Amelioration of Smoke Derived Taint in Wine by Membrane Filtration and Solid Phase Adsorption.



FINAL REPORT to

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1 Abstract:

The capacity of a combined reverse osmosis and solid phase adsorption treatment process to ameliorate smoke taint in wine following vineyard exposure to smoke was evaluated. The chemical composition and sensory attributes of wine were compared before and after the treatment process. The concentration of the smoke derived volatile phenols, guaiacol and 4-methylguaiacol, decreased with treatment; without any significant affect on other wine quality parameters, such as pH, titratable acidity, residual sugar content, alcohol content, wine colour and phenolic levels. Sensory analysis determined a perceptible difference between treated and untreated wines; with treated wine rated more favourably in acceptability trials.

2 Executive Summary:

Taint in grapes and wine as a consequence of vineyard exposure to smoke has resulted in a decline in product quality and financial losses for Australian grape and wine producers. Given the close proximity of many wine regions to bushland and forest area, vineyards are highly susceptible to smoke exposure. Since exposure cannot readily be predicted or prevented, amelioration techniques which remove smoke taint from wine would therefore be of great benefit to industry.

The current study evaluated the capacity of a combined membrane filtration and solid phase adsorption treatment process to improve the quality of smoke tainted wines, by reducing the concentration of volatile smoke components which contribute to the taint, in particular guaiacol and 4-methylguaiacol. The treatment process was able to reduce the volatile phenol concentrations of two commercial wines reportedly affected by smoke: a Sauvignon Blanc and a Pinot Noir. In the case of the Pinot Noir wine, sensory analysis also demonstrated an improvement in the acceptability of the wine's organoleptic properties. The treatment process had a negligible impact on other compositional attributes such as pH, titratable acidity, sugar concentration, alcohol content or wine colour; while reductions in wine total phenolics were attributed to the removal of low molecular weight phenolic compounds. The treatment process was therefore considered to represent a potential amelioration technique by which the intensity of smoke taint in wine can be reduced.

This research was undertaken as a collaboration involving Curtin University of Technology, the University of Adelaide and the Australian Wine Research Institute, with financial support from the Grape and Wine Research and Development Corporation and in-kind support from Memstar Pty. Ltd.

3 Background:

In recent years, significant forest fires have occurred in Asia, Africa, Europe, North America, South America and Australia, and the incidence of such fires is expected to escalate as a result of climate-induced weather changes, particularly increased temperature, drought, wind and natural ignition sources.[1] In some cases, fires have occurred in close proximity to wine regions resulting in vineyard smoke exposure and smoke tainted grapes and wine.[2] The taint, characterised by objectionable 'smoky', 'dirty', 'earthy' and 'burnt' aromas[2] and a lingering retro-nasal 'ash' character on the palate,[3] has caused significant financial loss for grape and wine producers and is therefore an issue of increasing concern.

In smoked food products, meat, fish and cheese for example, 'smoke aroma' has primarily been attributed to the presence of phenol derivatives[4,5] in particular guaiacol (2-methoxyphenol) and 4-methylguaiacol, which derive from the thermal degradation of lignin during the pyrolysis (combustion) of wood. Guaiacol and 4-methylguaiacol are routinely identified in wines matured in oak barrels, at concentrations between 10 and 100 μg/L for guaiacol and between 1 and 20 μg/L for 4-methylguaiacol.[6] Guaiacol and 4-methylguaiacol were quantified at unusually high levels (approximately 1000 μg/L and 300 μg/L respectively) in wines made from grape bunches experimentally exposed to smoke.[2] Since these compounds were not detected in corresponding wines made from unsmoked grape bunches, their origin was attributed to the application of smoke. At these concentrations, which far exceed published aroma detection threshold concentrations,[7,8] both guaiacol and 4-methylguaiacol would undoubtedly contribute to the intense smoke character evident in wines made from smoked grapes. Sensory studies indicated a perceivable difference between wines made from smoked and unsmoked grapes, which persisted even when the wines were diluted (blended) up to 95%.[2] At this dilution factor, both guaiacol and 4-methylguaiacol concentrations are sub-threshold, suggesting that while these compounds contribute to smoke taint, they are not solely responsible. However, since they can be readily quantified by gas chromatography-mass spectrometry (GC-MS), they represent useful marker compounds; with levels of guaiacol and 4-methylguaiacol being indicative of levels of smoke taint.

Where wine regions are located near areas of bushland and forest, vineyards may be susceptible to smoke exposure. Since vineyard smoke exposure cannot readily be predicted or prevented, methods which enable the removal or reduction of smoke taint

from wine would therefore be of great benefit to industry. Membrane filtration (also known as reverse osmosis) has previously been used to treat wines with high alcohol or volatile acidity problems. In combination with solid phase adsorption, membrane filtration offers a method by which smoke tainted wine might be ameliorated.

