



CHROMATOGRAPHY OF WINE

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The objectives of the review are the collection, concise description and evaluation of the various chromatographic technologies applied for the separation and quantitative determination of macro- and microcomponents present in wines.

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Introduction

Chromatographic methods have been developed and successfully employed for the separation and quantitative determination of a wide variety of organic and inorganic compounds even present in complicated accompanying matrices at the trace level. The rapid development of new chromatographic instrumentation, the increase of the precision and sensitivity of the newest apparatus facilitated the solution of separation problems which were impossible some years ago.

Wines are produced and consumed all over the world. Because of their considerable commercial importance the adequate quality control of wines is of paramount importance. Both traditional and up-to date techniques found application in the analysis of wines. Because of their advantageous separation characteristics chromatographic methods are frequently employed in the evaluation of wine quality.

The objectives of the review are the collection of the newest results obtained in the chromatographic analysis of wines, the critical evaluation of the results and the elucidation of the similarities and dissimilarities among the results obtained by various analytical procedures.

The application of sample preparation and chromatographic technologies in the analysis of selective biogenic amines, methylxanthines and water-soluble vitamins has been earlier reviewed.¹

Gas chromatography (GC)

Gas chromatographic (GC) technologies are generally employed for the separation and quantitative determination of volatile compounds. Non-volatile compounds can be derivatized to increase volatility, however, the method is time consuming and decreases the reliability of the procedure. As the majority of the constituents are volatile

or semi volatile GC methods have been frequently application in the analysis of wine. Wine contains not only natural constituents but also synthetic products to increase yield and to improve the quality of the end product. Both kind of analytes can be easily investigated by GC methods.

Gas chromatography of natural analytes

The volatile composition of alcoholic beverage was investigated by headspace solid-phase microextraction method (HS-SPME) followed by gas chromatography mass spectrometry (GC-MS). It was established that volatile compounds such as alcohols, esters and terpenes influence the flavor of fortified wines. It was further found that *m*-thymol, *o*-thymol, eugenol and their esters play a considerable role in the formation of aroma profile.² The impact of different over-lees ageing was also investigated in detail (ageing on fine white lees, on fine red lees, fine second passage lees, rough red lees). The measurements indicated that the type of lees exerts a considerable effect on the composition of Cabernet wine modifying polysaccharide and volatile composition of the end product.³ Both sensorial and chromatographic methods were simultaneously employed for the investigation of the aroma profile of *Garnacha Tintorera*-based sweet wines. It was established that the main volatile components were sotolon ($73 \mu\text{g L}^{-1}$) and acetoin ($122 \mu\text{g L}^{-1}$).⁴ Solid phase microextraction (SPME) combined with gas chromatography-olfactometry (GC-O) and cryogenic trapping was employed for the study of the aroma-active compounds of Shiraz wine. The preconcentration procedure was carried out by using various fibre coatings such as polyacrylate (PA), and triple-phase polydimethylsiloxane/divinylbenzene/carboxene (PDC).

It was concluded from the data that the method is suitable for the investigation of the aroma active compounds of Shiraz wine.⁵ The impact of soil management on the composition of aroma compounds of Negroamaro wine was elucidated by using a GC-MS method. The influence of two agronomic practices (cover cropping, and soil tillage) on the free and bound aroma compounds was measured. The investigations revealed the presence of alcohols (55.7 mg L^{-1}), fatty acids (7.0 mg L^{-1}), and esters (6.6 mg L^{-1}). It was established that soil tillage enhances the amount of aroma compounds such as esters, carboxylic acids, alcohols, acetamides and phenols. It was further established that the concentration of sulfur compounds decreased while the soil

