Review

White wine phenolics: current methods of analysis

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Abstract

White wine phenolic analyses are less common in the literature than analyses of red wine phenolics. Analytical techniques for white wine phenolic analyses using spectrophotometric, chromatographic, spectroscopic, and electrochemical methods are reported. The interest of research in this area combined with the advances in technology aimed at the winemaking industry are promoting the establishment of novel approaches for identifying, quantifying, and classifying phenolic compounds in white wine. This review article provides an overview of the current research into white wine phenolics through a critical discussion of the analytical methods employed.
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Keywords: phenolic compounds; white wines; chromatography; spectroscopy; electrochemistry

INTRODUCTION

Phenolic compounds are complex molecules that occur in both red and white wine. They appear at lower concentrations in white wines than in red, but are important contributors to the appearance, antioxidant capacity and sensory aspects of the wine. Phenolic compounds are divided into two major classes based on their chemical structure: flavonoids (diphenylpropanoids) and non-flavonoids (phenylpropanoids). Flavonoids are classified by a three-ring structure of which the central ring is a pyran ring. Flavonoids make up approximately 20% of the total phenolics found in white wine.[1] The subclasses of flavonoids, their distinct subunits, source of compound and concentrations in white wine, based on the work reported by Waterhouse[2] and Jackson,[3] are outlined in Table 1. Within them, flavanols are highly responsible of browning in white wines due to their participation in chemical oxidation reactions. Moreover, these compounds are involved in the mouthfeel properties of white wines.

The subclasses of non-flavonoids, their distinct subunits, source of compound and concentrations in white wine, as reported by Waterhouse[2] and Jackson,[3] are outlined in Table 2. Hydroxycinnamic acids account for approximately 50% of white wines' total phenolic content (TPC).[1] These compounds are easily oxidised by polyphenol oxidase enzymes (PPO), such as tyrosinase or laccase, when grey rot is present. PPO are therefore responsible for the browning that occurs in white wine musts.[2-4] The hydroxycinnamic acids are characterised by an ethylene group between a benzene ring and carboxylic acid group[5] but commonly exist as esters of tartaric acid, giving coutaric acid, caftaric acid and fertaric acid.[2] Hydroxybenzoic acids consist of a single benzene ring and a hydroxyl group with a carboxylic acid substitution.[5] Gallic acid is the most common hydroxybenzoic acid found in white wine.[2]

Tyrosol is produced from tyrosine in yeast during fermentation and its concentration depends on the yeast strain used.[5]

Another minor class of phenolic compounds are stilbenes, the most important of which is resveratrol. Vines produce resveratrol in response to fungal infection.[2] The resveratrol derivatives are only found in grape skins and at low concentrations in white wine (~0.5 mg L^{-1}).[2] In addition, white wines might also contain hydrolysable tannins from wood origin if wood contact occurs during the winemaking process. These compounds can be found at varying levels in the wines based on the duration of the wood contact process, among other factors such as wood origin or wood age. Alternatively to wood contact, the use of oenological tannins can also incorporate hydrolysable tannins in white wines. Hydrolysable tannins are classified as gallotannins or ellagitannins. Gallotannins are formed by the esterification of gallic acid and D-glucose with nut galls and tara as the primary source of these compounds.[6] Ellagitannins are polymers of ellagic, gallic or hexahydroxydiphenic acids obtained from oak and chestnut. Oenological hydolysable tannins act as antioxidants and antioxidasics, reducing enzymatic oxidation activity and potentially reducing

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Table 1. Summary table of flavonoid subclasses, their subunits, source, and concentration

Flavonoid	Subunit	Source	Concentration
Flavan-3-ols	(+)-Catechin (−)-Epicatechin (−)-Epicatechin gallate (−)-Epigallocatechin Procyanidins Condensed Tannins	Grape berry skin and seeds	15–25 mg L^{-1} (monomers) 20–25 mg L^{-1} (polymers)
Flavonols	Quercetin Kaempferol Myricetin (often exist as glucosides)	Grape berry skin	Low concentration
Anthocyanins	Cyanin-3-glucoside Delphinin-3-glucoside Petunin-3-glucoside Peonin-3-glucoside Malvin-3-glucoside	Red pigments in grape berry skin	Extremely minute levels

Adapted from Waterhouse[2] and Jackson.[3]

Table 2. Summary table of non-flavonoid subclasses, their subunits, source, and concentration

Non-flavonoid	Subunit	Source	Concentration
Hydroxycinnamic acids	Coumaric acid *p*-Coutaric acid Ferulic acid *S*-Glutathionyl caftaric acid	Grape berry pulp	130–155 mg L^{-1}
Hydroxybenzoic acids	Gallic acid Benzoic acid Protocatechuic acid Syringic acid Hydrolysable tannins	Grape berry seed	~10 mg L^{-1}
Tyrosol	Tyrosol	Yeast	N/A

Adapted from Waterhouse[2] and Jackson.[3]

A high total phenol content (TPC) gives higher levels of bitterness and astringency and intensifies the wine's perceived viscosity.[5] Increased TPC was reported to provide increased varietal character and complexity, and decreases acidity.[15] In white wines, phenolic compounds are also directly responsible for protein haze formation. Initially soluble, flavanol protein complexes might precipitate from solution after the protein complex grows and becomes insoluble, thereby causing turbidity.[16]

Phenolic compounds also participate in aroma changes during winemaking and ageing. Polyphenols and especially flavanols are readily oxidisable compounds that modulate the presence of desirable (4-methyl-4-mercaptopentanone (4MMP), 3-mercaptohexanol (3MH) or 3-mercaptohexyl acetate (MHA)) and undesirable (hydrogen sulphide (H_2S)) nucleophilic volatile polyfunctional mercaptans (PFMs).[17] During the wine exposure to oxygen, reactive chemical species in the form of quinones are formed and are therefore available to react with nucleophilic compounds.[18] Phenolic oxidation processes are thus involved in removing these sulfur-containing nucleophilic species. The extent of these reactions also depends on the varying levels of the most commonly used preservatives, i.e. sulfur dioxide, ascorbic acid or glutathione. These compounds are well known for their ability to reduce or scavenge quinones, avoiding the interaction of quinones with aroma compounds, and the consequent loss of flavour and aromatic intensity.[19] In addition, the formation and presence of Strecker aldehydes in wine are also influenced by the presence of phenolic compounds. Strecker aldehydes are powerful volatiles responsible for the oxidative aroma of wines. The Strecker degradation of amino acids with the involvement of quinones from phenolic molecules is one of the most important pathways in the formation of Strecker aldehydes.[17,20]

It has been shown that phenolic concentration is associated with *in vitro* antioxidant activity.[21] The structure of phenolic compounds allows them to react with oxidants via free radical scavenging and transition metal chelation[22] due to the ease with which hydrogen atoms can be abstracted.[23] These reactions have important health benefits as they inhibit processes that attenuate inflammatory responses, thereby serving as possible cardioprotective, neuroprotective, and chemopreventive agents.[24] This has been highlighted by the fact that over the last 20 years coronary heart disease has

SO$_2$ additions. These compounds also aid in protein stabilisation and precipitation, clarification in conjunction with bentonite, or modifying mouthfeel properties of white wines.[7]

The phenolic composition and overall content of white wines vary and are consistent with grape variety.[8] Pre-fermentative maceration and increased skin contact time lead to increased phenolic content.[9-11] Wines aged in oak showed increased total phenol content (TPC) compared to wines aged in stainless steel.[12] In addition, syringaldehyde, coniferaldehyde, sinapinaldehyde, scopoletin (non-volatile phenols) and 4-ethyl-guaiacol and eugenol (volatile phenols) along with increased gallic acid content were all found in wines aged in oak.[12] Storage of wine with fluctuating temperatures showed an impact on TPC of the wines compared to wines stored at a constant temperature.[13] Studies that explore the role and evolution of phenolic compounds in wine throughout the winemaking process provide insight for informed decision making in the wineries.

Phenolic compounds can bind to salivary proteins at various positions via hydrogen bonding and hydrophobic interactions.[14]

occurred less among the populations of countries with regular and moderate consumptions of wine.[25] A study showed that 1 h after consuming white wine the levels of hydroxycinnamic acids in human plasma increased significantly.[26] In another study, juice supplemented with red wine polyphenols was suggested to prevent neurodegenerative diseases.[27] A review study also showed the importance of dietary polyphenols in the development of metabolic diseases, citing mainly the critical role of polyphenols as potent anti-inflammatory and antioxidant compounds.[28] Furthermore, work published by Moreno-Arribas et al.[29] highlighted the role played by phenolic compounds in oral and gut microbiota and subsequently in the incidence of Alzheimer's disease. The study reports the potential role played by wine polyphenols in the prevention of neurodegenerative diseases. Nevertheless, excessive alcohol consumption can lead to health risks.[30] Alcohol consumption was found to be linearly associated with a higher risk of stroke and coronary disease. However, myocardial infarction risk decreased log-linearly with alcohol consumption, heart failure, fatal hypertensive disease and fatal aortic aneurysm.[31]

Phenolic compounds are extracted from the grape skin, seeds and stems into white wine during the cold maceration process,[32] which is described as the process whereby the skins of crushed and destemmed grapes are macerated in their juices under controlled conditions.[11] This process only lasts a couple of hours for white winemaking and is extended for red winemaking, where it could proceed for weeks. In some cases, the only maceration that takes place in white winemaking occurs in the press before separating the skins and juice. It is an optimisation of phenolic extraction that creates a balanced, good-quality white wine.[32] The pressing operation is therefore crucial and factors such as pressing method (destemming/crushing or direct pressing), type of press, applied pressure and must fractionation define the polyphenol content of the wines.[33] In addition, in the production of 'Blanc de Noirs', in which white wines are obtained from red varieties, the pressing process is even more relevant as the goal is to limit any diffusion of phenolics into the must.

