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Determination of Trace Elements in Wine by Atomic Spectroscopy and Electroanalytical Methods

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Additional information is available at the end of the chapter

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Abstract

The chapter will outline the basic theory, advantages and disadvantages, experimental considerations and set up of various atomic spectroscopy, and electroanalytical quantification methods and their specific application to trace element determination in wines. The reader will gain an introduction to most popular elemental analysis methods used in beverage analysis. Copper, iron, manganese, and zinc will be used as examples of essential trace elements throughout the chapter that at high levels may affect the properties of wine as well as the sensory experience of the consumer. Furthermore, special considerations that should be given to wine as a sample matrix for quantitative analysis of inorganic elements and the use of standard addition methods will be described.

Keywords: trace element determination, atomic spectroscopy, electroanalytical methods, wine, standard addition methods, stripping voltammetry

1. Introduction

Wine is a widely consumed alcoholic beverage produced by yeast fermentation of natural sugars contained in grape juice. Wine has been produced and consumed for thousands of years and is thought to have originated from current Georgia where wine stained pottery from circa 6000 BC has been found [1]. Drinking wine daily is common in many cultures ranging from countries with old, well-established wine cultures in Europe and America to rapidly growing wine markets such as China. In some countries, alcoholic beverages, including wine, account for >12% of the daily intake of beverages [2]. Although the per capita consumption of wine by Americans was only 9.42 L per person in 2010, the United States is the single largest wine

market in the world due to the large number of American consumers [3]. However, Old World wine countries such as France, Italy, and Portugal had the highest per capita wine consumption in 2010 (45.7, 42.15, and 41.81 L, respectively) out of the selected wine producing countries (**Figure 1**) [3]. Algeria and Israel had the lowest wine consumption per person of the selected countries at 0.97 L in 2010 [3].