The treatment process works by fractionating wine components on the basis of molecular size, yielding permeate and retentate fractions, according to the diagram shown in Appendix 5. Low molecular weight molecules permeate membrane filters preferentially to high molecular weight molecules. 'Tight' membranes exclude molecules with molecular weights exceeding approximately 90 atomic mass units; but allow small wine components such as water, acetaldehyde, ethanol, acetic acid, ethyl acetate and lactic acid to permeate. 'Loose' membranes exclude molecules with molecular weights exceeding approximately 150 atomic mass units; theoretically allowing volatile compounds contributing to smoke taint, such as guaiacol and 4-methylguaiacol, to permeate. Higher molecular weight wine components, including sugars and phenolic compounds do not permeate and are retained in the retentate fraction. The permeate fraction can be subsequently treated by solid phase adsorption, using activated carbon or other adsorbent resins for example, to remove undesirable constituents. The treated permeate and the retentate are then recombined, with the resulting treated wine exhibiting a less intense smoke taint and an overall improvement in quality.

Guaiacol and 4-methylguaiacol have molecular weights of 124 and 138 atomic mass units (amu) respectively. Since these compounds would therefore be expected to permeate 'loose' membranes and are readily quantitated by gas chromatography-mass spectrometry, they provide a means by which the efficacy of membrane filtration and solid phase adsorption can be evaluated for the treatment of smoke tainted wine.

The outcomes of the project are expected to enable industry to make informed decisions on membrane filtration and solid phase adsorption as a treatment option for reducing or removing smoke taint from wine that may otherwise be unsaleable.

4 Project Aims and Performance Targets:

This project aimed to:

- Evaluate the capacity of a combined membrane filtration and solid phase adsorption process to improve the quality of smoke tainted wine, by reducing the concentration of smoke derived volatile compounds contributing to the taint, (e.g. guaiacol and 4-methylguaiacol);
- Determine which wine constituents (both desirable and undesirable) permeate the membrane filter and are subsequently removed by solid phase adsorption treatment;
- Optimise the operating conditions of the filtration and solid phase adsorption processes;
- Evaluate the commercial feasibility of employing membrane filtration and solid phase adsorption to the treatment of smoke tainted wines; and
- Deliver project findings and outcomes to industry.

The project's outputs and performance targets comprised:

Outputs	Performance Targets
Evaluate capacity of treatment process to ameliorate smoke taint in wine.	Wine treated by membrane filtration and solid phase adsorption and chemical analysis (pH, titratable acidity, colour and phenolics, ethanol content, sugar concentration and quantitative GC-MS analysis) and sensory analysis (difference and preference testing) completed.
Evaluate commercial feasibility of treatment process.	Consider operating costs associated with wine treatment to determine the cost of producing a kL of treated wine.
Delivery of research findings to industry.	Presentation of research findings and outcomes to industry post-2008 vintage.
Publication of research findings.	Preparation of a paper for publication in an industry or scientific journal.
Submission of final report to GWRDC.	Final report to be submitted to GWRDC.

5 Method:

Wine treatment

Two commercial wines, a 2007 Sauvignon Blanc and a 2007 Pinot Noir sourced from two different wineries in Victoria, were treated using a combined membrane filtration and solid phase adsorption process to ameliorate a taint resulting from vineyard exposure to smoke, following severe bushfires that occurred in north-east Victoria during the 2006/07 growing season. In particular, two periods of high intensity smoke conditions were reported, occurring from the 3rd to the 20th of December 2006 and from the 7th to the 15th of January 2007.[9] The treatment process was conducted by Memstar Pty. Ltd. using: (i) an R41670 membrane separator (Memstar Pty. Ltd., Victoria, Australia) and activated carbon based adsorbent for treatment of the Sauvignon Blanc wine; and (ii) an R80940 membrane separator (Memstar Pty. Ltd., Victoria, Australia) and polystyrene based adsorbent for treatment of the Pinot Noir wine. In each case the operating conditions employed (membrane size, pressure, temperature and flow rate), were optimised in-house.

Sampling

For treatment of the Sauvignon Blanc, wine samples were collected prior to treatment; permeate and wine samples were then also collected at the completion of each of five separate treatment cycles; each cycle being equivalent to the time taken to circulate the original volume of wine (2000 L) through the system. Permeate samples (750 mL) were collected before and after activated carbon treatment and wine samples (12 x 750 mL) were collected following recombination of retentate and treated permeate fractions (sampling points shown in Appendix 5). For treatment of the Pinot Noir, only wine samples (48 x 750 mL) were collected, before and then after the treatment process. All samples were immediately bottled under screwcap and cellared at between 12 and 15 °C until required for chemical and sensory analysis.

