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METHODS FOR DETERMINATION AND SPECIATION OF TRACE ELEMENTS IN WINE

(Review)

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Abstract: This article reviews methods for the determination and speciation of trace elements in wine. Wine is one of the most widely consumed beverages and strict analytical control of trace elements content is required during the whole process of wine production from grape to the final product. Levels of trace elements in wine are important from several points of view: organoleptic - Fe, Cu, Mn and Zn concentrations are directly related to the destabilization and oxidative evolution of wines, toxicological – toxic elements content should be under allowable limit and wine adulteration – definition of the authenticity of wine through its trace element composition and pattern recognition. The speciation of metals in wine is subject of increasing interest since complexation may reduce their toxicity and bioavailability. Two main approaches used for trace element determination in wines – sample digestion followed by instrumental determination and direct instrumental determination are reviewed and discussed. Procedures for sample pre-treatment, for trace element separation and preconcentration are presented. The possibilities, advantages and disadvantages of different analytical methods (atomic absorption spectrometry, atomic emission spectrometry, atomic emission spectrometry with inductively coupled plasma, inductively coupled plasma with mass spectrometry, electroanalytical methods etc.) for wine analyses are compared. Advances in metal speciation studies in wines are presented.

Key words: *wine, trace element determination, speciation, review*

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Introduction

Wine is a natural product, widely consumed in the world with thousands years of tradition. The chemical composition of wine is very complex: besides ethanol, sugars and organic acids, wine contains tannins, aromatic and coloring substances and microelements. The information about the quantitative concentration of various components of wine at all stages of winemaking allows viticulturists to control the process of obtaining high quality wine that posses a certain taste, bouquet, color, flavor and transparency [1]. Another point of view of wine analysis is "analytical detection of wine adulterations" – suitable analytical information for wine that ensures exact determination of wine variety, vintage and geographical origin. Suitable analytical information means multi-elemental, multi-factorial, statistical approach including organic trace and aroma components, inorganic trace components and stable isotopes [2].

Another point of view on the importance of wine analysis is that recent data suggest that beverages can significantly contribute to the total dietary intake of some trace elements with the possibility of influencing the levels in tissues and body fluids. Wine is among the beverages which contributes to increasing the total dietary intake of trace elements to an extend greater than 10 % [3]. Numerous studies have shown that a moderate consumption of wine, especially red, improves good health and longevity when it is combined with a balanced diet [4]. Daily consumption of wine in moderate quantities contributes significantly to the requirements of the human organism for essential elements (B, Co, Mn, Ni, Mo, Se, Zn), albeit with elements like As, Pb, Cd which are well known as toxic. Beverages of different kinds have been investigated for their

content of Pb, Cd, Ni, Cr, As and Hg [5]. About a ten times higher Pb content was found in wine than in most other beverages, so wine is the most significant source of Pb. Evidently strict analytical control of trace elements levels in wine is important to asses the dietary intake of essential as well as toxic elements for humans. Maximum acceptable limits for trace element contents in wine have been established by the Office International de la Vigne et du Vin (OIV) but national legislation concerning allowable limits of these elements exists in almost all countries.

Grape variety, processing method and even the year of vinification can have a dramatic impact on the organoleptic and visual characteristics of wines. Although it is not clear that trace elements in wine can substantially affect taste, it is well known their influence on sophisticated equilibrium between different compounds in wine matrix. A plethora of substances and processes can affect the element composition of wine during production and packing. The most important factors that determine the metal content in wines are: (i) contribution from soil on which vineyards are located and capacity of grapes to assume mineral substances; (ii) contribution from various steps of the production cycle, from grape to the finished wine (treatments preliminary to grape-harvest, fermentation reactions, addition of compounds with various functions); (iii) contribution from wine processing equipment, conservation and bottling. Unless exposed to significant airborne pollution grapes accumulate a small amounts of toxic metals by translocation from the roots or by direct contact with vineyard sprays. Investigations carried out on the migration of toxic elements in the system soil-grapevine-grape for polluted region showed that major amount of toxic elements in grapevine are mainly due to the toxic metal containing aerosols falling from the atmosphere [6]. However Orescanin et al. [7] determined V, Cr, Mn, Fe, Ni, Cu, Zn, As and Pb in soil, grape and wine and concluded that the main source of heavy metals in grapes is absorption from the soil. Almost the same conclusion has been done from Mackenzie et al. [8]. They found that soil cation chemistry does influence the wine grape composition. Trace elements are normally absorbed onto the yeast cell and are removed from the final product during the prefermentation clarification (a process of removal of substances that produce unwanted flavors, favor the fermentation to dryness and increase the fermentation rate) [9]. Both toxic elements Cd and Pb are greatly eliminated by clarification [9]. In most cases their final elevated concentrations in wine result from contamination during post-fermentation processing, sources include contact with nonstainless steel equipment and impurities in fining agents and filter media [10, 11]. In a model investigation, ten different bentonites have been used for wine fining and as a result statistically significant increases of the most elements was observed but in significant lower levels of Cu, K, Rb and Zn. The addition of yeast hulls caused a statistically significant depletion of the contents of Ce, Cu, Fe, La, Sb, U, V and Y [12]. Therefore it is clear that trace element composition of grapes and wines is influenced by the type of soil, wine processing equipment and vinification but in very specific manner for different elements [13, 14].

Trace elements in wine

Potassium is a natural component of grape and its concentrations in wine reflects the levels in grapevine in the final stages of berry ripening. High K levels affect the stability of wine with respect to the potassium hydrogen L-(+)-tartarate precipitation.

Calcium is a natural component of wine although the concentration of calcium in wine can be affected by the traditional practices of de-acidification ($CaCO_3$ addition) or plastering ($CaSO_4$ addition). Elevated calcium levels can lead in some wines to calcium L-(+)-tartarate precipitation. It should be pointed that total calcium content in wine is not informative enough to predict the stability of wine and data for the free metal concentration are required [16].

Aluminum is found in grape juice, but the concentration in both juice and wine is elevated because of the use of bentonite and to a lesser extent from contact with aluminum surfaces. It has become apparent that aluminum is strongly complexed in wine which affects its bioavailability from one side and makes haze formation unlikely from the other side.

At low concentration *iron* plays an important role in metabolism and fermentation processes as an enzyme activator, solubilizer and functional component of proteins. Above trace levels, iron

has other roles: altering redox system of the wine in favor of oxidation, participation in the formation of complexes with tannins and phosphates thus resulting in instabilities.

Almost the same is valid for *copper*: in trace amounts is an important inorganic catalyst for metabolic activities of microorganisms; at high levels it plays an important role in catalyzing oxidation of wine polyphenols. It should be pointed out that copper and copper complexes are more active than iron and its complexes [16]. However for both elements copper-induced and iron-induced spoilage are not related to the total metal concentration. For copper, the free active metal concentration is important and for iron the valence state determines the potential for iron-induced oxidation.

Sources of *lead* in wine were inferred from systematic assay of grapes must and wine during winemaking. It was found that Pb concentration in fermenting must vary during vinification. Lead concentration increased significantly in open-top vessels, in holding bins, and during pressing. Juice and wine stored in concrete or waxed wood have significantly higher concentration of lead compared to juice and wine stored in stainless steel. Moreover fining with bentonite or filtering with diatomaceous earth contribute further to final Pb concentration, while fermentation, both primary and secondary, removed Pb [17]. In another study measurements of 7000 wines were used to identify possible sources of Pb in wine and these showed that atmospheric–related contamination (leaded gasoline) was not responsible for elevated Pb levels in wine. It was also shown that the presence or absence of tin-lead capsules as well as the stare of tin-lead capsule corrosion had only a very minor influence on the Pb concentration in wine. It has been concluded that brass is the main contamination source for elevated Pb content in wine [18].

Cadmium levels have been determined during wine making in 21 locations in France. During the alcoholic fermentation, Cd elimination is almost completed with losses between 87 to 100% [19].

An interesting study for statistical evaluation of aroma and metal content in Tokay wine answers the question – how qualitative and quantitative relations of volatile organic and metal components present in traditional wines depend on the vintage, the location on which it is grown, as well as the type of wine grape and to what extent these are characteristics of wines of given type and vintage [20]. Wines from Jordan has been characterized for pesticides and trace metals contents and it has been shown that heavy metals showed higher values in grapes than in wines which is attributed to the removal of solids during wine preparation processes [21].

The influence of Fe, Cu and Mn on wine oxidation was studied and it was found that these three cations intervene ‘somehow’ the evolution of different compounds: anthocyanins, tannins, total phenol content and acetaldehyde which are sensitive to oxidation. Iron catalyzes acetaldehyde combination with phenolic compounds [22].

Methods for trace element determination in wines based on sample digestion followed by instrumental determination

Atomic Absorption Spectrometry in Flame (FAAS), Electrothermal (ETAAS) and Hydride generation (HG) modes is one of the most widely used techniques for trace element determination in wines applied almost routinely in oenological laboratories and recommended by the OIV, European Economic Community and the American Society of Enologists [23, 24]. The sample preparation step e.g. preliminary digestion of wine sample was included to destroy the organic matrix and/or to extract the metal ions bound in inorganic and organic complexes. In the wine industry dry ashing dates from very beginning of wine analysis: it involves the complete removal of organic matter, although volatilization losses at high temperatures are not always easy to assess and low recoveries have been observed at trace analytes levels [24]. Comparison between two mineralization methods: microwave (MW) digestion versus dry ashing for Pb determination in wines does not offer noticeable differences, but authors inclined to the microwave digestion due to the more reproducible results and considerable gain of time [25]. Acid wet digestion is the preferred pretreatment procedure, but reagent blanks for some elements are close to their natural contents in wine [26–34]. In some cases vanadium pentaoxide was added as a catalyst to improve completeness of sample digestion [35–37] In order to prevent analyte losses, PTFE bombs [38] or Savillex vessel [26]

have been used. As an alternative a microwave oven digestion offers advantages such as reduced losses due to volatilization, low reagents consumption, fast and complete matrix mineralization [3, 35, 39–47]. On-line MW sample digestion was used in flow injection HGAAS determination of Pb in wine [48]. Simple and very reliable sample preparation method in wine analysis is UV-photolysis which allows low blanks with minimal analyte losses [49, 50]. Wine sample digestion is unavoidable and highly recommended (OIV) procedure when HGAAS was applied in wine analysis [51, 52]. Complete digestion of wine organic matter was required in order to obtain accurate and reliable results. Flow-injection HGAAS with on line MW oxidation was used for Pb determination in wines [47, 53]; a mixture of HNO_3+$HClO_4$ has been proposed for wine digestion in thermostatted vessel for Se determination by HGAAS [54]; MW digestion with HNO_3 has been applied to Hg and Se determination in wines from Canary Islands [50]. An interesting approach was applied by Chuachuad et al for Cd determination in wines by flow injection cold vapour AAS (CVAAS) [44, 56] and Pb determination by HGAAS [44] after wine MW digestion by mixture of HNO_3+H_2O_2. A volatile derivative was formed on passage of an acidified cadmium solution through a strong-anion-exchange resin (Amberlite IRA-400) in the tetrahydroborate(III) form and atomized in a quartz T-atomizer [43] or graphite furnace [56]. Strong-anion-exchange resin (Amberlist A-26) in the tetrahydroborate(III) form as reductant was used for Pb determination in wines in the presence of $K_3Fe(CN)_6$ [43]. Ozone treatment as wine pre-treatment procedure was applied for Hg determination in wine by CV AAS [57]. It is known that ethanol as main volatile component is a serious depressant in HGAAS and recently has been shown that simple ethanol evaporation is efficient for wine pre-treatment before As determination by HGAAS [29].

