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A thermometric enthalpy titration (TET) study of some Australian wines

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Abstract

The "titratable acid" and "total phenolics" content of selected Australian wines have been determined by thermometric enthalpy titration (TET) via thermometric titration with hydroxide ion. The "titratable acid" and "total phenolics" content have also been determined by the routine potentiometric and spectrophotometric methods and the sensitivity of the TET procedure has been assessed in comparison with that of the routine procedures. A separate TET study of tartaric and gallic acids has provided further insight into the complex interactions prevalent in the wine matrix.

INTRODUCTION

Wine is a complex mixture of compounds, consisting of at least two major categories: organic acids such as tartaric and gallic acids, and phenolics such as anthocyanins, hydroxycinnamates and flavonoids [1]. The acidic components of wine are known to affect both the taste of the wine and its resistance to spoilage. In some wines, additional acids such as sorbic acid and ascorbic acid are added as preservatives or anti-oxidants. The phenolic components also contribute to the colour, odour and taste of wines and provide an oxygen-reducing reservoir. Thus the acids and phenolics in wine collectively play a major role in the development of wine "character". In terms of quantifying such character, it is necessary to determine the "titratable acid" and the "total phenolics" content. Existing recommended procedures involve the measurement of these contents separately via potentiometry and UV–visible spectrophotometry respectively [1–3]. It is well known that when wine samples are titrated potentiometrically with a strong base, such as sodium hydroxide, one

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major end-point is observed which can be used to determine the titratable acid content of the wine.

However, because the typical organic acids in wine have pK values that are well separated from those of typical wine phenolics, thermometric titrimetry is able to differentiate between these two classes of "weak acids": hence in a thermometric titration of a wine sample with a strong base, such as hydroxide, two discernible end-points are obtained; the first corresponds to titratable acid and the second to the total phenolics contents, respectively [4]. Thus the significant advantage of the thermometric titration procedure over the conventional titration procedure is that with the former, titratable acid and total phenolic contents are determined in a single operation, which is a distinct advantage for the routine determination of these major components in wine. However, the thermometric titration procedure has not been highly developed for wine analysis, thereby suggesting a basis for the present investigation. A bonus from such an investigation is that with the thermometric titration procedure, multiple end-points are detected within the titratable acid region which correspond to the individual component acids in wine. However, at this stage, due primarily to a lack of available pK_a data for the minor acidic components in wine, these additional end-points cannot be correlated with individual acids.

The present project involves determination of the titratable acid and total phenolics contents by the conventional recommended procedures and by thermometric titrimetry, and demonstrates that with the latter technique, unambiguous identification of the titratable acid and total phenolics end-points in the thermometric titrations of the wine samples is possible by "spiking" with tartaric acid and phenol, respectively. A separate thermometric titrimetry study of typical acids in wine, such as tartaric and gallic acids, indicates that individual end-points corresponding to stepwise proton losses from these acids are identified. Optimisation of the thermometric titrimetry system for the determination of titratable acid and total phenolics content of wine is investigated.

EXPERIMENTAL

TET system and accessories

The TET system used and the associated data analysis procedures have been described in detail by bin Ahmad et al. [5, 6]. A Tronac (Model 450) thermometric enthalpy titration system (Tronac Inc., Orem, Utah, USA) was used throughout, comprising a 100 cm^3 capacity vacuum dewar reaction-vessel, a 6 cm^3 capacity glass delivery burette (delivery rate, 1.035 $cm^3\ min^{-1}$) and an all-glass stirrer. The reaction vessel temperature sensor is a 100 kW thermistor and the overall sensitivity with respect to

energy measurement is 2600 mV K^{-1}. Isoperibol operation conditions were achieved by suspending the reaction vessel and burette delivery system in a water bath, maintained at 298.00 ± 0.01 K.

Analytical procedure

The reaction heat Q_R and molar reaction enthalpy $\Delta_R H_m^{\ominus}$ (kJ mol^{-1}) were calculated on the basis of the determined temperature variation ΔT (mV) for the relevant quantitative calorimetric reaction and the associated average heat capacity $\bar{C}_p$ (kJ mV^{-1}), determined from the measured heat capacities of the calorimeter and contents before (C_{pB}) and after (C_{pA}) the thermometric titration

$$Q_R = -\bar{C}_p \Delta T = n_p \Delta_R H_m^{\ominus}$$

where n_p is the number of moles of product formed.

