THE GENERAL RELATIONSHIP BETWEEN POTASSIUM, SODIUM AND pH IN GRAPE JUICE AND WINE

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ABSTRACT

The general relationship between the concentrations of the cations, potassium and sodium, and acidity measures of grape juices and wines are presented. The pH is expressed as a function of the titratable acidity, the potassium and sodium contents and the tartrate to malate ratio. The graphical representation of the relationship provides a means of following the changes in the organic acid content, titratable acidity, mineral uptake and pH during the maturation of grapes. It can also be used to estimate the tartrate to malate ratio in the juice, an important consideration in the selection of a deacidification procedure for juices that are high in total and titratable acidity.

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pH is perhaps the most important measure of juice and wine acidity. It has a controlling influence on the incidence of the malo-lactic fermentation (12) and on the susceptibility to microbial contamination (10). It plays an important role in the sourness of taste, in the stability of soluble grape proteins (15), in the extent of potassium bitartrate precipitation (4) and in color stability of red table wines (24). The titratable acidity, while of some importance in sourness of taste plays no role in any kind of wine stability and is a poor indicator of organic acid content. In grape tissue (6), the titratable acidity accounts for only approximately 68% of the total acidity (as indicated by the equivalance of the organic acid anions) while in wines (5), it represents approximately 74% of the total acidity.

Early studies which considered anion and cation balances in wines (9,13,17,18,19,28) and juices (20,21) showed that the sum of the titratable protons and mineral metal cations was approximately equal to the sum of the organic and inorganic anions. The effect of mineral cations on the titratable acidity does not appear to have been noted presumably because of the overriding effects of total acidity which are usually not considered. Relationships between potassium and pH have been noted as a result of empirical correlation studies by Wejnar (30,31) in 1971 and Somers (25,26) in 1975 and 1977. Wejnar found a linear relationship between potassium concentration and free hydrogen ion concentration in 32 juices (30) and in 50 wines (31) of several cultivars grown in Germany,

$$[K^+] = A + B\,[H^+]_{\text{free}}$$

where A and B are empirical constants.

Somers (25) presented an inverse relationship between potassium concentration and the free hydrogen ion concentration of 75 Australian red table wines,

$$[K^+] = A' + \frac{B'}{[H^+]_{\text{free}}}$$

where A' and B' are empirical constants.

The apparent conflict in the form of these relationships is further complicated in that both correlations are statistically significant. However, neither is exact.

There is no corresponding relationship between sodium concentration and pH in juices or wines or any previous suggestion that potassium and sodium are transported by the same carrier.

It has recently been shown (5,6) that a more specific ion balance, considering only acid anions, titratable protons and monovalent metal cations (primarily potassium and sodium), provides a means of predicting the titratable acidity and pH in juices and wines. This result has prompted the suggestion (7) of an enzyme system in the cellular tissue of grapevines which exchanges cations such as potassium and sodium for protons derived from the organic acids. It has also enabled the development of the generalized relationship between the pH and the potassium and sodium concentrations of grape products which is the subject of this paper.

MATERIALS AND METHODS

The pH is predicted from the concentrations of the major acids and the potassium and sodium concentrations (8). In this form, contributions to the pH due to citric, phosphoric and amino acids are neglected, as are those due to the uptake of other monovalent metal cations.

The uptake of potassium and sodium has previously been shown (6) to be at the expense of protons from the organic acids and can therefore be considered to be analogous to titration of protons by a strong base. Pursuing this analogy further, the simplest representation of a titration is a plot of pH against the quantity of base added. The corresponding plot for a juice or a wine would be a plot of pH against amount of potassium and sodium present.

Plots of this kind are not of a general nature, however, because the shape of a resulting curve depends on the total acidity and the relative amounts of the major organic acids (malic and tartaric in the case of juices, together with lactic, succinic, acetic and sulfurous in wines). In order to develop general relationships of this kind, it is necessary to scale the potassium and sodium concentrations by the total acidity making a dimensionless variable which is described here as the "fractional exchange" or the "extent of exchange." It has been shown (5,6) that the total acidity is numerically equal to the sum of the titratable protons, the potassium and sodium concentrations:

$$\text{Total acidity} = [H^+]_T + [K^+] + [Na^+] \qquad \text{(I)}$$

where $[H^+]_T$ represents the titratable protons, and $[K^+]$, $[Na^+]$, the concentrations of potassium and sodium, all expressed in molar quantities. The extent of exchange can then be expressed as:

$$\text{Extent of exchange} = \frac{[K^+] + [Na^+]}{[H^+]_T + [K^+] + [Na^+]} \qquad \text{(II)}$$

The other major factors which affect the pH are the relative proportions and strengths of the acids present in the juice or wine.