Although direct ETAAS is used for trace elements determination in wines, reliable results for elements like As and Sb cannot be obtained without preliminary wine digestion [27, 28, 58, 59]. Very strong matrix interferences leading to strong signal depression by 40– 60 % have been observed in direct determinations, even in the presence of suitable modifier. It could be suggested that wine organic matter as well as high phosphate and sulfate contents [58] are responsible for the observed interference. As far as phosphate and sulfate contents do not change after wine digestion, remarkable depression still exist and requires standard addition method to be used for calibration [28, 59]. Relatively low concentrations of Pd and Ni modifiers have been recommended for efficient thermal stabilization of As, Sb [28] and Se [58] in wine digests. Complete wine decomposition in the presence of HNO_3+H_2O_2 in two different digestion systems (Tecator and Bethge) was achieved without any analyte losses [59]. Summary of the methods based on ETAAS together with detection limits (LOD) achieved are present in Table 1. In Table 2, HG and CV method combined with AAS, ETAAS and AFS are presented.

ICP-AES and ICP-MS.

Both methods permit multielement analysis in wide dynamic range and this explains their wide applications for trace element determinations in wines [105]. Low detection limits achieved by ICP-MS together with the possibilities for element isotope ratios determination rank this method as an excellent tool for detailed characterization of the elemental composition of wines. Detailed investigations on the spectral and non-spectral interferences due to the complex wine matrix have been conducted [106, 107]. Ethanol is well known to cause matrix effects in ICP techniques because carbon deposition on the sample introduction system, plasma instability and signal enchantment/depression for some elements [60]. Therefore varieties of methods for preliminary wine sample decomposition have been suggested: ethanol evaporation [108, 109], digestion in the presence of HNO_3+H_2O_2 [26, 30, 110–115], UV-irradiation [112, 113, 116–118].

Two methodologies for multielement (26 elements) analysis of wine samples: direct ICP-MS determination of trace elements and preliminary sample decomposition by UV-irradiation, performed in two different laboratories with two different ICP-MS instruments have been compared [118]. Their

Table 1. The application of ETAAS in wine analysis

Element(s)	Sample pretreatment	Modifier(s)	LOD	Ref.
Al	Direct after dilution	No modifier	40 μg L^{-1}	60
Al	Direct (dilution)	$Na_2Cr_2O_7$	2.8 μg L^{-1}	61
Al	Direct after dilution	No modifier	1 μg L^{-1}	62
Al	Digestion with HNO_3+V_2O_5	$Mg(NO_3)_2$	0.4 μg L^{-1}	36
Al	Direct	No modifier	1.5 μg L^{-1}	63, 64
Ag, Co, Si, Zn	Direct		0.20 μg L^{-1} Ag 1.6 μg L^{-1} Co 7.9 μg L^{-1} Si 21 μg L^{-1} Zn	66
As	Digestion with HNO_3+H_2O_2	Pd	5 μg L^{-1}	28
As	Digestion with HNO_3	Pd	6.6 μg L^{-1}	27
As, Sb	Direct/better after digestion	$Pd(NO_3)_2$	-	59
Cd	Digestion/HNO_3/V_2O_5		0.5 pg	38
Cd	Digestion with $HClO_4$ and HNO_3	-	0.008 μg L^{-1}	30
Cd	Direct	$Pd(NO_3)_2$+HNO_3	0.03 μg L^{-1}	67
Cd	Direct	Pd	0.08 μg L^{-1}	68
Cd, Pb	Dilution with HNO_3	$Pd(NO_3)_2$+$Mg(NO_3)_2$	0.03 μg L^{-1} Cd 0.8 μg L^{-1} Pb	37
Cd, Pb	Microwave digestion with HNO_3	$NH_4H_2PO_4$+$Mg(NO_3)_2$	0.1 μg L^{-1} Cd 1.0 μg L^{-1} Pb	41
Cd, Cr, Pb	Direct		0.5 μg L^{-1} Cd 1 μg L^{-1} Cr 3 μg L^{-1} Pb	69–71
Cd, Cr, Pb	MW digestion	$Pd(NO_3)_2$ for Cd and Pb $Mg(NO_3)_2$ for Cr		72
Cd, Co, Cr, Mn, Pb	MW digestion	Cd: $Pd(NO_3)_2$;; Co, Mn, and Cr: $Mg(NO_3)_2$; Pb: $Pd(NO_3)_2$+$NH_4H_2PO_4$		73
Cr	Direct	No modifier or Pd	0.1–1 μg L^{-1}	74–76
Cu	Direct	No modifier	5.75 μg L^{-1}	77, 78
Cu, Pb	Direct	No modifier		79,80
Cu, Fe	Direct/dilution (1+9) with Milli-Q water	No modifier		81
Cu	Direct	$Pd(NO_3)_2$+ $Mg(NO_3)_2$	5.0 μg L^{-1}	82
Hg	MW digestion and extraction with APDC into MIBK	Pd	0.2 μg L^{-1}	83
Ni	Direct	Pd	1.0 μg L^{-1}	84, 85
Pb	Dilution with HNO_3	Pd+Mg	15.5 μg L^{-1}	27
Pb	Direct after dilution	$Pd(NO_3)_2$+$Mg(NO_3)_2$	19 μg L^{-1} Pb	60
Pb	Interlaboratory study by using ETAAS			86
Pb	Direct	Pd+$Mg(NO_3)_2$	0.9 μg L^{-1}	87
Pb	Direct/dilution (1+4 v/v) Triton X-100	No modifier	Not present	88
Pb	Dilution with HNO_3	$NH_4H_2PO_4$+$Mg(NO_3)_2$	6.2 μg L^{-1}	89
Pb	Dilution with HNO_3	$NH_4H_2PO_4$	LOD 4 μg L^{-1} LOQ 14 μg L^{-1}	90
Pb	Digestion with HNO_3+UV photolysis	$NH_4H_2PO_4$+$Mg(NO_3)_2$	0.12 μg L^{-1}	91

Continue Table 1

Pb	Direct	$NH_4H_2PO_4$		92, 93
Pt	Direct and mineralization	-	10 μg L^{-1}	94
Se	Digestion with HNO_3+H_2O_2	$Ni(NO_3)_2$+$Sr(NO_3)_2$	1 μg L^{-1}	58
Se	Extraction with APDC into MIBK	Ag or $Ni(NO_3)_2$+$Sr(NO_3)_2$	0.2 μg L^{-1}	58, 95
Se	Direct	Pd + hydroxylamine hydrochloride	9 μg L^{-1}	96
Tl	Extraction from 0.5 mol L^{-1} KI solution into MIBK	Pd+ascorbic acid; Ag	0.05 μg L^{-1}	97
V	Direct		4.2 μg L^{-1}	98, 50

Table 2. HG and CV methods with AAS, ETAAS and AFS detection in wine analysis

Element(s)	Technique	Sample pretreatment	Reaction media	Reductant	LOD	Ref.
As(III), As(V) total As	HGAAS	Direct (ethanol evaporation) MW digestion	8 mol L^{-1} HCl	$NaBH_4$ (0.2% or 0.6% m/v)	0.1 μg L^{-1} As(III), As(V), total As	29
As (III), As(V), MMA, DMA, Total As	HGAFS	direct	Citric buffer: As(III) 0.2 mol L^{-1} CH_3 COOH: As(III)+DMA 8 mol L^{-1} HCl: As(III)+As(V) 1 % m/v L-cysteine	$NaBH_4$ (0.2% or 0.6 % m/v)	0.4 μg L^{-1} As(III) 0.4 μg L^{-1} As(V), DMA	99
As	HGAFS	Direct, flow injection; Digestion	6 mol L^{-1} HCL	$NaBH_4$ (1% m/v)	0.3 μg L^{-1}	101
Cd	FI-CVAAS	Digestion	0.2 mol L^{-1} HNO_3; 1% m/v thiourea, 1 mg L^{-1} Co	Amberlite IRA-400) tetrahydroborate (III) form	0.032 μg L^{-1}	43
Cd	FI-CV ETAAS	Digestion	0.2 mol L^{-1} HNO_3; 1% m/v thiourea, 1 mg L^{-1} Co	Amberlite IRA-400) tetrahydroborate (III) form	0.09 μg L^{-1}	56
Hg	CVAAS	Digestion	1 mol L^{-1} HCl	$SnCl_2$ (20% m/v)	1.0 μg L^{-1}	40
Hg (white wines)	FI-CVAAS	Ozonation	1 mol L^{-1} HCl	$SnCl_2$ (20% m/v)	0.5 μg L^{-1}	57
Hg	CVAFS	Direct	HCl (20 % v/v)	Ethanol	0.07 μg L^{-1}	102
Pb	FI-HGAAS	Direct	0.1 mol L^{-1} HNO_3 3% m/v $K[Fe(CN)_6]_3$	Amberlite IRA-400) tetrahydroborate (III) form	3.1–5.2 μg L^{-1}	44
Pb	FI-HGAAS	Digestion	HNO_3+H_2O_2	$NaBH_4$ (6 % m/v)	10 μg L^{-1}	48
Pb	FI-HGAAS	Direct	HNO_3	H_2O_2	10 μg L^{-1}	53
Pb	HGAAS	Direct (dilution with HCl)	HCl H_2O_2 (7.5%)	$NaBH_4$ (21% m/v)	24 μg L^{-1}	103
Sb	HGETAAS	Direct (Pd modifier)	HCl+thiourea	$NaBH_4$ (1 % m/v)	0.13 μg L^{-1} Sb	104
Se	HGAAS	Digestion with HNO_3	7 mol L^{-1} HCl	$NaBH_4$ (0.6% m/v)	0.1 μg L^{-1} Se	40

results demonstrate a very good agreement for most elements, although some discrepancies for the REE's, As and Ga have been observed. The application of ICP-AES and ICP-MS in wine analysis is presented in Table 3.