Phenolic research has become increasingly popular due to the influence of phenolic compounds on the appearance, health benefits and perception of the quality of white wines. Many studies have been put forward where phenolic compounds in white wines are being identified, quantified, and used as markers for the discrimination of wines based on many factors. This article will review the analytical methods researchers use to increase knowledge of the role of phenolic compounds in white wines. This includes spectrophotometric, chromatographic, spectroscopic, and electrochemical methods of phenolic analysis.

SPECTROPHOTOMETRIC METHODS FOR THE ANALYSIS OF PHENOLIC COMPOUNDS

Folin–Ciocalteu reagent (FCR)
FCR is commonly used as a total phenol assay for wine samples.[22,34] FCR measures a sample's reducing (antioxidant) capacity and many studies have shown a linear correlation between a sample's total phenolic profile and its antioxidant capacity.[35] FCR is composed of sodium tungstate and sodium molybdate dissolved in water, hydrochloric acid and phosphoric acid, with an addition of lithium sulfate.[34] The reagent is yellow, which, when it undergoes an electron transfer reaction, forms a blue species via reduction of the molybdate compound: $Mo(VI) + e^- \rightarrow Mo(V)$.[35] The quantification of total phenols is then possible spectrophotometrically at an absorbance maximum of 765 nm.[36] A reduction reaction occurs

between FCR and phenolics under basic conditions, whereby dissociation of the phenolic proton leads to a phenolate anion, which can reduce the reagent.[35] The most common method to calculate TPC using FCR is a calibration curve using gallic acid as a standard,[37] although catechin may also be used as a standard.[38,39]

While FCR analysis is convenient, there are still some limitations associated with it, namely interference due to SO_2, sugars and ascorbic acid which cause an issue when using FCR to analyse white wine phenolics.[34,40] It was demonstrated that the SO_2 content in white wines amplifies the reaction of FCR with phenols and that correcting this interference is impossible.[40] Sugars interfere with the FC reaction, which is linked to temperature, but approximate corrections are available.[34,41] Ascorbic acid creates an augmentation effect on the amount of FCR reacting with the phenols present. It is suggested that this is due to the reduction of quinones as they form, which prolongs the reaction.[34]

The effects of SO_2 on the FCR were explored and it was found that there is a decrease in the apparent polyphenol concentration measured by FCR when the SO_2 was removed from a wine sample.[36] This decrease was most noticeable in samples with a high initial free SO_2 concentration. It was noted that bound SO_2 did not have the same augmentation effect on the phenolic concentration and did not need to be removed. Furthermore, it was shown that the previously proposed correction for SO_2[42] was too small compared to the effect shown in this study.[36]

When white wine FCR results are compared to those of high-performance liquid chromatography–diode array detection (HPLC-DAD) and UV–visible spectrophotometry (absorbance = 280 nm), it was found that the TPC, in gallic acid equivalents (GAE), was generally higher for the FCR than for the other analyses;[43-45] this was attributed to the fact that FCR is non-specific to phenolic compounds due to its ability to be reduced by other compounds present in wine.

As FCR measures the reduction reaction, it is often linked to the antioxidant capacity of wines. TPC and antioxidant capacity are highly correlated,[22,46] with a higher TPC having a greater antioxidant capacity. High correlation coefficients have also been found between TPC measured by FCR and antioxidant capacity measured by ABTS, DPPH and ORAC methods.[38,47]

FCR was used to demonstrate that white wines made with a maceration step produced a product higher in phenolic content and hence higher radical scavenging abilities.[37] Table 3 outlines the TPC ranges obtained from FCR analysis of wines from different geographical origins. The differences between the values might be attributed to the different cultivars examined.

The interferences of the FCR method may act as a hindrance to the success of this method for phenolic analysis. Pre-treatment of samples is recommended to eliminate the interferences as precise correction calculations are not currently available.[34,39] The interferences are more noticeable in white wine samples and, along with the fact that the method is non-specific, great caution should be taken when interpreting TPC from FCR. However, FCR as an analysis technique alongside other reference analyses provides useful information on TPC of wines.

UV–visible spectrophotometry
TPC can be successfully determined using UV–visible spectrophotometry by applying the Beer–Lambert law due to the dependency of absorbance on concentration and light path length.[52] Absorbance at 280 nm is frequently used to determine the TPC, as the aromatic rings of the phenolic compounds absorb UV light at 280 nm, causing a characteristic sharp absorbance peak at this

Table 3. Summary of total phenol content (TPC) ranges from studies from various geographical origins, where *n* indicates the number of samples in the study

Geographical origin	TPC range from FCR analysis (mg L^{-1} GAE)	Reference
Spain	178.3–292.7 (*n* = 5)	48
Croatia	292–402 (*n* = 4)	49
Greece	213–277 (*n* = 4)	44
China	189–495 (*n* = 11)	50
Serbia	238.3–420.6 (*n* = 10)	51
Cyprus	224 (*n* = 1)	43

FCR, Folin–Ciocalteu reagent; GAE, gallic acid equivalents.

wavelength.[53] Hydroxycinnamic acids and their derivatives can also be determined using the absorbance at 320 nm.[54]

While all phenolic compounds absorb some UV light at ~280 nm, the signal produced from this analysis gives no information about the phenolic subclasses.[52,55] Moreover, some information is not captured at the 280 nm absorbance due to some phenolic compounds not having an absorbance maximum at this wavelength.[54] Sorbic acid may also distort the 280 nm absorbance results for white wines; however, sorbic acid can be removed using iso-octane. Ascorbic acid and proteins are shown to interfere with the 280 nm signal but only have a minor effect.[54]

UV–visible spectrophotometry was used with principal component analysis (PCA) to successfully create a spectral phenolic fingerprint of Chardonnay juice press fractions over a spectral range of 200–600 nm.[56] The cuvée juice samples could be discriminated from taille samples using spectral fingerprints. This study showed that UV–visible spectrophotometry could not only accurately quantify the total polyphenol content (TPC) of white wines but also act as a reliable discrimination tool. UV–visible spectrophotometry uses reliable instrumentation and offers rapid and cost-effective analysis advantages. UV–visible spectrophotometry can be considered one of the most consistent reference techniques available for total polyphenol content analysis of white wine. However, this method may encounter interferences, which must be considered when interpreting the results of the analysis.

Visible spectrophotometry can also be used to assess the colour properties of wines. In the case of white wines, the relevant phenomena of browning could be assessed. The absorption at 420 nm and 440 nm measures the intensity of the yellow and brown colour of the wines, respectively, with the absorption at 440 nm proposed as the browning index.[53] The CIElab colour space, proposed by the Commission International de l'Eclairage,[57] could also be used to measure the extent of colour oxidation. The method is based on a trichromatic system that simulates the perception of colour by real observers. The coordinates *L*, *a** and *b** provide information about the wine's clarity, red/green and blue/yellow colour, respectively.[53] In the case of white juices and wines the *b** coordinate could be used as an indication of colour oxidation.

CHROMATOGRAPHIC METHODS OF ANALYSIS AND CAPILLARY ELECTROPHORESIS

Gas chromatography–mass spectrometry (GC-MS)

GC-MS allows fast and accurate analysis of complex mixtures. However, it requires a derivatisation step, is prone to thermal degradation and is less capable of analysing compounds of high molecular weight.[58] The derivatisation step is required to reduce the polarity of polyphenolic compounds in order to make them more easily detectable by GC-MS.[59]

The use of GC-MS for the analysis of phenolic compounds is not as popular as liquid chromatography (LC) analysis; however, GC-MS has been successfully employed to identify benzoic acids in white wine samples.[60] GC-MS detected nine phenolic compounds from white wine samples (before and after natural precipitation) in another study.[16] GC-MS was also used to detect the stereoisomers of catechin and epicatechin and five other phenolic compounds in wine samples.[59]

The studies mentioned above employed GC-MS analysis in selected ion monitoring (SIM) mode. GC-MS in SIM mode is suitable for sensitive analyses of phenolic compounds; however, interferences are uncontrollable and may result in inaccuracies.[59] Due to this fact and the need for a derivatisation step GC-MS is not the preferred chromatographic analysis method for white wine phenolics.

Liquid chromatography (LC) and high-performance liquid chromatography (HPLC)

LC and more specifically HPLC can be used with a range of detectors for phenolic analysis in white wine.[61] LC has been proven superior to GC, and has been used in many configurations for a wide range of white wine phenolic analyses. The other advantages of LC, compared to GC, includes sensitivity and accuracy due to lack of thermal degradation and no limitation on the molecular size of compounds that can be analysed.[62] On the other hand, HPLC runs a shorter analysis time than standard LC due to the use of a high-pressure pump to move the solvent, overcoming the pressure drop at the back of the column and reducing elution times. A summary table (Table 4) provides the phenolic compounds detected in each study using LC in its different analytical techniques.