The general pH/extent of exchange plots were prepared by using an algorithm (8) which solves the hydrolysis equations for the acids present by successive approximations. The calculations were performed on a Tektronix 4051 computer.

RESULTS

The data from 95 published juice analyses (11,14,22,30) are shown in the form of pH as a function of potassium concentration in Fig. 1. The corresponding plot for 125 published wine analyses (2,3,5,9,13,16,18,19,22,23,28,29,31) is given in Fig. 2 together with the correlations proposed by Wejnar (31) and Somers (26).

The pH is presented as a function of the extent of exchange for 109 juices (11,21,22,30) in Fig. 3, together with the predicted pH curves for various tartrate to malate ratios. The corresponding plot of 67 wine analyses (5,9,13,16,18,19,22,23,28,29) is shown in Fig. 4. Table 1 presents the computed values of the generalized pH relationship for juices, tabulated for convenience.

DISCUSSION

The data for the potassium concentration and pH in juices (Fig. 1) show considerable scatter and a general trend which indicates that when plotted in this manner, pH is practically independent of the potassium concentration.

The data for the potassium concentration and pH in

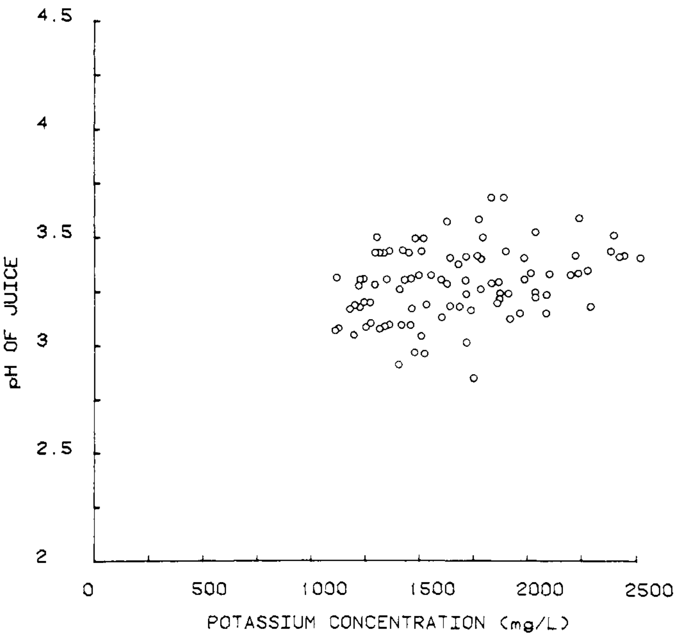

Fig. 1. Effect of potassium concentration on the pH of grape juices.

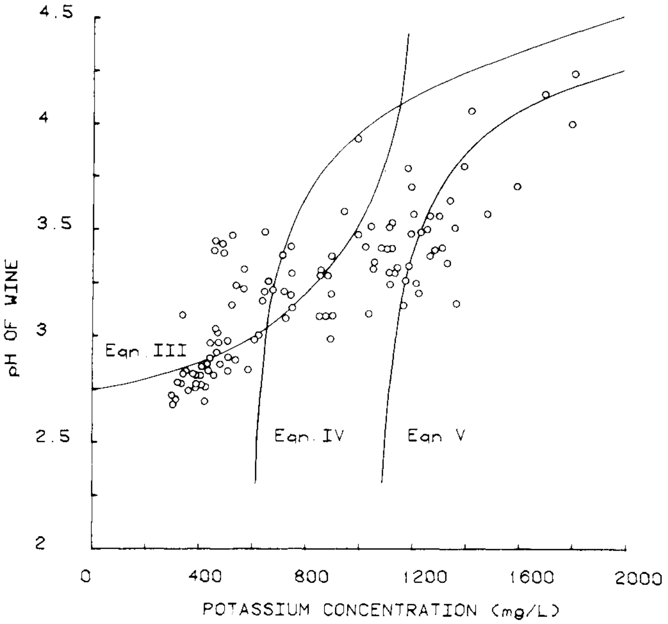

Fig. 2. Effect of potassium concentration on the pH of wines.