Voltammetry:

Electroanalytical methods are particularly suitable for both purposes total trace element determination and speciation - more precisely determination of different metal fractions in wines. The most commonly used stripping techniques are differential pulse anodic stripping voltammetry (DPASV) and stripping potentiometry (SP). The remarkable sensitivity of both methods is attributed to their effective in situ preconcentration of the metal of interest generally into a mercury drop (or other electrode) of both conventional and microscopic dimensions. The difference between methods is in the second stripping step. In ASV the metal is re-oxidized electrochemically from the amalgam state resulting in an anodic current, the magnitude of which is proportional to the analyte metal concentration. In (SP) stripping is achieved chemically, dissolved oxygen and mercury ions, either together or separately are commonly used. One of most common interferences in voltammetric analysis is the passivation of working electrode due to adsorption of organic constituents, more pronounced for DPASV and in less so extend for SP. That is why the application of DPASV for trace element determination in wine is typically combined with a previous digestion step for decomposition of the organic matter of wine; dry mineralization [157, 158], acid digestion with strong oxidizing agents (HNO_3, H_2O_2, $HClO_4$) [159, 160] and ultraviolet irradiation in the presence of oxidizing agents or photocatalyst [49, 161–163] are the most extensively employed. Digestion procedures were carefully optimized prior to Ni determination in wines by DPASV [163] or Cu and Pb determination by ASV using mercury microelectrodes [161]. Determination of Cr in wine by ASV was performed after UV-digestion [162]. Ion-selective electrodes with summing operational amplifier have been employed for Ca, K and Mg determination in wines after dry ashing [157]. New idea for fast electrochemical sample preparation for ASV determination of Cu, Pb and Zn was proposed [164]. The summary of the electroanalytical methods used for trace elements determination in wine is presented in Table 4.

Total reflection X-ray fluorescence spectrometry (TXRF).

Important advantage of this method when compared with widely used FAAS and ETAAS is the possibility for fast, multi element analysis of wine samples [39, 192–194]. It is really rapid and very small amounts of wine samples are needed [194]. Owing to the complex matrix of wine in most cases it is necessary to mineralize the sample in the presence of HNO_3+H_2O_2 [39, 192]. However detection limits achieved for most frequently determined elements like As, Cd, Cu, Cr, Pb are worse than those by ETAAS.

Direct methods for trace elements determination in wine

Atomic Absorption Spectrometry in Flame, Electrothermal and Hydride generation modes is particularly suitable for direct determination of trace elements in wine. However wine is a complex matrix containing ethanol and other organic compounds which influence the transport properties of the sample toward atomization device due to the changes in viscosity and surface tension in comparison with aqueous standard solutions. Wine contains high concentrations of K, which acts as natural ionization buffer and should be taken into account in calibration procedures. Inorganic components in wine like sulphates and phosphates could interfere with the atomization of elements (FAAS) or cause strong background absorption due to radicals formed in ETAAS. FAAS is most widely used and easily accessible technique for the determination of Ag, Ca, Fe, K, Mn, Mg, Na and Zn in wines [32, 65, 195–197]. Conventional ionization buffers (CsCl) and ethanol are added to the calibration solution in order to obtain matrix-matched standard solutions and La(III) chloride is used as releasing agent to overcome phosphate atomization interferences in the determination of Ba, Ca, Mg and Sr.

Table 3. ICP methods in wine analysis

Element(s)	Sample pretreatment	Type of instrument	Calibration/ correction	Isotope(s)	Ref.
Al, Ba, Cd, Co, Cr, Cu, Fe, Ga, Li, Mn, Ni, Pb, Rb, Sr, V, Zn, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	digestion by UV irradiation	ICP-MS (quadrupole mass analyzers)	External calibration Semiquantitavive mode	^{111}Cd, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{160}Gd, ^{159}Tb, ^{63}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{173}Yb, ^{75}Lu, ^{7}Li, ^{51}V, ^{59}Co, ^{69}Ga, ^{71}Ga, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{53}Cr, ^{60}Ni, ^{65}Cu, ^{75}As, ^{138}Ba, ^{27}Al, ^{55}Mn, ^{64}Zn, ^{85}Rb, ^{88}Sr, ^{57}Fe	117
Li, V, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Pb	Direct with micro-concentric nebulizer Digestion by UV irradiation in the presence of H_2O_2 Comparative study	ICP-MS (quadrupole mass analyzers)	Direct: set of external standards and two BCR wines (dry white and red) for quality control Digestion: internal standard (Rh) for digestion procedure	^{111}Cd, ^{125}Te, ^{141}Pr, ^{147}Sm, ^{151}Eu, ^{158}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu ^{185}Re, ^{192}Os, ^{195}Pt, ^{197}Au, ^{209}Bi, ^{9}Be, ^{93}Nb, ^{99}Ru, ^{105}Pd, ^{133}Cs, ^{139}La, ^{140}Ce, ^{146}Nd, ^{205}Tl, ^{232}Th, ^{238}U, ^{59}Co, ^{69}Ga, ^{90}Zr, ^{127}I, ^{182}W, ^{7}Li, ^{51}V, ^{60}Ni, ^{208}Pb, ^{118}Sn ^{121}Sb, ^{75}As	118
Co, Ga, As, Zr, Sn, Sb, W, I, Li, V, Ni, Pb, Be, Nb, Pd, La, Ru, Ce, Tl, Th, U, Cs, Cd, Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Te, Re, Os, Pt, Au, Bi, Y, Rh, In Pb isotope ratios	Direct	ICP-MS (quadrupole mass analyzers)	External calibration by using set of ethanol matched standard solutions, Internal standards – Y and Rh, BCR wines for quality control	^{9}Be, ^{51}V, ^{60}Ni, ^{48}Ti, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{75}As, ^{85}Rb, ^{88}Sr, ^{90}Zr, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{125}Te, ^{133}Cs, ^{135}Ba ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{158}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{173}Yb, ^{175}Lu, ^{185}Re, ^{195}Pt, ^{197}Au, ^{205}Tl, ^{232}Th, ^{238}U, ^{182}W $^{208/207}$Pb, $^{206/207}$Pb, $^{206/204}$Pb	119
Li, Be, Al, Sc, Ti, V, Sr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb, Lu, Hf, Ta, Re, W, Pt, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U, Pu	Direct: Wine+1% v/v HNO_3 (1+1 v/v) dilution	ICP-MS	Calibration by using set of ethanol matched standard solutions, Internal standard– Y, BCR wines for quality control	^{7}Li, ^{9}Be, ^{27}Al, ^{45}Sc, ^{48}Ti, ^{51}V, ^{52}Sr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{62}Ni, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{69}Ga, ^{73}Ge, ^{75}As, ^{78}Se, ^{81}Br, ^{85}Rb, ^{86}Sr, ^{87}Sr, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{93}Nb, ^{95}Mo, ^{102}Ru, ^{103}Rh, ^{106}Pd, ^{107}Ag, ^{111}Cd, ^{114}Cd, ^{115}In, ^{120}Sn, ^{121}Sb, ^{125}Te, ^{127}I, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{152}Sm, ^{153}Eu, ^{154}Gd, ^{159}Tb, ^{162}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{174}Yb, ^{175}Lu, ^{178}Hf, ^{181}Ta, ^{185}Re, ^{182}W, ^{195}Pt, ^{192}Os, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{2002}Hg, ^{205}Tl, ^{206}Pb, ^{207}Pb, ^{207}Pb, ^{209}Bi, ^{232}Th, ^{238}U, ^{239}Pu	120
Al, Li, Fe	Sonication (CO_2 removal)	Cold plasma ICP-MS	External standard calibration	^{7}Li, ^{27}A, ^{56}Fel	122

Continue Table 3

Al, B, Ba, Cu, Fe, Mn, Zn	MW digestion	ICP-AES	External calibration		123
Li, B, Al, Ca, Mn, Fe, Ni, Cu, Zn, As, Rb, Sr, Cd, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Pb, P, S	Direct: wine+twice distilled water (1+1 v/v) dilution and addition of 100 µl conc. HNO_3	ICP-MS (quadrupole mass analyzers) comparison of nebulizers	Semi-quantitative mode by using internal standard In	-	124
Li, B, Na, Mg, Al, Si, Cl, Ca, Sc, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ru, Cd, Sn, Sb, Te, Cs, Ba, La, Ce, Nd, W, Tl, Pb, U	Dilution: 1+1 with 0.14 mol L^{-1} HNO_3 MW digestion	ICP-MS quadropole mass analyzer Cross-flow nebulizer	Matrix matched (6% ethanol, nitric acid) standards Internal standard - In	^{51}Cr, ^{55}Mn, ^{85}Rb, ^{88}Sr, ^{98}Mo, ^{133}Cs, ^{138}Ba, ^{139}La, ^{140}Ce, ^{146}Nd, ^{205}Tl, ^{208}Pb, ^{238}U for quantitative mode	125
Ag, Al, Cd, Ca, Co, Cr, Cu, Fe, Hg, K, Mn, Mg, Na, Ni, Pb, V, Zn	Direct and after digestion	ICP-AES Two different instruments tested	Standard addition, matrix matched (ethanol) standards	-	110
Ag, Al, As, B, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Rb, Sb, Se, Sn, Sr, Zn	Digestion	ICP-AES	External calibration	Viticulture products Mozhe da se slogi v teksta	126
Fe, Pb, Al, Zn, Cu, Na, Ca, Mg	Digestion	ICP-AES	External calibration	-	127
Al, B, Ba, Ca, Fe, Mg, Mn, Na, Rb, Sr, Zn	Digestion	ICP-AES	External calibration	-	128
Ag, Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Li, Ni, Pb, Rb, Sr, Sb, Tl, U, V, Zn	Direct (stabilizatiion with HNO_3), Mineralization in Savillex teflon vessels with (HNO_3+H_2O_2)	ICP-MS (quadrupole mass analyzers)	Internal standards Sc, In, Re	^{7}Li, ^{9}Be, ^{27}Al, ^{51}V, ^{59}Co, ^{53}Cr, ^{62}Ni, ^{65}Cu, ^{66}Zn, ^{75}As, ^{85}Rb, ^{88}Sr, ^{109}Ag, ^{111}Cd, ^{121}Sb, ^{133}Cs, ^{138}Ba, ^{208}Tl, ^{208}Pb, ^{238}U	26
Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Na, Ni, Pb, Rb, Sn, Sr, V, Zn	Digestion with HNO_3	ICP-AES	External calibration	-	129
Al, B, Cu, Fe, Hg, Mg, Ni, Pb, Si, V	Direct	ICP-AES PTFE membrane desolvator	Standard addition calibration	-	130