LC coupled with mass spectrometry (LC-MS) can be used to identify the chemical structure of phenolic compounds and hence help classify which compounds are present in a wine sample.[61] LC coupled with diode array detection (DAD) was also successfully used to quantify the concentration of a wide range of white wine phenolics.[63] The detector was programmed to record at 240 nm and 450 nm and the spectra obtained were compared with spectra of pure standards to obtain the concentration of each phenolic compound. The results are shown in Table 4.[63]

White wine samples were analysed using LC-MS with electron spray ionisation and atmospheric pressure chemical ionisation (APCI).[61] Higher sensitivity for the majority of the phenolic compounds was obtained in the APCI negative mode. However, resveratrol detection was achieved only in the positive polarity mode. Gallic acid, protocatechuic acid, caffeic acid, catechin, epicatechin, *trans*-piceid and quercetin glycosides were identified using the MS data. The samples were then analysed with LC-DAD with electrochemical detection (ECD) and fluorescence detection (FD) at 280/325 nm, 260/400 nm and 300–390 nm. The chromatograms obtained with LC-DAD-FD-ECD did not differ significantly from those obtained with the LC-MS. The FD did allow discrimination of fluorescent and non-fluorescent overlapping peaks, and fluorescent compounds, such as resveratrol and piceid, could be identified.[61]

LC-MS was used to analyse phenolic concentrations of wine stored in bottles of varying colours. This shows LC-MS applicability for analysing phenolic compound development in wine.[72] Five

Table 4. Summary of HPLC phenolic analysis for white wine samples

Reference:	4	64*	65**	9***	26*	32***	11***	66*	13*	63*	1*	67*	68*	69*	70*	71*
Instrumentation:	HPLC-DAD-MS/MS	HPLC-DAD	HPLC-DAD-FD	HPLC-DAD and ESI-MS	HPLC-ECD	HPLC-DAD	HPLC-DAD	HPLC-DAD	HPLC-DAD	LC-DAD	RP-HPLC-DAD and HPLC-ESI-MS	RP-HPLC-DAD with monolithic column	HPLC	HPLC-DAD	RP-HPLC-DAD	HPLC (UV detection at 365 nm)
Compound																
Kaempferol	d	nd	0.40	0.02–0.55	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Quercetin	nd	nd	nd	0.05–2.37	nd	2.74–6.45	2.69–8.97	1.4–4.1	nd	nd	0.08–0.12	1.7	1.0–8.07	nd	nd	10.0–185.0
Myricetin	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.26	nd	nd	nd	nd
Rutin	nd	nd	0.17	nd	nd	nd	nd	nd	0.75–0.84	nd	nd	2.7	nd	0.19	nd	nd
Caftaric acid	d	8.33–54.88	nd	1.77–4.76	164.4	13.43–57.14	15.95–87.13	0.5–92.6	9.21–14.67	3.86–53.5	29.00–31.00	12.0–79.0	65.7–116.0	0.02	0.92–1.36	nd
Caffeic acid	d	0.93–3.26	nd	nd	nd	0.04–4.11	2.26–15.29	0.7–25.9	0.92–2.39	nd–2.71	1.3–1.6	0.6–7.7	6.10–8.21	nd	0.92–1.36	nd
Caffeic acid derivatives	d	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Coutaric acid	d	2.78–13.87	nd	0.05–4.37	31.0	0.76–4.94	0.94–3.92	0.6–8.4	0.28–0.65	nd–14.4	0.36–1.2	1.2–18.0	8.72–38.2	0.62	nd	nd
Coumaric acid	d	0.34–1.52	nd	0.03–0.08	0.5	nd	0.28–0.78	0.8–47.2	0.18–1.3	nd–3.04	0.34–0.62	1.4	2.9–3.36	d	d	nd
Fertaric acid	d	1.62–6.12	nd	2.96–5.21	4.7	0.03–4.20	1.14–5.83	1.1–5.8	0.64–1.19	nd	0.7–0.9	nd	1.17–1.74	nd	nd	nd
Chlorogenic acid	Nd	nd	0.14	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Gallic acid	d	0.68–1.42	2.43	1.01–4.36	nd	nd	0.19–6.22	0.6–32	nd	nd–8.37	0.42–0.83	1.6–13.0	0.63–3.20	0.19	0.003–1.2	nd
GRP	d	nd	nd	13.35–28.15	1.3	nd	nd	1.5–18.6	nd	nd	2.3–3.3	nd	4.94–6.87	nd	nd	nd
p-Hydroxybenzoic acid	nd	0.40–1.28	nd	nd	nd	0.56–4.27	0.89–7.97	0.2–38.3	0.26–1.16	nd	0.07–0.10	nd	nd	nd	0.34–4.78	nd
3,4-Dihydroxybenzoic acid	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.47	nd	nd	nd	nd
Ferulic acid	d	0.45–1.76	nd	nd	0.1	0.04–1.44	0.56–1.50	0.3–5.5	0.54–2.00	nd–3.04	d	0.5–1.2	nd	nd	nd	nd
Protocatechuic acid	nd	0.73–2.14	nd	nd	nd	0.03–1.27	0.48–2.20	0.7–11	nd	nd–4.74	0.15–0.32	0.5–1.2	5.37–10.7	0.06	nd	nd
Vanillic acid	nd	nd	nd	nd	nd	nd	nd	nd	Nd	nd	0.22–0.33	0.4	nd	0.05	nd	nd
Syringic acid	nd	0.43–1.13	nd	nd	nd	nd	nd	0.6–2.1	nd	nd–0.47	D	0.41–0.98	nd	0.44	0.009–0.057	nd
Ellagic acid	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.09	0.006–0.19	nd
Sinapic acid	nd	nd	nd	nd	nd	nd	nd	0.1–5.1	nd	nd	nd	nd	nd	nd	0.003–0.76	nd
Astilbin	nd	nd	nd	nd	nd	nd	nd	0.3–102	nd	nd	d	nd	nd	nd	nd	nd
Tryptophol	nd	nd	nd	nd	nd	nd	nd	nd	0.99–1.73	nd–3.04	0.68–1.07	nd	nd	0.10	nd	nd
Engeletin	nd	nd	nd	nd	nd	nd	nd	nd	0.42–0.76	nd–3.47	D	nd	nd	nd	nd	nd
(−)-epicatechin	d	3.16–12.62	1.30	3.35–10.3	nd	nd	1.54–12.37	0.1–1.7	0.13–0.36	nd–10.4	0.5–1.15	2.0–4.4	nd	nd	nd	nd
(−)-epigallocatechin gallate	nd	nd	0.60	nd	nd	nd	nd	nd	nd	nd–15.6	nd	nd	nd	nd	nd	nd
(+)-catechin	d	4.68–17.69	2.20	0.45–9.75	nd	0.06–15.70	3.44–14.85	0.3–102	0.98–1.52	nd–11.1	0.71–2.2	3.1–13.0	2.11–8.38	0.39	nd	nd
Ethyl gallate	nd	nd	nd	nd	nd	0.02–1.56	0.97–1.93	nd	nd	nd	nd	nd	nd	nd	nd	nd
Ethyl caffeate	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd–3.47	nd	nd	nd	nd	nd	nd
Ethyl p-coumarate	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
trans-Resveratrol	nd	0.26–1.61	nd	nd	nd	nd	nd	nd	nd	nd	0.08–0.10	0.32	0.22–0.62	nd	nd	nd
cis-Resveratrol	d	0.36–2.27	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.04–0.60	nd	nd	nd
trans-Piceid	d	0.05–0.87	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.33–1.26	nd	nd	nd
cis-Piceid	d	0.32–3.39	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	1.09–2.70	nd	nd	nd
Tyrosol	d	nd	nd	nd	nd	nd	10.69–39.17	3.5–4.07	8.88–22.6	nd–11.9	31.0–36.0	nd	7.14–8.16	1.69	nd	nd

Table 4. Continued

Reference:	4	64*	65**	9***	26*	32***	11***	66*	13*	63*	1*	67*	68*	69*	70*	71*
Instrumentation:	HPLC-DAD-MS/MS	HPLC-DAD	HPLC-DAD-FD	HPLC-DAD and ESI-MS	HPLC-ECD	HPLC-DAD	HPLC-DAD	HPLC-DAD	HPLC-DAD	LC-DAD	RP-HPLC-DAD and HPLC-ESI-MS	RP-HPLC-DAD with monolithic column	HPLC	HPLC-DAD	RP-HPLC-DAD	HPLC (UV detection at 365 nm)
Compound																
Hydroxytyrosol	d	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Procyanidin A2	nd	nd	0.36	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Procyanidin B1	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd–8.6	nd	nd	nd	nd	nd	nd
Procyanidin B2	nd	nd	nd	nd	nd	nd	nd	0.3–65.1	nd	nd	nd	nd	nd	nd	nd	nd
Total phenols	na	na	7.6	143–297	416	na	15.74–112.37	96–509	na	nd	42–77	na	132–247	na	na	na

Detected (d)/not detected (nd)/not applicable (na)/values expressed as mg L^{-1}; *wine, **grape juices, ***grape juices and wines.
DAD, diode array detection; ECD, electrochemical detection; ESI, electrospray ionisation; FD, fluorescence detection; HPLC, high-performance liquid chromatography; MS/MS, tandem mass spectrometry; RP, reverse phase.

peaks were identified on their chromatograms and were assigned in Table 5 as follows.[72] These phenolic pigments were ascribed to be responsible for the brown colouration (absorption maxima at 440 or 460 nm) of wines exposed to bottle ageing.

Reverse-phase liquid chromatography (RP-LC) has become popular for phenolic analysis. RP-LC differs from standard LC by using a non-polar stationary phase with polar mobile phase allowing for the polar molecules to elute faster than the non-polar molecules. South African white wines were successfully discriminated based on cultivar with the use of RP-LC-DAD for phenolic analysis.[73] The data from this research indicated that epicatechin, caftaric acid and protocatechuic acid were the phenolic compounds that differed significantly between cultivars and hence aided in the discrimination of samples using chemometrics.

HPLC analyses could discriminate white wine samples based on cultivar,[1,66,70,74] and geographical origin.[64,69,75,76] Monitoring the influence of pre-fermentative maceration on phenolic content in white wine is commonly done using HPLC,[9,11,15] as well as the effect of storage conditions on phenolic content.[11,77]

LC as a technique for phenolic analysis is very popular due to its reliability and accuracy. It has become a well-researched area for phenolic content quantification and discrimination. These methods provide detailed information which can be used as reference data for many fields of wine research.

Capillary electrophoresis (CE)

CE is an established analysis method for phenolic compounds in wine samples.[78] CE has the capability of high separation efficiency with a short analysis time and small sample volume. CE can be miniaturised, making it a good candidate for field analysis of phenolic compounds.[78] CE is a separation method of analysis and uses electro-osmotic flow between an anode and cathode as the driving force of the separation.[79] It can be used as an alternative method of analysis to HPLC. Compounds are separated according to their charge-to-mass ratio as the migration time for compounds increases with charge.[79] For separation optimisation in CE analysis, voltage, temperature and electrolyte concentration can be varied as well as the use of additives.[79] A summary table with the phenolic levels reported in CE analysis is presented in Table 6.