Stoichiometry factors were determined on the basis of the ratio of the moles of titrant consumed at a specified end-point to the moles of titrate in the reaction vessel. The thermochemical data derived refer to 298 K and the relevant uncertainty is quoted as the standard deviation from the mean.

Calibration

Two test reactions were employed: NaOH/HCl and THAM/HCl. The derived $\Delta_R H_m^{\ominus}$ values for these reactions were −55.26 ± 1.99 kJ mol^{-1} (−55.75 kJ mol^{-1} [7]) and −47.28 ± 0.67 kJ mol^{-1} (−47.36 mol^{-1} [8]), respectively.

Wine samples

The commercially available wine samples used were Cabernet Sauvignon, Pinot Noir and Dry White.

Potentiometric titrations

The titratable acid content of these wines was determined potentiometrically using a PHM83 pH meter (Radiometer, Copenhagen) which was standardised using Radiometer pH 4 and 7 standard buffer solutions. A wine sample (10 cm^3) was diluted with 'neutralised water' (phenolphthalein end-point) (20 cm^3) and the solution was stirred vigorously throughout the titration with 0.1 M NaOH to the titratable end-point at approximately pH 8.4 [1]. The titratable acid end-point was derived from the pH/volume "first derivative" profile.

Thermometric titrations

The titratable acid and total phenolics contents of these wines were determined by thermometric titrimetry. A wine sample (5 cm^3) contained in the reaction vessel was diluted to 90 cm^3 with deionised distilled water and thermometrically titrated with 1.0 M NaOH standard solution.

Spiking procedures

Wine samples (5 cm^3) were spiked with either phenol (BDH, AR grade) or tartaric acid (BHD, AR grade) in amounts equivalent to 10% of the measured contents of these components in the corresponding "undisturbed" wines. Thermometric titrations, using 1.0 M standard NaOH solution as titrant, were conducted and the percent recovery calculated.

Reference study of tartaric and gallic acids

Potentiometric and thermometric titrations were performed using 0.1 M and 1.0 M NaOH, respectively, as titrant and either tartaric acid or gallic acid as titrate.

Tartaric acid (BDH, AR grade) (1.53858 g) was dissolved in deionised distilled water and the solution was made up to 100 cm^3 (0.1025 M). Gallic acid (BDH, AR grade) (0.96686 g) was dissolved in 50:50 v/v deionised distilled water/absolute alcohol and the resulting solution was made up to 250 cm^3 (0.0228 M). The acid solutions (5 × 10 cm^3 aliquots) were thermometrically titrated with 1.0 M standard NaOH solution. For comparison, the acid solutions were also potentiometrically titrated as described above for the wine samples.

Spectroscopic evaluation of total phenolics content

The spectroscopic method for the determination of total phenolics in wine described by Somers and Ziemelis [2] was used. A Shimadzu 240 UV–visible recording spectrophotometer was employed using 1 cm path-width quartz cells and deionised distilled water as solvent reference. The absorbance of red wine samples (10–20-fold dilution) and white wine samples (4-fold dilution) was determined at 280 and 320 nm. Correction factors of (−4) and (−1.4) were applied at 280 nm and 320 nm, respectively.

RESULTS AND DISCUSSION

Table 1 gives the results for the titratable acidity determined by both potentiometric titration and thermometric titration for three wine samples

TABLE 1

Titratable acid and total phenolics content of selected wines

Wine type		Titratable acid (mol l^{-1})	Tartaric acid equiv. (g l^{-1})	Total phenolics (mol l^{-1})
Cabernet Sauvignon	T/T [a]	0.109 ± 0.001	8.18 ± 0.01	0.153 ± 0.001
	P/T [b]	0.100 ± 0.050	7.85 ± 0.05	
Pinot Noir	T/T [a]	0.097 ± 0.001	7.26 ± 0.01	0.072 ± 0.001
	P/T [b]	0.090 ± 0.050	6.64 ± 0.05	
Dry white	T/T [a]	0.078 ± 0.003	5.85 ± 0.01	0.048 ± 0.001
	P/T [b]	0.070 ± 0.050	5.44 ± 0.05	

[a] T/T, thermometric titration. [b] P/T, potentiometric titration.

in terms of the molar concentration, based on the moles of hydroxide consumed at the end-point, and the tartaric acid equivalent (units of g l^{-1}). The latter is the common procedure for expressing the titratable acidity of wine [1]. Typical thermograms are shown in Fig. 1. The overall results obtained for titratable acid content by thermometric titrimetry are slightly greater than those obtained by potentiometric titration. This is in part a consequence of selecting the end-point in the potentiometric titration by the derivative method (generally around pH 7.6–7.8), rather than titrating to the normally accepted pH value of 8.3 [1]. Thus, the thermometric procedure is more able to detect the weaker acid components of the wine and does not require titration to a set pH value.

