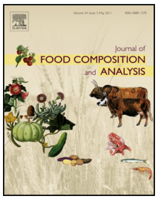
Journal of Food Composition and Analysis 33 (2014) 105–110

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca



Original Research Article

Investigation of heavy metal concentrations in some Turkish wines

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ARTICLE INFO

Article history:
Received 4 April 2012
Received in revised form 3 October 2013
Accepted 11 November 2013

Keywords:
Metal contamination
Turkish wine
AAS
ETAAS
Heavy metal profile
Power plant effect
Trace elements
Minerals
Environmental pollution of the food chain
Food safety
Food composition
Food analysis

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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http://dx.doi.org/10.1016/j.jfca.2013.11.006

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	80	5	5	700	0	1.5	2300	1.5	2400	1	Ar
	5	120	10									
Cr	5	80	5	5	750	0	1.5	2500	1.5	2500	1	Ar
	5	120	10									
Fe	5	80	5	5	750	0	1.5	2400	1.5	2500	1	Ar
	5	120	10									
Co	5	80	5	5	750	0	1.5	2200	1.5	2400	1	Ar
	5	120	10									
Ni	5	80	5	5	700	0	1.5	2000	1.5	2200	1	Ar
	5	120	10									
Cu	5	80	5	5	600	0	1.5	2000	1.5	2400	1	Ar
	5	120	10									
Zn	5	80	5	5	550	0	1.5	2000	1.5	2400	1	Ar
	5	120	10									
Cd	5	80	5	5	550	0	1.5	2000	1.5	2400	1	Ar
	5	120	10									
Pb	5	80	5	5	550	0	1.5	2200	1.5	2300	1	Ar
	5	120	10									

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 where SO_4^{2-} and Cu^{2+} ions have been detected simultaneously in wine (Tamasi et al., 2010). Accepting the SO_4^{2-} ion concentration to be in acceptable limits very high matrix modifiers have not been used during the study. Similar studies have been encountered in literature (Paneque et al., 2010; Sardans et al., 2010). All results are given in Tables 2–4 according to the type of wine, region and winemaker.

The results reveal the amounts of Cd and Pb metals to be extremely low. In some cases, Cd and Pb concentrations remained below the limit of quantitation and could not be detected. Although Co is an essential metal for living beings, the results showed it to be below 10 ppb. However, we have taken this is to be normal since there are no other suggestions reported in literature. The results reveal the Fe, Mn and Zn content to be higher than the other elements in question. The mean value of these elements shows that they can be determined with the FAAS method. On the other hand the Cr, Co, Ni, Cu, Cd and Pb concentrations were far too low to be determined by the FAAS method. There are many papers dealing with FAAS but these mostly deal with enrichment rather than content (Pohl, 2009; Bakırcıoğlu et al., 2003). Only Fe determination was achieved using FAAS due to its concentration. Table 2 shows the standard deviation to be minimal. Other elements were detected using the ETAAS method.

If relative abundances of the essential elements in red wines are compared, the tendency at the ranking is as follows:

$$\mathrm{Fe} > \mathrm{Mn} > \mathrm{Zn} > \mathrm{Cu} \geq \mathrm{Ni} > \mathrm{Cr}$$

Comparison of the relative abundances of the essential elements in white wines reveals the following tendency:

$$\mathrm{Zn} > \mathrm{Fe} > \mathrm{Ni} > \mathrm{Cu} > \mathrm{Mn} > \mathrm{Cr}$$

This ranking is not to be taken as exact because there are many variables in wine production, such as region, company, soil and climate. For this reason, the amount of an element may be found in a wide variety of ranges for different wines even if they were produced from the same type of grapes. For example, the amount of Mn was found to be between 120 mg/L and 1789 mg/L in Cabernet red wines which is quite a wide range.

The following general conclusions can be made from data in Table 2:

- Fe and Mn content of red wines is higher than that of white wines.
- Zn and Ni content of white wines are higher than those of red wines.
- Co, Cr and Cu contents of red wines are the same or very close to those of white wines.

Due to the significantly high concentrations of Ni and Zn in the analyzed wine samples a prediction can be made: it is possible that Ni and Zn are dissolved into the wine during the production steps in metal vessels. It sounds probable considering the acidic nature of the wine.