Table 1. Computed pH values for grape juices.

Extent of exchange[a]	pH ∞^b	$3/1^b$	$2/1^b$	$1/1^b$	$1/2^b$	$1/3^b$	0^b
0.10	2.54	2.60	2.63	2.68	2.73	2.76	2.86
0.20	2.85	2.93	2.96	3.02	3.09	3.12	3.23
0.30	3.13	3.22	3.25	3.32	3.39	3.43	3.54
0.40	3.39	3.50	3.54	3.61	3.69	3.73	3.86
0.50	3.66	3.78	3.82	3.90	4.01	4.05	4.23

[a] Defined in Equation I.

[b] Tartrate/malate ratio on molar basis.

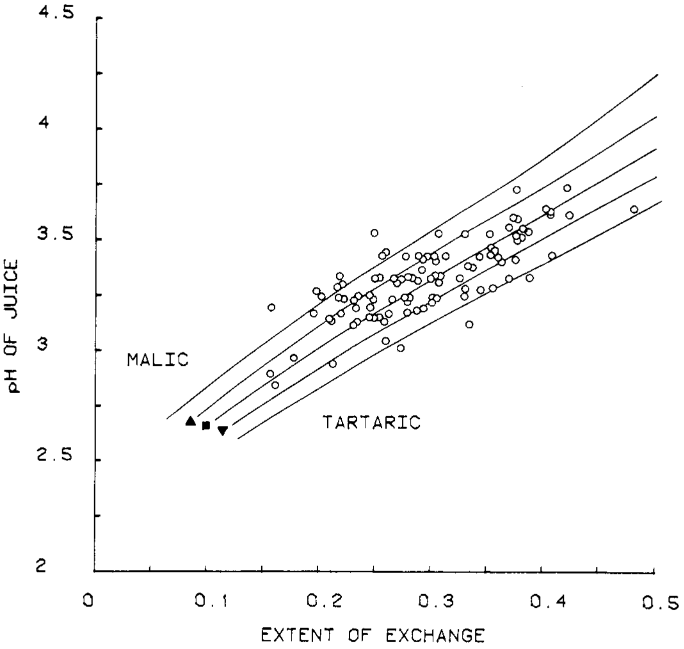

Fig. 3. Effect of extent of exchange on the pH of grape juices for various acid proportions. The molar ratios of tartrate to malate are 2:1 (▼), 1:1 (■), and 1:2 (▲).

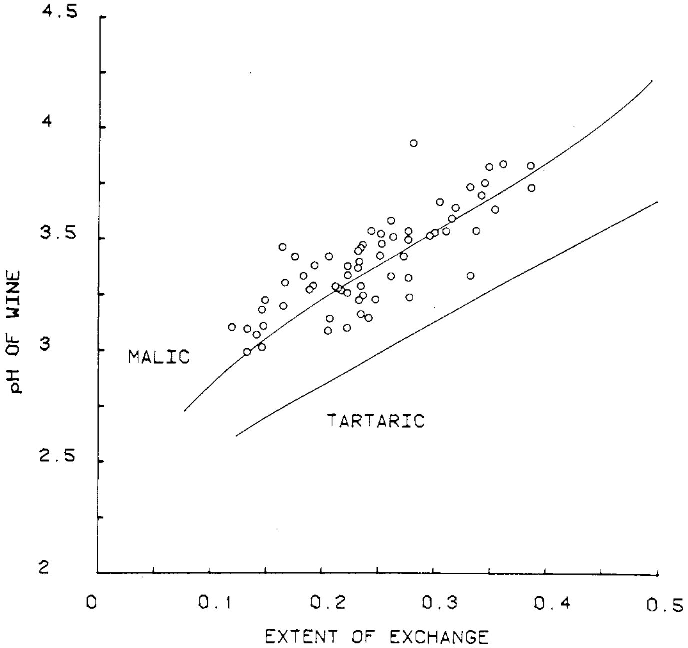

Fig. 4. Effect of extent of exchange on the pH of wines.