management did not influence the amount of glycoside volatile compounds.⁶ The application of various SPME methods has been earlier discussed in various accompanying matrices and their use was discussed in detail.⁷ The impact of deficit irrigation and kaolin particle film on the grape composition and volatile compounds in Merlo grape (*Vitis vinifera*) was investigated in detail. The analytes were separated and quantitatively determined by stir-bar sorptive extraction-gas chromatography-mass-spectrometry (SBSE-GC-MS). It was established that the treatments modify considerably the following volatile compounds: hexanal, trans-2-hexenal, 1-hexanol, nerol, geraniol, β -damascenone, 3-hydroxy- β -damascenone, 1,1,6-trimethyl-1,2-dihydro-naphthalene, 3-oxo- α -ionol, 13-norisoprenoids and anthocyanins.⁸ The addition of oak chips on the composition of volatiles in *Moravia Agria* wines has been investigated by GC-MS. Chips were added during alcoholic fermentation, during malolactic fermentation and in young red *Moravia Agria* wines. The results indicated that the addition of oak chips to the fermentation broth influences the amount of ethyl esters of straight-chain fatty acids, ethyl, hexyl, isoamyl acetates and superior alcohols. It was further found that the presence of oak chips increases the concentration of benzene compounds, oak lactones and furanic compounds.⁹

Gas chromatography of synthetic analytes

Besides of natural components wines contain various organic and inorganic pollutants added to the wine intentionally (i.e. pesticides) or unintentionally. These additional compounds may increase the yield, and may modify the aroma profile of the wine. An easy and reliable GC method using electron capture detector (ECD) was developed for the detection of chlorpyrifos (CP) and its metabolite chlorpyrifos-oxon (CPO) in wine. The quick, easy and cheap preparation method employs extraction with acetonitrile, followed by dispers phase extraction using primary secondary amine. It was found that the accuracy of the method was $(92.3 \pm 18.2) \%$ for chlorpyrifos and $(96.6 \pm 16.1) \%$ for chlorpyrifos-oxon. LOD and LOQ values were 0.04 and 0.15 ng mL⁻¹ for CP and 0.49 and 1.62 ng mL⁻¹ for CPO.¹⁰

Both high performance liquid chromatography-photodiode-array detection electrospray ionization mass spectrometry (HPLC-DAD-ESI/MS) and solid-phase micro extraction-gas chromatography-mass spectrometry (SPME-GC-MS) were employed for the identification and isolation of spoilage yeasts. It was established that the combined method is suitable for the identification of this class of yeasts¹¹. A new extraction procedure was developed and tested for the determination of volatile compounds in white and red wines. The investigations indicated that the recovery values of the method are good and depend considerably on the character of the volatile compound under investigation. It was further established that the employment of matrix-matched calibration curve is necessary to obtain reliable quantitative results.¹² A new SPE-GC method was developed for the analysis of alpha- and beta tujone in alcoholic beverages. It was stated that the yield of extraction is high (over 98%), the LOD is 0.033 mg L⁻¹, RSD is below 1.8 % and the relationship between the amount of analytes and the detector response is linear.¹³ Membrane ethanol biosensor was prepared using *Methylobacterium*

organophilum-immobilized egg: shell membrane and an oxygen electrode.

It was established that the relationship between the amount of ethanol in the sample and the biosensor response was linear between 0.050 – 0.75 mmol L⁻¹, the detection limit was 0.025 mmol L⁻¹, RSD was 2.1 %. The results were compared with those obtained by GC, it was stated that the biosensor is suitable for the determination of the alcohol content in alcoholic beverages.¹⁴ An automatic headspace in-tube extraction (ITEX) technique was developed for the determination of volatile components in wine and beer. It was stated that the method is suitable for the analysis of very volatile compounds (acetaldehyde, ethyl acetate, diacetyl) in different matrices.¹⁵ A new GC-MS method was developed for the determination of aldehydes in grape pomace distillates (Orujo). Samples were diluted and derivatised with O-(2,3,4,5,6-pentafluorobenzyl) hydroxyl amine, then microextracted by SPME before GC-MS analysis. The LOD value was 0.7 ng L⁻¹, the repeatability was excellent.