Continue Table 3

Al, As, B, Ba, Be, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, I, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pd, Pr, Rb, Rh, Sb, Si, Sm, Sn, Sr, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn,Zr	Direct 1+4 dilution with 1% v/v HNO_3	ICP-MS Pneumatic nebulizer	Matrix matched (2.5% ethanol) multielemnt standard solutions	^{7}Al, ^{75}As, ^{7}B, ^{138}Ba, ^{44}Ca, ^{114}Cd, ^{140}Ce, ^{59}Co, ^{52}Cr, ^{133}Cs, ^{63}Cu, ^{56}Fe, ^{69}Ga, ^{73}Ge, ^{39}K, ^{139}La, ^{7}Li, ^{24}Mg, ^{55}Mn, ^{95}Mo, ^{58}Ni, ^{47}P, ^{208}Pb, ^{141}Pr, ^{85}Rb, ^{121}Sb, ^{28}Si, ^{120}Sn, ^{88}Sr, ^{232}Th, ^{48}Ti, ^{238}U, ^{51}V, ^{182}W, ^{89}Y, ^{174}Yb, ^{66}Zn, ^{90}Zr	131
Li, Be, B, Al, Sc, Ti, V, Ni, Mn, Co, Cu, Zn, Ge, As, Se, Rb, Sr, Nb, Zr, Mo, Rh, Pd, Ag, Cd, Sn, Sb, La, Ba, Ce, Eu, Gd, W , Pt, Au, Hg, T1, Bi, Pb, Th, U	MW digestion with HNO_3	ICP-MS (quadrupole mass analyzers)	Standard addition calibration	^{7}Li, ^{9}Be, ^{10}B ^{27}Al, ^{45}Sc, ^{49}Ti, ^{51}V, $^{60(61)}Ni$, ^{55}Mn, ^{59}Co, ^{63}Cu, ^{66}Zn, ^{74}Ge, ^{75}As, ^{82}Se, ^{85}Rb, ^{88}Sr, ^{93}Nb, ^{94}Zr, ^{95}Mo, ^{103}Rh, ^{105}Pd, ^{107}Ag, ^{ll4}Cd, ^{115}In, ^{120}Sn, ^{121}Sb, ^{139}La, ^{138}Ba, ^{140}Ce, ^{153}Eu, ^{156}Gd, ^{182}W, ^{195}Pt, ^{197}Au, ^{202}Hg, $^{205}T1$, ^{209}Bi, ^{208}Pb, ^{232}Th, ^{238}U	3
A1, B, Cu, Mn, Sr, Ti, Zn	MW digestion with HNO_3	ICP-AES	External calibration	-	3
Al, Ca, Cr, Cu, Fe, Pb, Zn	Decomposition with $HClO_4$+HNO_3	ICP-AES Ultrasonic nebulizer	External calibration	-	30
Mg, Na, K, Ca, Fe, Al, Cr, Mn, Cu, Zn, Se, Sr, Br, Rb, Li, Ti, Ni, As, I, Ba, Pb, Sc, V, Co, Y, Zr, Mo, Sn, Cs, Ga, Nb, Pd, Cd, Sb, Hf, W, Hg, Tl, Th, U	Direct: wine+twice distilled water (1+1 v/v) dilution addition of 100 µl conc. HNO_3	ICP-MS (quadrupole mass analyzers) Cross flow nebulizer	Quantitative and Semi-quantitative mode by using set of standard solutions and internal standard Rh	^{24}Mg, ^{23}Na, ^{39}K, ^{44}Ca, ^{56}Fe, ^{55}Mn, ^{63}Cu, ^{64}Zn, Se, ^{88}Sr, ^{138}Br, ^{85}Rb, ^{58}Ni, ^{75}As, ^{209}Pb, ^{59}Co, ^{133}Cs, ^{69}Ga, ^{114}Cd, ^{202}Hg, ^{208}Tl monitored in quantitative mode.	132
Al, As, Ba, Ca, Ce, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sn, Sr, Th, U, Y, Zn	Direct: dilution with a factor from 2 to 20 depending of the element	ICP-MS	Internal standard		133
Pb isotope ratio, Ag, Ni, Al, As, Pb, Au, Pd, B, Pt, Ba, Rb, Be, Re, Bi, Rh, Br, Cd, Sb, Ce, Sc, Co, Sn, Cr, Sr, Cs, Ta, Cu, Te, Fe, Th, Hf, Ti, Tl, Ir, U, La, V, Li, W, Mn, Y, Mo, Zn, Nb, Zr	Direct, acidification	ICP-SF-MS In low and medium resolution mode	Matrix matched (ethanol) blanks and standards SRM 981(Common Lead) and SRM 982 (Equal-Atom Lead)	The precision of Pb isotope ratio measurements is superior to that obtained by quadrupole systems.	107

Continue Table 3

Li, Be, Mg, Al, P, Cl, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, I, Cs, Ba, La, Ce, Tl, Pb, Bi, Th, U	Direct: Wine+0.2 mol L^{-1} HNO_3 (1+1 v/v) dilution	ICP-MS (quadrupole mass analyzer) Concentric nebulizer	Calibration by using set of ethanol matched standard solutions. Two in-house reference wines for quality control.		134
Al, As, Ba, Ca, Ce, Co, Cr, Cs, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sn, Sr, Th, U, V, Y, Zn	Evaporatation to dryness; residue disolved with 0.1 mol l^{-1} HNO_3	ICP-MS	Standard addition calibration		135
B, V, Mn, Zn, Fe, Al, Cu, Sr, Ba, Rb, Na, P, Ca, Mg, K	Decomposition in Kjeldahl flask $(H_2O_2)+H_2SO_4$	ICP-OES Cross-flow nebulizer	External calibration		111
B, V, Mn, Zn, Fe, Al, Cu, Sr, Ba, Rb, Na, Ca, mg, P, K	Direct Decomposition in Kjeldahl flask $(H_2O_2)+H_2SO_4$	ICP-OES	Ethanol matched standards External calibtration		136
Ag, Ba, Cr, Cu, Ni, Pb, Sb, Tl, U, As, Cd, Co, Th, V, Zn, Ce	Direct	ICP-MS	Standard addition calibration	^{107}Ag, ^{52}Cr, ^{63}Cu, ^{60}Ni, ^{121}Sb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{137}Ba, ^{238}U, ^{205}Tl, ^{111}Cd, ^{108}Cd, ^{106}Cd, ^{232}Th, ^{66}Zn, ^{75}As, ^{51}V, ^{53}V, ^{140}Ce	141
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Direct after acidification	ICP-MS Microconcentric nebulizer	A multi element REE calibrant solution. Internal standard - In	^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{158}Gd, ^{159}Tb, ^{164}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{171}Yb, ^{175}Lu	108
Cu, Fe, Zn, Mn	MW digestion	ICP-AES	-	-	142
Pb isotope ratio	Digestion with $HNO_3+H_2O_2$ Pb separation by ion exchange chromatography	Multi collector ICP-MS	Isotope dilution $^{205}Tl/^{203}Tl$ isotope ratio used for mass bias correction	$^{206}Pb/^{208}Pb$	115
Pb	Direct after 10 times dilution	ICP-MS	External calibration		143
Pb	Direct after dilution	Flow injection ICP-MS	Standard addition	$^{208}Pb/^{206}Pb$; $^{208}Pb/^{204}Pb$; $^{208}Pb/^{207}Pb$	144

Continue Table 3

Pb isotope ratio	UV irradiation	ICP-MS	Pb isotopic standard/internal correction with Tl as internal standard	Precison: 0.3% for $^{207}Pb^{+}/^{206}Pb^{+}$, and $^{208}Pb^{+}/^{206}Pb^{+}$; 0.8% for $^{204}Pb^{+}/^{206}Pb^{+}$	112, 113
Pb isotopes	Digestion with HNO_3 evaporation	ICP-MS comparison with TIMS	External calibration/isotope dilution	$^{206}Pb/^{208}Pb$, $^{206}Pb/^{207}Pb$, $^{206}Pb/^{204}Pb$	145
Pb isotope ratio	Direct	ICP-MS Quadrupole,Multi collector and time-of flight analyzers	External calibration	$^{206}Pb/^{208}Pb$, $^{206}Pb/^{207}Pb$, $^{206}Pb/^{204}Pb$ Comparison of precision and accuracy.	146
La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	MW digestion with HNO_3	ICP-MS	Internal standard	^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{166}Er, ^{169}Tm, ^{174}Yb, ^{165}Lu	114
Pb	Direct	ICP-MS coupled with GC		^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{203}Tl, ^{205}Tl, ^{202}Hg	148
Pb	Direct	ICP-MS	External standard	$^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$	149
Pb	Direct	ICP-MS	External standard	$^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$	150
Pb	Digestion with HNO_3	ICP-MS (ID)	Internal standard	^{204}Pb, ^{206}Pb ^{207}Pb, ^{208}Pb	151
Pb	Direct; digestion with HNO_3	ICP-MS	Internal standard	^{208}Pb	91
Pb	Direct (dilution)	ICP-MS	Internal standard	^{204}Pb, ^{206}Pb ^{207}Pb, ^{208}Pb	152
Pb		ICP-MS		$^{206}Pb/^{207}Pb$	153
Pb	Ion exchange	ICP-AES			154
Sr isotope ratio	UV irradiation, separation between Sr and Rb by cation exchange chromatography	ICP-MS (quadrupole mass analyzers)	Mass bias correction by $^{88}Sr/^{86}Sr$ isotope ratio. Quality control by NIST SRM 987 ($SrCO_3$, isotopic form)	$^{87}Sr/^{86}Sr$ Precision 0.15%–0.5%	116
Sr isotope ratio	Digestion, Sr separated by cation ion exchange (Bio-Rad AG50 resin)	ICP-SF-MS	Mass bias correction by $^{88}Sr/^{86}Sr$ isotope ratio. Quality control by NIST SRM 987 ($SrCO_3$, isotopic form)	$^{87}Sr/^{86}Sr$ Precision: 0.001%–0.002% at Sr levels > 1mg L^{-1}; 0.005%–0.02% at Sr levels < 200 µg L^{-1}	155,156

Table 4. Electroanalytical methods in wine analysis

Element(s)	Sample preparation	Technique	Working electrode	LOD	Ref.
As (speciation)	Direct	Differential pulse anodic stripping voltammetry (DPASV)	Gold film electrode	0.08 μg l^{-1}	165
Bi, Cd, Cu, Pb, Tl	High pressure digestion with HNO_3	Potentiometric stripping analysis (PSA)	Mercury film electrode	1 μg l^{-1} for Pb	166
Ca	Direct	Ion selective electrode (ISE)	Ca ion selective electrode		167
Ca, K	Direct	Flow injection potentiometry	Ca and K ion selective electrodes	2.0 mg l^{-1} for Ca and K	168
Ca, K	Evaporation; ashes disolved in 10 ml 2 mol l^{-1} HCL	ISE	Ca and K ion selective electrodes	0.782 mg l^{-1} for Ca 1.202 mg l^{-1} for K	157
Cd, Pb, Zn	Direct; diluted 1:5	DPASV	Solid silver amalgam electrode		169
Cd, Pb, Zn	Direct; acidified to pH 1.5	Anodic stripping voltammetry (ASV)	Naflon-coated bismuth-film electrode	0.1 μg l^{-1} for Cd and Pb 0.4 μg l^{-1} for Zn	170
Cd, Pb, Zn	Direct	ASV	Glassy carbon electrode (RDE)		171
Cd, Cu, Pb	Digestion with HNO_3 under a pressure into quarz tube	PPSV	Mercury film electrode		158
Cd, Cu, Pb	Direct	ASV	Bismuth coated carbon microdisk electrode	0.88 μg l^{-1} for Cd 2.9 nmol l^{-1} for Pb	172
Cd, Cu, Pb, Zn	Direct, acidified to pH 2 with 5 mol l^{-1} HCl	Derivative anodic stripping chrono potentiometry (DASCP)	Glassy carbon electrode	0.05 μg l^{-1} for Cd, Pb 0.07 μg l^{-1} for Cu, Zn	173
Cd, Cu, Pb, Zn	Direct, acidified	ASV	Hanging mercury drop electrode		174
Cd, Cu, Pb, Zn	Wet digestion with with H_2SO_4 and H_2O_2	DPASV	Hanging mercury drop electrode		175
Cd, Cu, Pb, Zn	Digestion with H_2SO_4 and H_2O_2	ASV	Thick-film modified electrode (TFMGE)		159
Cd, Co, Cu, Fe, Pb, Ni, Zn	UV photolysis	DPASV	Multimode working electrode	5 μg l^{-1} Cd, Ni 10 μg l^{-1} Co, Cu, Pb 20 μg l^{-1} Zn	49
Cd, Cu, Pb, Zn (specia-tion)	Direct	DPASV	Static mercury drop electrode	2 μg l^{-1} Cd 50 μg l^{-1} Pb 90 μg l^{-1} Cu	176
Cd, Pb, Cu, Zn	Direct, acidified with HCl	SV and PSA	Hg-coated screen printed electrode	0.1 μg l^{-1} for Pb	177
Cd, Cu, Pb, Zn	Direct, acidified with HCl	DPSA	Glassy carbon -thin mercury film	1.4 μg l^{-1} for Cd 1.7 μg l^{-1} for Cu and Zn 1.1 μg l^{-1} for Pb	178
Cd, Cu, Pb, Zn	Decomposition and acidified with HCl	PSA	Mercury film electrode	0.034 mg l^{-1} for Zn	160