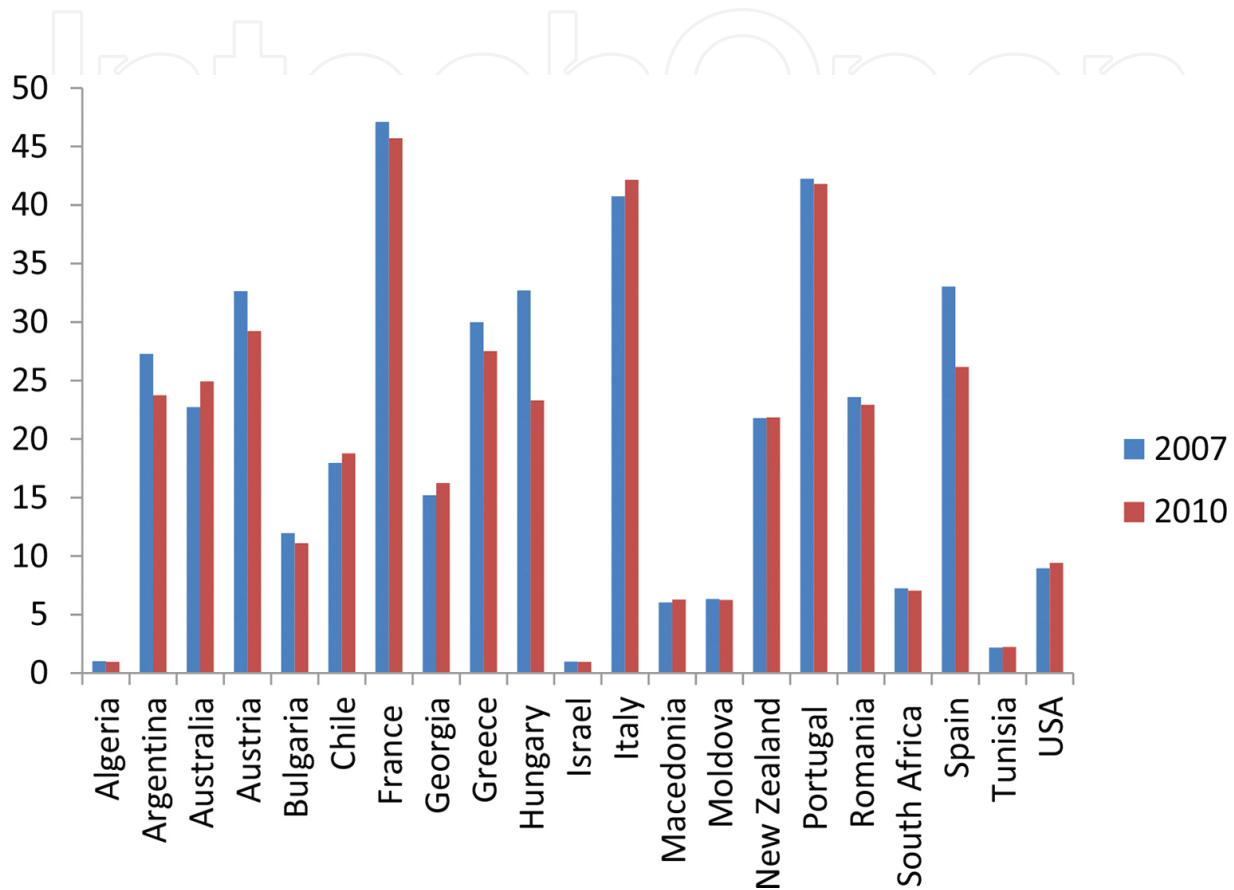


Figure 1. Per capita wine consumption by country (L per person) in 2007 and 2010 from selected wine-producing countries (Wine Institute, Trade Data and Analysis, 2012).

Although fewer studies have been published on trace metal content in alcoholic beverages compared to elemental analysis of foods such as fish, produce, peanuts, and tea, wines are one of the most studied alcoholic beverages. Most studies have focused on quantification of metals such as As, Ni, Cu, Cr, Cd, Pb, Zn, and others in wines from specific countries such as Spain [4, 5], Italy [6–10], Argentina [11–13], Australia [14], Turkey [15–17], Romania [18], and Croatia [19–21] and/or focused on studying regional variation in mineral content from wine-producing regions and grape varieties within a single country.

Wine has significant economic impact and commercial value in addition to its social importance. Wine production is one of the most important agricultural activities in many regions of the world. Wine has a complex sample matrix that contains various components such as macro- and microelements as well as lanthanides that contribute to its nutritional value. Wine composition also greatly affects its quality. The concentration of metals in wine is of great

significance as it affects their conservation and color, in addition to impacting the organoleptic properties of wine, thereby affecting human consumption and the sensory experience [2, 22, 23]. Trace metals affect the organoleptic properties such as aroma, color, flavor, freshness, and taste. Cu, Fe, and Zn, for example, contribute to haze formation and taste effects in wine [24]. However, these minor metals are also favorable for yeast as they are an essential part required for prosthetic group of metalloenzymes that serve as biological catalysts. Other elements such as Ca, K, Mg, and Na are involved in regulating the cellular metabolism of yeasts by helping to maintain adequate ionic balance and pH [25]. Since metal species participate in oxidation-reduction reactions, physical properties of the wine such as color, turbidity, and astringency are largely dependent on metal composition of the wine [23]. Browning, the oxidative spoilage of wine which ultimately results in the loss of aromatic freshness and the appearance of precipitates of condensed phenolic material in the bottled wine, is activated and accelerated by the presence of Fe, Mn, and Cu [2, 22]. The presence and the levels of specific metals can also be used in quality control and the authentication of wines [5, 26]. In addition, metal profile from trace element analysis can act as a fingerprint that may be used to determine the origin, variety, and/or the type of wine and other beverages [27–31]. Therefore, trace element characterization of wine is powerful in fraud detection in commercially sold wines. The trace element composition of wine is influenced by factors such as grape varieties, soil at the vineyard, and viticultural practices [32, 33]. Knowledge of metal concentrations in wine is also of great importance in quality assurance (QA) of branded wines [34].

There are endogenous and exogenous sources of metals in commercial wines. Endogenous metals of natural origin mostly come from the soil on which vines are grown and reach the wine through the harvested grapes [34]. These primary metals make up for the largest part of total metal content in wine [35–37]. Concentrations of these metals are also characteristic of the type of soil at the vineyard, the climate conditions during the growth of the grapes, grape variety, and the maturity of the grapes [38]. The metals of secondary origin are introduced during growth of grapes or at different stages in winemaking starting with harvesting and finishing with storing bottled wine at a cellar. Environmental pollution, addition of fertilizers used in cultivation, as well as application of fungicides and pesticides during the growing season of the grapes increases the amounts of metals such as Cd, Cu, Mn, Pb, and Zn in the finished wine [11, 39–43]. Variation in levels of K, Ca, and Cu in wine may also result from fertilizers applied at the vineyard [44]. The environmental pollution introducing metals into the soil, grapes, and ultimately the wine could be due to nearby industry, waste management practices, traffic, and even mining operations. For example, wines produced at vineyards located near industrial areas or close to major highways often contain higher levels of Cd and Pb due to vehicle exhaust fumes and other emissions to air, water, and/or soil [11, 39, 41, 42]. During winemaking process, the long contact of acidic wine with materials such as aluminum, brass, glass, stainless steel, and wood used in wine-making machinery and pipes, casks, and barrels used for handling and storing wine may also introduce metal contamination to the wine. The steps during the winemaking process often introduce elements such as Al, Cd, Cr, Cu, Fe, and Zn into the finished wine [11, 35]. Metal wine casks at a Sonoma Valley winery are shown in **Figure 2**.



