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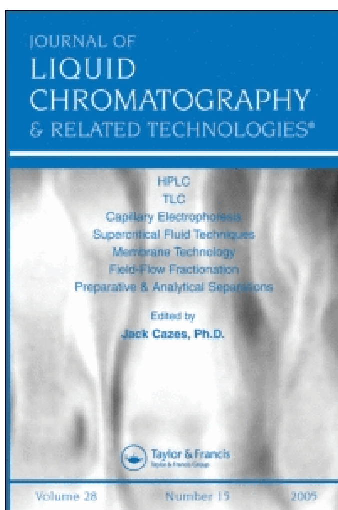

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High Performance Liquid Chromatography in Oenology

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HIGH PERFORMANCE LIQUID CHROMATOGRAPHY IN OENOLOGY

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INTRODUCTION

In this review I have included every reference I have been able to find in which h.p.l.c. has been used in analysing wines and musts. Clearly an article such as this would be incomplete if allied fields like brewing, food chemistry, and phytochemistry were ignored. I have therefore used my discretion in selecting from the huge number of publications in these areas those papers which seem to me likely to be of value to oenologists.

ORGANIC ACIDS

A review of analysis of organic acids in wine has appeared[1]. Palmer and List[2] separated organic acids on Aminex A25 resin in the formate form, eluting with aqueous sodium formate and using R.I. detection. The acids were trapped on a short column of the same resin which was then washed with water prior to elution of the acids onto the separation column. Rapp and Ziegler[3] described separation of citric, malic, tartaric, and succinic acids on Aminex A6 resin eluting with an isobutyl acetate-isobutyl alcohol-water mixture and using R.I. detection;

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with wines enrichment with ion exchange resin was necessary. The same authors[4] used an anion exchange resin to split wine into acid and neutral fractions, then analysed each fraction with a cation exchange resin column eluting with aqueous methanol and using R.I. detection. The neutral fraction contained sugars, ethanol, glycerol, and butane 2,3 - diols and the acid fraction the wine acids. Rajakkyla[5] separated organic acids, including the major wine acids, on Aminex HPX - 87 resin at 65° eluting with 0.01N H_3PO_4 and employing detection at 210nm. The author has seen chromatograms of wines and of standard mixtures of acids using essentially the same conditions as Rajakkyla, separations were excellent and most of the other U.V. absorbing materials from the wine eluted before the acids. The wines were simply filtered before injection and several hundred samples were run without deterioration of the colum performance[6].

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Lee[7] separated wine acids on a column of macroporous poly (styrene-divinylbenzene) resin eluting with pH 2.6 buffer and detecting at 210nm. Separation of a standard mixture was excellent but a chromatogram of a Californian wine was congested in the region around tartaric acid. Gump and Kupina[8] investigated analyses of gluconic and other wine acids both on a C-18 column and on Aminex 50W x 4, with R.I. detection. Schneyder and Flak[9] concentrated acids from wine on Lewatit M5020 resin then separated them on a C18 column eluting with a phosphate buffer and using R.I. detection. Jeuring et al[10] separated malic and citric acids by direct injection of filtered apple juice onto a C-8 column, eluting with phosphate buffer and employing detection at 220nm. Bush et al[11] similarly separated C_2 - C_5 fatty acids on a C18 column using a phosphate buffer containing 10% methanol with detection at 210nm. Droz and Tanner[12] separated acids in fruit juices and wine on a C18 column

eluting with an aqueous buffer containing KH_2PO_4, $Bu_4N\ PO_4$ and H_3PO_4 and employing detection at 225nm. Gonnet and Marichy[13] investigated the chromatography of wine acids using a variety of reverse phase columns and solvents but decided that the best separation they obtained was unsatisfactory. Stahl and Laub[14] determined acids in wines and fruit juices on a column of microcrystalline cellulose eluting with ethyl acetate-n-propanol-water and using conductivity, U.V., R.I., and pH detectors in series. Stahl et al[15] compared this method with official methods of analysis and obtained good agreement. Israelian[16] discussed briefly the application of h.p.l.c. to wine analysis and separated wine acids on an ion exchange column. Friberg[17] separated low m.wt. acids (as well as saccharinic acids, aldonic acids, and monosacharides) in various systems including wines and discussed potential applications in the food industry with special reference to winemaking.