Continue Table 4

Cr	Digestion by UV irradiation and addition of H_2O_2	Differential pulse adsorptive stripping voltammetry (DPAdSV)	Hanging mercury drop electrode (HMDE)	0.97 μg l^{-1}	162
Cu	Direct	DPASV	Hanging mercury drop electrode (HMDE)		179
Cr, Mn	Dry mineralization	Square wave voltammetry	Static mercury drop electrode (SMDE)		180
Cu (labile and tightly bond)	Direct	DPASV; Potentiometry	SMDE; Ion selective electrode		181
Cu	Direct	SP	Glassy carbon electrode		182
Cu	Direct	ASV	Chemically modified carbon paste electrode (CMCPE)	0.1 μg l^{-1}	183
Cu	Direct, acidified with H_2SO_4 (v/v white wine : 1 mol l^{-1} H_2SO_4 is 9:1)	Underpotential deposition stripping voltammetry (UPD-SV)	Disorganized monolayer gold electrode		184
Cu	MW digestion with HNO_3, evaporate to drayness and the residue dissolved in 2 ml with HCL to pH 2	Square wave voltammetry (SWV; PSA	Hg electrode (drop and film)	0.06 μg l^{-1} with SWV 0.04 μg l^{-1} with PSA	185
Cu, Pb	Direct, dilution	SP	Glassy carbon electrode	50 μg l^{-1} for Cu	186
Cu, Pb	Digestion with HCl, UV irradiation	ASV	Mercury microelectrode	1 μg l^{-1} for Pb	187
Cu, Pb	Digestion, UV irradiation	Anodic stripping voltammetry	Mercury coated platinum microelectrode	0.03 μg l^{-1} for Pb	188
Cu, Zn	Digestion with H_2SO_4 and H_2O_2	DPAdSV	Hanging mercury drop electrode (HMDE)		9
Cu, Pb, Zn	Electrochemical preparation forming TMGE surface (D)	Voltammetry	Thin-film graphite-containing electrode modified with calomel	-	163
Ni	Digestion with H_2SO_4 + H_2O_2; UV irradiation and addition of H_2O_2	DPAdSV	HMDE	Not present	163
Pb	Direct	SV	Glassy carbon electrode		189
Pb	Direct	SV	Mercury plated platinum disc electrode		190
Pb, Zn	Direct	PSA	Dental amalgam electrode	2.9 μg l^{-1} for Pb	191

Sample dilution with HNO_3 is recommended for FAAS determination of transition metals Cu, Fe, Mn and Zn. In order to increase sample throughput, an automatic flow injection system based on zone sampling technique has been developed for the determination of Ca, K, Mg and Na in wines [1988] as well as a flow injection system based on stream splitting for Cu determination in wines [199]. Direct application of HGAAS with quartz tube or quartz burner with Ar/H_2 flame as atomizers in wine analysis is limited because of drastic ethanol interference [29, 99, 101, 103]. It was shown recently that ethanol probably enters as an aerosol from gas/liquid separator into the atomizer, thus interfering with the atomization of hydrides [29, 99]. The magnitude of this interference strongly depends on the type of the atomizer used – it is not so strong if hydride trapping in graphite furnace or inductively coupled plasma is employed as atomizers. This fact is well documented as successful direct determination of Sb in wine using HGAAS with hydride trapping into the graphite furnace [104]. Sample dilution [99, 103] or flow injection mode [101] are proposed to overcome ethanol interference and to achieve successful determination of As in wine samples. Recently sample matrix-assisted photo-induced chemical vapor generation has been proposed for ultrasensitive detection of Hg in wines [102]. Ethanol e.g. wine matrix under UV-irradiation reduces mercury compounds or ions to atomic mercury thus playing a role of reductant for CVAAS determination of Hg. The application of direct hydride generation with different detectors is summarized in Table 2.

ETAAS permits determination of toxic trace elements in wine samples much below their permissible limits (OIV, national legislation) and therefore is widely used for wine quality control. The choice of efficient modifier for trace element thermal stabilization, optimal temperature program for the graphite furnace and suitable calibration method are the most popular topics of investigation. An advantage of ETAAS is the possibility to develop accurate direct methods for trace element determination in wine without any sample pretreatment. Expected matrix interferences are associated with wine organic matter which may cause high values of nonspecific absorption and ethanol content in wine sample which impairs sample delivery into the graphite furnace. Problems connected with reproducible sample injection are most frequently solved by injection into a preheated platform or graphite tube (‘hot injection’), while sample sputtering is avoided by applying two-stage drying step [60]. The use of Zeeman background correction is preferable to overcome high nonspecific absorbance, thus greatly improving the accuracy of measurements. Stabilized temperature platform furnace (STPF) conditions should be fulfilled in order to obtain accurate and reliable results [77]. Aluminum levels in wine are high enough to permit high dilution factors so as thus to minimize matrix effects and allow for external calibration in assays. [60, 62, 64]. For port wine, however, a product with the most complex matrix which composition differs considerably from traditional table wines, potassium dichromate was proposed as modifier for Al determination together with end-capped Transverse Heated Graphite Atomizers (THGA®) [61]. Trace elements (Ag, Co, Si, and Zn) were determined in port wine by ETAAS, and FAAS [66]. Cadmium and Pd are elements predominantly determined in wine samples by ETAAS moreover that ETAAS is an official method of analysis for Cd and Pd in wine by European regulations [23, 69, 70]. Typically sample dilution with HNO_3 is the only sample pretreatment and the chemical modifiers used for thermal stabilization of both elements in wine samples are $Pd(NO_3)_2$ [35, 67, 72, 87], $Pd(NO_3)_2 + Mg(NO_3)_2$ [36, 75], $NH_4H_2PO_4$ [90, 92, 93], and $NH_4H_2PO_4 + Mg(NO_3)_2$ [89]. Standard additions are frequently recommended as calibration procedure for Cd and Pb quantification in wines. An alternative approach is presented by Jorhem et al. [88]: Pb is determined in wine without any modifier by utilizing relatively low atomization temperature. It could be mention that the wine matrix contains by itself enough phosphate and Mg to act as a content so some thermal stabilizer (‘internal modifier’). Successful simultaneous determination of Cd and Pb in wines is reported in the presence of $Pd(NO_3)_2$ as modifier and by using two stage ashing to avoid formation of carbonaceous residue inside the atomizer [36]. Although it is not very typical for ETAAS, Bi as an internal standard has been proposed for Pb determination in wine [87]. The employment of internal standard could minimize absorbance

variations due to changes in experimental conditions such as atomizer temperature, integration time, graphite tube surface, sample composition etc. Chromium levels in French wine and grapes and in Spanish wines were determined by direct ETAAS after careful optimization of temperature programs [74, 76]. Fast temperature programs with high sample throughput were developed for Cu determination in wines [82]. Useful models which permit the detection of possible sources of bias errors were applied to the determination of Cu in wine [78]. Manganese, Ni and V levels were defined in French wines and grapes from different regions and in Californian wines by using ETAAS [84, 98, 200]. Vanadium determination by ETAAS from the view point of matrix interferences and calibration procedures was discussed [50]. Selenium is an essential element, unfortunately presents at very low levels in wine. Direct determinations are hampered by strong matrix interferences [58] and even by different behavior of both oxidation states [96].

Comparison of results obtained for trace elements content by ETAAS and ICP-AES with ultrasonic nebulization shows very good agreement [30]. Methods for direct trace element determination in wines by ETAAS are complied in Table 1.

ICP-AES and ICP-MS.

Direct determination of trace elements coupled with fast multielement measurement method is the most effective way of wine analysis. Various approaches have been designed and applied to ensure accurate and reliable results by overcoming matrix interferences observed without sample pretreatment. A solvent matched (ethanol) standards is the only requirement to determine 16 elements in wines by ICP-AES [141] or 22 elements in wines from Trentino (Italy) [129]. Micro-porous PTFE membrane desolvator coupled to a microconcentric nebulizer was applied in ICP-AES analysis of wine from the market in Korea [130]. Matrix effects caused by the presence of ethanol in ICP-MS analysis of wines were studied by Rodushkin et al. [107]. Significant intensity losses in ethanol matrix were encountered if operating parameters were optimized by using a non-matrix-matched solutions. The phenomenon is explained with increased vapor pressure in the spray chamber due to increased solvent evaporation from the aerosol, resulting in higher gas flow through the torch injector and shorter residence time for the analytes in plasma [107]. Another matrix effect is signal enhancement for elements with high ionization potential; the magnitude of this effect depends on the ionization potential and ranges from 10–15 % to 400 % in 5 % *v/v* ethanol solution. The most effective way to correct for these effects is [106]:

- To utilize a matrix-matched tuning solution for instrument optimization and to maintain the same ethanol concentration in blanks, standards and samples. In most cases ethanol 2–5 % (v/v) was chosen as compromise between signal intensity and the prevention of carbon deposition on the sample orifice [120, 121, 131, 132, 134, 156, 201]. Experimental design could be used for accurate optimization of instrumental parameters [122].
- To employ a suitable internal standard for calibration in order to correct for small differences in ethanol content in different samples. Internal standards most frequently used in wine analysis are In [124, 125, 138] or Rh [117, 121].
- To apply mathematical corrections to overcome isobaric interferences.