CE and HPLC were compared for the analysis of phenolic compounds in white wine samples and no qualitative or significant quantitative differences between the results of the two techniques were found.[79] The concentration values for the phenolics analysed were found to be slightly lower in HPLC *versus* the CE analysis; this was attributed to the capability of CE to give a higher resolution of separation allowing for better quantification. It was shown in this study that CE gives better peak shapes and separation and is a faster analysis when compared to HPLC and was recommended as an appropriate alternative to HPLC for phenolic compound analysis.[79]

Thai white wine samples were analysed with CE to obtain a phenolic profile for these samples. Prior to analysis of the samples, calibration and recovery data were found for 14 standard phenolic compounds.[80] Resveratrol, epicatechin and gentisic acid were not detected in any of the white wine samples;[80] yet, in a similar study, these compounds were detected in their Italian white wine samples.[81] This discrepancy between the two studies may be due to the differences in phenolic composition between white wines of different varieties and geographical origin or the difference in method optimisations that were selected. Great care must be

Table 5. Summary of liquid chromatographic–mass spectrometric data from Maury et al.[72]

Peak	Relative absorbance at 440 nm	MS data (m/z)	UV–visible data	Assignment
Peak 1	100	617	Maxima at 280 and 440 nm with shoulder at 310 nm	(−)-Epicatechin-derived xanthylium cation
Peak 2	97.4	645	Maxima at 280 and 460 nm with shoulder at 310 nm	Ethyl ester of (−)-epicatechin-derived xanthylium cation
Peaks 3 and 4*	99.6 and 99.8	617	Maxima at 280 and 440 nm with shoulder at 310 nm	(+)-Catechin-derived xanthylium cations
Peak 5*	100	645	Maxima at 280 and 460 nm with shoulder at 310 nm	Ethyl ester of (+)-catechin-derived xanthylium cation

All retention times were identical to published data except for peaks indicated with an asterisk (*).

taken when selecting the optimum technique for the CE in relation to the compounds being analysed.

A study was performed which developed an optimum method for analysing phenolic compounds in white wine samples with reasonable limits of detection, linearity, peak area and migration times repeatability.[84] Prior to the analysis of white wine samples using CE, the chromatographic resolution statistic (CRS) equation was used to determine the optimum method for analysis. CRS is a mathematical function that gives a lower value when the chromatographic peaks are well resolved and uniformly spaced.[84] The condition which gave the lowest CRS value in this study was found unsuitable for separating phenolic compounds in wine, so a further optimisation step – response surface analysis – was required.[84] Response surface analysis can determine the influence of various factors and their interactions on the CRS value,[85] and it is commonly used for method optimisation. Calibration methods by recovery, at three concentration levels of ten phenolic standards, were performed prior to the analysis. In this study, kaempferol was the only phenolic compound tested that was not found in any white wine samples.[84] This phenolic compound was not included in the detection profiles in the other studies discussed.[80,81]

One of the disadvantages of CE compared to HPLC is its low sensitivity.[82,86] This is because the phenolic compounds are present at low concentrations in matrices that are highly complex.[87] On-line pre-concentration of samples prior to CE analysis is beneficial as it increases the sensitivity of the method without any loss in separation efficiency[82,88,89] and also simplifies the electropherograms.[87] Pre-concentration steps eliminate the need for sample concentration prior to CE analysis, which minimises the consumption of equipment and solvents and reduces resources and analysis costs.[82]

On-line solid-phase extraction (SPE) was used as a potential pre-concentration step prior to CE analysis of white wine samples.[87] The CE method was coupled with a flow injection system in conjunction with a C18 mini-column, which was used to clean up the wine samples by SPE before the CE analysis was carried out, and this allowed for lower detection limits with the avoidance of interference from other compounds. This method achieved detection of resveratrol and other phenolic compounds, namely gentisic acid, and allowed for reasonable limits of detection, linearity, accuracy and sensitivity.[87]

Large-volume sample stacking (LVSS) was used as a pre-concentration step prior to CE analysis of white wine samples.[82] LVSS works by applying a voltage of opposite polarity in the electrophoretic run after a large sample volume is injected. The polarity is then switched back a few seconds before the analysis. This method allows the sample to be concentrated at the head of the capillary and gives more accurate migration times when the analysis is performed.[88] In this research it was found that LVSS caused a co-elution of ferulic acid and kaempferol; hence another pre-concentration method – reverse electrode polarity stacking (REPSM) – was examined.[82] The REPSM allowed for the separation of ferulic acid and kaempferol peaks. Narirutin, (−)-epicatechin, kaempferol, vanillic acid, rutin, myricetin, morin, cinnamic acid, ferulic acid and p-coumaric acid were not detected in the white wine samples when analysed with CE and REPSM pre-concentration.[82] Further optimisation of both CE and the REPSM pre-concentration step would need to be done for this method to allow for comprehensive detection of more phenolic compounds in white wine samples.

Despite the wide use of UV detection with DAD, electrochemical detection (ED) is also a valid alternative due to the high oxidation ability of polyphenols. ED was reported to have higher sensitivity when compared with UV detection in CE methods.[86] The use of a bare glassy carbon electrode was compared to the use of a glassy carbon electrode modified with multi-walled carbon nanotubes (MWCNT) for CE analysis with amperometric electrochemical detection. This was done to establish the optimum type of electrode needed for analysing white wine phenolics.[83] It was found that glassy carbon/MWCNT electrodes allowed for an increase in sensitivity of signals due to improved resolution and efficiency compared to when the bare glassy carbon electrodes were used.[83] Using the glassy carbon/MWCNT electrode and phenolic standards, detection of phenolic compounds in white wine samples to a high degree of accuracy was possible without the need for a pre-concentration step. The MWCNT electrode also retained its stability despite fouling substances in the wine samples which could cause degradation.[83] The proposed method showed great potential for phenolic compound detection and quantification of some compounds using direct analysis of white wine.

None of the research methods discussed fully comprehensively detect of phenolic compounds in white wine samples. Optimisation of CE for the use in the detection and quantification of phenolic compounds still needs to be performed. However, CE has proven to be a suitable analytical method for the identification of some phenolic compounds as well as providing the option for fast and accurate analysis that may be used in an industrial setting at a reduced cost. However, the necessity of a pre-concentration step and low sensitivity when analysing

low-concentration samples means that HPLC as a method for phenolic analysis is still preferred throughout the industry.

Ultra-performance liquid chromatography (UPLC)

UPLC uses a narrow-bore column packed with very small particles with a mobile phase delivery system operating at high back-pressures.[90] The advantages of UPLC over HPLC are improved resolution, shorter retention times and higher sensitivity.[90] Table 7 summarises the phenolic compounds identified in white wines with UPLC.

Several publications reported phenolic analysis making use of UPLC. Although several of them investigated red wine phenolics, there was also a significant number of studies reporting phenolic content in white wines (Table 7). This might indicate the suitability of this technique to quantify low levels of polyphenols such as those found in white juices and wines. An example of this is presented in work reported by Canedo-Reis *et al.*[100] in which UPLC-MS was used to characterise the phenolic content of juices from multiple varieties.

UPLC was used to characterise the polyphenol composition of Polish wines.[97,102] Moreover, in a study using interspecific hybrid cultivars, minor differences were observed for the phenolic content of white wines when compared to red wines. However, detailed phenolic profiling of the white wines was obtained.[94] The effect of different yeast treatments and fermentation temperatures on the phenolic content was also assessed

with UPLC.[92] In this case, the concentration of the main phenolic families was obtained from calibration curves of selected standards. The total content of phenolic acids, flavan-3-ols and flavonols was calculated as the sum of each compound. Similarly, other publications reported the total content of phenolic families or the total content of polyphenols using UPLC.[90,94,95] UPLC analysis was also applied to quantify the TPC of sparkling wine juices during pressing. The study aimed to generate the reference data needed to build spectroscopy calibrations with an in-line UV–visible spectrometer.[101] Successful calibrations were reported highlighting the potential of UPLC for phenolic analysis. This technique's improved resolution and increased sensitivity showed its suitability to quantify the polyphenol content in sparkling wine juices.