Figure 2. Shows wine storage containers at a Sonoma Valley winery at California (USA).

Many studies have shown that moderate consumption of red wine may improve health and longevity when it is done in combination with a balanced diet [45]. Much attention has been given in the research and medical communities to the properties and activity of polyphenols. Polyphenols have been shown to provide some possible health benefits by acting as antioxidants that helps prevent cell damage. Many of these health benefits of wine are associated with polyphenol antioxidants such as resveratrol (3,5,4'-trihydroxystilbene) that is common in grapes and many other plants [46]. Resveratrol obtained from moderate wine consumption was found to decrease the risk of cardiovascular events and decrease tumor growth in animal models [47, 48]. The powerful antioxidant properties of resveratrol are thought to reduce the oxidation of low-density lipoproteins (LDL) and to inhibit platelet aggregation that is involved in the formation of atherosclerotic lesions [49–51]. However, due to the complex structure, properties, and activity, many of the possible positive effects of polyphenols on animal and human health are not yet fully understood. The structure of resveratrol (3,5,4'-trihydroxystilbene) is shown in **Figure 3** as an example of a potent, well-studied organic antioxidant.

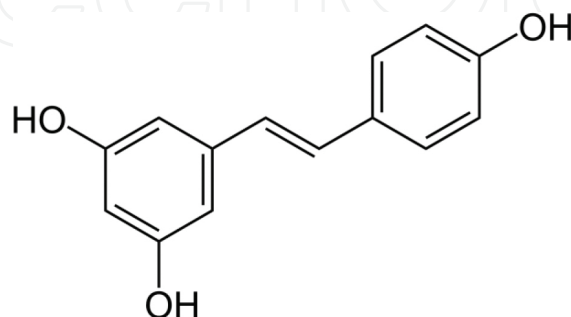


Figure 3. Structure of resveratrol (3,5,4'-trihydroxystilbene), a potent and commonly found polyphenol in red wines with known antioxidant properties.

While wine when used in moderation may also be a good nutritional source for dietary intake of some essential minerals such as iron (Fe) and zinc (Zn) [34, 52], and other metals such as copper (Cu) are considered both an essential and a potentially toxic element. Copper in excess may cause serious health consequences or result in the long-term bioaccumulation and toxicity in the body [53]. Excessive iron intake above the tolerable upper intake level (UL) causes gastrointestinal distress while excess copper intake is likely to result in liver damage. It has been established that even moderate daily consumption of wine contributes significantly to the human nutritional requirements for essential trace elements such as Cr, Co, Fe, Cu, Mn, Mo, Ni, Se, and Zn [54]. The estimated safe intake levels of Cu, Fe, Mn, and Zn established by the US and the European Union (EU) are summarized in **Table 1** [55–57].

Mineral		USA RDA (mg/day)	USA UL (mg/day)	EU PRI (mg/day)	EU SCF (mg/day)
Cu	Adults	0.9	10	1.1	
Fe	Female	18.0	45		15–20
	Pregnant female	27.0	45		30
	Male and postmenopausal female	8.0	45		8–10
Mn	Female	1.8	11 ^a		1–10 ^b
	Male	2.3	11 ^a		1–10 ^b
Zn	Female	8.0	40	7	
	Male	11.0	40	9.5	

^a The estimated safe and adequate dietary intake for Mn was reported as 2–5 mg/day for adults [55].

^b Scientific Committee on Food of the EU has reported 1–10 mg/day as an acceptable range of Mn intake [56]. The EU does not have a RDA for Mn.

Table 1. Recommended dietary allowance (RDA) and tolerable upper intake level (UL) of selected trace minerals by the Food and Nutrition Board (Washington DC) [57]. Population reference intake (PRI) recommendations by the European Union. The Scientific Committee on Food (SCF) guidelines by the European Union [56].