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The above methods all use R.I. or short wavelength U.V. detection. In the authors experience R.I. detection can give solvent and other peaks which may interfere with the peaks of interest. For example when using a Waters Rad-Pak C-18 column with a phosphate buffer of pH 2.6, water gives a negative peak very close to tartaric acid, reducing the height of the latter peak. Short wavelength U.V. is absorbed by many wine components and broad peaks eluting after the acids can delay injection of the next sample.

A number of other methods of detection have been described which may merit investigation for wine acids. Farinotti et al[18] separated various short chain acids on a C18 column with aqueous acetonitrile, the effluent was mixed with bromocresol purple and the absorbance at 425nm was monitored, it is claimed that this method is ten times more sensitive than using U.V. absorbance at 205nm. Cochrane and Hillman[19] separated anions

on a Vydoc 302 column, eluting with .005M potassium hydrogen phthalate, the eluate was monitored at 302nm and the ions were seen as peaks of decreased U.V. absorbance. Buytenhuis[20] used a similar principle, eluting anions from anion exchange resin with mobile phases of high refractive index to increase the difference in R.I. between the eluant and the eluted ions.

Organic acids in wines can be separated with Dionex Ion Chromatographs[21], these are very costly however. Molnar et al[22] described a similar system in which the suppressor column can be omitted, though at some loss of baseline stability. Both these systems use conductivity detection.

Organic acids can also be analysed after derivatisation and much excellent work has been published using this approach. Methylanthracene derivatives[23] for fluorescence detection and napthyl derivatives[24] for U.V. detection may be prepared by reaction of acids with diazo derivatising agents. Napthacyl[25] and phenacyl[26-31] derivatives have been described, these have very high U.V. absorbance and are readily separated by normal and reverse phase chromatography. Crown ether catalysts[28,29] enable dibasic acids to be esterified and such a catalyst has been used by Gonnet and Marichy[32] as a basis for analysing acids in wines by reverse phase chromatography. Potassium fluoride, which is cheaper than crown ethers, can also be used to catalyse phenacyl ester formation[30,31] however it does not bring about esterification of tartaric, malic, and succinic acids under conditions which esterify acetic and benzoic acids[33].

The author[33] has found that ω -tosyloxy acetophenone (prepared from styrene glycol by tosylation and oxidation) is a useful alternative to phenacyl bromide as it is widely separated from the latter compound in

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reverse phase chromatography. This is advantageous where the phenacyl ester of interest and phenacyl bromide chromatograph close together. Also the tosyl compound is not lachrimatory.

Organic acids may also be derivatised with 4-bromomethyl-7-methoxycoumarin[34-36] and the derivatives can be separated by reverse phase chromatography with fluorescence detection. Again the use of crown ether catalysts[36] makes possible derivatisation of dicarboxylic acids.

Shimazu and Watanabe[37] separated organic acids in wines and musts by a new h.p.l.c. analyser using 'a highly specific and highly sensitive detection method'.

Monk et al[38] have separated wine acids by low pressure chromatography on Dowex 50W x 2 eluting with dilute butyric acid and using conductivity detection.

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BENZOIC, SORBIC, ASCORBIC, AND ISOASCORBIC ACID

McCalla et al[39] analysed sorbic acid in wine on an anion exchange column eluting with a borate buffer and employing detection at 254nm. Eisenbeiss et al[40] and Clasodonte et al[41] determined sorbic acid in wine in the presence of benzoic acid. Froehlich[42] optimised reverse phase separation of benzoic acid and sorbic acid from each other and from the matrix in wine and in cherry and sauerkraut juices. Kubota[43] determined sorbic acid on an anion exchange column with a phosphate buffer and U.V. detection.

Bui-Nguyen[44] determined ascorbic and isoascorbic acids on a LiChrosorb NH_2 column using aqueous acetonitrile containing KH_2PO_4. Dennison et al[45] employed a similar system with methanol in place of acetonitrile to determine ascorbic acid and deoxy ascorbic acid. The

latter compound was reduced by DL homocysteine to ascorbic acid before analysis. Geigert et al[46] analysed ascorbic and isoascorbic acids on a Waters Carbohydrate analysis column eluting with aqueous acetonitrile containing phosphate buffer.

SUGARS

Palmer and Brandes[47] separated sugars in deionised grape juice on Aminex Q150S K^+ at 60° eluting with water. Rapp et al[48] analysed wine for sucrose, glucose, fructose, glycerol and ethanol by direct injection onto a column of Aminex A6 resin and eluting with water. Rapp et al[49] used this method to study the inversion of sucrose in grapes.