Chemical analysis

Permeate and wine samples collected during the Sauvignon Blanc treatment were analysed to determine: pH and titratable acidity (TA), as tartaric acid equivalents to an end-point of pH 8.2; glucose concentration, using an enzymatic test-kit[10] (R-Biopharm., Mannheim, Germany); ethanol content, using an Anton Paar alcolyzer (MEP Instruments, North Ryde, NSW, Australia); and phenolic concentration and brown pigmentation (A_{420}), according to the method of Iland et al.[11] Wine samples collected during the Pinot Noir treatment were analysed to determine pH, titratable acidity, glucose, ethanol and phenolic

concentrations as above; wine colour density and colour hue were also measured according to Iland et al.[11] All analyses were conducted in duplicate.

Gas chromatography-mass spectrometry analysis of smoke derived volatile phenols

Guaiacol, 4-methylguaiacol, 4-ethylguaiacol, 4-ethyphenol and eugenol were quantified by the stable isotope dilution assay methods reported previously.[6,12,13] These publications include details of the syntheses of the internal standards used herein. For all analytes: the linear dynamic range was 0, and 1-1000 μg/L; the limit of detection was 1 μg/L; and the precision was <5% relative standard deviation. Sauvignon Blanc wine and permeate samples were analysed once after bottling; whereas Pinot Noir wine samples were analysed after bottling and again 12 months post-bottling.

Preparation of samples for analysis.

A deuterated internal standards (IS) solution containing d_3-guaiacol (1.13 μg), d_3-4-methylguaiacol (0.840 μg) and d_4-4-ethylphenol (0.721 μg), in ethanol (100 μL) was added to the wine or permeate sample (5 mL) in a screw cap vial using a glass syringe (100 μL Hamilton). The organic solvent (diethyl ether/n-pentane 1:2 (v/v) ca. 3 mL) was added, and the mixture was shaken briefly. A portion of the organic layer (ca. 2 mL) was then placed in a vial ready for analysis.

Reference standards.

Reference standards containing 100 μL of deuterated internal standards ethanolic solution (as described above) and 100 μL of normal unlabeled analytes ethanolic solution (guaiacol (4.646 μg), 4-methylguaiacol (1.536 μg), 4-ethylguaiacol (2.025 μg), 4-ethylphenol (1.798 μg) and eugenol (2.108 μg)) in diethyl ether/n-pentane (1:2 (v/v), approximately 2 mL) were used.

Gas chromatography-mass spectrometry analysis.

An Agilent Technologies 6890 gas chromatograph (GC) was equipped with a Gerstel MPS2 multi-purpose sampler and coupled to an Agilent 5973N mass selective detector. The gas chromatograph was fitted with an approx. 30 m x 0.25 mm, 0.25 μm J&W DB-Wax fused silica capillary column. The carrier gas was helium (BOC Gases, high purity), linear velocity 50 cm/sec; flow rate 1.2 mL/min. vacuum compensated at the mass spectrometer interface. The oven temperature was started at 50 ℃, held at this temperature for 1 min, increased to 240 °C at 10 °C/min, and held at this temperature for

20 min. The injector temperature was 200 °C and the transfer line was held at 240 °C. A 2 μL sample volume was injected. The splitter, at 30:1, was opened after 36 s, and the liner used was resilanized borosilicate glass, tapered, with a plug (2-4 mm) of resilanized glass wool at the column interface. The instrument was controlled with Agilent G1701CA ChemStation software in conjunction with the Gerstel MASter software (version 1.81). For quantification of the smoke derived volatile phenols, positive ion electron impact mass spectra at 70 eV were recorded in Selective Ion Monitoring (SIM) mode using conditions published previously.[6,12,13] The data was analysed with Agilent MSD ChemStation software.

Sensory analysis

No discernible smoke taint could be detected in the untreated Sauvignon Blanc wine during informal 'benchtop' sensory evaluations. These evaluations were supported by the results obtained from quantitative GC-MS analysis (Table 1) and so no formal sensory trials are reported for the Sauvignon Blanc wine treatment.

Difference testing of untreated and treated Pinot Noir wines.

Difference tests were conducted using the triangle test method described by Meilgaard et al.,[14] using a panel of 48 members. Panellists were of European origin, aged between 18 and 55, with similar numbers of males and females. Wines were presented to the panel using a balanced, randomised presentation order where all possible configurations (i.e. ABB, BAA, AAB, BBA, ABA and BAB, where A denotes the Pinot Noir wine before treatment and B denotes the Pinot Noir wine after treatment) were presented an equal number of times. Panellists smelt, but did not taste the samples, and were asked to identify the sample within each set that was different.

Consumer acceptance testing of untreated and treated Pinot Noir wines.

