentration in vapor phase according to the  $V_{\text{liq}}$  values. For the most volatile compound the values increase for the whole range of  $V_{\text{liq}}$  values, but for the less volatile compound, these values stagnate for  $V_{\text{liq}} > 0.75$  mL.

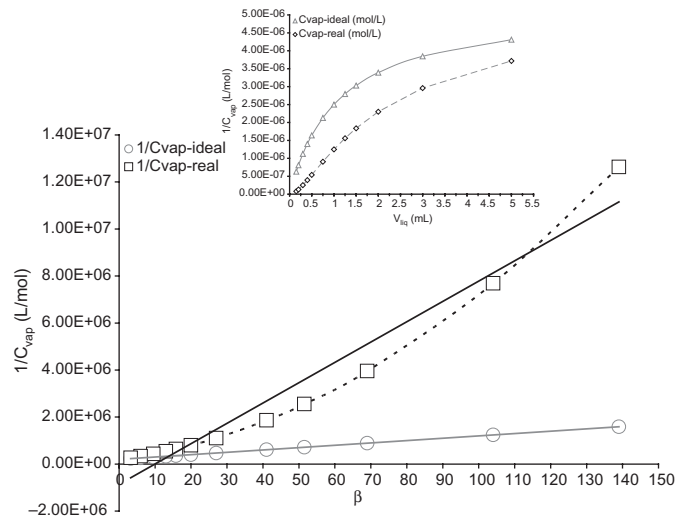
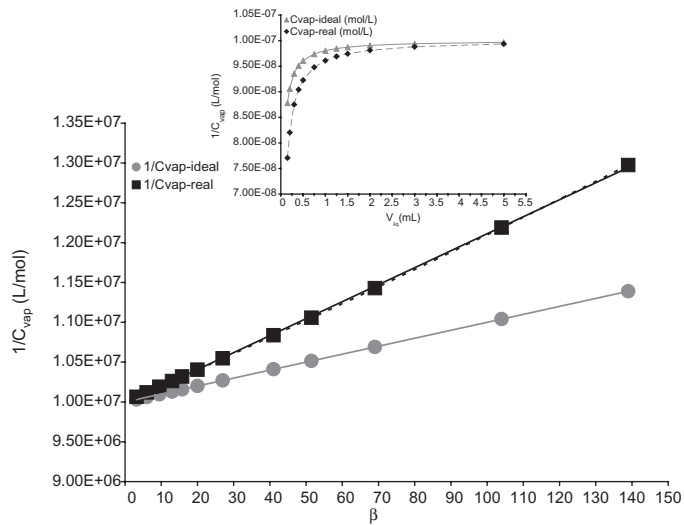
## 75.4 DISCUSSION AND CONCLUSION

The results summarized in Figure 75.1 highlight a deviation between the ideal PRV calculation, obtained using  $C_{\text{vap-ideal}}$  values, and a more realistic result obtained using  $C_{\text{vap-real}}$  that should reflect experimental conditions. This deviation remains low for the less volatile compound but significantly increases when volatility increases: the higher the volatility, the greater the deviation. Examination of the slope and intercept values obtained for  $K_2 = 0.05$  reveals a dramatic risk in providing erroneous K values.

In this way, the more reliable points are obtained for low  $\beta$  values, so that large liquid volume and a good alternative would be to choose  $\beta$  range corresponding to larger liquid volume ( $\beta \leq 20$  so that  $V_{\text{liq}} \geq 1$  mL). It is already the best choice for the volatile compounds, but there is a technical limitation for the less volatile compounds. Indeed, because of the stagnation of concentrations in the vapor phase for volumes of liquid phase higher than 2 mL (inserts in Figure 75.1(a)), the weak experimental increase of chromatographic area values may be masked by background noise.

The study of the two examples given shows the crucial importance of an adequate choice of liquid volumes and  $\beta$  range for an optimal use of PRV method and reliable determination of liquid-vapor partition coefficient values.





**Figure 75.1** Graphical representation of regression plots  $1/C_{vap}$  vs.  $\beta$  (left (a)  $K_1 = 0.001$ ; right (b)  $K_2 = 0.05$ ). Variations of  $C_{vap}$  vs. volume of liquid phase are displayed in the inserts.

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