It was found that the application of demethylant column considerably modified the quality profile of the distillate.¹⁶

High performance liquid chromatography

Because of high separation capacity and variability high performance liquid chromatographic technologies (HPLC) have been frequently employed in the up-to date analytical chemistry even in the separation and quantitative determination of the macro- and microcomponents of wines and in the determination of environmental pollutants. The application of cyclic voltametry and HPLC have been simultaneously employed for the determination of caffeine in aqueous, acid, and alcoholic media. The investigations were motivated by the pharmacological properties of caffeine (stimulation of the central nervous system, peripheral vasoconstriction, relaxation of the smooth muscle and myocardial stimulation).¹⁷ Gas- diffusion microextraction (GDME) was applied for the extraction of some aliphatic amines such as methylamine, dimethylamine, and ethylamine in fermented beverages (white, red and rose wines, dark and pilsner beers). Analytes were derivatised by phenyl isothiocyanate and analysed by HPLC. It was found that LOD varied between 12 – 46 $\mu\text{g L}^{-1}$, while LOQ ranged 39 – 153 $\mu\text{g L}^{-1}$. Because of its simplicity the method was proposed for the analysis of these compounds.¹⁸ Biogenic amines (histamine, tyramine, spermine, spermidine, putrescine, cadaverine and phenylethylamine were also investigated by reversed phase (RP-)HPLC. Analytes were pre-column derivatised using phase-centered central composite design. The optimal conditions for the derivatization with dansyl chloride were 60 °C and 60 min. Biogenic amines were separated on an octadecylsilica (ODS) column at a column temperature of 40 °C using gradient elution of acetonitrile-water. Analytes were detected at 254 nm. Calibration in matrix fitted resulted in $R^2 > 0.997$. Repeatability ($n = 6$) and intermediate precision ($n = 3$) in matrix showed RSD values $> 2.34 \%$ and 3.16% , respectively. It was established that the concentration of biogenic amines in Chilean young varietal wines varied between 18.12 – 39.84 mg L⁻¹.¹⁹ The phenolic profile of *Sercial* and *Tinta Negra Vitis vinifera L.* grape skins was investigated by HPLC-DAD-ESI-MS (high performance

liquid chromatography-diode array detection-electrospray ionisation tandem mass spectrometry). The presence of 3-hydroxybenzoic acids, 8-hydroxycinnamic acids, 4-flavanols, 5-flavanones, 8-flavonols, 4-silbenes and 8-anthocyanins was established. It was stated that 10 new compounds were identified in the grape skins of *Sercial* and *Tinta Negra Vitis vinifera L.*: protocatechic acid glucoside, p-hydroxybenzoyl glucoside, caffaric and vanilloyl pentoside, p-coumaric acid-erythroside, naringenin hexose derivate, eriodictyol-glucoside, taxifolin-pentoside, quercetin-gluronide-glucoside, malylated kaempferol-glucoside and resveratrol dimer. Grape skins were proposed as sources of bioactive compounds.²⁰ A new generic sample treatment method was developed for the simultaneous analysis of multiclass pesticides and mycotoxins. Analytes were extracted by SPE and separated by HPLC TOF method. It was established that the retention capacity of cartridges showed considerable differences. The analytes were identified according to the retention time and accurate mass measurements of the protonated analyte molecules. LOD were lower than $1 \mu\text{g L}^{-1}$ for the 87% of the molecules included in the investigation.²¹ The application of molecularly imprinted polysiloxane microspheres (MIPS) for the improved selective extraction of 3,3'-dichlorobenzidine has been recently reported. The interest in the analysis of dichlorobenzidine and degradation products was motivated by the carcinogen character of this class of molecules. It was established that MIPS show marked selectivity toward 3,3'-dichlorobenzidine the binding capacity being seven times larger than for diphenylamine. The new microspheres were proposed for the selective extraction of 3,3'-dichlorobenzidine from different accompanying matrices.²² A combined method including derivatisation, solid-liquid extraction, solid-phase purification and HPLC-DAD was employed for the determination of dithiocarbamate (DTC) fungicide in various matrices such as apples, wine grapes, lettuces, peppers, tomatoes and strawberries. Fungicide residues exceeding maximum residue limit was found only in 6% of the samples.²³ A HPLC method combined with tandem mass spectrometry detection was employed for the study of the migration of phthalates into 12% ethanol simulating alcoholic beverages. Measurements were carried out on a RP-HPLC column (50 x 3.0 mm; 2.5 μm). Analytes were separated by gradient elution using water-methanol mixtures as mobile phase containing 0.1% acetic acid, the flow rate was $300 \mu\text{L min}^{-1}$. The target compounds dibutylphthalate, di-isononylphthalate, di-isodecylphthalate and butyl-benzyl phthalate were applied for the validation of the procedure. It was found that the detection limit of the method allows its application in legislation procedures.²⁴ The retention of bioactive anthocyanins by wine polymers was investigated by RP-HPLC. The investigations were motivated by the fact that red wine is important source in the dietary intake of phenolic derivatives showing marked antioxidant activity. Moreover, anthocyanins play a considerable role in the prevention of cardiovascular diseases and cancer. The measurements indicated that anthocyanins bind to wine polymers and the strength of the binding depends on the chemical character of the interacting compounds. It was further established that the results may facilitate the rational dosage of wine anthocyanins.²⁵ The reaction between malvidin-3-glucoside-(O)-catechin, catechin and malvidin-3-glucoside was studied by LC-DAD/ESI-MS. Measurements were performed both in the positive and