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Shimazu et al[50] analysed sugars, polyols and ethanol in wine and must on a Diaion CK08S (Ca^{2+}) resin column. Schmidt et al[51] determined mono and oligosaccharides in beer and wort on Aminex HPX-42 resin at 85° eluting with water. Dunsmire and Otto[52] described a general procedure for analysing sugars in a variety of matrices using a µBondapak/Carbohydrate column eluting with aqueous acetonitrile. Wong-Chong and Martin[53] used a similar method with flow programming to speed analysis, these authors[54] also examined ion exchange resins for sugar separations and obtained excellent resolution on Aminex Q150S(K^+) at 60°, eluting with water. Czerny et al[55] determined sugars and polyols in foods with a µBondapak/Carbohydrate column eluting with aqueous acetonitrile. Palla[56] separated sugars on µBondapak C18 eluting with water. Flak[57] removed acids from wines with ion exchange resin in the acetate form then separated the sugars on either a µBondapak/Carbohydrate column or an amino bonded column. Muller and Siepe[58] separated sugars on

LiChrosorb NH_2 and recommended ethyl acetate-acetone-water as a less toxic alternative to aqueous acetonitrile. Aitzetmuller[59] described a method for the analysis of sugars and glycerol on silica, eluting with aqueous acetonitrile containing an amine modifier, this is claimed to show advantages over a bonded NH_2 packing whilst giving similar separations. Johncock and Wagstaffe[61] used Aitzetmullers' method and discussed the sources of baseline instability in R.I. detection and the need for thermostatting the various parts of the chromatograph to obtain increased sensitivity.

Goiffon et al[62] analysed glycerol and sugars in wines on an amino bonded column eluting with aqueous acetonitrile. Stahl et al[63] using a column of microcrystalline cellulose, a mobile phase of ethyl acetate-n-propyl alcohol-water, and R.I. and microadsorbtion detectors analysed wines for polyhydric alcohols. The same column could be employed to determine C_1-C_5 monohydric alcohols using benzene as the eluent. Iverson and Bueno[64] using a method similar to that of Palmer and Brandes[47] compared h.p.l.c. and g.l.c. for analysis of sugars and concluded that h.p.l.c. was both quicker and more accurate.

All the methods in this section used R.I. detection. It should be noted that sugars can be detected also with short wavelength U.V. although the problems mentioned in the section on acids would apply with sugars also.

BIOGENIC AMINES

Subden et al[65] described a method for determining histamine in wine as its o-phthaldialdehyde derivative on a μBondapak C18 column

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eluting with a phosphate buffer in aqueous acetonitrile and with detection at 200nm and 220nm. The same group reported[66] results obtained with Canadian wines. Buteau et al[67] looked at the stability of the o-phthaldialdehyde complex and showed that after derivatisation, acidification or extraction into ethyl acetate was desirable to prevent a rapid decrease in absorbance. Battaglia and Froehlich[68] determined histamine in wine by dansylation, separation on Spherisorb 5SW and fluorimetric detection. This method was later extended[69] to incorporate a step gradient, this separated more than 20 biogenic amines. Woidich et al[70] analysed biogenic amines in wines with a Liquimat 11 amino acid analyser.

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CARBONYL COMPOUNDS

Okamato et al[71] analysed acetaldehyde in wines as its lutidine derivative on either a 3-aminopropyltriethoxysilane treated silica column or a bonded amino column, eluting with ethanol-hexane and with U.V. or fluorescence detection. Suzuki and Maruyama[72] determined aldehydes by injecting them in aqueous solution into a heated column of 2,4-dinitrophenylhydrazine on celite which was connected to the h.p.l.c. column, wines analysed this way showed acetaldehyde levels of 24-100mg/l.

Numerous publications have dealt with determination of carbonyl compounds as their 2,4-dinitrophenylhydrazones. Selim[73] showed that the reaction between carbonyl compounds and 2,4-dinitrophenylhydrazine is an equilibrium which on a macroscale is driven to completion by precipitation of the product. On a microscale the reaction may not go to completion due to the hydrazone remaining in solution. The reaction may be driven to

completion by addition of an immiscible organic phase to extract the product. Selim's method appears quite suitable for determination of carbonyl compounds in wines. 2,4-Dinitrophenylhydrazones are readily separated by reversed phase chromatography[73-76].