UPLC was also used for the authentication of white wine Greek varieties. In this study, 22 phenolic compounds were identified. Multivariate statistical analysis, using random forest and phenolic data, was able to discriminate between local Greek white wine cultivars.[91] In addition, discrimination of single cultivar wines was attempted with UPLC phenolic analysis, with successful results reported, and with the identification of the phenolic compounds with the highest discrimination ability.[93] The ability of the UPLC systems, often coupled with MS, to provide detailed phenolic composition, even in matrices with low polyphenol content such as white juices or wines, makes this technique one of the most preferred analytical tools for wine scientists. The successful

Table 6. Summary of phenolic analysis by capillary electrophoresis for white wine samples

| Compound | Reference | | | | | |
	82	83	84	80	81	79
Quercetin	0.96–2.92	nd	1.7	2.12	nd	nd
Myricetin	nd	nd	1.6	nd	nd	nd
Rutin	nd	nd	3.2–8.9	3.46	nd	nd
Caftaric acid	nd	nd	nd	nd	nd	1.61–11.37
Caffeic acid	0.99–2.03	nd	1.8–4.4	0.64–4.28	0.5–2.2	0.70–4.06
Coutaric acid	nd	nd	nd	nd	nd	0.29–8.77
o-Coumaric acid	nd	nd	nd	nd	0.3–0.7	nd
p-Coumaric acid	nd	nd	2,1	1.15–1.13	0.8–1.0	0.21–7.47
Cinnamic acid	nd	nd	nd	0.49–1.54	nd	nd
Gallic acid	0.97–1.63	2.00–12.0	1.6–2.9	1.25	0.6–3.5	5.52–20.67
p-Hydroxybenzoic acid	nd	nd	nd	0.73–0.75	0.2	nd
3-4-Dihydroxybenzoic acid	0.99–1.24	nd	nd	nd	nd	1.25–12.86
Ferulic acid	nd	nd	nd	nd	nd	0.31–1.07
Protocatechuic acid	nd	nd	nd	0.60–0.94	0.1–1.1	nd
Vanillic acid	nd	nd	nd	nd	0.1–0.6	nd
Sinapic acid	nd	nd	nd	nd	0.1–0.4	nd
Syringic acid	nd	nd	1,3	2.64–6.09	0.1–0.2	0.01–1.37
Salicylic acid	nd	nd	nd	0.50–0.60	0.2–1.0	nd
Gentisic acid	nd	nd	nd	nd	0.2–0.3	nd
(+)-Catechin	1.36–2.96	11.0–38.0	12.4–23.4	0.92–1.7	0.1–4.9	nd
(−)-Epicatechin	nd	nd	nd	nd	0.3–2.8	3.16–158.1
Epicatechin gallate	nd	nd	nd	nd	1.2–1.3	nd
trans-Resveratrol	3.31	nd	0,9	nd	0.1–0.3	nd
cis-Resveratrol	nd	nd	nd	nd	0.2–0.3	nd
Tyrosol	nd	nd	nd	nd	1.1–3.0	0.95–3.73
Hydroxytyrosol	nd	nd	nd	nd	1.6–2.7	nd

Results are in units of mg L^{-1}; non detected (nd).

application of UPLC analysis for quantification/profiling, authentication or discrimination seems also to indicate the potential of this technique.

ELECTROCHEMICAL METHODS OF ANALYSIS

Voltammetry

Cyclic voltammetry (CV)

Cyclic voltammetry (CV) has proven to be a powerful and rapid tool for characterising the antioxidant properties of white wines and their phenolic content.[102-105] The structure of phenolic compounds allows them to act as antioxidants, making them detectable through CV analysis. Quantification is performed using the area under the anodic peaks in the cyclic voltammograms. The anodic current is produced when the phenolic compounds in a sample are oxidised. Kilmartin has been a significant contributor to this field of research[106] and some of his studies will be discussed in this chapter, along with other research that uses CV for analysing the phenolic content of white wine.

CV has been used to characterise phenolic acids and flavonoids in white wine samples.[102] FCR was used as the reference method for TPC and it was found that the CV measurements were generally four to five times lower than the FCR results. This was attributed to the fact that a lot of the white wine phenolics are only detectable by CV when a potential greater than 500 mV is used, which was not the case in this study.[102]

In another study, a significant CV current was generated from white wine samples when operating with a potential greater than 750 mV and was attributed to vanillic, coumaric and coutaric acid.[105] However, GAE data for TPC was collected using a potential of 500 mV (Q_{500}). When this was compared to FCR data it was found that there was a 20–30% increase in the TPC measured with FCR as GAE.[105] Nonetheless, a good correlation was observed between the total phenols measured and the electrochemical response, shown by a straight line when CV Q_{500} values were plotted against FCR values.

Furthermore, in this study, seven phenolic compounds were detected and their concentrations were quantified by HPLC analysis for the white wines,[105] and these results correlated very well with the CV analysis performed. The correlation was performed by creating simulated voltammograms using the HPLC data and CV data for phenolic standards and comparing the simulated voltammograms to the experimental voltammograms.[105]

CV as a method for phenolic analysis was compared with normal-phase HPLC, reverse-phase HPLC and FCR in a study.[107] Again, only the Q_{500} measurements were used; hence the CV results only reflected the TPC of compounds containing pyrogallol, gallate and catechol groups such as flavanols, proanthocyanidins, flavonols and phenolic acids, and therefore a major part of white wine phenols were not included in the measurement.[107] No significant correlation was found between the FCR results and the CV results and it was suggested that the difficulties in quantifying total current in voltages above 500 mV would need to be overcome to obtain more accurate results for CV analysis of phenolic compounds. However, it was concluded that CV under 500 mV does provide qualitative and semiquantitative information about the easily oxidisable polyphenols.[107]

Another study used CV at a glassy-carbon electrode to characterise the phenolic content of Sauvignon Blanc grape juice.[108] The electrochemical method results were compared with RP-HPLC and the FCR method. Using the RP-HPLC data, the peaks of the voltammograms were assigned to caftaric acid, 2-S-glutathionyl caftaric acid (grape reaction product), cis- and trans-coutaric acids, quercetin 3-O-glucoside and quercetin 3-O-glucuronide, and two non-phenolic compounds. Furthermore, a good correlation between the TPC of the juices, determined by FCR, and the area under anodic current for scans taken to 700 mV.[108]

CV voltammograms were recorded in the potential range of −100 to 1200 mV and, therefore, all of the TPC of white wine samples could be detected.[104] The voltammograms showed a peak at 480 mV, which was attributed to catechol-containing hydroxycinnamic acids and a further peak at 900–1000 mV, which was ascribed to polyphenolics with a higher formal potential, such as coumaric acid and its derivatives.[104] The TPC of the wines was successfully measured by the size of the voltammetric peaks, once the SO_2 had been removed.[104] The CV approach for quantitative analysis of the phenolic compounds in white wine proved very effective in this research.[104]

CV was used to evaluate electrochemically active components in wine for identification purposes.[109] Voltammograms called 'redox spectra of wines' were resolved into a set of peaks corresponding to the redox potential of the different phenolic groups. CV could therefore be used for wine identification using this simple approach. However, this technique still requires further investigation to account for the numerous factors affecting the redox spectra of wines.[109]

The principle put forward by the study previously discussed was used to establish a method of phenolic characterisation for wines using CV.[110] One white wine was analysed in this study and it was concluded that wine characterisation could be accomplished by evaluating the electrochemical properties of phenolic compounds present in the wines.[110] The distribution of the phenolic compounds in the wines when analysed with CV could be used for identification and authentication purposes.[110] Furthermore, disposable graphite-based screen-printed electrodes (SPEs) were successfully used to carry out the analysis. It was suggested that SPEs are beneficial to use as they are inexpensive and can be mass produced, and the fact that they are disposable means the problem of electrode fouling is avoided.[110] Therefore, going forward, this method could be efficient for wine authentication analysis due to its low cost and applicability.

CV was compared to FCR and the DPPH assay for white Croatian wines.[111] The TPC results for the CV analysis were lower than that of the FCR method, but once again only analysis up to a potential of 500 mV was used, ignoring a high proportion of white wine phenolics that register at voltages above 500 mV.[111] The TPC coefficient of determination between the Q_{500} and the FCR results was moderately good ($r^2 = 0.830$), while a better coefficient of determination, of $r^2 = 935$ was found when the TPC was derived from the anodic peak current (I_A) for white wines.[111] However, the coefficient of determination between the white wine TPC and the antioxidant activity, as measured by the DPPH assay, was relatively poor ($r^2 = 0.686$), and this discrepancy was attributed to the fact that white wines have a lower concentration of phenolic compounds with radical scavenging ability than red wines.[111]

CV shows excellent promise as a method of phenolic analysis and could potentially be used as an alternative to FCR and UV–visible absorbance spectroscopy.[104] While some limitations are still associated with this method, such as the inaccuracies in measurements for applied voltages above 500 mV, CV methods are still being developed, and ways of overcoming these limitations are being established.

Table 7. Summary of phenolic analysis by ultra-performance liquid chromatography (UPLC) for white wine samples