Consumer acceptance tests were conducted using a hedonic rating method described by Meilgaard et al.,[14] with a panel of 48 members. Panellists were of European origin, aged between 18 and 55, with similar numbers of males and females. Wines were presented to the panel using a balanced, randomised presentation order. Panellists smelt, but did not taste the samples, and by placing a vertical line on the 9-point scale (Figure 1), rated the acceptability of each wine. The scale was divided into segments, with word anchors placed at segments 1, 5, and 9, corresponding to 'don't like the wine at all', 'neither like nor dislike the wine' and ' like the wine very much', respectively. The ratings for each wine from each judge were then measured in cm from the left hand end for statistical analyses.

Figure 1. Hedonic scale used to rate consumer acceptability.



Statistical analysis

Data were analysed by one-way analysis of variance (ANOVA) using GenStat (9th Edition, VSN International Limited, Herts, UK). Mean comparisons were performed by least significant difference (LSD) multiple comparison test at $P < 0.05$.

6 Results/Discussion:

The membrane filtration and solid phase adsorption treatment process reduced the concentration of smoke derived volatile phenols in the wines treated, and in the case of the Pinot Noir, improved the acceptability of the wine's organoleptic properties, without any significant impact on other compositional attributes such as pH, titratable acidity (TA), sugar concentration, alcohol content or wine colour. The treatment process therefore affords a potential amelioration technique by which the intensity of smoke taint in wine, following vineyard exposure to smoke, can be reduced.

Effect of treatment process on composition of Sauvignon Blanc wine and permeate.

Chemical analysis was carried out on Sauvignon Blanc wine before treatment, and on wine and permeate (pre- and post-activated carbon adsorption) samples collected following each of 5 successive treatment cycles (Table 1).

Table 1. Effect of membrane filtration and solid phase adsorption treatment on the chemical composition of Sauvignon Blanc wine and permeate samples.

	sample	pH	TA (g/L)	glucose (mg/L)	alcohol (%, v/v)	total phenolics (au)	brown pigments (au)
wine	untreated	3.38	6.3 a	182 a	14.8 a	6.36 a	0.110 a
	after 1 treatment cycle	3.40	6.4 a	215 a	14.6 a	5.97 a	0.109 a
	after 2 treatment cycles	3.50	6.1 a	177 a	14.7 a	5.80 a	0.114 a
	after 3 treatment cycles	3.57	5.9 a	189 a	14.7 a	5.74 a	0.114 a
	after 4 treatment cycles	3.50	5.9 a	167 a	14.5 a	5.75 a	0.107 a
	after 5 treatment cycles	3.62	5.9 a	192 a	14.6 a	5.34 a	0.119 a
permeate pre-AC	after 1 treatment cycle	3.53	2.5 b	9 b	14.1 b	-2.31 b	0.007 b
	after 2 treatment cycles	3.57	2.5 b	8 b	14.2 b	-2.39 b	0.009 b
	after 3 treatment cycles	3.46	2.4 b	9 b	14.1 b	-2.50 b	0.005 b
	after 4 treatment cycles	3.54	2.5 b	7 b	14.2 b	-2.55 b	0.004 b
	after 5 treatment cycles	3.72	2.5 b	9 b	14.2 b	-2.60 b	0.004 b
permeate post-AC	after 1 treatment cycle	3.46	2.4 c	6 b	14.2 b	-3.43 c	0.001 c
	after 2 treatment cycles	3.62	2.4 c	7 b	14.2 b	-3.27 c	0.002 c
	after 3 treatment cycles	3.51	2.4 c	6 b	14.1 b	-3.16 c	0.001 c
	after 4 treatment cycles	3.45	2.4 c	4 b	14.0 b	-3.09 c	0.002 c
	after 5 treatment cycles	3.48	2.5 c	6 b	14.2 b	-3.03 c	0.002 c

Mean values from duplicate analyses, values were in agreement to ca. 5%.
Values followed by a different letter within columns are significantly different ($P < 0.05$).

Throughout the five successive treatment cycles, wine pH, TA, sugar, alcohol and colour measurements remained relatively constant, although a slight increase in pH was observed, from 3.38 to 3.62, corresponding to a slight decrease in TA, from 6.3 g/L to 5.9 g/L. It is not clear if this resulted from the treatment process, but the observed changes were not considered to be meaningfully different, especially given the ease with which pH and TA can be adjusted by tartaric acid additions. Variations in glucose and ethanol content were within accepted levels of experimental error and were also not considered to be meaningful. Interestingly, the total phenolics concentration progressively decreased from 6.36 to 5.34 with treatment. Since high molecular weight phenolic compounds (e.g. flavonoids) would not be expected to permeate the membrane, the observed decrease is most likely due to the removal of low molecular weight phenolic compounds; possibly including smoke derived phenols.

Compositional differences were observed between wine and permeate samples; TA, glucose, ethanol and phenolic concentrations, and wine colour in particular. The organic acids present in wine have low molecular weights, 150 amu for tartaric acid for example, and so were expected to permeate the membrane filters. The 60% decrease in permeate TA observed was therefore attributed to ionic-based membrane interactions, rather than size-based membrane exclusion. As expected, higher molecular weight wine components, including glucose and some phenolic compounds, did not permeate the membrane. Those components responsible for white wine colour were also excluded; i.e. permeate samples were completely colourless (Figure 2).