wines (Fig. 2) show a similar scatter of points, with the wine pH being more sensitive to the potassium concentration than that of the juice. Also shown on Fig. 2 are the empirical correlations presented by Wejnar (31) and Somers (26). Interpretation of Wejnar's linear correlation of free hydrogen ions with potassium concentration (31) leads to the following approximate relationship:

$$[K^+]_{mg/L} = 1200 + 6 \times 10^5 \, [H^+]_{free} \qquad \text{(III)}$$

where $[H^+]$ is expressed in moles per liter. This function suggests that a pH of 2.75 results when no potassium is present, and that the potassium concentration cannot exceed 1200 mg/L at higher pH values, as shown in Fig. 2. Clearly, both of these limits and the general form of the relationship do not describe the observed pattern. The other two curves shown in Fig. 2 represent the general correlation for table wines and the particular correlation for blended red table wines reported by Somers (26). In these cases, the approximate relationships are:

$$[K^+]_{mg/L} = 600 + \frac{4 \times 10^{-2}}{[H^+]_{free}} \qquad \text{(General for table wines)} \quad \text{(IV)}$$

and

$$[K^+]_{mg/L} = 1100 + \frac{4 \times 10^{-2}}{[H^+]_{free}} \qquad \text{(Blended red table wines)} \quad \text{(V)}$$

At low pH conditions, potassium concentrations of below 600 mg/L (1100 mg/L for the blended red wines) should not occur, while at high pH values the quantity of potassium required to get a further increase in pH, rises rapidly. Neither of these empirical relationships shows a pattern which adequately describes the range of conditions found in wines. They have both been derived from limited ranges of conditions and show unrealistic trends when extrapolated. The main objections to this approach are that only one variable is considered, when in fact several are involved, and that dependent and independent variables have been confused. The pH is dependent on the potassium concentration (and several other factors). It does not determine the potassium concentration of wine as is implied by these correlations.

A widespread misconception is that a high potassium concentration (> 1500 mg/L) generally leads to a high pH (> 3.50). The data (Fig. 1) show several juices with potassium concentrations at this level, but with pH values less than 3.25, with some in the range 2.80 to 3.00. This is because the juice pH also depends on the total acidity, and the relative proportions of the major organic acids.

The general plots of pH as a function of the extent of exchange (Figs. 3, 4) provide a more realistic means of relating the potassium and sodium levels to pH. The observed pH is primarily a reflection of the extent to which protons from the total acidity have been exchanged for potassium and sodium ions. Fig. 3 also shows predicted pH curves for various ratios of tartaric to malic acid in juices. The vertical displacement between these curves shows the range in pH that can result from different ratios of tartaric to malic acids at the same extent of exchange. The horizontal displacement shows the ranges in the extent of exchange and tartaric to malic acid ratio that can lead to the same pH. The reported values generally lie within the limits of the curves of tartaric and malic acid. Less than 10% of the points lie outside this range, and all of these are based on pH values reported to only one decimal place (11) or potassium and sodium contents estimated from the alkalinity of ash values (18,19). Fig. 4 shows the predicted pH curves for tartaric acid and malic acid and the corresponding data for wines. In general, the extent of exchange is less than that of the juice due to the precipitation of potassium bitartrate and the pH is higher due to the formation of the weaker acids such as lactic and succinic acids during the primary and secondary fermentations.

The pH/extent of exchange diagrams are general in nature because they take into account the principal factors involved in the pH equilibrium. They are independent of the level of total acidity and are not limited to certain potassium or pH ranges. Only one diagram is required to represent all juices. A large number of wine diagrams could be developed, covering the whole range of the relative proportions of the five major acids, but this is not considered necessary.