negative ion mode. The results of HPLC measurements indicated the formation of methylmethine-linked cat-mv3glc-(O)-cat ([M-H]⁻ m/z 1097) and mv3glc-mv3glc-(O)-cat(+)[m/z 1301] adducts.²⁶ As mannoproteins improve considerably the quality of wine many analytical methods have been developed for their determination in various wine varieties. A new chromatographic method was developed for the quantitative determination of mannoproteins in wines. Target analytes were isolated by size exclusion chromatography followed by acid hydrolysis, elimination of acids by weak anionic exchange solid phase extraction. The method was proposed for the analysis on monosaccharides by ion exclusion HPLC. It was stated that the method uses low volume samples, makes possible the parallel measurement of multiple samples and the absence of precipitation steps.²⁷ A versatile targeted metabolomics method was developed for the rapid quantification of phenolics in fruits and beverages. The investigations were motivated by the well known health benefits of these classes of molecules. It was established that the procedure suitable for the analysis of 135 phenolics such as benzoates, phenylpropanoids, coumarins, stilbenes, dihydrochalcones, and flavonoids. It was stated that the method is suitable for the evaluation of food quality.²⁸ The profile of low molecular weight phenolic composition of various chips (Portuguese chestnut, French, American and Portuguese oak chips) were investigated using HPLC-DAD and LC-DAD/ESI-MS. Target compounds (phenolic acids, phenolic aldehydes, and furanic derivatives) were separated by pressurized liquid extraction and analysed by HPLC technologies. The results indicated that the botanical species exerts higher influence on the composition of phenolic compounds than the geographic origin.²⁹ The importance of cork taint as a major organoleptic defect in wine, the analytical methods applied for the separation and quantitative determination of the compounds responsible for the cork taint, the enumeration and short discussion of the analytical procedures (solid-phase microextraction, stir-bar sorptive extraction, microextraction in packed syringe) has been recently published.³⁰