Reference:	91	92	93	94	95	96	97	98	99	90
Instrumentation: Compound	UPLC-QTOF/MS	UPLC-PDA	UPLC-QqQ-MS/MS	UPLC-PDA MS/MS	UPLC-DAD-fluorometer	UPLC-MRM-MS	UPLC-PDA	UPLC-PAD	UPLC-PDA	UPLC MS/MS
Quercetin 3, 7, 4'-tri-glucoside	nd	nd	nd	tr-0.09	nd	nd	nd	nd	nd	nd
Quercetin 3, 4'-diglucoside	nd	nd	0.01–0.06	nd	nd	nd	nd	nd	nd	nd
Quercetin 3, 7– di-glucoside	nd	nd	nd	0.01–0.08	nd	nd	nd	nd	nd	nd
Myricetin 3-rutinoside	nd	nd	nd	0.11–0.35	nd	nd	nd	nd	nd	nd
Myricetin 3-glucoside	nd	nd	nd	4.57–9.97	nd	nd	nd	nd	nd	nd
Quercetin 3-rutinoside	nd	nd	nd	0.67–1.34	nd	nd	nd	nd	nd	nd
Quercetin 4'-glucoside	nd	nd	nd	0.94–1.77	nd	nd	nd	nd	nd	nd
Quercetin 3-glucoside	nd–1.2	nd	nd	3.10–13.37	nd	nd	2.2	nd	nd	nd
Dihydroquercetin 3-rhamnoside	nd	nd	nd	0.55–1.59	nd	nd	nd	nd	nd	nd
Kaempherol 3-glucoside	nd	nd	nd–0.04	0.35–0.98	nd	nd	1.1	nd	nd	nd
Kaempherol 3-gluconoride	nd	nd	nd–0.03	nd	nd	nd	nd	nd	nd	nd
Quercetin 3-rhamnoside	nd	nd	nd	0.45–1.30	nd	nd	nd	nd	nd	nd
Quercetin 3-glucuronide	nd	nd	0.03–0.88	0.22–0.39	nd	nd	nd	nd	nd	nd
Isorhamnetine 3-glucoside	nd	nd	nd	0.08–0.48	nd	nd	nd	nd	nd	nd
Rutin	nd	nd	nd–0.22	nd	nd	nd	nd	nd	nd–2.77	nd
Naringenin	nd–0.47	nd	nd	nd	nd	nd	nd	nd	nd	nd
Taxifolin	nd–0.2	nd	0.23–1.11	nd	nd	nd	nd	nd	nd	nd
Astringin	nd	nd	nd–0.09	nd	nd	nd	nd	nd	nd	nd
Procynidin B1	nd	nd	2.11–18.59	1.94–6.76	nd	nd	nd	nd	nd	nd
Procyanidin B3	nd	nd	0.21–1.48	0.36–2.18	nd	nd	nd	nd	nd	nd
(+)-Catechin	0.71–16	nd	3.10–17.92	8.43–33.32	nd	nd	0.9–1.2	0.73–23	nd–5.34	nd
Procyanidin B4	nd	nd	nd	0.29–2.38	nd	nd	nd	nd	nd	nd
Procyanidin B2	nd	nd	nd	0.62–5.03	nd	nd	nd	nd	nd	nd
(−)-Epicatechin	nd–16	nd	1.51–3.33	11.53–27.73	nd	nd	9.8–36.9	nd	nd–30.42	nd
(−)-Epicatechin 3-gallate	nd	nd	nd	0.59–3.21	nd	nd	nd	nd	nd	nd
Epigallocatechin	nd	nd	0.05–1.62	nd	nd	nd	nd	nd	nd	nd
Gallocatechin	nd	nd	0.24–1.53	nd	nd	nd	nd	nd	nd	nd
Gallic acid	nd–15	nd	6.62–16.68	0.51–1.21	nd	61.09–84.75	0.2–0.4	nd	nd	3.68
GRP	nd	nd	nd	nd	2.69–3.67	69.16–114.91	nd	nd	nd	nd
Caftaric acid	nd	nd	9.38–41.03	9.42–21.44	nd	nd	nd	nd	nd	nd
Protocatechuic acid	nd–3.5	nd	nd	0.16–1.48	nd	nd	4.3	nd	nd	2.52
Coutaric acid	nd	nd	0.98–16.67	4.43–10.18	nd	75.24–84.93	nd	nd	nd	nd
Caffeic acid	0.39–25	nd	0.43–1.17	1.33–3.21	nd	2.39–5.21	nd	0.16–19.4	nd	1.25
p-Coumaric acid	0.57–25	nd	nd	0.19–1.16	nd	0.24–0.66	1.8–2.9	nd	nd	0.3
m-Coumaric acid	nd	nd	nd	nd	nd	nd	0.1–0.2	nd	nd	nd
Ferulic acid	nd–1.2	nd	0.05–0.16	0.03–0.44	nd	0.6–0.7	nd	nd	nd	0.15
4-Hydroxybenzoic acid	nd–0.76	nd	0.01–0.18	nd	nd	nd	nd	nd	nd	5.83

Table 7. Continued

Compound	91 UPLC-QTOF/MS	92 UPLC-PDA	93 UPLC-QqQ-MS/MS	94 UPLC-PDA MS/MS	95 UPLC-DAD-fluorometer	96 UPLC-MRM-MS	97 UPLC-PDA	98 UPLC-PAD	99 UPLC-PDA	90 UPLC MS/MS
2,5-Dihydroxybenzoic acid	nd	nd	0.25–0.35	nd	nd	nd	nd	nd	nd	nd
Salicylic acid	nd–1.4	nd	nd	nd	nd	nd	nd	nd	nd	0.34
Gentisic acid	nd–1.6	nd	nd	nd	nd	nd	nd	nd	nd	0.77
Vanillic acid	nd–0.58	nd	0.03–0.13	nd	nd	nd	nd	nd	nd	0.38
Syringic acid	nd–1.3	nd	nd	nd	nd	nd	0.3–1.7	nd	nd	nd
Fertaric acid	nd	nd	2.01–3.2	nd	nd	19.48–21.06	nd	nd	nd	nd
Hydroxytyrosol	nd–4.2	nd	nd	nd	nd	nd	nd	nd	nd	nd
Tyrosol	0.21–35	nd	nd	nd	21.97–25.70	nd	nd	nd	nd	nd
trans-Piceid	nd	nd	nd–0.09	0.01–0.08	nd	nd	nd	nd	nd	nd
cis-Piceid	nd	nd	0.40–1.96	0.02–0.25	nd	nd	nd	nd	nd	nd
trans-Resveratrol	nd–1.7	nd	nd	0.02–0.13	nd	nd	2.4	nd	nd–0.16	nd
cis-Resveratrol	nd	nd	nd	0.15–0.33	nd	nd	nd	nd	nd	nd
Flavonols	NA	0.1–1	NA	14.62–26.22	NA	NA	NA	NA	NA	NA
Flavan-3-ols	NA	123.3–355.1	NA	37.06–66.13	0.25–1.31	NA	NA	NA	NA	NA
Phenolic acids	NA	9.7–45.6	NA	16.83–36.10	45.88–63.08	NA	NA	NA	NA	NA
Stilbenes	NA	nd	NA	0.24–0.68	NA	NA	NA	NA	NA	NA
Total	NA	143.3–394.2	NA	87.62–105.56	NA	NA	NA	NA	NA	15 215

Not detected (nd)/not applicable (NA)/values expressed as mg L^{-1}.
DAD, diode array detection; MRM, multiple reactions monitoring; MS/MS, tandem mass spectrometry; PDA, photodiode array; QqQ, triple quadrupole; QTOF, quadrupole time of flight.

17
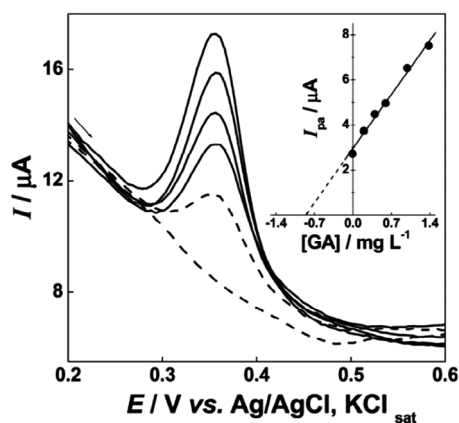
Figure 1. Differential pulse voltammetry response curve with calibration curve (insert) obtained for determination of gallic acid (GA) in white wine samples. Dashed and solid lines represent a black measurement and actual sample measurements, respectively.[114]

Differential pulse voltammetry (DPV)

The use of DPV *versus* CV for the analysis of wine samples has been explored.[115,116] It has been determined that DPV is less sensitive to the interferences caused by SO_2 content compared to CV[112,114] and hence may be more applicable to white wine analysis. DPV results for wine have not shown a good correlation with TPC yet have proven to correlate well with the results from antioxidant assays.[113] CV and DPV differ substantially in their electrochemical responses by their susceptibility to residual current, the time base of the analysis and the shape of the voltammetric curve.[112] DPV is less sensitive to residual current, and the contribution for polyphenolic compounds is more significant when compared to CV.[112] DPV use for phenolic analysis in wines is less explored than CV analysis but it has promise due to its lower sensitivity to interferences caused by SO_2 and poison species.[112-115] While TPC of white wines may be difficult to determine using DPV, the results have shown to have a good correlation with antioxidant capacities of white wine as well as FCR results (GAE).[113-115]

DPV was used to determine the antioxidant capacity of white wine samples.[114] The authors were specifically demonstrating the effectiveness of carbon nanotube-modified electrodes for this purpose. FCR was used as a reference method to determine the TPC as GAE, which the authors then compared to the results of DPV.[114]

The GAE for the DPV analysis for the white wine samples were determined using a calibration curve obtained with gallic acid standard solutions.[114] The DPV curve for the wine samples and the calibration curve are shown in Fig. 1. The relative error for the DPV and FCR results, by comparison, was low (Table 8) and hence from these results it was concluded that the TPC could be estimated as GAE using DPV.[114]

A similar study was performed in which DPV was used to determine the antioxidant capacity of white wines and FCR was again used as a reference method for TPC determination.[115] The DPV curve obtained showed two peaks: one which was related to *ortho*-diphenolic compounds (quercetin, rutin, caffeic acid and gallic acid), and the other which was associated with monophenols such as ferulic acid, resveratrol, malvidin and coumaric acid.[115] A good correlation was obtained between the TPC results from the FCR and the DPV, demonstrating that DPV could be used to estimate TPC for white wine samples.[115]

DPV as a method for phenolic analysis for white wines will need to be examined further in order to establish the full potential of this method, but it does present a valid alternative to CV as it allows for the correction and minimisation of distortions caused by SO_2 and other wine additives, which CV does not.[112-115] As well as this, it is a stable, reproducible and inexpensive form of analysis, significantly when carbon nanotube-modified electrodes are used, which allow for a longer lifetime of the apparatus and less waste of wine samples.[114]

While the advantages of electrochemical analysis for white wine phenolics are clear, there is an essential requirement for method optimisation in this field of analysis. As more research is pursued, the documentation of the benefits and limitations associated with method optimisation and modifications will allow for better analyses to be performed using electrochemical techniques.

Linear sweep voltammetry

Linear sweep voltammetry using disposable electrochemical sensors with carbon paste working electrodes for the rapid fingerprinting of oxidisable phenolics in white wines has been successfully explored.[116] The deposable sensors used was a commercial Nomasense Polyscan electrochemical analyser. The analysis was run in less than 1 min and no sample preparation was necessary. This analysis gives rise to a portable device that can be used in wineries for the voltammetric analysis of white wine. Using an electrochemical technique such as linear sweep voltammetry coupled with disposable carbon paste sensors allows for rapid, simple measurements[116] superior to others discussed in this section.