The World Health Organization and various regulatory agencies have established recommended maximum limits for the concentration of metals in beverages and water utilized in human consumption. In addition, individual countries have rules restricting maximum metal content in wines, which have to be met in order to export wine to these consumer markets. For example, Cu and Zn content must be <5 mg/L by law in wines sold in Australia and Germany [58]. The Office International de la Vigne et du Vin (OIV) sets the limits for Cu at 1 mg/L and Zn at 5 mg/L [58, 59]. Italy has established the following legal levels in wine: 1 mg/mL Br, 1 mg/L Cu, 0.2 mg/L Pb, and 5 mg/L Zn [60]. Wine quality is also greatly affected by their metal content. For example, concentrations of Fe >5 mg/L generally induces haze formation and oxidative spoilage of the wine [2]. Concentration of Cu(II) above 1 µg/mL and Fe(III) ions above 7 µg/mL can give unpleasant, astringent tastes in addition to producing cloudiness in wines

that have high pH or high concentration of tannic substances [35, 61]. Typically, the limits on metal concentration imposed for alcoholic beverages are higher than those established for drinking water as the expected intake of alcoholic beverages such as wine is lower [62]. Most of the trace metals are thought to originate from the atmospheric deposition of airborne particulate matter on grapes, composition of the soil, residues of metal containing agrochemical products, transfer of metals from the soil via the roots to the grapes and the wine, vinification methods, and contamination from contact with the metal apparatus during winemaking, production, and packaging processes [2, 54]. For example, some of the copper in finished wine may be due to copper sulfate used for spraying the wines to prevent mildew growth. Most of the iron in wine is determined by the composition of the soil where the grapes for the wine are produced [39]. Elements such as As, Cd, Pb, and Br are considered to be potentially toxic [63].

The ability for discriminating wines regionally within or between countries based on their trace element profile suggests that the elements mainly originate from their movement from the rock to soil and from the soil to grapes used to produce the commercially sold wine [64, 65]. Ability to determine the region of production for a wine greatly benefits the distributors, producers, as well as the consumers. The denomination origin controlled (DOC) system is used in some wine-producing countries to track the origin, to guarantee the wine quality, and to help eliminate fraud [66, 67]. Chemical characterization of finished wine is one of the key requirements to obtaining DOC certification. Wine authenticity may be examined by quantifying suitable geographic tracers in finished wine. For example, the origin may be tracked by examining the specific content of organic constituents that vary regionally such as anthocyanins, flavanols, flavonols, and organic acids [68, 69], by studying the elemental composition profile of inorganic species and by analysis of variation in selected stable isotopes [70]. Chemometric approaches have been applied to large analytical data sets that are generated during wine composition analysis and authenticity determination [12, 21, 66, 67, 70, 71].

The multielemental composition profile in soils appears to be strongly affected by the solubility of inorganic species in the soil. This connection between soil composition and that of finished wine has been confirmed in studies where soil and wine samples were systematically characterized. Strong consensus has been demonstrated between soil and wine samples' element composition while clear differences were shown between the studied regions [70]. In addition to Argentinian wines, statistically significant correlation between vineyard soils and finished Czech wines has been reported [35]. Ultimately, this multielement profile creates a sort of geochemical "fingerprint" that is unique to the vineyard or at least the grape growing region. These regional trace element patterns have been well established in chemical literature using instruments such as inductively coupled plasma-mass spectrometry, ICP-MS [72–84]. Characterization of the geographic origin of wine is even more accurate when natural isotopic abundance ratio of a key element, such as strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) that is independent of the grape variety, is combined with trace element profile analysis [70].

As described above, concentrations of metals in finished wine are characteristic of the type of soil at the vineyard but are also influenced by the climate conditions during the growth of the grapes, the variety of grapes, and their maturity [38]. An example of a vineyard located in the

northern United States will now be described. **Figure 4** shows the scenery at Chateau Grand Traverse in northern Michigan. The soil at the vineyard consists of loamy sand/glacial till and has a pH of 7.2–8.0. Chateau Grand Traverse vineyards lie directly on the 45° North Parallel at the elevation of 640–850 feet (or 195–259 m). The climate on the Old Mission Peninsula is also moderated by the surrounding deep waters of the Traverse Bay, helping to prevent frost during the growing season. Growing season at the Old Mission Peninsula is usually 145–160 days and the heat units have a 5-year average = 2260° days (+50°F or +10°C). Five-year average rain fall is 24.69" (or 62.7 cm) with 80.00" (or 203.2 cm) average snowfall.



Figure 4. Shows the scenery at Chateau Grand Traverse, one of the oldest wineries in northern Michigan. The vineyard is located on a narrow peninsula, north of Traverse City on the shores of Lake Michigan.

The typical composition and properties of wine as a sample matrix for various quantitative analyses will be described in the next section. The sample composition and properties impact important decisions such as what type of sample preparation is needed (if any), should the use of standard addition methods be considered, what is the best instrumental analysis method for characterization of the sample and the quantification of target analytes, etc.