Carbonyl compounds in beer have been detected down to .1 ug/l by low pressure distillation and trapping in 2,4-dinitrophenylhydrazine solution followed by reverse phase chromatography, and also by a combination of steam distillation and liquid-liquid extraction followed by reaction with o-nitrobenzylhydroxylamine and reverse phase chromatography. The latter reagent is claimed to be superior to 2,4-dinitrophenylhydrazine as a derivatising reagent.

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PHENOLIC COMPOUNDS

Anthocyanidins and Anthocyanins

Manley and Shubiak[79] separated the 3-glucosides of malvidin, petunidin, and peonidin on Pellidon (polyamide bonded onto glass beads) eluting with chloroform-methanol. In all later reports of anthocyan(id)in separations reverse phase chromatography has been the method of choice. Adamovics and Stermitz[80] separated delphinidin, cyanidin and pelargonidin (and also the 3-O-rutinosides of quercetin, kaempferol, and isorhamnetin) on a C18 column eluting with aqueous methanolic acetic acid. Wilkinson et al[81] separated the anthocyanidins on a µBondapak C18 column also using aqueous methanolic acetic acid. Akavia and Strack[82] reported that this separation could not be achieved on other reverse phase columns and recommended the use of aqueous acetonitrile containing 1.5% H_3PO_4

as the mobile phase. Akavia et al[83] also described a method for identifying anthocyanins by following the appearance and disappearance of the products of graded acidic hydrolysis. Williams et al[84] separated anthocyanidin 3-glucosides, 3,5-diglucosides, and their p-courmaryl derivatives on a µBondapak C18 column. Wulf and Nagel[85] obtained excellent separations of anthocyanidin 3-glucosides and their acetate, coumarate, and caffeoate derivatives on a octadecylsilyl column, they also examined the products of alkaline hydrolysis and degradation to aid in identification of the pigments. McCloskey and Yengoyan[86] studied wine colour during aging but the reference[87] given for their chromatographic method is not available to the author. Pergiovanni and Volonterio[88] separated anthocyanins with a formic acid-water-methanol gradient on a µBondapak C18 column or a LiChrosorb RP18 column, and the aglycones with methanol-water-acetic acid on the µBondapak C18 column. Bertrand et al[89] used essentially the same conditions to follow changes in anthocyanin levels during fermentations of Cabernet Sauvignon and Merlot grapes. Preston and Timberlake[90] separated the flavilium and chalcone forms of malvidin 3-glucoside and 3,5-diglucoside on a column of Spherisorb hexyl eluting with a gradient of aqueous methanol containing .6% of perchloric acid. Israelian[16] analysed anthocyanins on a C18 column.

Other Phenolics

Wulf and Nagel[91] separated phenolic acids and D-catechin on a C18 column with acetic acid-methanol-water eluants. They also chromatographed flavanoids and flavanoid glycosides but complete resolution was not possible as some groups of compounds, e.g. aglycones and monoglucosides, overlapped. Ong and Nagel[92] separated caffeoyl, p-

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coumaryl, and feruoyl esters of tartaric acid on a C18 column with water-acetonitrile-H_3PO_4 mixtures and also described[93] changes in levels of these compounds during maturation of White Riesling grapes. Nagel et al[94] used a similar method to examine hydroxycinnamic esters of tartaric acid in grapes and wines from the Pacific Northwest of the U.S.A. Nagel and Wulf[95] followed changes in the concentrations of various phenolics during the aging of Cabernet Sauvignon and Merlot wines. Using a C18 column hydroxycinnamic esters were eluted with water-acetonitrile-acetic acid, anthocyanins and polymeric pigments with water-acetone-acetic acid, and ethyl acetate extractable phenolics with water-acetonitrile-acetic acid adjusted to pH4. At pH4 the hydroxycinnamic esters eluted rapidly and did not interfere with examination of other phenolics in the extract. Wulf and Nagel[96] used preparative reverse phase chromatography with recycling to isolate flavanoids from Cabernet Sauvignon and Merlot wines, and Baranowski and Nagel[97] similarly isolated hydroxycinnamic esters from White Riesling grapes.

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Symonds[98] partly decolourised wine with 50W x 8 resin, then analysed the organic acids by the method of Palmer and List[2], whilst the phenolic acids were either extracted with ether or into acetone after saturating the wine with salt, then analysed by reverse phase chromatography. Okamura and Watanabe[99,100] looked at phenolic constituents of wine and must on a C18 column eluting with a methanolic aqueous phosphate buffer, the effect of phenolic acid esters of tartaric acid on wine quality was investigated. Nickenig and Pfeilsticker[101] fractionated oxidised wine on Sephadex G25 and examined the fractions for phenolics with a water-methanol-acetic acid gradient on a Nucleosil-7 C8 column, using an esterase to cleave ethyl hydroxycinnamates. On the same

column dicarboxylic acids were separated by elution with .3% phosphoric acid and detection at 195 and 220 nm.