Liquid chromatography combined with tandem mass spectrometry was employed for the analysis of pesticides in drinking water and beverages. Pesticide samples were extracted by shaking a mixture of 10 mg of sample and 20 mL of extracting agent (acetonitrile). After shaking vigorously the mixture 1 g of sodium chloride and 4 g of magnesium sulfate were added to the mixture. The organic phase was treated with graphitic carbon black/PSA column. The samples were concentrated and reconstituted with 25 % methanol containing aqueous solution than analysed with LC-MS/MS. The measurements indicated that the recovery from alcoholic beverages was lower than of nonalcoholic ones. It was tentatively explained by the impact of ethanol on the separation process. It was stated that the method can be applied to monitor pesticide residues in drinking water and various beverages.³¹ The metabolic profile of resveratrol has been investigated in healthy men using SPE coupled to LC-ESI-MS/MS. It was established that the food matrix influences considerably the bioavailability of resveratrol. The method identified 17 resveratrol and piceid derivatives. The results indicated that that supplement intake may be used to bring resveratrol to humans.³² The impact of non-volatile compounds on the different in-mouth attributes such as astringency has been studied in detail. The target

compounds were separated with various HPLC technologies. It was found that aconitic acids, polymeric proanthocyanidins, caftaric, caffeic, coumaric and quercetins can considerably influence the astringency of Spanish red wines. Marked antagonisms was observed between the pairs cis/trans-acetic acids, between aconitic acid and caffeic acids, and caffeic acids and quercetin-3-O-galactoside and quercetin-3-O-glucoside. It was concluded from the data that the interaction between the target molecules is a very complicated one and needs further investigations.³³ A RP-HPLC technology was developed and successfully applied for the measurement of Total Antioxidant Potential (TAP) It was stated that the method can be employed both for the analysis of pure compounds and complex mixtures. Hydroxyl radicals can be analysed indirectly as products of their reaction with p-hydroxybenzoic acid (pHBA) or terephthalic (TPA) acids. The 3,4-dihydroxybenzoic or hydroxyterephthalic acids can be separated with RP-HPLC method. Target compounds can be detected with electrochemical or fluorescence methods. It was stated that the method can be used for the determination of TAP values of some alcoholic beverages.³⁴ A similar HPLC method combined with fluorometric detection was applied for the determination of TAP values of low molecular mass molecules such as biogenic polyamines (spermidine, spermine, 1,7-diaminoheptane, putrescine and cadaverine). It was found that the HPLC procedure is suitable for the determination of the TAP values of complicated mixtures such as foods, herbal extracts, blood, alcoholic, and non alcoholic beverages, etc.³⁵ In situ C-13 labelling coupled with LC-DAD-MS/MS was employed for the study of the phenolic biosynthesis in *Vitis vinifera*. The measurements indicated that the method can be used for the investigation of the biosynthesis of phenolics.³⁶ A reversed-phase HPLC column was applied for the separation and quantification of 9 organic acids (acetic, formic, citric, tartaric, lactic, malic, succinic, oxalic, and fumaric). The column dimensions were: 300 x 3 mm; mobile phase: consisted of Li₂SO₄, the flow rate was 0.5 mL min⁻¹. The standard deviation of the method was below 5 %.³⁷ A novel, simple and rapid method was developed for the separation and quantitative determination of pesticide residues in red wine. Pesticide residues were extracted into acetonitrile by QuEChERS (quick, easy, cheap, effective, rugged and safe). Samples were further purified with dSPE (dispersive solid phase extraction) followed by the separation of organic acids, sugars and polyphenolic pigments. Recoveries were between 81.6 % and 112.2 %. Final separation step was carried out by LC-MS-MS. The LOD and LOQ values varied 0.01-0.40 and 0.05-1.33 ng mL⁻¹, respectively.³⁸ Chromatographic profiles of wines were measured at different UV-Vis absorption wavelengths (280, 310, 370, and 520 nm) and by fluorescence at 260 nm excitation and at 360 emission. Principal component analysis (PCA) established that thirteen phenolic compound makes possible the differentiation between the Spanish varieties (*Penedes*, *Rioja* and *Ribera del Duero*). The selected compounds were employed to build partial least squares discriminant analysis (PLS1-DA and PLS2-DA). Characteristic compounds were tentatively identified by LC-MS. It was found that the gallic acid characteristic for *Penedes*; trans-coumaroyltartaric acid and trans-caffeoyltartaric acids for *Rioja* and myricetin for *Ribera del Duero* wines.³⁹ The simultaneous determination of 17 free amino acids and 8 biogenic amines was carried out on an RP-HPLC column. Target compounds were