2. Wine as a sample matrix and winemaking treatments

The sample matrix is, by definition, everything in the sample of interest other than the analyte being quantified. Wine is a relatively complex aqueous sample matrix for quantitative chemical analysis due to containing about 12–15% ethanol (by percent volume) and mixture of hundreds of different organic compounds (such as polyhydroxyalcohols, polyphenols, organic acids, polysaccharides, peptides, etc.) in addition to various inorganic species (such as selenium, iron,

zinc, nickel, copper, etc.). Major metals in wine, Ca, K, Na, and Mg are typically at levels in the range of $10\text{--}10^3$ $\mu\text{g/mL}$ [36]. The concentration of K is usually the highest [85]. Al, Cu, Fe, Mn, Rb, Sr, and Zn are called minor metals that are usually found in the range of $0.1\text{--}10$ $\mu\text{g/mL}$ [34]. Trace metals include Ba, Cd, Co, Cr, Li, Ni, Pb, V, and others in the range of $0.1\text{--}100$ ng/mL or less [34].

It is also important to note whether or not allowed additives, adjuvants, or fining agents were used in the winemaking process as these do affect the trace-element levels in wine. Ca concentration in wines is often affected by the addition of CaCO_3 or CaSO_4 during winemaking to deacidify must and wine [11, 43]. Clarifying products such as bentonites are allowed in winemaking. It has been reported that some winemaking treatments such as bentonites and yeast hulls can affect the final trace element composition of wine [6]. Bentonite, for example, is a natural highly absorbent clay containing sheet silicates that is widely used in winemaking. Bentonite contains exchangeable cations such as Ca, Mg, and Na. Bentonite, which mostly consists of montmorillonite-type phyllosilicate, acts as a settling aid to clarify wine and to remove amino acids, minerals, polyphenols, and protein, thus minimizing the risk of haze formation in wine. Proteins are depleted in wines due to their adsorption on the surface of the silica layers. Yeast hulls, living and nonliving biomass of *Saccharomyces cerevisiae*, have also been reported to significantly lower heavy metal content of wines by biosorption [86–88].

Nicolini et al. quantified changes of several minerals in red and white wines resulting from the addition of bentonites and yeast hulls using inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry [6]. They studied the changes in trace element composition resulting from Italian wines treated with 10 different types of bentonite at 1 g/L (the highest doses routinely used in winemaking) and two different yeast hulls at doses of 180 and 360 mg/L. The authors found that bentonite fining significantly lowered concentrations of K, Cu, Rb, and Zn [6]. Cu depletion of -43% was observed with bentonite fining. Meanwhile, certain elements such as Ce, Gd, La, Nd, Pr, and Y increased by about one order of magnitude due to bentonite fining that was used. Also, concentrations of Be, Tl, and U increased by about 4–6 times after bentonite fining [6]. Therefore, depending on the specific element, its concentration may increase or decrease in the wine upon treatment with bentonites.

Nonliving yeast cell walls have also been reported to reduce concentrations of certain cations due to biosorption-involving protein-polysaccharide complexes [89]. Treatment of wine by yeast hulls induced significant decreases of Ce, Cu, Fe, La, Sb, U, V, and Y content in red and white wines as reported in [6]. Higher depletion of the elements was seen at the higher doses of 360 mg/L yeast hulls exposed to wines for 3 h.

3. Matrix effect and the use of standard addition methods

Quantification of certain inorganic trace and ultratrace elements such as arsenic, cadmium, and lead in complex sample matrix such as wine is often challenging due to their very low concentrations. Including a preconcentration step prior to quantitative analysis is often

necessary for these types of dilute analytes as the analyte concentrations may be below the detection limit of the instrumental analysis technique. The preconcentration step may also help to isolate the analyte of interest from the complex sample matrix, thereby improving selectivity of the detection step and stability of the analyte. Evaporation of some solvent including ethanol and water is usually sufficient to preconcentrate wine samples to a high enough level for quantification of trace elements such as iron, copper, zinc, and manganese by spectroscopy. However, electrolytic deposition is a very efficient method for isolation and preconcentration of many inorganic trace elements prior to quantification using an electrochemical detection method such as stripping voltammetry (SV). Selected examples of spectroscopic and electroanalytical detection methods will be described later in this chapter.

Matrix effect is a detectable change (i.e., an increase or a decrease) in the analytical signal response caused by sample components other than the analyte. Matrix interferences that are sometimes observed in atomic spectroscopy (AS) are often due to differences between surface tension and viscosity of test solutions that are often used to simulate the samples and real samples undergoing quantification. Standard addition is especially useful when the exact sample composition is not known, the composition varies between samples, or the sample is complex and the sample matrix affects the observed analytical signal. Therefore, standard addition methods are well suited for analyzing complex aqueous samples such as wine in which the likelihood of matrix effects is substantial. In standard addition, all samples undergoing analysis are in the same matrix. The standard being added in standard addition procedures is the same substance as the analyte of interest. For example, a certified reference standard purchased from a chemical company for aqueous Zn at ppm levels will be added into aliquots of wines undergoing quantitative analysis for zinc based on standard addition approach. The additions result in an increased signal response such as an increase in absorbance, which is directly proportional to the amount of zinc standard added. The standard addition methods will now be described in more detail.