Figure 2. Sauvignon Blanc wine and permeate samples collected prior to, and following one cycle of the amelioration treatment process.



The negative values obtained for permeate total phenolics are thought to be a function of the associated calculations, which include a correction to allow for the absorbance of non-phenolic material.[11] Nevertheless, the results strongly suggest a proportion of phenolic material that permeated the membrane filter was subsequently adsorbed by the activated carbon, reducing the total phenolics content of treated wine. It is possible this is due to absorption of low molecular weight smoke derived phenols. The activated carbon treatment had no apparent effect on TA, or glucose and ethanol concentrations.

Effect of treatment process on composition of Pinot Noir wine.

Chemical analysis was carried out on Pinot Noir wine sampled before and after the treatment process (Table 2). Again a decrease in TA was observed with treatment, from 9.0 g/L to 7.8 g/L, although pH remained constant at 3.38. At this stage it's not clear how the treatment process affected TA, although it doesn't appear to be a function of the solid phase adsorption step. However, as with the Sauvignon Blanc, this should not present a significant problem with regards to wine quality, given the capacity to pH adjust wine. Slight variations in glucose and ethanol content were again observed following treatment, but were not considered to have any meaningful impact on wine quality. Importantly, wine colour (both density and hue) remained constant. The direct addition of activated carbon to a red wine would be expected to cause a noticeable loss of colour. However, since high molecular weight anthocyanins and pigmented polymers are excluded from membrane permeation and retained in the retentate fraction, they are protected from adsorption during the solid phase treatment. A reduction in total phenolics was also observed during the Pinot Noir treatment, similar to that observed with the Sauvignon Blanc treatment. Again this could be due to the adsorption of low molecular weight smoke derived phenols by the adsorbent resin.

Table 2. Effect of membrane filtration and solid phase adsorption treatment on the chemical composition of Pinot Noir wine.

sample	pH	TA (g/L)	glucose (mg/L)	alcohol (%, v/v)	total phenolics (au)	colour density (au)	colour hue
untreated wine	3.38	9.0	900	14.1	39.13	5.19	0.80
treated wine	3.38	7.8	515	13.7	34.79	5.00	0.77

Mean values from duplicate analyses; values were in agreement to ca. 5%.

Effect of treatment process on volatile phenol composition of Sauvignon Blanc wine and permeate.

Quantitative GC-MS analysis was carried out on Sauvignon Blanc wine collected before treatment, and on wine and permeate (pre- and post-activated carbon adsorption) samples collected after each of 5 treatment cycles, in order to evaluate the permeability and rate of adsorption of various volatile phenols associated with smoke taint (Table 3).

Table 3. Effect of membrane filtration and solid phase adsorption treatment on the concentration of smoke derived volatile phenols in Sauvignon Blanc wine and permeate samples.

sample		concentration (μg/L)				
		guaiacol	4-methyl guaiacol	4-ethyl guaiacol	4-ethyl phenol	eugenol
wine	untreated	8	2	tr	1	1
	after 1 treatment cycle	7	tr	tr	tr	1
	after 2 treatment cycles	6	tr	tr	tr	1
	after 3 treatment cycles	5	tr	tr	tr	1
	after 4 treatment cycles	5	tr	tr	tr	tr
	after 5 treatment cycles	5	tr	tr	tr	tr
permeate pre-AC	after 1 treatment cycle	6	tr	tr	1	2
	after 2 treatment cycles	5	tr	tr	tr	1
	after 3 treatment cycles	5	tr	tr	tr	1
	after 4 treatment cycles	6	tr	tr	tr	nd
	after 5 treatment cycles	5	tr	tr	tr	tr
permeate post-AC	after 1 treatment cycle	Tr	nd	nd	nd	nd
	after 2 treatment cycles	1.5	tr	nd	nd	nd
	after 3 treatment cycles	3	nd	nd	nd	nd
	after 4 treatment cycles	3.5	tr	nd	tr	tr
	after 5 treatment cycles	4.5	tr	nd	tr	d

Mean values from duplicate analyses.
nd = not detected; tr = trace (i.e. positive identification but < 1 μg/L limit of detection).