Linear sweep voltammetry using disposable carbon paste electrodes was used to analyse the evolution of 13 commercial white wines under conditions of controlled oxidation.[117] The voltammograms correlated well with oxygen consumption rates as well as giving an 'oxidation signature' of the wines using the easily oxidisable flavanols and ascorbic acid.[117]

Another study performed monitored white wine's antioxidant pattern during early winemaking steps.[118] This study was performed using linear sweep voltammetry with disposable single-use electrodes at an industrial scale. The methodology was successful and insights into the impact of different winemaking techniques on the oxidisation of phenolic compounds was established.[118]

SPECTROSCOPIC METHODS FOR THE ANALYSIS OF PHENOLIC COMPOUNDS

Infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy
FTIR spectroscopy is a method for obtaining the entire infrared spectrum of a sample.[119] FTIR is often used with attenuated total reflectance (ATR) cells as opposed to regular sample spectroscopic cells. The use of ATR cells minimises the effect that sample turbidity and window wear may have on the path length due to the cleaning of transmission cells.[120] FTIR offers a method of analysis which has improved signal-to-noise ratio and accurate spectra can be obtained.[119]

FTIR successfully provides information related to the chemical composition and structure of polyphenols.[121] The region used for identifying phenolic compounds is known as the 'fingerprint region' of the spectrum and is in the range of 1800–900 cm^{-1}. Focusing on this region allows for the interference caused by the intense band of —OH groups absorbance at 3600–

2900 cm^{-1} to be ignored. This band occurs due to water and ethanol found in wine samples.[122] In the 'fingerprint region' several peaks were found that correlated with different chemical compositional aspects of phenolic compounds. These are outlined in Table 9.[123] In a second study,[124] FTIR was used for the analysis of phenolic compounds in white wine samples but the 'fingerprint region' was not focused on the range of wavelengths where there is a more significant contribution from the ethanol and water in the samples. This may have caused inaccuracies in their results.

FTIR was also used to predict total phenolics in Moscatel dessert wines.[122] For this study, partial least squares (PLS) models were developed to allow for the prediction of the TPC of the wines. This was done by performing spectrophotometric analysis using FCR and a reference standard of gallic acid to quantify the TPC of the wines. The average TPC was found to be 1090 ± 123 GAE mg L^{-1}. FTIR-ATR was performed for each sample over the spectral range of 4000–650 cm^{-1}, though only the 'fingerprint region' was selected for the operating range.[122] The FTIR results were combined with the results of the reference method for TPC in order to establish a calibration range using the PLS model. A good correlation coefficient, $r = 0.933$, was found for the TPC and FTIR data.[122] The conclusion was that FTIR-ATR is a valuable tool for the analysis of TPC.

A similar study confirmed this conclusion once again. In this study, FTIR-ATR was used to analyse white wine throughout the winemaking process (at various stages from crushing to final wine) alongside a TPC reference method to monitor the evolution of the phenolic compounds during the winemaking process.[125] The wine analysed in this study was a blend of Pinot Blanc, Traminer Rot and Sauvignon. The reference method for TPC used was UV–visible absorbance at 280 nm, where quantification was achieved using a calibration curve built with gallic acid standards of varying concentrations.[125] PLS regression was used in this study to construct calibration models and allowed for the determination of TPC using FTIR analysis.[125] The corroboration of the conclusions of these studies shows that FTIR is a method that can be applied successfully to white wine of different cultivars and styles during the entire winemaking process.

FTIR-ATR could discriminate white wine based on its cultivar using UV–visible spectrophotometry reference data for TPC.[121] Two different white wine cultivars were analysed: Dafni and Vilana. The analysis was focused on the 'fingerprint region', and categorising the wines based on cultivar was done using PCA and linear discriminant analysis. Complete discrimination of the wine samples based on cultivar was achieved using this method.[121]

These studies demonstrate that FTIR can be used as a method of analysis for phenolic compounds found in white wines and can allow for the determination of TPC and discrimination of samples based on cultivar. It appears to be a suitable method of analysis with potential implementation in the industry due to its versatility, rapidness, and non-invasive and low-cost nature;[121] however,

the interpretation of the spectra does require professional knowledge. Commercial infrared instruments do exist, but calibrations for white wine phenolics are often not provided. Further studies could be attempted to establish a database for TPC using FTIR spectra and to investigate the ability of FTIR for discrimination of samples based on other factors.

Near-infrared (NIR) spectroscopy

NIR spectroscopy has been used for the discrimination of white wine samples based on cultivar and geographical origin,[126,127] but these studies focus on the overall chemical contributions to the spectra and not specifically on the contributions of the phenolic compounds to the spectra. However the contribution of the phenolic content of the samples influenced the discrimination factors.[126] NIR hyperspectral imaging is a non-destructive, rapid and accurate form of analysis that has been explored for the determination of TPI in white grapes.[128,129]

NIR hyperspectral imaging has been explored to determine the TPC in white grapes. NIR hyperspectral imaging combines the advantages of NIR spectroscopy and microscopy, and allows for non-destructive, rapid and accurate analysis.[128,129]

NIR hyperspectral imaging was also used to determine TPC in white wine samples.[128] FCR was used as the reference method for TPC determination, and calibration models were constructed by combining the reference data and the results from the hyperspectral imaging.

The standard error of prediction for the TPC of the samples was found to be too large for accurate predictions to be performed from the calibration model. It was concluded that these errors resulted from high spectral variability in the white grape samples.[128] These errors may have been more minor if another reference method for the TPC had been used, as it is well documented that there are many interferences, such as SO$_2$ and ascorbic acid content,[1,34,36] that may cause inaccuracies in the FCR results for white wine samples.

A similar study, where the phenolic compounds were determined in white grape pomace,[129] was performed. The reference analysis methods used for quantifying the individual phenolic compounds were rapid-resolution liquid chromatography, UV–visible absorption spectroscopy and mass spectrometry. A calibration model was then produced from each sample's reference data and the NIR spectra. Twenty-seven individual phenolic compounds, as well as TPC for the samples, were able to be determined quantitatively.[129] The R^2 value for the TPC was 0.92, which indicates that the calibration model could determine the TPC quantities with a high degree of accuracy.[129]

While this study[129] was done for grape pomace, the method employed could also be applicable to white wine samples. Further studies will be needed to confirm whether NIR hyperspectral imaging can be applied to the determination of the TPC of white wines. Infrared spectroscopy offers a non-invasive and destructive

Table 8. TPC determination (gallic acid equivalents, GAE) of white wine samples using differential pulse voltammetry (DPV) and Folin–Ciocalteu reagent (FCR)[114]

Sample	DPV (GAE mg L^{-1})	FCR (GAE mg L^{-1})	Relative error (%)
White wine 1	229.1	244.2	−6.59
White wine 2	219.6	224.5	−2.18
White wine 3	265.8	275.3	−3.45

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19

Table 9. Fourier transform infrared spectral bands and wavenumbers associated with characteristic vibrational modes of phenolic compounds[123]

Vibrational mode	Wavenumber
$C=O$ stretching	1712–1704 cm^{-1}
$C=C$ stretching	1609–1608 cm^{-1} and 1519–1516 cm^{-1}
—CH_3 antisymmetric in-plane bending	1448–1444 cm^{-1}
—CH_3 symmetric in-plane bending	1376–1373 cm^{-1}
CH bending and CH_2 wagging	1340–1339 cm^{-1}
O—H in-plane bending	1281–1278 cm^{-1}
C—O stretching	1207, 1110–1107, 1068–1062 cm^{-1}

approach to analysis and would be very applicable to the wine industry if used to its full potential.

Fluorescence spectroscopy

Fluorescence spectroscopy has become a method of increased interest for analysing the phenolic compounds in wine over the last few years. It is a rapid, low-cost, non-destructive, non-invasive, sensitive and specific form of analysis.[130-133] Fluorescence spectroscopy works well for phenolic analysis as most of the phenolic compounds found in wine are intrinsically fluorescent due to the presence of conjugation in the molecules.[134] The use of fluorescence spectroscopy for classifying white wine based on cultivar and geographical origin has been explored,[135,136] and fluorescence spectroscopy has been used to determine the quality of sparkling wines.[133] Little research has been done into applying fluorescence spectroscopy to quantify the TPC of white wines.

Fluorescence spectroscopy was used to investigate how different concentrations of sulfur dioxide addition to grape must affect the phenolic content of white wines.[132] The wines were analysed with the reference method of UPLC-DAD to establish the phenolic composition of the wines. After bottle aging, the SO_2-treated wines were analysed, and assessed using a calibration model.[132] There were three SO_2 concentrations used in the treatments: 0, 4 and 8 g hL^{-1}. The fluorescence landscapes and UPLC data suggested that the phenolic composition of the wines was unchanged with the level of SO_2 used, yet the intensity of the fluorescence signal increased with increasing SO_2 concentrations. It was suggested that this was because the phenolic compounds were better preserved with the higher additions of SO_2, as supported by the results of the UPLC analysis.[132] A scores and loading plot of PLS-DA analysis of the parallel factor analysis (PARAFAC) data for the treated wines showed clustering of wines based on treatment. The conclusion from this was that fluorescence spectroscopy can discriminate wine based on winemaking practices such as SO_2 addition.[132] Studies to establish the range of winemaking practices that could be identified using fluorescence spectroscopy are not currently available.