By following the standard addition approach, sample constituents including the possible matrix effect that may suppress or enhance the signal response should be identical in each case because the standards are prepared in aliquots of the same sample. Standard addition methods are also advantageous when the amount of sample is limited. For example, in clinical laboratory setting, limited sample size could be encountered when blood or urine samples are obtained from premature babies or dehydrated elderly patients. In this scenario, standard additions can be carried out by successive introductions of increments of the standard to a single measured volume of the unknown sample. Signal measurements are then made on the original sample and on the sample plus the standard after each addition. In most cases, the sample matrix is nearly identical after each standard addition, the only difference being the concentration of the analyte that has increased leading to detectable increases in the signal response. For direct metal determination in wines without any pretreatments, the usage of ethanol-containing standards or using the standard addition method is recommended in order to minimize chemical and physical interferences [90–93].

As described, standard addition method can take several forms. For example, the wine sample may be spiked by adding one or more increments of a standard solution containing known

concentration of the trace element analyte, such as Zn^{2+} , to sample aliquots containing identical volumes of wine. The standard being added should ideally be relatively concentrated so that the addition of small volumes is sufficient and the sample matrix is not significantly altered. Each solution is then diluted to a constant total volume using deionized water before measurement of the signal. **Figure 5** helps one to visualize stepwise a typical standard addition experiment with constant total volume. This procedure is sometimes called a graphic procedure for standard addition. This graphic procedure is necessary when the analysis method such as atomic spectroscopy consumes some of the prepared solution during the quantification step. Flame atomic absorption, for example, may consume 2–5 mL of the prepared solution when multiple absorbances are obtained in order to determine a more representative mean absorbance value. The sample introduction and atomization steps in flame-atomic absorption spectroscopy (flame-AAS) are very wasteful as the aerosol containing the analyte reaching the flame contains only about 5% of the initial sample. The excess liquid drawn from the sample solution through a capillary tube flows out to drain and ultimately a waste container.

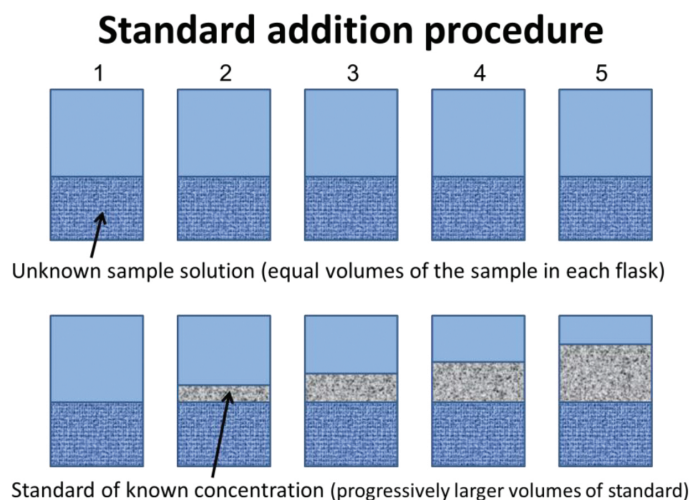


Figure 5. Standard addition procedure shows the addition of equal volume aliquots of the unknown sample (wine) to be quantified to five identical containers, the addition of progressively larger volumes of standard of known concentration and composition (middle layer), and finally, filling the flasks to the same total volume using deionized water prior to the quantitative analysis. Ultimately, all samples undergoing quantitative analysis are in the same sample matrix.

The signal response is determined and recorded for each resulting solution to help quantify the analyte or analytes of interest. It is critical in quantitative analysis, regardless of the detection method chosen, that the signal response to the added analyte is linear. Ideally, each aliquot of added standard in a graphic standard addition procedure should increase the signal by a factor of 1.5–3. The quantification by this procedure usually involves the following steps:

1. Calculate the concentration of added standard for each flask as measured after dilution.
2. Plot analytical signal versus concentration of added standard on a xy graph.
3. Add a linear regression line and the equation for the line.

- The equation for the line ($y = mx + b$) will be used to find the concentration of the analyte in flask 1 by setting y -value equal to zero, and solving for x ($x = -b/m$). The magnitude (absolute value) of the x -axis intercept is the original concentration of the unknown (in units matching the x -axis).