The untreated Sauvignon Blanc wine contained 8 μg/L of guaiacol and 2 μg/L of 4-methylguaiacol. Since only trace levels (≤ 1μg/L) of 4-ethylguaiacol, 4-ethylphenol or eugenol were detected, these compounds are not discussed in further detail. The results indicate that during the 5 successive treatment cycles, guaiacol permeated the membrane readily, with each permeate fraction containing at least 70% as much guaiacol as the

corresponding wine from which it derived. As expected, the highest rates of guaiacol removal occurred during the first two treatment cycles; the rate of adsorption subsequently decreased due to saturation of the activated carbon substrate. For this reason, subsequent treatments, including the Pinot Noir treatment, employed a polystyrene based adsorbent resin, in preference to the activated carbon substrate. Following wine treatment, guaiacol content had been reduced to 5 μg/L and only trace levels of 4-methylguaiacol remained. These results demonstrate the treatment process is capable of removing smoke derived volatile phenols. However, the extent of amelioration is highly dependent on the duration of treatment, the nature of the solid phase substrate, and in the case of the activated carbon substrate, adsorption performance should be monitored to ensure efficiency. It should also be noted that the adsorption process could potentially remove desirable low molecular weight volatiles, but this was not investigated in the current study and is the focus of ongoing research.

Effect of treatment process on volatile phenol composition of Pinot Noir wine.

Quantitative GC-MS analysis was carried out on Pinot Noir wine collected before and after the treatment process, and again 12 months post-bottling (Table 4). Anecdotal evidence from winemakers has suggested that the intensity of smoke taint can increase with bottle age, so the 12 month post-bottling analysis was included to investigate this hypothesis.

Table 4. Effect of membrane filtration and solid phase adsorption treatment on the concentration of smoke derived volatile phenols in Pinot Noir wine.

Sample		concentration (μg/L)				
		guaiacol	4-methyl guaiacol	4-ethyl guaiacol	4-ethyl phenol	eugenol
untreated wine	post-bottling	12	3	n.d.	n.d.	n.d.
	12 months post-bottling	15	4	n.d.	n.d.	n.d.
treated wine	post-bottling	5	2	n.d.	n.d.	n.d.
	12 months post-bottling	6	3	n.d.	n.d.	n.d.

n.d. = not detected

As with the Sauvignon Blanc, a reduction in guaiacol and 4-methylguaiacol concentrations were observed in the Pinot Noir wine following treatment: from 12 μg/L to 5 μg/L for guaiacol and from 3 μg/L to 2 μg/L for 4-methylguaiacol. (4-Ethylguaiacol, 4-ethylphenol and eugenol were not detected in any of the wines). This further demonstrates the capacity of the treatment process to remove smoke derived volatile phenols from wine and

to a lesser extent their soluble precursors. Slight increases in guaiacol and 4-methylguaiacol levels were observed in both untreated and treated wines following 12 months bottle age. This is thought to be due to the hydrolysis of conjugated precursors, as discussed in previous studies.[15] The guaiacol content of the treated wine 12 months post-bottling was still well below that measured prior to treatment. It should again be noted, the concentrations of guaiacol and 4-methylguaiacol measured were below the aroma detection thresholds reported in the literature,[7,8] although it has been suggested the published thresholds may be too high.[16] Irrespective, guaiacol and 4-methylguaiacol proved useful smoke taint marker compounds in the current study. In combination with sensory analysis, using difference and acceptability tests, quantitative GC-MS analysis has demonstrated the capacity of the treatment process to moderate the chemical composition and organoleptic properties of smoke tainted wine.

Effect of treatment process on sensory properties and consumer acceptability of wine.
Although guaiacol and 4-methylguaiacol were observed in the untreated Sauvignon Blanc wine (Table 1), indicative of the presence of smoke taint, no discernible smoke-related aroma characters could be detected during informal 'benchtop' sensory evaluations, so formal sensory trials were not performed and are not reported for this wine.

A triangular difference test[14] was conducted to establish whether or not there was a perceptible difference in the sensory properties of the untreated and treated Pinot Noir wines. Wines were presented to a panel of 48 judges, 22 of whom responded correctly. These data show that the treatment process had a significant impact on wine aroma (at the 95% confidence level). In order to establish whether this organoleptic impact was positive or negative, an acceptability test[14] was subsequently performed. Wines were again presented to a panel of 48 judges, who indicated their preference for each wine on a 9 point scale; with 1 corresponding to 'don't like the wine at all' and 9 corresponding to 'like the wine very much'. The panel gave the untreated wine a 3.64 rating and the treated wine a 4.51 rating; corresponding to a statistically significant preference for the treated wine (at the 95% confidence level), albeit a moderate preference only. Interestingly, the panel did not specifically associate smoke-related aroma characters with the untreated wine, but the treated wine was informally described as 'cleaner' and more 'fruit-driven'. The treatment process is therefore considered to have improved the overall sensory properties and consumer acceptability of the tainted wine.

7 Outcome/Conclusion:

- *Evaluate the capacity of a combined membrane filtration and solid phase adsorption process to improve the quality of smoke tainted wine, by reducing the concentration of smoke derived volatile compounds contributing to the taint, (e.g. guaiacol and 4-methylguaiacol).*

The quantitative GC-MS data obtained in the current study demonstrates the membrane filtration/solid phase adsorption treatment process can be employed to reduce the concentration of smoke derived volatile phenols in tainted wine; with both wines containing lower levels of guaiacol and 4-methylguaiacol following treatment. This conclusion was further supported by sensory analysis, which confirmed the treatment process improved the overall sensory properties and consumer acceptability of the tainted Pinot Noir; which can at least partially be attributed to the removal of guaiacol and 4-methylguaiacol.