ICP-MS offers different quantification procedures depending on the accuracy and precision required: (i) the isotope dilution (ID) mode of analysis when the highest quality of results is needed; (ii) quantitative mode of analysis which requires external calibration using a set of multielement standards; (iii) semiquantitative mode of analysis based on a pre-calibrated internal response for all elements, which can be updated with a single point calibration. External calibration is a time consuming procedure which requires a set of multielement standards not always available. That is why simple semiquantitative mode of ICP-MS analysis of wine after UV-irradiated digestion [117] or only dilution 1+1 or 1+2 with 0.1–0.2 M nitric acid is studied [114, 124, 132]. The results demonstrate that this approach is very useful for fast provenance testing of wine samples. Accurate determination of REEs is a difficult task taking into account their low concentration often < 0.1 μg l^{-1} and fairly complex wine matrix. Microconcentric nebulizer used for sample introduction with reduced solution consumption allows reduction of matrix interferences thus increasing the sensitivity of direct analysis and

making possible determination of REEs in without any preconcentration [108]. However recently Castineira et al. compared micro-concentric nebulizer with a membrane desolvator (MCN 6000) with conventional Meinhard nebulizer and concluded that the former one is not suitable for wine analysis [124]. Flow injection mode is another useful approach for sample introduction and automatic dilution for ICP-MS analysis of wine samples with high sample throughput [141]. A microscale flow injection system employing a microconcentric nebulizer for efficient sample introduction into the ICP-MS was successfully applied for As determination in wines [138]. Lead content is very important wine parameter and analytical procedures for precise Pb determination in wines by using DI-ICP-MS were developed and used for metrological purposes [115, 151, 202]. Comparison among several calibration techniques e.g. standard addition calibration, internal standard calibration and isotope dilution for Pd determination by FI-ICP-MS have been presented. Authors concluded that from the view point of accuracy, precision and flexibility the standard addition calibration is the most preferable procedure [143, 144]. Direct ICP-MS was used for lead isotope ratio determination in different wines [17, 107, 145, 146], results obtained were compared with Pb isotope ratios measured by thermal ionization mass spectrometry (TIMS) and very good agreement was achieved. ICP-MS after sample digestion by UV-irradiation should be used for the same purpose in port wine due to higher ethanol and organic matter content in this type of wine [112, 113]. Strontium isotope ratios in wines are important characteristic used as a fingerprint of its regional origin and are determined by ICP-MS after Sr separation from wine matrix by cation exchange [116, 156, 203]. Direct ICP-MS methods for multielement determinations in wines and their characteristics are presented in Table 4.

Voltammetry:

Taking into account that digestion step is time consuming and prone to analyte losses or contamination several approaches have been developed for direct application of DPASV and SP in wine analysis [158, 177, 178, 184, 186]. Anionic surfactant sodium dodecyl sulphate was used to suppress organic adsorption interferences in ASV determination of Cd, Cu and Pb in wine [171]. Bismuth-coated carbon microdisk electrode and uncoated carbon microdisk electrode were applied for direct DPASV determination of Cd, Pb and Cu in wine [172]. Mercury microelectrode was used for direct determination of the free fraction of Cd, Pb and Zn at natural wine pH and the total metal content in acidified wine samples by DPASV [176]. Multiple standard additions with latent variables are proposed as a method design to overcome the difficulties in DPASV (mercury electrode) determination of Cu in a complex matrix as wine [179]. Potentiometric stripping analysis is used for the determination of Cd, Cu, Bi, Pb and Tl in wines after simple sample dilution with appropriate supporting electrolyte [167] and sensitivity achieved for Pb is significantly higher versus that of ETAAS [167, 204]. Recently a novel nontoxic dental amalgam electrode was introduced for SP analysis of Pb and Zn in wine [172, 191]. Derivative SP analysis allows the direct determination of Cd, Cu, Pb and Zn in acidified wines without any sample pretreatment because the glassy carbon mercury film working electrode remains inert to organic molecules interferences during the signal collection phase [165, 181]. The determination of Cu by SP is generally successful although difficulties have been observed with some wine styles [205]. Medium exchange SP present the possibility of solving many of the problems encountered allowing sensitive and accurate determination of Cu in white wines [182]. Total Cu is determined after wine acidification by using SP and square wave ASV with mercury film electrode in the presence of ethylene diamine [185]. In order to avoid highly toxic mercury electrode method for direct determination of Cd, Cu and Pb by ASV using thick-film electrode is developed [159].

X-ray fluorescence.

Proton induced X-ray fluorescence spectrometry (PIXE permits direct determination of trace elements in wine without any sample pretreatment. Wine samples are carefully dried under IR lamp on the target. Internal standard calibration is recommended for quantification thus eliminating the errors due to the different sample thicknesses on the target [206, 207]. Determination of Pb is achieved after

preconcentration by repeat evaporation of wine sample and analyte addition method as calibration procedure [208]. The levels of trace elements in Brazilian wines were defined by direct TXRF. Relatively light matrix of these wines permits wine analysis without sample pretreatment: 5 μl of wine is simply deposited by evaporation on a suitable reflector. Internal standard calibration procedure (Ga) is recommended for trace element quantification.

Ion chromatography (IC) and capillary electrophoresis (CE).

Both methods are widely and successfully used for anions determination in wine samples. CE is very suitable method for alkali and alkali earth elements determination in wine samples. Separation of six cations (Na, K, Mg, Ca, Mn, Li) has been achieved on a fused silica capillary column (UV-CAT-1). Analytical procedure includes only simple sample dilution with doubly distilled water [209, 210]. Hydrostatic injection for 30 s was used for sample introduction, running buffer solution (pH 4.5) consists of 6.5 mmol l^{-1} α-hydroxyisobutiric acid and 2 mmol l^{-1} 18-crown-6-ether, indirect UV detection at 214 nm was used. The precision was better than 2.5–3.4%, recoveries were in the 92–102% and detection limits for all elements between 0.1–0.06 mg L^{-1}. Lithium ion can be added as a denaturing agent in wines and legal controls of Li levels is important analytical task. IC was recommended for Li determination in wines. Analytical procedure developed is less subject to matrix interferences than ICP-OES since analyte peaks are very well resolved and the accuracy depends mostly on the optimization of the instrumental parameters [211].

An unusual alternative approach has been tested for the determination of Cu, Fe, K, Na, Ca and Mg in white wines. Selected elements have been determined by FAAS and by transmission near infrared spectrometry (NIR). Different chemometric methods have been used to create models for metals determination in wines by NIR. Models obtained for K, Na, Ca and Mg are acceptable, however those for Cu and Fe are not. Results indicate that NIR spectrometry may provide a suitable, rapid method for analysis after further investigations using a larger number of wine samples [212].

Trace elements separation and preconcentration prior to wine analysis

Separation and preconcentration procedures have been recommended for trace analytes determination in wines in cases when the concentration of elements are below the detection limits of instrumental method available in laboratory or strong matrix interferences restricted direct application of instrumental method. Liquid/liquid extraction is proposed for the determination of Se [58, 95], Tl [97] and Hg [34] due to their extremely low content in wine samples – typically less than 0.1 μg l^{-1}. Liquid/liquid extraction is typically combined with FAAS and ETAAS and extraction systems are based on chelate extraction of dithiocarbamate or ion associate complex of the analyte. Solid phase extraction is more frequently used in wine analysis due to the possibility to achieve fast automatic analysis of trace elements and to combine with less expensive and easily available FAAS or spectrophotometry [213–215].

As can be expected most of papers are dedicated to Pb determination in wines applying flow injection analytical mode [9, 31, 42, 216, 217]. A specially designed for Pb^{2+} imprinted polymer Pb-Spec allows direct determination of Pb in wine without any sample pretreatment and without any significant matrix interferences [40]. Automatic on-line sorbent extraction preconcentration system (diethylammonium-N,N-diethyldithiocarbamate complexes are collected in a column packed with bonded silica reversed-phase sorbent with octadecyl functional groups) combined with FAAS allows determination of Pb with sampling rate of 65 samples/hour and for Cu sampling rate is from 150–300 samples/hour [9]. Determination of free Pb^{2+} and total Pb after sample digestion could be preformed by using sorption of Pb on packed polyurethane foam column, modified by addition of 2-(2-benzothiazolylazo)-p-cresol [31]. The main idea of a series papers for trace element preconcentration from wine samples is sorption of analyte complexes with different reagents e.g. bathocuproinedisulfonic acid [45], dithizone [44], KSCN [45] on inert sorbents like Chromosorb 108, diaion HP-2MG or XAD-7 respectively. Very low Cd concentrations in wine have been determined by on-line preconcentration in a knotted reactor coupled to ICP-OES with ultrasonic nebulization [140]. A natural sorbent

modified rice husks was characterized and successfully applied for Cd and Pb determinations in wines [218]. Rice husks have been shown to be a homogeneous and stable adsorbent in which more than 100 preconcentration/elution cycles provide a relative standard deviation of less than 6 %. Liquid/liquid extraction and head-space micro-extraction have been used as preconcentration procedures for the determination of butyltin compounds in wines [219, 220]. Several experimental parameters (tetramethylammonium hydroxide pretreatment, pH, matrix modification, extraction mode, fiber type, extraction time, extraction temperature, derivatization) for quantitative extraction of butyltin compounds and their derivatization have been optimized and defined. Detection limits of analytical procedure developed are in the range 0.02–0.03 μg l^{-1} as Sn for tributyltin and 0.03–0.04 μg l^{-1} as Sn for dibutyltin, RSD is in the range from 8 % (monobutyltin) to 6 % (dibutyltin, tributyltin). The method has been applied to Portuguese table and Port wines and dibutyltin was found in the range 0.07–0.15 μg l^{-1}, monobutyltin is observed in few wines at levels <0.05 μg l^{-1} and tributyltin is not detected in any sample. Most important procedures recommended for trace element speciation are presented in Table 5.

Fractionation and speciation of trace elements in wine

The understanding of the physicochemical forms under which a metal is present in wines deserves interest because complexation with wine organic matter may reduce their toxicity and their bioavailability for humans. It is recognized that extend of the toxic effects caused by trace metals (As, Cd, Pb, Hg) is not governed by their total concentration it is regulated by the forms of the metals that can efficiently interact with biologically active ligands [79]. It also well known that wine instability and haze formation depends on the exact chemical form of trace elements like Fe, Cu, Mn and Zn [22]. Wine is a very complex matrix and the accurate determination of exact chemical species of trace metals in wine is real analytical challenge. The possible physical form of trace elements e.g. dissolved or suspended can be determined by using filters of different pore size [232] and these results are enologically very important because this colloid fraction destroys the quality of wine [232].