An example of a standard addition plot obtained using graphical standard addition treatment is shown in **Figure 6** for the quantification of Zn in a white wine using flame-atomic absorption spectroscopy. The increases in mean absorbance were proportional to the aliquots of Zn standard added, allowing the reliable determination of Zn in the original wine using linear regression. Each standard addition increased the absorbance signal by a factor of 1.8.

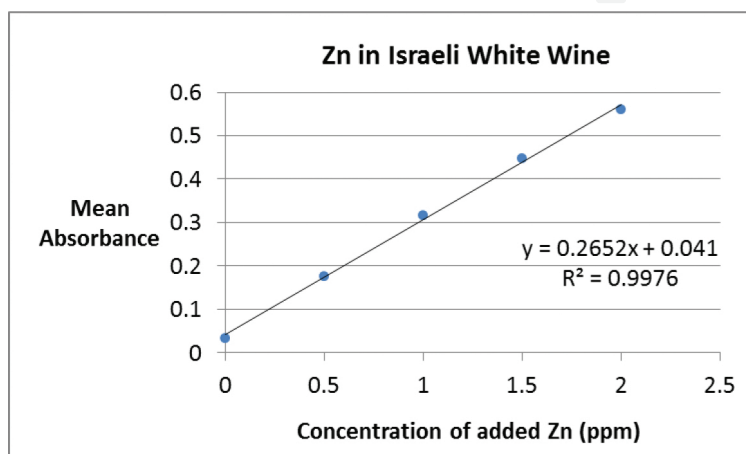


Figure 6. Graphical treatment of standard addition data in quantification of zinc. Concentration of Zn in a white wine from Golan Heights in Israel was determined using 0, 2.5, 5, 7.5, and 10 mL additions 10 ppm zinc standard (from PerkinElmer) to 50 mL volumetric flasks already containing the white wine samples. The first flask with mean absorbance of 0.017 only contained the wine sample and deionized water. Based on the standard addition experiment, this Vintage 2012 Galilee wine from Golan Heights (Israel) contained 1.16 mg/L or ppm of zinc.

4. Common analytical methods for trace element analysis

Various analytical techniques have been used for metal analysis in water, foods, and beverages. The electroanalytical methods include stripping voltammetry and stripping polarography [4, 10, 94–97]. Other analysis methods include X-ray fluorescence [98, 99] and near-IR spectroscopy [14, 29, 30]. Ion chromatography and capillary zone electrophoresis can also be applied to the analysis of metal cations in wines [5, 100, 101].

Atomic absorption and emission spectroscopy methods such as inductively coupled plasma-optical emission spectroscopy, inductively coupled plasma-mass spectroscopy, graphite furnace-atomic absorption spectroscopy (GF-AAS), and flame-atomic absorption spectroscopy are the most commonly used techniques in the determination of metal concentrations due to their high sensitivity and rapid results [7, 14, 30, 58, 102–107]. **Figure 7** shows an F-AAS by PerkinElmer, which is very affordable and reliable for quantification of many trace elements using standard addition methods.



Figure 7. Flame-atomic absorption spectrometer (F-AAS), type AAAnalyst 200 by PerkinElmer is shown.

Despite wine being a relatively complex aqueous sample matrix for chemical analysis due to containing ethanol and hundreds of different larger organic compounds (such as polyhydroxyalcohols, organic acids, polyphenols, polysaccharides, peptides, etc.) in addition to various inorganic species, very few of these compounds actually interfere with atomic spectroscopy due to the high temperatures involved in the sample atomization steps [58]. Also, AAS, the official method of analysis for determination of elements such as Fe and Zn by the European Union Regulation [108], and recommended by the OIV and the American Society of Enologists, is affordable, selective, highly sensitive, often capable of direct measurements, and relatively easy to operate. Fe, Cu, Zn, and Mn, for example, are relatively simple to quantify using F-AAS. These four elements have significant impact on wine quality by contributing to haze formation and leading to undesirable changes in wine taste and aroma [23]. These elements may also impact human health via contributing to total dietary intake (in addition to other sources such as multivitamin supplements, food, and other beverages) and ultimately possible bioaccumulation and toxicity in the event of excessive intake [23]. The most common fuel/oxidant combination for quantification of trace elements such as Cu, Fe, Mn, and Zn by F-AAS in aqueous sample matrix is acetylene/air.