Fluorescence spectroscopy was used to determine the quality of sparkling wines, defined by degree of browning.[133] The degree of browning was examined after storage of the wines after an accelerated browning process. The fluorescence data were compared to UV–visible absorbance at 420 nm (A_{420}) and hydroxymethylfurfural (5-HMF) content, which are standard quality parameter analysis methods. This research found that a linear and highly correlated trend existed between the two fluorescence peaks, at 465 nm(ex) and 530 nm(em) and 280 nm(ex) and 380 nm(em), and the data from the A_{420} and 5-HMF content analysis.[133] This allowed for the conclusion that fluorescence spectroscopy could provide an efficient and accurate determination of non-enzymatic browning of white wines, which can be used as an alternative to the usual indication methods, such as UV–visible spectroscopy, HPLC and tristimulus colourimetry, which are expensive and time consuming.[133]

In another study, white wines were discriminated based on cultivar using fluorescence spectroscopy and chemometrics.[135] Three cultivars – Torrontés, Chardonnay and Sauvignon Blanc – could be well discriminated using the successive projection algorithm with linear discriminant analysis and also with unfolding–partial least squares discriminate analysis.[135] A similar study demonstrated that white wines could be discriminated based on cultivar and geographical origin using PARAFAC, PCA and soft independent modelling of class analogy. In this study, wines of four cultivars – Chardonnay, Pinot Gris, Riesling and Sauvignon Blanc – and from two geographical origins – France and Romania – were discriminated.[136] The excitation–emission matrices produced by the fluorescence spectroscopy, in these studies, show profiles evidentially specific to each cultivar and geographical origin based on fluorophores present as well as the intensities of the signals.[135,136] This supports the idea that fluorescence spectroscopy is a valuable tool for the discrimination of different wine samples based on these parameters and can be applied in the future for authentication purposes. Fluorescence spectroscopy coupled with advanced mathematical modelling, using benchtop instruments[131,137] or even portable devices,[138] has proven to have specificity for phenolic compounds in red wine. However, such calibrations have not yet been explored in white wines. Applications of this method, with the aid of calibration models for quantifying phenolic compounds in white juices and wines, should be explored in the future. Fluorescence spectroscopy measurements can easily be adapted for handheld devices and for on-/in-line process monitoring.[138] These developments are being explored in research for industries beyond wine.[139] There seem to be good prospects for future developments in fluorescence spectroscopy for quantification analysis of fluorescing phenolic compounds.

Raman spectroscopy

Raman spectroscopy was used to analyse white wine phenolic acids and sugar components.[143,144] This research was proposed to fill a gap in the literature as only one paper[142] had so far been published documenting the use of Raman spectroscopy for white wine analysis, where the ethanol content of the wine was determined.

One Bordeaux dry wine and one Bergerac medium-dry wine were analysed alongside reference samples, made with pure phenolic compounds or sugars dissolved in a model wine solution.[140] From the UV–visible spectra for these samples it was clear that the hydroxycinnamic acids present in the wines showed a peak at 326 nm, a peak at 263 nm for the medium-dry wine, and a 273 nm peak for the dry wine, which were assigned to the hydroxybenzoic acid: gallic acid.[140]

The UV–visible analysis results were correlated with the results of the laser-induced fluorescence spectra when 325 nm excitation was used, and a maximum was observed at 440 nm for the hydroxycinnamic acids present in each wine. The maxima differed in intensity due to the compositional differences in hydroxycinnamic acids for the dry and medium-dry wine.[140] The

hydroxybenzoic acids did not display any fluorescence at 325 nm and neither of the phenolic acids displayed significant fluorescence for the 532 nm and 785 nm excitation wavelengths.

The Raman spectra for each sample were recorded for 325 nm, 532 nm and 785 nm excitation wavelengths. The 325 nm spectra, once it had been corrected for fluorescence background using fit by a polynomial, showed two strong lines at 1600 cm^{-1} and a few weaker signals at around 879 cm^{-1}. These peaks corresponded to those displayed by the caffeic acid and gallic acid model solutions, respectively, when they were analysed using Raman spectroscopy at 325 nm.[140]

These results allowed the team to conclude that it would be possible to identify the main species of hydroxycinnamic acids in white wine using Raman spectroscopy.[140] This research group performed another study to explore this use of Raman spectroscopy further.[141] Model wine solutions were prepared for gallic acid and each of the main hydroxycinnamic acids: caffeic, caftaric, p-coumaric, ferulic and sinapic acid.

The resonance Raman spectra (RRS) and normal Raman spectra for each model solution were obtained. RRS at 325 nm enhanced the peaks for caffeic acid and additional peaks for gallic acid compared to that of normal Raman spectra at 532 nm. The peaks for gallic acid in RRS were negligible in comparison to the intensities of the peaks for the hydroxycinnamic acids.[141] The RRS for the individual hydroxycinnamic acids were then obtained by subtracting the spectrum of the model wine solution.

A comparison was then made between the RRS of a dry wine sample and a synthetic solution, made by weighted addition of the RRS of the model wine solution with those of p-coumaric acid and caftaric acids. These spectra were seen to be similar as indicated by the observation of peaks at 1600 cm^{-1} seen in the spectra. The peak at 1174 cm^{-1} could be attributed to p-coumaric acid.[141] These spectra were comparable by the observation of the peaks at 1600 cm^{-1}, seen in both of the RRS, after subtraction of the model wine solution, for these hydroxycinnamic acids as well as a peak at 1174 cm^{-1} seen in the RRS, after subtraction of the model wine solution, for p-coumaric acid.[141] This research concluded that hydroxycinnamic acids could be qualitatively analysed in white wine samples using Raman spectroscopy.[140]

The use of a dry white wine for this study was beneficial as it eliminated the Raman signals caused by sugars present in the wine, as seen in the medium white wine sample from the first study discussed in this chapter.[140] This may indicate that Raman spectroscopy for analysing the hydroxycinnamic acids in wine samples that still contain high levels of sugar would not be as straightforward. These studies[140,141] do not demonstrate how Raman spectroscopy can be used for the quantitative analysis of these phenolic compounds, and further research may be needed to unlock this analytical method's true power. Investigations into improvements of this method would be advisable due to its benefits, such as a small sample volumes and non-destructive nature, and its suitability for in situ measurements with the use of fibre optics.[140] It should be noted that surface-enhanced Raman spectroscopy (SERS) can be employed to improve the signals obtained from samples for low-concentration applications. The signal is increased through electric field enhancement with the aid of a noble metal substrate.[143]

FUTURE PROSPECTS

As the wine industry grows, process control strategies are becoming apparent.[144] These strategies are analytical tools which help ensure that quality standards are met. The tools provide real-time information about the process and the future product. These methods should be efficient, cost effective and non-destructive to maximise their beneficial effect.

Spectral analysis meets these method requirements and is becoming frequently used as a process control strategy in the food industry. Spectroscopy offers rapid analysis with minimal sample preparation and applies to on-line or in-line analysis.[144] The advancement of chemometric methods has aided in the popularity of spectroscopy as a process control tool. Chemometric methods allow for extracting relevant information from the chemical data to create calibration models for a range of information. Spectroscopic methods are currently being used in the food and wine industry as tools for quantification, classification, discrimination, identification and detection of adulteration of products.[144]

Having discussed the importance of white wine phenolics, it is easy to understand why there is much interest in developing process control strategies with the capability of monitoring phenolic compounds during the winemaking process. The ideal process monitoring system should not be invasive and able to provide detailed information without interfering with the process itself.[145] Hence the focus on creating a portable, on-line/in-line monitoring device for phenolic compounds is clear from the studies being performed.

For a method of analysis to be compatible with a commercial setup, the linkage between the analysis performed, the data processing and the calibration model construction must be robust and accurate. The spectrometric analysis methods, such as infrared and fluorescence spectroscopy, have shown the potential to create comprehensive calibration models. These models have been used to explore the relationship between fluorescence spectroscopy and white wine quality (based on the degree of browning),[133] among other examples discussed in this paper.

The concept of a portable NIR device for phenolic analysis was explored[146] and the potential of IR spectroscopy for in-line and on-line application in the industry.[147] Similarly, there is a focus on research that explores fluorescence spectroscopy's use for process control monitoring. The implementation of process control will allow for consistent quality standards, reducing wastage and increasing yield.[148] Knowledge of phenolic concentrations throughout the winemaking process would allow winemakers to better construct wines with desirable mouthfeel and distinct styles.[5] For sparkling and white winemaking, knowledge of the levels of phenolics during the pressing stages may increase product yield and allow more control over the flavour and acid development in the wine as it ferments.[5,149] Hence, there is a growing demand for a portable device that could quantify phenolic levels in wine during the winemaking process.[144]

Easy-to-operate, handheld devices are available, but their implementation in commercial setups has not yet been investigated thoroughly.[150] However, advances in the field are predicted in the future due to the dedication of the scientific community to research on phenolic compounds and their analysis.

A possible obstacle experienced currently is the apprehension of the industry to adopt the experimental and scientific approaches in the wineries. As most studies discussed have been performed in laboratory setups, it is clear that for the winemakers to fully understanding what benefit a technique of analysis might have in the wine industry, the technology must be employed. Like most industries, technology is being incorporated into the traditional art of winemaking, and there are clear benefits in doing so, but it is happening slowly. It can be hoped that the future will

only bring more openness to the wine industry to embrace the technological advancements that could be offered them. As science is trying to run alongside the wine industry, the scientific approaches must be compatible with the methodologies of the winemakers in the cellar. The communication between researchers and industry could be strengthened and, in doing so, more applied research and experimental devices could be done and created which could positively impact the wine industry for years to come.

CONCLUSIONS

As the importance of the role of phenolic compounds in white wine becomes more apparent to winemakers, there is increasing interest in this area of research. It is expected that better quality wines can be produced with more understanding of the phenolic levels, during the winemaking process.

This review paper is to serve as a compilation of all standard methods of white wine phenolic analysis. All forms of the analysis showed great promise and many advantages for phenolic analysis. The methods discussed were used to gain insight into phenolic quantification and phenolic compounds as markers for geographical locations, winemaking practices, and quality, among others, of white wines.

Due to the inherent difficulty of white wine phenolic analysis, it is hoped that this paper can be a guide for researchers looking to previous research performed by their peers in this field of study for inspiration and knowledge on this subject. Due to the interest among researchers in wine phenolics, there are sure to be further advancements in this field very soon. The technology being explored has the prospect of being able to fulfil an indispensable role in the industry. When reliable and easy-to-use instrumentation is developed it is hoped that it can be utilised in the industry in many positive ways.

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