derivatized with a precolumn method using o-phthalaldehyde (OPA) and detected with fluorescence detector. It was concluded from the results that the most abundant free amino acids are Glu, Arg, Ala, Asp and Lys. Histamine (HIM), cadaverine (CAD), methylamine (MEA) and Tyramine (TYM) have not been found in the samples. The tryptamine (TRM) content was high in aged wines but the concentration of ethanolamine (ETA) was lower. These results were employed for the preliminary classification of the samples using cluster analysis.⁴⁰ The vascular effects of an enzymatic extract of grape pomace (GP-EE) was investigated and the concentration of polyphenols in the extract was determined by HPLC. The presence of kaempferol, catechin, quercetin and procyanidines B1 and B2, resveratrol, gallic acid and anthocyanidines was established. It has been found that GP-EE possess antioxidant and protective vascular properties and can be applied as a functional food.⁴¹ Capillary HPLC combined with laser-induced fluorescence detection (LIF) was employed for the determination of ochratoxin A in wines. Dispersive liquid-liquid microextraction (DLLME) was applied for the preconcentration of the target analyte. The LOD was 5.5 ng L⁻¹, recoveries ranged from 91.7 to 98.1%.⁴² Both GC and HPLC were employed for the study of the effect of mixed culture fermentation (*Candida*, *Hanseniaspora*, *Saccharomyces*) on yeast populations and aroma profile. The measurements revealed considerable differences between the behaviour of mixed cultures.⁴³ HPLC-DAD was employed for the investigation of the distribution and concentration of anthocyanins and flavonols berries from *Vitis vinifera* L. cv. The measurement revealed the presence of the derivatives of five anthocyanins (malvidin, peonidin, petunidin, delphinidin and cyanidin) and six flavonols (quercetin, myricetin, kaempferol, laricitrin, isohamnetin and syringetin). It was stated that the berries from *Vitis vinifera* L. cv. *Brancellao* are suitable for the production of high quality red wine.⁴⁴ The phenolic profile of various grape skins was measured by HPLC-DAD-electrospray ionisation tandem mass spectrometry (HPLC-DAD-ESI-MS). The method identified 40 phenolic compounds including 3 hydroxybenzoic acids, 8 hydroxycinnamic acids, 4 flavanols, 5 flavanones, 3 flavonols, 4 stilbenes and 8 anthocyanins. The investigation found new compounds in grape skins such as protocatechuic acid-glucoside, p-hydroxybenzoyl glucoside, caffeic acid vanilloyl pentoside, β -coumaric acid-erythroside, naringenin hexose derivative, eriodictiol-glucoside, taxifolin-pentoside, quercetin-glucuronide, methylated kaempferol-glucoside, and resveratrol dimer. The application of grape skins as sources of bioactive compounds was proposed.⁴⁵ The phenolic profile of some spine grape varieties was determined using wet methods and HPLC. It was established that variety *Junzi*1* has the highest phenol content (total phenolic, flavonoids, flavanols, and anthocyanins) and the highest antioxidant capacity (DPPH radical-scavenging capacity, cupric-reducing capacity, and hydroxyl radical-scavenging activity). HPLC analysis of the samples established that (+)-catechin is the most abundant phenol derivatives and hydroxycinnamic acids are the most important phenolic acids. It was concluded from the results that *Junzi*1* has the best health promoting properties.⁴⁶ The conditions influencing the release of anthocyanins from the berry skins was investigated in detail. Samples were analysed by HPLC and the date were compared. The measurements indicated that the anthocyanin profile of berry skins depended