Dumont[102] determined chlorogenic acid in grape juice and wines, inter alia, by enzymic cleavage followed by chromatography of the liberated caffeic and quinic acids on a LiChrosorb RP18 column. Slinkard[103] used h.p.l.c. among other techniques to study phenolics of grape skins.

Villeneuve et al[104] described a general procedure for analysing plant phenolics by reverse phase chromatography with methanol-water-acetic acid mixtures, changes in phenolic acids in grape juice during storage were followed. Murphy and Stutte[105] separated various substituted benzoic and cinnamic acids on a μ Bondapak C18 column using gradient elution with mixtures of n-butanol-methanol-water and acetic acid containing ammonium acetate. The latter compound inhibited intramolecular bonding and made possible separation of all 13 acids examined. Krause and Strack[106] separated a range of hydroxycinnamic acid derivatives on an RP8 column with gradient elution using aqueous methanolic acetic acid or citrate buffer in place of acetic acid, (but note that Waters Associates state[107] that citrate buffers should not be used with their reverse phase columns). It was found that varying the proportion of acetic acid in the solvent produced marked changes in retention times and selectivity which can be used to optimize separations.

The separations described above all used alkylsilyl bonded column packings but other bonded materials can also be utilised. Vanhaelen and Vanhaelen-Fastré[108] used an alkylphenyl column with a gradient of water,

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ethanol, and acetic acid to resolve various aromatic acids and phenolics. Also some flavonoids were separated with isocratic elution. The authors note that ethanol gives better separations than does methanol. Nagels et al[109] chromatographed glucose- and quinic acid-cinnamates and benzoates on both RP8 and diol columns. The diol column gave separations similar to adsorbtion chromatography but without the sensitivity to water shown by alumina and silica columns. The elution order was not simply the reverse of that given by the RP8 column, thus offering a different selectivity. A preliminary separation on ECTEOLA cellulose (separation based on charge differences at pH7) was a useful adjunct to the hplc separations. Becker et al[110] used an aqueous acetonitrile gradient on a LiChrosorb NH_2 column to separate the polar flavonoids isoorientin 3'-O- and 4'-O-glucosides which were not resolved on LiChrosorb RP8.

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McMurrough[111] analysed phenolics from hops and barley on a µBondapak C18 column and found that for separating flavonol glycosides tetrahydrofuran as the organic modifier gives better resolution than acetonitrile although the latter solvent gives better resolution than methanol.

In one of the few reports of h.p.l.c. of phenolics which did not rely on U.V. detection Roston and Kissinger[112] used electrochemical detection and showed that the current-potential responses of eluted compounds can be used as an aid in identification. Similarly Sontag et al[113] examined electrochemical detection for methyl and ethyl esters of various hydroxycinnamic acids, the esters of different acids are oxidised at different potentials giving scope for selective detection. The methyl and ethyl esters of each acid are oxidised at the same potential. Galensa

and Herrmann[114,115] separated flavones, flavanols, and flavanones by acetylation followed by chromatography on LiChrosorb Si 60, eluting with various mixtures of organic solvents. Of interest in connection with this method is the observation of Coutts et al[116] that phenols may be acetylated in aqueous solution with quantitative recoveries.

There has been an increased interest recently in the role of procyanidins in wine[117,118] and it is appropriate to note here h.p.l.c. of these compounds although most publications have been in non-oenological areas. Lea[119] separated cider procyanidins by reverse phase chromatography using aqueous methanol containing perchloric acid as the mobile phase. The same author subsequently reported[120] the use of Snyder's procedures to optimise separation of procyanidin oligomers showing that shallow gradients are required and that a sharp increase in solvent strength elutes oxidised materials as a fairly sharp band. This may be useful in studying these intractable materials. Lea also suggested[120] that Snyder's procedures could be used to estimate molecular weights of procyanidin polymers.

