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Original Research Article

Investigation of heavy metal concentrations in some Turkish wines

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ABSTRACT

Research studies analysing heavy metal or trace elements in Turkish wines is scarce. This study was designed to fill this gap, analysing 43 wines produced in 4 different regions in Turkey. A total of 37 red and 6 white wines produced from various grapes from 2006 to 2008 in Marmara, Aegean, Central Anatolia and Eastern Anatolia regions were studied. Wines were analyzed for Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb using atomic absorption spectrometer equipped (AAS) with electrothermal atomization unit (ET). Average results for red and white wines, respectively, were: Cr, 38.6 and 29.4 μg/L; Mn, 697 and 101 μg/L; Fe, 1.7 and 0.7 mg/L; Co, 6.3 and 0.5 μg/L; Ni, 134 and 573 μg/L; Cu, 131 and 158 μg/L; Zn, 389 and 2099 μg/L; Cd, 2.8 (red wine; white wine results were under limit of detection); Pb, 6.3 (red wine; white wine results were under limit of detection). These results were interpreted for grape types and regions. Accuracy was tested with standard addition method. Recoveries ranged from 96% to 107% after standard addition. Cr, Fe and Mn in red wines were higher in comparison to white wines, whereas white wines were higher in Ni and Zn. Non-essential Cd and Pb concentrations were very low in both red and white wines. Comparison with literature shows all heavy metal concentrations in the analyzed Turkish wines to be below the limits designated by World Health Organization.

1. Introduction

Research on accumulation of heavy metals in food, especially canned tuna, oil, dry tea, mushrooms and peanuts has been seen in the literature since the early 1970s (Reilly, 2002a,b; Eschnauer, 1986). However the number of analysis in alcoholic beverages is considerably limited. Only a few studies dealing with heavy metal content of high alcoholic drinks has been reported in literature. Among the reported studies wine samples are not rare. Different methods of rare metal analysis were employed in these studies the majority being atomic absorption and atomic emission. The following methods have been reported for studies in relation to atomic absorption techniques; FAAS (Flame Atomic Absorption Spectrometry) (Sauvage et al., 2002; Bakırcıoğlu et al., 2003; Monasterio & Wuilloud, 2009; Paneque et al., 2010; Fabani et al., 2010; Trujillo et al., 2011; Calin et al., 2012), ETAAS (Electrothermal Atomic Absorption spectrometry) (Freschi et al., 2001; Nikolakaki et al., 2002; Lara et al., 2005), HGAAS (Hydride Generated Atomic Absorption spectrometry) (Elçi et al., 2009; Klarić et al., 2011). On the other hand studies dealing with the following methods in relation to atomic emission techniques have also been reported; ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) (Kallithraka et al., 2001; Kment et al., 2005; Catarino et al., 2006; Moreno et al., 2007; Chopin et al., 2008; Cozzolino et al., 2008; Serepinas et al., 2008; Capron et al., 2007; Fabani et al., 2010; Ferreira et al., 2008; Gonzalves et al., 2009; Grindlay et al., 2009; Provenzano et al., 2010; Santos et al., 2010; Vrcek et al., 2011; Fiket et al., 2011; Rodrigues et al., 2011; Geana et al., 2013). Alongside these other rare metal analysis techniques like anodic stripping (Brainina et al., 2004), Spectrophotometric analysis (Riganakos and Veltsistas, 2003), XRF (X-Ray Fluorescence) (Santos et al., 2010) and Near IR Spectroscopy (Cozzolino et al., 2008) have been reported. The majority of the studies are focused mostly on Italian and Spanish wines. Studies dealing with Argentinian (Lara et al., 2005; Fabani et al., 2010) Romanian (Geana et al., 2013), Croatian (Fiket et al., 2011) and Turkish (Elçi et al., 2009; Aydın et al., 2010) wines are in the minority. However, although Turkey is a winemaker of grapes and wine, there are only a few case studies dealing with heavy metal analysis in alcoholic beverages produced in Turkey.

In this study, 17 wine samples from the Marmara Region, 15 from the Aegean Region, 6 from Central Anatolian Region and 5 from Eastern Anatolian Region were taken for analysis. Of these, 37

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Table 1
Temperature programming of graphite cuvette using ETAAS method.