From the thermometric titration curves in Fig. 1, it is apparent that a

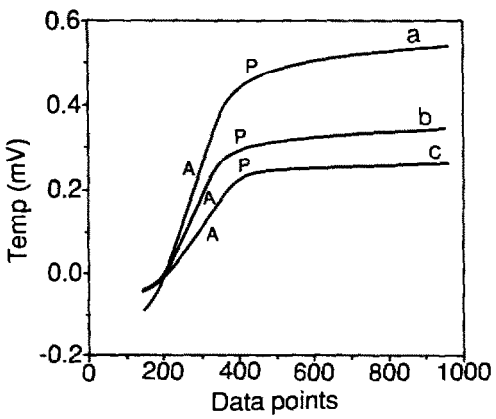

Fig. 1. Thermometric titration of dry white (curve a), Cabernet Sauvignon (curve b), and Pinot Noir (curve c) with sodium hydroxide. A: titratable acid end-point; P: total phenolics end-point.

TABLE 2

Tartaric acid spiking studies

Wine identification		Tartaric acid added (moles × 10^4)	Tartaric acid recovered (moles × 10^4)	Recovery ratio	Mean
Cabernet Sauvignon	P/T [a]	2.050	1.950	0.95	0.96
		2.050	1.985	0.97	
	T/T [b]	1.333	1.398	0.95	1.10
		1.333	1.654	1.20	
Pinot Noir	P/T [a]	2.050	1.954	0.97	0.97
		2.050	1.980	0.97	
	T/T [b]	0.868	0.638	0.74	0.81
		0.868	0.765	0.88	
Dry white	P/T [a]	2.050	1.990	0.97	0.98
		2.050	2.010	0.98	
	T/T [b]	0.868	0.895	1.00	1.05
		0.868	0.855	1.10	

[a] Potentiometric titration. [b] Thermometric titration.

second end-point exists. This can be taken as a measure of the phenolic content of the sample and the calculated values are listed in Table 1.

Spiking experiments, in the context of wine analysis by thermometric titrimetry, are most useful for the identification of the titratable acid and total phenolics end-points, via the shifts obtained with such end-points. The present spiking studies involve the addition of tartaric and gallic acids and phenol to selected wines. The results obtained for spiking wines with tartaric acid and phenol are shown in Tables 2 and 3. Figure 2 shows the effect of spiking on the thermometric end-points. Recoveries for tartaric acid are close to unity, indicating that the thermometric titration

TABLE 3

Phenol spiking studies

Wine identification		Phenol added (moles × 10^5)	Phenol recovered (moles × 10^5)	Recovery ratio	Mean
Cabernet Sauvignon	T/T [a]	3.966	6.000	1.50	1.50
		3.966	6.010	1.50	
Pinot Noir	T/T [a]	5.988	8.800	1.50	1.50
		7.485	11.340	1.50	
Dry white	T/T [a]	7.485	7.700	1.00	0.93
		7.485	6.428	0.86	

[a] Thermometric titration.

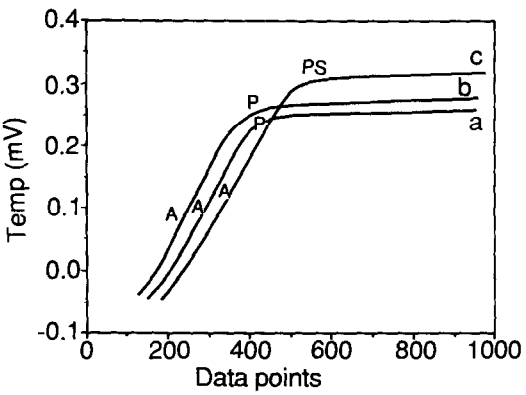

Fig. 2. The effect of spiking wine (curve a) with tartaric acid (curve b) and phenol (curve c) on the shape of the thermometric titration curve. A: titratable acid end-point; P: total phenolics end-point; PS: total phenolics end-point after spiking with phenol.

procedure is capable of identifying accurately the titratable acid content of the wine samples. Recovery with phenol was close to unity for the white wine, but considerably greater than unity for the red wines. The noted experimental effect in the thermometric titrations of phenol-spiked red wines is that the second major end-point, which corresponds to the total phenolics end-point, is greatly increased by the spiking procedure and this is possibly a consequence of phenol not being a natural phenolic constituent of wines [1].