considerably on the environmental conditions such as ripeness, extraction kinetics. It was concluded from the results of the investigation that the data can be applied for the improvement of wine quality and for purposeful creation of different styles of wines.⁴⁷ The application possibility of LC-MS technologies for the analysis of foods and food products has been earlier discussed and it was established that LC-MS can be successfully employed for the solution of problems of authentication and adulteration. Moreover the review deals with an outlook on future tendencies.⁴⁸ Ochratoxin A (OTA) is a possible human carcinogenic (IARC). The impact of alcoholic fermentation on the concentration of OTA has been investigated by HPLC-fluorescence detection (HPLC-FL). The measurements proved the detoxifying effect of alcoholic fermentation. It was further established that 5-12% of OTA is adsorbed on grape skins and both commercial strain were suitable for the reduction of the concentration of OTA during the alcoholic fermentation process.⁴⁹ A HPLC method was developed for the separation and quantitative determination of biogenic amines such as histamine, tyramine, spermine, spermidine, putrescine, cadaverine and phenylethylamine. The investigations indicated that wines show marked differences in the composition and concentration of biogenic amines, the amount of putrescine being the highest in each sample.⁵⁰ A new effective extraction and separation method was developed for the analysis of anthocyanins from black grapes. The possible application of grape anthocyanins in electronic and photonic devices is discussed in detail⁵¹. The aroma profile and phenolic content of some grapes grown in Italy were determined by various chromatographic technique and the result were compared by using multivariate mathematical statistical evaluation methods (cluster analysis, principal component analysis). Volatiles were extracted by using headspace solid phase microextraction (HS-SPME) carried out on PDMS fiber and were analysed by GC-MS. Ethyl hexanoate, ethyl decanoate, and ethyl octanoate were the dominating esters while phenyl ethanol, 3-methyl-1-butanol were the dominating alcohols.

HPLC-MS detected gallic acid, p-coumaric acid, trans ferulic acid, caffeic acid, trans-resveratrol, (+)-catechin and (-)-epicatechin. The total phenolic content of the wines varied between 30.4 – 61.9 mg L⁻¹.⁵² HPLC and spectrophotometry were employed for the study of copigmentation and anti-copigmentation in grape extract. The investigations established that many components in wine are able for copigmentation modifying in this manner the color of the wine.⁵³ A HPLC procedure was optimized for the determination of biogenic amines (histamine, methylamine, ethylamine, tyramine, putrescine, cadaverine, phenethylamine, isoamilamine).⁵⁴

Abbreviations

CAD	cadaverine
CP	chlorpyrophos
CPO	chlorpyrophos-oxon
CT	cryogenic trapping
DAD	diode array detection

dSPE	dispersive solid phase extraction
DTC	dithiocarbamate
ESI-MS	electrospray ionisation tandem mass spectrometry
ETA	ethanolamine
FL	fluorescence detection
GC-O	gas chromatography-olfactometry
GC-MS	gas chromatography – mass spectrometry
HIM	histamine
HPLC	high performance liquid chromatography
HPLC-DAD-ESI-MS	high-performance liquid chromatography-photodiode-array detection-electrospray ionization mass spectrometry
HS-SPME	headspace solid-phase microextraction
LOD	limit of detection
ITEX	headspace in-tube extraction
LOQ	limit of quantitation
MEA	methylamine
MIPS	molecularly imprinted polysiloxane microspheres
ODS	octadecyl silica
OPA	o-phthaldialdehyde
OTA	ochratoxin A
PA	polyacrylate
PDC	triple-phase polydimethylsiloxane/carboxane
pHBA	p-hydroxybenzoic acid
QuEChERS	quick, easy, cheap, effective, rugged and safe
SBSE-GC-MS	stir bar sorptive extraction-gas-chromatography-mass spectrometry
SPME-GC-MS	solid phase microextraction-gas-chromatography
SPME	solid phase microextraction
TAP	total antioxidant potential
TPA	terephthalic acid
TRM	tryptamine
TYR	tyramine

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