Voltammetry:

Electrochemical methods are very useful for metal ions fractionation in wine samples e.g. determination of free or labile metal species, labile and tightly bound metal species, and metal fraction bound to wine colloids [175, 186, 233-235]. Both DPASV and SP are widely used for Cu fractionation due to remarkable influence of labile Cu species on the stability of wine [77, 181, 185, 186]. An interesting study has been carried out to study the complex formation of Cu, Fe, Mn, and Zn with wine polyphenols. ASV was used for metals measurement and liquid chromatography was applied for the determination of wine polyphenol fractionation [142, 235, 236]. A good correlation have been found for both Fe and Cu with total content of wine polyphenols and antocyannins. The individual correlation of both Zn and Cu with cyaniding-3-glucoside is established. Further Zn and Cu interaction with three selected flavonoids (cathechin, quercetin and rutin) in model solution as well as in real samples was studied. Authors [236] concluded that complexing ability of wine is due mainly to the cathechin although the presence and contribution of other ligands is not precluded. Lead is a toxic element however its toxicity and bioavailabilty depends on the particular chemical species and their ability to interact with other biologically active ligands so complexation behavior of Pb in wine is thoroughly investigated by DPASV and SP [237]. It is shown that lead is strongly complexed in wines and further studies on the gastrointestinal digestion were conducted [82]. Among the factors that affect the quality of wine, the cationic content and the form in which the cations exist in the must are important since they play a relevant part in the fermentative process [9]. The influence of two different prefermentation clarification treatment on total, acid-displaceable and labile metal (Cd, Cu, Pb, Zn) content was investigated by DPASV [9] and it was concluded that Cd and Pb with elevated toxicity were greatly eliminated by clarification.

Table 5. Speciation analysis of trace elements in wine

Element	Species	Separation procedure	Detection method	Ref.
As	As(III), As(V), MMA, DMA	IC, Ion Pac AS12 column (Dionex); gradient elution: 5 mmol L^{-1} NaOH+0.1 mmol L^{-1} Na_2CO_3 then10 mmol L^{-1} NaOH+10 mmol L^{-1} Na2CO3	HGAFS, 0.9% m/v $NaBH_4$, 1 mol L^{-1}HCl	99
As	As(III), As(V), MMA, DMA	IC, Wescan Anion/R column, gradient elution, eluent 1: propan-1-ol, eluent 2: 50 mmol L^{-1} carbonate buffer, pH 7.5	ICP-MS	137
As	As(III), As(V), MMA, DMA	Ion exchange, cation exchange resin AG 50 W-X8; anion exchange resin AG1-X8	HGAAS, 1.4% m/v $NaBH_4$	221
As	As(III), As(V), MMA, DMA	HPLC, C_{18} Supelco, narrow-bore column, mobile phase: 5 mmol L^{-1} tetrabutylammonium hydroxide, pH 6.28 with malonic acid	ICP-MS	139
As	As(III), As(V), MMA, DMA	HPLC, PRPX-100 column (Hamilton); mobile phase:10 mmol L^{-1} KH_2PO_4+10 mmol L^{-1} K_2HPO_4	HGAFS, 1.4% m/v $NaBH_4$, 1.5 mol L^{-1}HCl	100
As	Total, As(III), As(V)	As(III), As(V): selective reaction media Total: wine MW digestion	HGAAS	29
Al, Ca, Cu, Fe, K, Na, Pb	Metals in real solutions, colloids or suspensions	Ultrafiltration through 0.2 and 0.45 μm membrane filters	FAAS, ETAAS	222
Cd, Cu, Pb, Zn	Total and labile fraction	Total: wine digestion; labile fraction: acidification to pH 1	DPASV	9, 175
Cu	Total and labile copper(II)	Direct	DPASV; ion-selective electrode; kinetic photometric method	181
Cu	Total, fractionation	Fractions obtained by adding 0, 30 or 200 μl conc. HCl to 2 ml of wine sample	SWV with static mercury drop; PSA with mercury film electrode	185
Cu, Pb	Total Cu and Pb;bioavailable Cu and Pb, complexed Cu and Pb	RP-HPLC, C_{18}218TP54 column, gradient elution 0-30% ethanol in 20 mmol L^{-1} KH_2PO_4, off line. Bioavailable fractions: gastrointestinal digestion	Total Pb: ETAAS; Total Cu: FAAS; Pb and Cu in dialysates: ETAAS Complexed Pb: SWCV Complexed Cu: potentiometry, ISE	79, 80
Cu, Pb	Labile and total	Cu: stripping agent Hg(II); HCl (2 mol L^{-1}(total), 1 mol L^{-1}(labile); stripping medium $CaCl_2$(1 mol L^{-1}(total), 0.5 mol L^{-1}(labile); Pb: pH 1, stripping agent Hg(II)(total), stripping agent O_2 (labile).	SP	187
Cu, Fe, Zn	Fractionation	Fractions of Cu, Fe and Zn bound to polyphelons, proteins and polysaccharides. Labile species of Cu, Fe(II), Fe(III) and Zn.	FAAS ETAAS	223
Fe	Fe species	IC	FAAS	224
Fe	Total and Fe(III)	Fe(III):extraction of thiocyanate complex into MIBK, total Fe: FAAS	Sequential injection analysis by FAAS	225

Continue Table 5

Fe	Free and bounded Fe	Sequential cloud point extraction	FAAS	226
Fe	Fe(II), Fe(III), Organically bounded Fe	Liquid/liquid extractuion (thiocyanate, o-phenantroline) Column solid phase extraction	FAAS	227
Fe	Labile Fe(II) and Fe(III)	Solid phase extraction by using 1,10-phenantroline and 8-hydroxy-7-iodoquinoline-5-sulphonic acid	FAAS	228
Fe	Fe(III), total Fe	HPLC, Spherisorb S5 ODS 2 column, mobile phases: 50 mM CH_3COONH_4+CH_3OH (70+30 v/v) pH 4; CH_3COOSO_4/H_2SO_4 pH 2.5	Electrochemical Fe(II) FAAS	229
Fe	Fe(III), total Fe	Fluorescence reaction with 5-(4-methoxyphenylazo)-8-(4-toluenesulfonamido)quinoline in the presence of cetyltrimethylammonium bromide	Fluorimetry	230
Ni	Distribution of Ni in wine	Fractionation by liquid/liquid and thin-layer chromatography	Spectrophotometry	231
Pb	Biomolecular complex of Pb	Size exclusion HPLC, Superdex-75 column, TRIS buffer or formate buffer pH 3.5–7.5	ICP-MS	147

Flame and ETAAS:

Analytical procedures based on flame and ETAAS spectrometry in combination with solid-phase or liquid-liquid extraction have been developed for Cu, Fe and Zn fractionation in wines [223, 225–228, 230, 238]. Iron is one of the most widely investigated elements in wine. The efforts are concentrated for the determination of labile species of Fe(II) and Fe(III) as well as iron bounded to wine organic matter (wine polyphenols and proteins) and wine organic acids. Sequential cloud point extraction is used to differentiate between insoluble-suspended Fe and aqueous Fe [226]. The determination of labile Fe(II) and labile Fe(III) species in accordance with the redox processes in wines influenced by the pH-value, oxygen content and matrix constituents is very difficult. Most frequently solid phase extraction or liquid/liquid extraction is used for selective determination of Fe(II) or Fe(III) and rest other form is calculated by the difference from the total Fe content. HPLC with AAS and electrochemical detection is applied for Fe speciation in wines e.g. determination of Fe(II) and Fe(III) bound with wine organic acids and it was found that both Fe species are in complex with tartaric acid. However less than 12 % of total Fe is found in this fraction, the rest could be bound to other organic compounds of wine [229]. A scheme is presented for fractionation of wine components (polyphenols, proteins polysaccharides) and Fe, Cu and Zn determination in different fractions [223]. The resin XAD-8 is used for the separation of wine polyphenols in complex with wine proteins and polysaccharides. Around 20–30 % of Fe, 30 % of Cu and 15 % of Zn are found in this fraction. Dowex ion exchange resins were used for the separation of cationic and anionic species of Cu, Fe and Zn. As a rule the concentration of labile Fe(II) is higher than the concentration of labile Fe(III). Less than 5 % of Cu and Fe are bounded to wine polysaccharides and around 50 % of Cu and 60 % of Zn are presented in wines as a positively charged labile species. The ability of plant polysaccharides to bind cations is due to the presence of a high proportion of negatively charged glycosyl-residues. Their complexation capacities increase between pH 3 and pH 7 due to the dissociation of the carboxylic acid groups. The total capacity of pectic polysaccharides to complex metal ions is directly related to their degree of polymerization and their glycosyl-residue composition [238].

Recently it was shown that low molecular pectic polysaccharide rhamnogalacturonan II, which accounts for approximately 20 % of the

ethanol precipitable polysaccharides binds alkaline earth elements and 80–90 % of Pb in wines [147].

Arsenic is ubiquitous trace element, of which toxicity, biological availability and transport mechanism highly depend on particular physico/chemical forms present in sample. Therefore arsenic speciation in food and beverages is an important analytical task. Ion chromatography coupled to ICP-MS spectrometry or HG-AFS is the most widely used and efficient method for As speciation in wines [137]. The results published for major arsenic species in wines are rather controversial: only As (III) [139], As(III) plus As (V) [100] or elsewhere mostly organic arsenic species have been identified [221]. However authors opinion is that As(III) is major As species in wine samples [100].

HGAAS is very suitable technique for speciation purposes due to different response obtained from different analyte chemical species. Selective hydride generation of different arsenic species (As(III), As(V), DMA, MMA) is achieved by using different reaction media, hence e.g. arsenic speciation in wine could be performed. Applying this approach it was shown that As(III) is major arsenic species in wines [29, 99]. Wifladt et al [104] showed by using HGAAS that Sb(III) as well Sb(V) are present in wine samples.

Determination of authenticity of wine through its element composition or isotope ratios

The evaluation of quality of wine plays a very important role for both manufacture and sale. According to Eschnauer et al. [111] the term "*definitium vinum*" is understood as wine classification into groups, according to origin, vintage, grape variety or other criteria of quality. Historically the quality or geographical origin of wine was determined only through testing by wine experts. The development of precise methods for the classification of wines on a scientific bases according to their geographical origin and vine variety is becoming very important for the assignment of a "denomination of origin" - trade mark. Since prestige wines are often subject to adulteration the determination of fraud with regard to the product authenticity is another important challenge to modern analytical chemistry. Fingerprinting techniques based on chemical composition and multivariate statistical analysis of analytical data can be used for identification and classification of a specific agricultural product according to geographical origin. The chemical composition of wine depends on many factors, some of which are related to the specific production area: soil chemistry and regional geology, grape varieties and their capacity to assume mineral substances from soil; some related to the wine making processes from grapes to the finished and bottled wines (yeasts, fermentation reactions, addition of compounds with different functions, conservations, bottling, technological equipment); some related to anthropogenic factors as application of organic and mineral fertilizers, inorganic pesticides and other substances employed in growing practice, pollution of the surrounding area which is not directly associated with viticulture practice. All of these factors may influence the correlation between wine and soil composition and limit the usefulness of the fingerprinting procedure. Therefore, the key for successful application of chemometric methods for denomination of origin of wines depends on the selection of parameters that would reflect the link between particular wine and soil geochemistry of the region of production. Number of investigations discussed the relationship between wine composition, vineyard and wine color [109]; multielement composition and vineyard soil [26]; inorganic anions, heavy metals and ageing period, color and sugar content [166]. However results reported in the literature are still inconclusive and in many cases contradictory. In some cases various chemometrical methods are applied to as many as possible variables, in order to obtain good classification of wines [109, 111, 120, 136]. In other cases the content of selected trace elements is used to obtain a highly successful region classification. Even more it has been concluded that use of all variables is unnecessary and undesirable, because the use of variables with no extra discriminating information only introduces noise in the pattern recognition process [239]. In the most studies multivariate analysis of mineral and trace element data is used to determine geographic origin of wines: wines from Galicia [239, 240], Czech wines [26], German wines [110, 136], South African wines [125], Canary islands wines [55, 119], Canadian wines [134], English and Spanish wines [120], Okanagan valley wines [241], Italian wines [131,

173]. Various chemometric techniques: principal component analysis as well as SIMCA (Soft Independent Modeling Class Analogy) technique, various discriminant analysis, K nearest neighbours, multidimensional scaling, cluster analysis, factor analysis and artificial neural networks are applied as statistical methods. Some elements or set of elements have been recommended for wine fingerprinting: Li and Rb [239], Li and Fe [240], Mg [26], Sr [134], classification of South African wines is based on different combinations of elements characteristic for the particular wine region [125]. Kment et al. [26] concluded that both wine and soil samples are very well clustered according to their locality, however clustering of wines did not follow clustering of soils. Probably wine major and trace element fingerprint reflect all – soil composition, anthropogenic pollution and wine making process. Recently 53 samples of wine have been analyzed by Šperkova et al [133] for 27 elements by ICP-MS. The best results for identification of sample origin were achieved when determining the following parameters: the contents of Al, Ba, Ca, Co, K, Li, Mg, Mn, Mo, Rb, Sr, V and elements ratio Sr/Ba, Sr/Ca and Sr/Mg.