An index of the total phenolics content of both red and white wines used by the wine industry is based on the corrected absorbance at 280 nm: $A_{280} - 4$ is one accepted relationship [2]. Though this spectrophotometric procedure is somewhat empirical, it gives some estimate of the total phenolic composition of the wine and was used as a reference method in this study. Because this procedure gives the phenolic content in absorbance units, rather than mol l^{-1} as in the thermometric method, the ratios of the red to white wine values were used for comparison. Table 4 shows that the ratios for the total phenolic values as estimated from the absorbance values are considerably higher than those obtained by the thermometric measurements. However, this simple absorbance method ignores the flavonoid content of the white wine [3], and if an additional

TABLE 4

Comparison of total phenolics

Ratio	$E_{280} - 4$	Thermometric titration
Cabernet Sauvignon/dry white	4.2	3.2
Pinot Noir/dry white	2.1	1.5

correction is allowed for this class of phenolic, the ratios obtained from the spectrophotometric data are much closer to those obtained by thermometric titrimetry. Thus, the estimation of the phenolic content of wine by thermometric titrimetry is a reasonable alternative procedure to the spectrophotometric method.

A separate thermometric titrimetry study of tartaric acid and gallic acid in aqueous solution was undertaken using these acids as titrate and 1 M NaOH as titrant. Tartaric acid has been previously studied by thermometric titrimetry [10, 11], and in a titration with sodium hydroxide, two end-points were obtained and the enthalpy values corresponding to the loss of the first and second protons are $\Delta H_{R1} = -53.93$ and $\Delta H_{R2} = -55.93$ kJ mol^{-1} respectively. Because the pK_a values for tartaric acid are well separated (p$K_1 = 4.16$, p$K_2 = 2.52$ [11]), well-defined end-points should be obtained for the loss of the individual protons respectively. The results obtained for the potentiometric titration of tartaric acid with OH^- and the corresponding thermometric titration results are given in Table 5. The potentiometric titration data are consistent with tartaric acid behaving as a dibasic acid whereas the thermometric titrimetry data reveal stepwise proton loss and the corresponding mean enthalpy data are $\Delta H_1 =$

TABLE 5

Tartaric acid/sodium hydroxide system: comparison of potentiometric and thermometric titrations

(a) Potentiometric titration

End-point	Tartaric acid (moles × 10^3)	OH^- consumed at end-point (moles × 10^3)	Mole ratio at end-point n(hydroxide)/ n(tartaric acid)
1	1.025	2.040	1.99
1	1.025	2.035	1.99
1	1.025	2.040	1.99

(b) Thermometric titration

End-point	Tartaric acid (moles × 10^3)	ΔT_R (mV)	$\bar{C}_p$ (J mV^{-1})	$-Q_R$ (J)	$-\Delta H_R$ [a] (kJ mol^{-1})	Mole ratio at end-point n(hydroxide)/ n(tartaric acid)
1	0.5125	0.1828	148.1	27.074	52.82	0.98
2		0.1932		28.611	55.82	0.95
1	0.5125	0.1860	148.1	27.547	53.75	1.05
2		0.1940		28.731	56.06	0.97

[a] Mean $-\Delta H_{R1} = 53.29 \pm 0.66$ kJ mol^{-1}; mean $-\Delta H_{R2} = 55.94 \pm 0.17$ kJ mol^{-1}.

-53.29 ± 0.66 kJ mol^{-1} and $\Delta H_2 = -55.94 \pm 0.17$ kJ mol^{-1} which are in excellent agreement with previous such data [11]. It should be noted that the end-point corresponding to the first proton loss is not well-defined and mathematical regression techniques are required to identify the relevant slope change. It is interesting to note the coincidental approximate equivalence of ΔH_{R1} and ΔH_{R2} for tartaric acid.