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Jerumanis[121] separated polyphenol oligomers using a gradient of acetic acid in water and a C18 column. Oligomers isolated from beer showed very rapid depolymerisation. Mulkay et al[122] used Jerumanis' method to isolate polymers the structures of which were then elucidated by acetylation and n.m.r. spectroscopy. Kirby and Wheeler[123] analysed beer polyphenols on Spherisorb S5ODS with a water-methanol-KH_2PO_4 gradient and found only monomers and dimers. Jende-Strid and Møller[124] separated barley procyanidins with an aqueous acetic acid gradient on a µBondapak phenyl column. Wilson[125] analysed phenols from apple juice

ranging from dimeric to heptameric procyanidins by normal phase chromatography on a bonded CN column. The procyanidins were separated into groups according to their degree of polymerisation in this way. The isomers in each group were then resolved with a C18 column using methanol-water-KH_2PO_4.

AFLATOXINS

Takahashi[126,127] described analysis of wine for aflatoxins, normal or reverse phase chromatography were suitable but reverse phase was preferred, fluorescence and U.V. absorbance detection were both employed. Takahashi and Beebe[128] developed a general method for aflatoxins in foods and beveages including wines. Wei and Chang[129] analysed wines on a uPorasil column after clean up on silica gel and by thin layer chromatography. Sripathomswat and Thasnakorn[130] used h.p.l.c. in studies of aflatoxin producing fungi in a range of foodstuffs including wine.

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AMINO ACIDS

Ishida et al[131] separated amino acids in grape juice on a strong acid resin column with fluorescence detection after reaction with sodium hypochlorite then with 2-mercaptoethanol and o-phthaldialdehyde. Casoli and Colagrande[132,133] determined amino acids in sparkling wines by dansylation followed by reverse phase chromatography using a complex acetonitrile-water-phosphoric acid-acetic acid gradient and fluorescence detection. Schuster[134] analysed free amino acids and several vitamins in beverages (and intravenous solutions) on an amino bonded column eluting with an aqueous acetonitrile phosphate buffer and detecting the amino

acids at 200nm. Martin et al[135] determined amino acids in wines and musts as their dansyl derivatives which were separated on a radially compressed reverse phase column using gradient elution and fluorescence detection.

MISCELLANEOUS

Vialle et al[136] measured betaine in wine and beet sugar on a bonded NH_2 column eluting with aqueous acetonitrile and using R.I. detection. Initial sample cleanup was carried out on two ion exchange columns. Tyson et al[137] determined soluble protein in wine and must using a size exclusion column. Protein can however be determined far more cheaply by low pressure chromatography[138,139]. Tenenbaum and Martin[140] used h.p.l.c. to determine saccharin in alcoholic beverages.

Rhys-Williams and Slavin[141] determined methyl anthranilate in grape beverages by reverse phase chromatography with fluorescence detection. Qureschi et al[142] described a method of analysing beverages for purines, pyrimidines, nucleosides, nucleotides, phenolics, and pyrazines. It was found that addition of 1.5% acetic acid to the mobile phase sharpened the peaks but larger amounts impaired the resolution.

Micali et al[143] analysed alcoholic and non alcoholic beverages for β asarone by steam distillation and extraction followed by reverse phase chromatography with fluorimetric detection.

Steuerle[144] determined artificial dyes on a LiChrosorb NH_2 column. An aqueous solution of the dyes was pumped through the column, this concentrated the dyes in a narrow band at the top of the column. The

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unadsorbed materials were washed off with acetonitrile-water-acetic acid then the dyes were eluted with a pH gradient. Recovery of L-Red-12 from a spiked wine was quantitative. Martin et al[145] analysed acid fast dyes, including those often found in wines, by reverse phase chromatography and gradient elution after preliminary separation by adsorption onto wool.

Jeuring et al[146] and Frishkorn et al[147] determined furfural and hydroxymethyl furfural in spirits by reverse phase chromatography.

Sponholz and Lamberty[148] determined styrene in wine by direct injection onto a LiChrosorb RP8 column, elution with aqueous methanol and detection at 254nm. Jakob and Schaefer[149] extracted styrene into cychohexane then chromatographed the extract on an MY Porasil column, eluting with cyclohexane and monitoring at 254nm.

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Lazzarini et al[150] examined wines for imidazolidine-2-thione (a degradation product of some fungicides) by extraction with methylene chloride from salt saturated wine and chromatography of the extract on alumina. In a later publication[151] from the same group reverse phase chromatography was used. Caccialanza et al[152] also determined imidazolidine-2-thione by reverse phase chromatography.

Toussaint and Walker[153] used liquid chromatography to clean up cyclohexane extracts of wine, eluting polycyclic aromatic hydrocarbons as a group for subsequent analysis by gas liquid chromatography.

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