- *Determine which wine constituents (both desirable and undesirable) permeate the membrane filter and are subsequently removed by solid phase adsorption treatment.*

The treatment process comprises fractionation of wine primarily on the basis of molecular weight, to yield retentate and permeate fractions. In this way, many desirable wine components are retained in the retentate and protected from the solid phase adsorption process. The permeate only is passed over the adsorbent substrate, thereby improving the selectivity of this process. Some minor changes to compositional attributes including pH, TA, sugar and alcohol content were observed, but these differences were not considered to be detrimental to wine quality; while colour and hue were maintained during treatment of the Pinot Noir. Analysis of total phenolics indicated the adsorption of low molecular weight phenolic compounds from each permeate fraction by the activated carbon or polystyrene based resin substrates; including, based on the GC-MS analysis, smoke derived volatile phenols. However, desirable flavonoids were excluded from membrane permeation and were therefore retained in the retentate and treated wine. It is possible that other desirable aroma compounds may also permeate the membrane filter and be subsequently adsorbed. This was not investigated in the current project, but is the focus of ongoing research.

- *Optimise the operating conditions of the filtration and solid phase adsorption processes.*

Operating conditions, including membrane size, pressure, temperature and flow rate, were optimised in-house by Memstar Pty. Ltd. The polystyrene based resin was considered a more selective and efficient adsorption substrate than the activated carbon.

- *Evaluate the commercial feasibility of employing membrane filtration and solid phase adsorption to the treatment of smoke tainted wines.*

The operating costs for wine treatment have been estimated to be $60/kL; the treatment process is therefore considered to be viable for commercial applications. Nevertheless, commercial feasibility should still be determined on a wine by wine basis to take into account: the initial extent of smoke taint; their consumer market and intended price point; and the value of existing brands and reputation.

- *Deliver project findings and outcomes to industry.*

The major outcomes of this project have been communicated to industry via two technical workshop presentations (see Appendix 2) and now this report. A manuscript is also being prepared for publication in a refereed scientific journal and an abstract has been submitted for a poster presentation at the In Vino Analytica Scientia 2009 conference.

8 Recommendations:

o *Recommendations for technology uptake by industry*

In the current study, the membrane filtration/solid phase adsorption treatment process reduced the concentration of smoke derived volatile phenols in the wines treated, and in the case of the Pinot Noir, improved the acceptability of the wine's organoleptic properties, without any significant impact on other compositional attributes such as pH, TA, sugar and alcohol content or wine colour. The treatment process therefore affords a potential amelioration technique by which the intensity of smoke taint in wine, following vineyard exposure to smoke, can be reduced. Furthermore, since the wines included in this study had relatively low levels of smoke taint and concentrations of volatile phenols, the treatment process may prove more effective in the amelioration of more heavily tainted wines, which exhibit more intense smoke related aroma characters due to higher volatile phenol concentrations.

The data presented in this document is intended as an independent source of information only and should not be regarded as an endorsement. However, it is hoped that these results will enable more informed decisions to be made with regards to the suitability of this technique for the amelioration of smoke tainted wine. Individual wineries should determine for themselves the commercial feasibility of the treatment process, taking into account: the extent of smoke taint (the intensity of smoke related aromas exhibited); their consumer market and intended price point; and the value of existing brands and reputation.

o *Recommendations for future research*

Compared with the direct addition of activated carbon (or other substrate) to wine, the fractionation step of Memstar's amelioration technique reduces the range of wine constituents treated by solid phase adsorption, thereby improving both the selectivity and efficiency of the treatment process. However, it is entirely probable that low molecular weight wine constituents, in particular volatile compounds responsible for desirable aroma attributes, could also permeate the membrane and be adsorbed by the activated carbon or polystyrene based resin. Therefore, following on from the current study, investigations have commenced to investigate the impact of the treatment process on a broader range of volatile wine components.

Both the solid phase substrates utilised in the current study were capable of adsorbing the smoke derived volatile phenols of interest; i.e. guaiacol and 4-methylguaiacol. However,

the activated carbon's rate of adsorption decreased with time as it became saturated. Future work could therefore involve development of a rapid analytical method (possibly a spectroscopic technique) which could be used to monitor the solid phase substrate performance. The adsorption efficiency and selectivity of alternate solid phase substrates, including the polystyrene based resin, also warrant further investigation.