Gallic acid is also a major acidic component of wine. In principle, gallic acid has four acidic protons and generally behaves as a tribasic acid, the corresponding ionisation constants are $pK_1 = 4.27$, $pK_2 = 8.69$ and $pK_3 = 11.45$ [12]. Because these pK values are well-separated, three end-points should be obtained in a thermometric titration of gallic acid with OH^-.

TABLE 6

Gallic acid/sodium hydroxide system: comparison of potentiometric and thermometric titrations

(a) Potentiometric titration

End-point	gallic acid (moles × 10^4)	OH^- consumed at end-point (moles × 10^4)	Mole ratio (at end-point) n(gallic acid)/ n(hydroxide)
1	2.28	2.32	1.02
1	2.28	2.35	1.03
1	2.28	2.30	1.01

(b) Thermometric titration

End-point	Gallic acid (moles × 10^4)	ΔT_R (mV)	$\bar{C}_p$ (J mV^{-1})	$-Q_R$ (J)	$-\Delta H_R$[a] (kJ mol^{-1})	Mole ratio at end-point n(gallic acid)/ n(hydroxide)
1	2.278	0.0495	149.4	7.395	32.46	0.99
2		0.0585		8.740	38.37	0.94
3		0.0610		9.015	40.17	1.05
1	2.278	0.0486	150.5	7.314	32.12	0.95
2		0.0574		8.635	37.91	0.98
3		0.0600		9.030	39.64	1.10
1	2.278	0.0505	149.3	7.533	33.07	0.97
2		0.0595		8.890	39.03	0.99
3		0.0605		9.033	39.65	1.15
1	2.278	0.0495	148.7	7.367	32.34	0.96
2		0.0585		8.693	38.16	0.95
3		0.0595		8.850	38.85	0.97

[a] Mean $-\Delta H_{R1} = 32.50 \pm 0.41$ kJ mol^{-1}; mean mole ratio $= 0.97 \pm 0.002$. Mean $-\Delta H_{R2} = 38.37 \pm 0.48$ kJ mol^{-1}; mean mole ratio $= 0.97 \pm 0.002$. Mean $-\Delta H_{R3} = 39.02 \pm 0.30$ kJ mol^{-1}; mean mole ratio $= 1.07 \pm 0.08$.

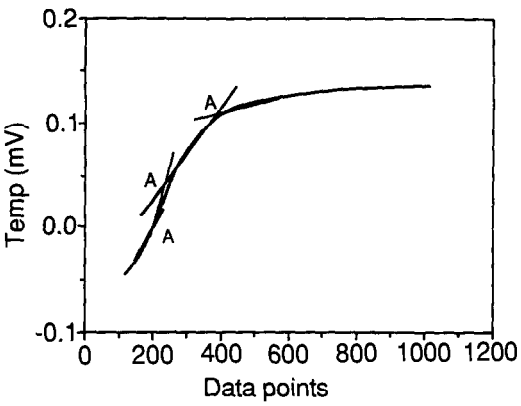

Fig. 3. Thermometric titration of gallic acid with sodium hydroxide. A: extrapolated end-points.

The results for the potentiometric titration of gallic acid with OH^- and the corresponding thermometric titration results are given in Table 6. The potentiometric titration data are consistent with gallic acid behaving as a monobasic acid–the phenolic protons cannot be determined by this technique. However, with the assistance of mathematical regression techniques, the thermometric titrimetry data reveal the stepwise loss of 3 protons with corresponding enthalpy values of $\Delta H_{R1} = -32.50 \pm 0.41$, $\Delta H_{R2} = -38.37 \pm 0.48$ and $\Delta H_{R3} = -39.02 \pm 0.30$ kJ mol^{-1}, respectively. Such enthalpy data for gallic acid have not been previously reported. A typical reaction period for a thermometric titration of gallic acid with OH^-, showing three poorly defined end-points, is given in Fig. 3.

SUMMARY

It appears that the thermometric enthalpy titration (TET) technique is, potentially, a valuable analytical technique for the sequential determination of the titratable acid and total phenolics content of wines. In addition, by refinement of the interpretation of the thermochemical data obtained, the stoichiometry of many of the acidic and phenolic components can be derived, thereby effecting further rationalisation of the wine matrix structure.

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