Various models based on metal content have been constructed for denomination of wines from Canary Island. Metals were grouped in three blocks – "rare earth", "Pb isotopes" and "other metals". Results obtained showed that model using all variables which means three blocks together has sufficient sensibility and specificity, close to the model using only other metals and Pb isotopes. Rare elements block alone as well as Pb isotopes alone did not allow wine classification and final conclusion is that the information is in "other" metals [156]. In some cases wine classification is achieved by using trace element content in combination with other wine analysis parameters [26, 123, 128, 240-243]. The discrimination of the geographical origin of Swiss wines [128] was achieved by using wine trace element content, NMR analysis ($^{2}H/^{1}H_{ethanol}$), IRMS analysis ($^{18}O/^{16}O_{wine\ water}$) and classical wine analysis (FT-IR). However as far as including so many variables, is not easy in routine practice. Authors recommend monovariate approaches based on elements like Sr and Rb, which are applied to demonstrate this correlation. It was concluded that significant dependence between the analyte contents in the vineyard soil and wine is exhibited only for Mg and in some extend similar transport Chemometric characterization and classification of Venetian white wines [243] was achieved by using trace elements, classical analysis and aroma compounds. The most important discriminating variables are cis-hexen-1-ol, 1-hexanol, K, nitrogen compounds and total polyphenols. For the characterization of geographical origin of Italian red wines (Apulia region) [123] chemical analysis (trace elements, inorganic anions, organic acids) is compared with NMR analysis (^{1}H) and it is concluded that proton NMR is very advantageous method for wine classification. Several studies comment and confirm that Sr isotope ratio $^{87}Sr/^{86}Sr$ is promising fingerprint of wine origin [116, 156, 203, 244]. The alkaline earth element Sr has four stable isotopes naturally occurring in the environment: ^{84}Sr, ^{86}Sr, ^{87}Sr and ^{88}Sr; only ^{87}Sr is radiogenic and in part comes from the natural β-decay of ^{87}Rb so its concentration in the minerals depends on the age of the rock and on the Rb/Sr ratio and is specific for geographical location [116, 156]. The $^{87}Sr/^{86}Sr$ isotope ratio do not change during biological processes and reflects in plants the environment of growth hence this ratio can be considered a parameter allowing the discrimination of wines of different origin. The soils from different wine-growing regions will show the same specific Sr isotope ratio as the wine produced from this region. It was demonstrate that by using Sr isotopes clear difference between wine produced on basaltic, mixed and granitic soils could be achieved [156]. To evaluate the roles of the soil composition and vinification process on the wine Sr isotope ratio, later was determined in the provenance soil, in the grape juices and in the wines. Total Sr concentration was determined in the grape juice, skins and seeds and in the samples collected in the different steps of each winemaking process and respective produced wines. The total Sr concentration increased during the vinification processes. The increase was attributed to the element liberation from grape seeds and skins (richer in Sr than pulp) during the initial mechanical pressing and fermentation. The $^{87}Sr/^{86}Sr$ values were statistically identical in the provenance soil, respective grape juice and wine, which indicates that $^{87}Sr/^{86}Sr$ is a suitable tracer of the origin of the studied wines [155]. However the

most important factor for adequate conclusions is the precision of the measurements. It has been shown that a minimum measurement precision of at least 0.01% is required which can be reached easily by TIMS. The application of quadrupole ICP-MS is limited due to the isobaric overlap of ^{87}Sr and ^{87}Rb. The problem is solved by cation exchange chromatography, but precision achieved between 0.15% to 0.5% [116] seems to be inadequate for more comprehensive applications and ICP-SF-MS is suggested as a better possibility [156].

Lead is composed of four stable isotopes, three of which are of radiogenic origin: the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th generates respectively ^{206}Pb, ^{207}Pb and ^{208}Pb; ^{204}Pb is non-radiogenic. It might be assumed that respective abundance of these Pb isotopes varies with geographical location of the sample. ICP-MS was applied for the determination of Pb isotopes in a series of French wines in order to study the influence of atmospheric pollution on the lead content in wines [149]. It was shown that in the post 1950 vintages, the lead isotope composition reflects dominant atmospheric fallout. Reflecting the airborne pollution the Pb isotopic signature is also specific of the continental origin of the wines and Pb isotope ratios determination in wines appears to be a promising tool for certifying wine authenticity.

Quality assurance

Validation of developed analytical procedures including quality control of analytical results obtained is important characteristic presented or discussed in most of the papers dealing with wine analysis. It is well known that analysis of certified reference materials is the best way to confirm accuracy and reliability of analytical methods however reference wines with certified concentrations of minor, trace or ultratrace elements are not available [245]. That is way in common case added/found method has been used to establish the accuracy and precision of analytical method developed. Another alternative widely used when direct method of analysis is tested is parallel determination of trace analytes by using previous wine sample digestion [29, 31, 37, 50, 58, 59, 69, 84, 101, 118]. Comparative analysis with other analytical techniques have been also applied as verification procedures for example results for the multi-element determination of trace elements in wine by ICP-MS (semiquantitative mode) are compared with those obtained by TXRF [124]. Unfortunately due to the quite different detection limits of both methods (31 elements have been determined by ICP-MS and only 12 by TXRF) conclusions for 8 element have been discussed: generally sufficient agreement (better than ±50% for Ca, Ni, Cu and better than±20% for Mn, Fe, Rb, Sr and Pb) was achieved [124]. The compatibility of two methods (AAS and TXRF) was validated by parallel analysis of five samples for Fe and Cu and agreement within the statistical uncertainty involved in both techniques was found [39]. The results obtained by quantitative mode ICP-MS and those obtained by NAA have been compared for Na, Mg, Al, Mn, Fe, Co, Zn, Rb and Cs in the natural wine samples analyzed. A correlation coefficient of 0.983 was calculated for the regression line between two data populations indicating that the results obtained by both techniques are similar [132]. Arsenic content determined by HG AAS or HG AFS is typically confirmed by ETAAS after wine sample digestion [29, 99].

Comparison 16 of the International Measurement Evaluation Programme (IMEP) aimed at the demonstration of the degree of equivalence of results of measurements of the Pb concentration and of the Pb isotopic composition in red wine (participants–129 laboratories). In parallel samples from IMEP-16 were offered to the Comité Consultatif pour la Quantité de Matière (CCQM) for its pilot study CCQM-P12 in which 14 National Metrology Institutes (NMIs) participated. Hence performance of field laboratories (IMEP-16) could be compared to performance of NMIs [152]. Reference value for the lead concentration in the average test wine sample was certified using a combination of a straightforward microwave sample digestion protocol and “direct” ID ICP-MS (quadrupole). Results obtained from both programmes have been presented and discussed [152]. IMEP-16: results were widely distributed around the reference value, about 40% of the results were accurate within ±10% uncertainty and nearly 33% were outside the ±50% uncertainty region. In comparison results from CCQM-P12 were in very good agreement, well within ±10% of the reference value. The conclusion is that the

capability and potential of the analytical technique used (if correctly employed) is not the most important factor producing accurate results. Underestimation of the uncertainty statement attached to the measurement result is very serious problem of field laboratories and responsible for worse results of some participants in IMEP-16.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
AFS	Atomic fluorescent spectrometry
APDC	Ammonium pyrolidinedithiocarbamate
ASV	Anodic stripping voltammetry
CE	Capillary electrophoresis
CPSA	Chronopotentiometric stripping analysis
CVAAS	Cold vapour atomic absorption spectrometry
DASPC	Derivative anodic stripping chronopotentiometry
DMA	dimethylarsinate
DPAdSV	Differential pulse adsorptive stripping voltammetry
DPASV	Differential pulse anodic stripping voltammetry
DPSA	Derivative potentiometric stripping analysis
ETAAS	Electrothermal atomic absorption spectrometry
FAAS	Flame atomic absorption spectrometry
HGAAS	Hydride generation atomic absorption spectrometry
DI	Direct injection
FI	Flow injection
GC	Gas chromatography
HMDE	Hanging mercury drop electrode
HPLC	High-performance liquid chromatography
IC	Ion chromatography
ICP-AES	Inductively coupled plasma - atomic emission spectrometry
ICP-MS	Inductively coupled plasma - mass spectrometry
ICP-SF-MS	Inductively coupled plasma-sector field-mass spectrometry
IE	Ion exchange
ISE	Ion selective electrode
LC	Liquid chromatography
LOD	Limit of detection
LOQ	Limit of quantification
MIBK	Methylisobutyl ketone
MMA	monomethylarsonate
MS	Mass spectrometry
MW	Microwave
OIV	Office International de la Vigne et du Vin
PSA	Potentiometric stripping analysis
PSV	Potentiometric stripping voltammetry
PTFE	Polytetrafluoroethylene
RDE	Glassy carbon electrode
REEs	Rare earth elements
RP-HPLC	Reverse phase high-performance liquid chromatography
SP	Stripping potentiometry
SPE	Solid phase extraction
SV	Stripping voltammetry
SWCV	Square wave cathodic voltammetry
SWV	Square wave voltammetry
TIMS	Thermal ionization mass spectrometry
TLC	Thin-layer chromatography
TXRF	Total reflex X-ray fluorescence spectrometry
UV	Ultraviolet
UV-Vis	Ultraviolet-visible
XRF	X-ray fluorescence spectrometry
NMR	Nuclear magnetic resonance
FT-IR	Fourie-trasform infrared spectroscopy
IRMS	Isotope relations mass spectrometry

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