Application to grape maturity: The general relationship for juices (Fig. 3) can provide important insights concerning acidity changes during ripening. If acid synthesis occurs, the total acidity will increase leading to a higher titratable acidity (Eqn. I). If acid degradation by gluconeogenesis or malic respiration occurs, the total acidity will decrease leading to a lower titratable acidity. The uptake of potassium and sodium at constant total acidity can only lead to a rise in pH. This is because the denominator of the extent of exchange term remains constant, while the numerator increases (Eqn. II). Since the ratio of tartaric to malic acids does not change under these conditions, the pH will rise as the extent of exchange increases. Acid degradation leads to a reduction in total acidity (the denominator of the extent of exchange) and an increase in the extent of exchange. The pH can either remain constant (as the tartaric to malic ratio increases by malic respiration) or it can rise (if there is mineral uptake at the same time). A fall in pH can only occur when acid synthesis is not accompanied by a similar relative increase in mineral uptake. This is because the total acidity would increase more rapidly than the mineral concentrations leading to a reduction in the extent of exchange. Examples of this short-lived phenomenon can often be observed following a post véraison rainfall (17) or irrigation.

Although the measurements of pH, titratable acidity, potassium and sodium are all that are required to use the diagram, estimates of the tartaric to malic acid ratio and even tartaric and malic contents can be made. The ratio can be estimated from the curves shown in Fig. 3, and this together with the total acidity (Eqn. I) can be used to estimate the individual acid concentrations. It is important to note that both the ratio and the concentrations have been expressed on a molar basis.

Application to juices and wines: The estimation of the ratio of tartaric to malic acid is of particular importance in selecting the method of deacidification for musts with high total acidity. The fraction of the total which is malic acid will also influence the pH and titratable acidity changes during the malo-lactic fermentation and should be known before fermentation occurs.

The addition of water to grape juice (or wine) can be shown to have a predictable effect on pH and titratable acidity. The total acidity is reduced in an inverse proportion to the increase in total volume. As a result, the titratable acidity is reduced in the same manner. The extent of exchange and therefore pH, however, remain constant. This is because the potassium and sodium contents are diluted to the same degree as the total acidity and the relative proportions of the major acids are unaltered. With wines, a slight fall in pH can occur due to the effects of ethanol concentration on the ionization of the acids (27).

The changes in pH and titratable acidity during fermentation and stabilization are not well explained in the wine literature (1). By yeast fermentation alone, that is excluding tartrate precipitation during fermentation, the pH can only rise because of the formation of weaker acids (succinic and lactic) at the expense of the stronger, malic acid. The formation of succinic acid, a weaker diprotic acid, would cause a slight rise in pH without causing any change in titratable acidity. Further, the formation of lactic, either during the alcoholic fermentation or the malo-lactic fermentation leads to a lowering of both the total acidity and the titratable acidity. The extent of exchange will therefore rise in this case (Fig. 4). A fall in titratable acidity and a rise in extent of exchange can also occur during skin contact, particularly during red wine fermentations. The precipitation of potassium bitartrate either during fermentation or stabilization will cause the pH to fall and will reduce both the total acidity and titratable acidity. At a typical extent of exchange of 30%, 30/(70 + 30), 30 milliequivalents will be due to potassium and sodium and 70 will be due to titratable acidity. The precipitation of 10 milliequivalents of potassium will ideally remove the same number of titratable protons in the form of bitartrate ions. The extent of exchange will then be 20/(60 + 20) or 25%. This fall in extent of exchange will result in a fall in pH, the magnitude being dependent on the fraction of the total acidity that is due to tartaric acid. Amerine (1) reports one study which concluded that if the pH is below 3.5, it will fall, while if above 3.5, it will rise during bitartrate precipitation. Somers (25) suggested that the higher potassium content in Australian red table wines could lead to more loss of tartaric acid as bitartrate during fermentation and stabilization causing higher pH values to result. Based on equilibrium considerations, the pH will at least remain constant, but generally fall due to potassium bitartrate precipitation.

The changes in pH during actual fermentations will be the combination of weak acid formation and bitartrate precipitation. The pH can either rise or fall, while titratable acidity will always fall. The only situation in which titratable acidity can rise is the formation of acetic or other acids from neutral substrates by spoilage organisms.

CONCLUSION

The general relationships between potassium, sodium and pH have been developed for juices and wines. These relationships, in the form of pH/extent of exchange diagrams, have been tested with reported juice and wine data from numerous cultivars, vineyard areas and vintages. The pH/extent of exchange diagrams have been used to explain the changes in the titratable acidity and pH associated with grape maturation and wine fermentation and stabilization.

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