Determined element	Drying				Ashing		Reading			Cleaning		Inert gas
	Ramp time (s)	°C	Hold. time (s)	Ramp time (s)	°C	Hold time (s)	Ramp time (s)	°C	Time (s)	°C	Time (s)	
Mn	5 5	80 120	5 10	5	700	0	1.5	2300	1.5	2400	1	Ar
Cr	5 5	80 120	5 10	5	750	0	1.5	2500	1.5	2500	1	Ar
Fe	5 5	80 120	5 10	5	750	0	1.5	2400	1.5	2500	1	Ar
Co	5 5	80 120	5 10	5	750	0	1.5	2200	1.5	2400	1	Ar
Ni	5 5	80 120	5 10	5	700	0	1.5	2000	1.5	2200	1	Ar
Cu	5 5	80 120	5 10	5	600	0	1.5	2000	1.5	2400	1	Ar
Zn	5 5	80 120	5 10	5	550	0	1.5	2000	1.5	2400	1	Ar
Cd	5 5	80 120	5 10	5	550	0	1.5	2000	1.5	2400	1	Ar
Pb	5 5	80 120	5 10	5	550	0	1.5	2200	1.5	2300	1	Ar

were red and the other 6 were white wine samples. All of the samples were produced by the four largest winemakers in Turkey. While some parts of the grapes used are local, there are also international brands and of the wines produced as 20% are exported to other countries. In some of the agricultural regions thermal power plants are found intensely. The effect of heavy metal contamination from these plants has not been reported until (Cayır et al., 2012; Baba et al., 2010).

A number of the studies in the literature were carried out to investigate the effects of thermal power plants and other similar industrial facilities on soil, plant and wine contents (Kallithraka et al., 2001; Jamali et al., 2009; Bajpai et al., 2010; Sanei et al., 2010). There are a large number of thermal power plants in Western Anatolia and Central Anatolia regions in Turkey. Therefore, the results of this study, especially for Cd and Pb, may be useful in showing the effects of thermal power plants.

2. Materials and methods

2.1. Materials

GBC Avanta PM model AAS (Atomic Absorption Spectrometer) with GF 3000 power supply and PAL 3000 auto sampler was used and atomization was achieved by graphite furnace electrothermally (GBC Scientific Equipment Pty. Ltd., Braeside, Victoria, Australia).

Only Fe analysis was carried out by a combination of ETAAS and FAAS, whereas the other metals were analyzed by ETAAS only. The matrix modifier has not been used in all the analysis (Sardans et al., 2010). FAAS was employed with air/acetylene (10/1.5) flames and lights at 248.30 nm wavelength was used for analysis of iron.

All solutions were prepared with de-ionized water with 0.55 μS/cm conductivity. Calibration curves were obtained for 1–200 μg/L standard solutions prepared from 1000 mg/L commercial stock solutions (Merck, Darmstadt, Germany). The graphite oven temperature programs are shown in Table 1.

LOQ values were assessed with respect to standard methods designated in literature (Skoog and Leary, 1992; Armbruster et al., 1994). The value where the standard deviation and signal/noise ratio values of the blank solution was 10, has been designated as LOQ. Also the adsorption values were measure using 0.1–3.0 μg/L standard solutions and the linear border region of the calibration curve was determined from the graph. The obtained LOQ values are as shown below:

Mn: 1.50 μg/L Cr: 1.80 μg/L Fe: 0.06 mg/L Co: 0.90 μg/L
Ni: 2.20 μg/L Cu: 1.30 μg/L Zn: 0.38 μg/L Cd: 0.35 μg/L
Pb: 2.50 μg/L

In addition, due to the lack of a reference standard material, accuracy of the analysis and the effect of the matrices in the media were controlled with the standard addition method. All studied elements were tested with standard addition method for 10 randomly selected samples

2.2. Preparation of the wine samples for analysis

The wine samples were treated with hot HNO_3–H_2O_2 for decomposition of organic matrix. For each sample; 25.00 mL of wine was put in a Kjeldahl flask. Then, 5.00 mL of the certificated HNO_3 (63%, d = 1.43 g/mL) and 5.00 mL of H_2O_2 were put in the flask and the mixture was boiled for about half an hour until colorless. Later, this solution was put in a 50.00 mL flask and diluted to 50 mL from where the samples were injected to the AAS.

In this study, two different samples were taken from each wine. After separate digestion, two different solutions were obtained for each sample all of which were analyzed three times with AAS. So each wine sample was analyzed 6 times.

3. Results and discussion

As the samples were digested in the HNO_3–H_2O_2 mixture the presence of an organic matrix is improbable. Ions which may cause interference like Cl^-, HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4 are very low in concentration. Only the existence of SO_4^{2-} ions in wines has been known for a very long time. Recently a study has been reported