9 Appendix 1: Communication:

The Sauvignon Blanc component of this project was undertaken by Ms Kathy Quinn towards a successful Honours degree under the supervision of Dr Kerry Wilkinson and Dr Hannah Williams at Curtin University of Technology. Research findings were published as a thesis:

> Quinn, K.C. The impact of reverse osmosis filtration on smoke taint in wine. Honours thesis, Curtin University of Technology, Australia, 2007.

The project's major research findings were presented at:

1) A GWRDC Smoke Taint Technical Workshop held on at the Melbourne Airport and Convention Centre, in Attwood on Tuesday 29th July 2008.
2) A 'Smoke Effect Working Group Consultative Forum' organised by the Wine Industry Association of Western Australia, held at the Manjimup Horticultural Research Institute in Manjimup on Friday 15th August 2008.

A manuscript is also being prepared for publication in a refereed scientific journal and an abstract has been submitted for a poster presentation at the In Vino Analytica Scientia 2009 conference.

10 Appendix 2: Intellectual Property:

Memstar Pty. Ltd. holds all intellectual property rights in relation to the membrane filtration and solid phase adsorption technology evaluated in this project. There was no further patentable intellectual property arising from this project.

11 Appendix 3: References:

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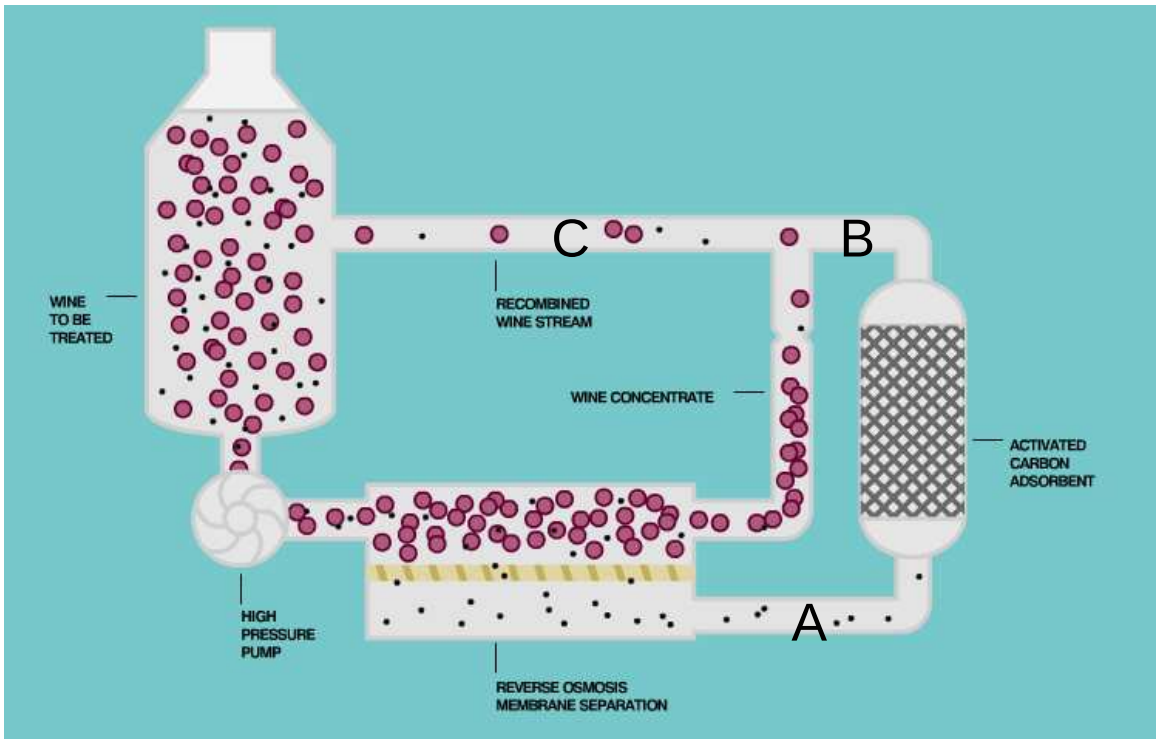
12 Appendix 4: Staff

The following staff and students were engaged in the project:

- Dr Kerry Wilkinson, Curtin/UA;
- Winery and laboratory staff from participating industry partners;
- Mr David Wollan, Memstar Pty. Ltd.;
- Dr Alan Pollnitz, The Australian Wine Research Institute;
- Dr Hannah Williams, Ms Kathy Quinn and Ms Jeanette Smith, Curtin; and
- Dr Sue Bastian, Mr Trent Johnson and Ms Anthea Fudge, UA.

13 Appendix 5: Other

Figure 3. Schematic diagram of combined membrane filtration and activated carbon treatment process; pre-AC permeate collected at sampling point A; post-AC permeate collected at sampling point B; and treated wine collected at sampling point C. (Courtesy of Memstar Pty. Ltd.)



14 Appendix 6: Budget Reconciliation

The Budget Reconciliation is provided separately using GWRDC Form B.