Quantitative analysis by atomic spectroscopy consists of an atomization step where the solid sample components are broken into atoms at high temperature (2000–8000 K) flame, furnace, or plasma after liquid portion of the sample has already evaporated. The inorganic analyte species is quantified based on absorption or emission of monochromatic ultraviolet or visible electromagnetic radiation of characteristic wavelength by the gas-phase analyte. The analytes are typically at parts per million ($\mu\text{g/g}$) to parts per trillion (pg/g) levels for AS.

In ICP-MS, the analyte trace elements are ionized by collisions with excited Ar^+ or energetic electrons in plasma. ICP-MS has detection limits that are 5–7 orders of magnitude lower than atomic spectroscopy based on F-AAS. In addition, the linear range for ICP-MS is 10^8 versus 10^2 for F-AAS. The sample throughput for ICP-MS is greater as most elements may be analyzed

in one run and the sample volumes required for analysis are also less. ICP-MS outperforms even other multielement techniques in element analysis due to its extremely low detection limits. However, the purchase cost and maintenance cost of an ICP-MS system is substantially higher and the instrument requires a skilled operator. ICP-MS has been utilized by many especially as an instrumental tool for characterizing wines according to their geographical origin [72–80, 109].

Stripping voltammetry is a very sensitive, low cost, and a popular electroanalytical chemistry method due to incorporating an electrolytic preconcentration step prior to the analysis of trace concentrations of electroactive species in solution. Multiple elements such as Cd and Cu may also sometimes be quantified from the same sample using SV during the same experiment. Extremely low detection limits for metal ions at sub-ppb (or 10^{-10} – 10^{-11} M) concentrations have been reported for SV. There are three parts in a stripping experiment: deposition, quiet time, and stripping. During the deposition step, the analyte of interest is accumulated onto the working electrode that may have been chemically modified previously. Deposition of the target species may be increased by forced convection such as stirring the solution, rotation of the working electrode, or creating flow conditions during the deposition step. The required deposition time (of typically 1–10 min) depends on the concentration of the analyte species in the sample. In anodic stripping voltammetry (ASV), the working electrode is held at a potential at least 0.4 V cathodic to the standard potential of the least easily reduced ion being quantified. The stirring is stopped and the system is allowed to reach equilibrium during a quiet time of about 10–15 s. Finally, the accumulated material is reduced or oxidized back into the solution during the stripping step. Change in electrochemical response (i.e., signal) during the stripping step is proportional to the concentration of the analyte that was in or on the working electrode. Anodic stripping voltammetry involves the reduction of a metal ion analyte from the sample during the preconcentration step. SV method for trace metal analysis in dry wines will be described briefly below as an example of sample preparation, solution conditions, and time required for electroanalytical quantification.

Brainina et al. [96] developed and reported a method for quantification of cadmium, copper, lead, and zinc in dry wines by stripping voltammetry with a thick-film modified graphite-containing electrode (TFMGE). The reported method has an advantage of not requiring acid digestion of the wine samples or any other sample preparation approaches for the destruction of organic substances. Supporting electrolyte of 0.5 M HCl was for Cu, Pb, and Cd, and 0.1 M acetate buffer (pH 5.5) and 0.35 M NaCl for Zn. The deposition potentials were –0.8 V for Cu, –1.2 V for Pb and Cd, and –1.4 V for Zn. The wine samples were diluted with the supporting electrolyte prior to deposition step. The deposition times were 30–60 s for Cu, 120 s for Pb and Cd, and 10–30 s for Zn. Results obtained by the TFMGE analysis were compared with quantification of the selected elements in the same samples done using ICP-MS. Of note, the fast and simple analysis method with TFMGE actually provided better reproducibility than methods involving wine decomposition prior to analysis. More recently, Burmakina et al. [110] developed a procedure for determining manganese(II) in wines by SV on a graphite electrode. The detection limit of manganese(II) was 50 $\mu\text{g/L}$ with a linear range 0.1–3 mg/L [110].

5. Conclusions

Wine is a common beverage that has immense economic impact on certain regions of the world. The theory, advantages and disadvantages, experimental considerations and set up of various sensitive atomic spectroscopy, and electroanalytical quantification methods were described in this chapter. Examples of quantification methods suitable for essential trace element as well as the determination of toxic elements generally found at considerably lower concentrations in wine were provided throughout the chapter. Many inorganic elements have been found to affect the properties of wine, how well it stores, as well as the sensory perception of the wine consumer. The unique trace element profile may also be used as a fingerprint to identify the authenticity of the wine if a fraud is suspected or provide information about the growing region of the grapes and the location of the vineyard. The complexity of wine as a sample matrix for quantification of inorganic elements and the use of standard addition methods to improve the reliability of the selected detection methods were described. Examples of common methods, the common origins of the inorganic elements in the finished wine, and reported levels of trace elements in wines were heavily referenced throughout the chapter.

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