Table 3 features the observed concentration ranges and averages for each metal, according to different winemakers, to render an opportunity to compare the possible differences emerging from the wineries. Among the analyzed samples, 6 were produced by Büyülübağ, 7 by Bak Bağcılık, 2 by Umurbey and 22 by Doluca making a total of 37 red wines (Table 3). The remaining samples are white wines.

In Table 3, the most noticeable factor is that in wines produced by Büyülübağ and Bak Bağcılık companies, Mn and Fe amounts are relatively high whereas in wines produced by Umurbey Company; Zn and Ni amounts are higher. This is in accordance with literature. Heavy metal concentration of wines varies in a wider range with respect to other alcoholic beverages (Ibanez et al., 2008).

The results given in Table 4 show that Mn amounts of Central Anatolian wines and Eastern Anatolian wines are relatively high which is also related with the type of wines. The mentioned wines are red wines.

WHO does not specify a maximum for Cd in wine. But at this point, drinking water specifications are useful considering all other food samples. According to WHO, Cd concentration must be below 5.0 ppb in drinking water (Reilly, 2002a,b). The outcome of this study reveals that the amount of Cd to be below the allowed limit for every analyzed sample. In literature, comments have been made about the effects of thermal power plants on accumulation of non-essential metals like Cd in similar studies (Kallithraka et al., 2001; Bajpai et al., 2010; Dragovic et al., 2013). However such interpretation of our study would not support Kallithtraka's reasoning; since the determined Cd concentrations are very low. In fact, there are many thermal power plants in the Marmara, Aegean and Central Anatolian regions. However, gas emissions of thermal power plants should be evaluated according to physical-geographical conditions. The Cd values were measured to be 7.42 ± 0.24 and 11.5 ± 1.45 μg/L (Tables 2 and 3) which are way over the designated 5.0 μg/L value. These high values are mostly encountered in the wines produced from grapes grown in the Marmara region a highly industrialized region with a vast number of thermal plants. The effect can be easily seen. On the other hand values reported by Kallithraka are much higher leading to the notion that thermal power plants are not the only reason for contamination.

Observed Pb values are very much lower than those allowed by the International Organization of Vine and Wine The highest value found for Pb 25.92 ± 1.50 μg/L which is much lower than the upper limit value given by the International Organization of Vine and Wine of 0.15 mg/L (OIV, 2011). Early studies in England have reported Pb values as high as 1840 μg/L resulting from lead cauldrons (Sherlock et al., 1986). As stainless steel boilers are used presently this problem has seemed to disappear. All data from the analysis are in agreement with literature. Values for Cr, Mn, Fe, Co, Ni, Cu and Zn have no difference than the ones given in the literature and can be considered approximately the same (Catarino et al., 2006; Chopin et al., 2008; Cozzolino et al., 2008; Fabani et al., 2010; Ferreira et al., 2008; Grindlay et al., 2009; Kment et al., 2005; Moreno et al., 2007; Reilly, 2002a,b; Santos et al., 2010; Serepinas et al., 2008; Vrcek et al., 2011).

The literature contains data of average heavy metal content in alcoholic beverages (Reilly, 2002a,b). In that study, it was reported that alcoholic beverages contain 400 μg/L Mn, 400 μg/L Fe, 1 μg/L Co, 30 μg/L Ni, 100 μg/L Cu and 300 μg/L Zn in average. Average chromium concentration was given as ~100 μg/L in the same study. The results observed in our study are overall comparable with these values with the exception of nickel concentration. However, Reilly's work was targeted at all alcoholic beverages whereas this study focuses on wine. Also, the findings are consistent with more recent literature (Alvarez et al., 2007; Fabani et al., 2009; Fiket et al., 2011; Vrcek et al., 2011). The most considerable difference between our findings and the ones in the literature is that nickel and zinc concentrations in two particular white wine samples were found to be significantly high. Nevertheless, it should be noted that these two samples were produced by the same company. Therefore, it would not be accurate to generalize such results. They were probably due to a defect during winemaking. With regards to the low standard deviation and repeatable results, high Mn, Ni and Zn findings are acceptable.

Table 2
Heavy metal content of wine by type.

Type of wine		*n*		Cr	Mn	Fe*	Co	Ni	Cu	Zn	Cd	Pb
Name of grape	Color											
Cabernet	Red	10	Range	10.83 ± 2.06	120.56 ± 10.43	0.89 ± 0.17	2.30 ± 0.33	65.21 ± 6.03	44.81 ± 0.90	80.74 ± 11.70	1.96 ± 0.41	1.60 ± 0.34
				91.86 ± 9.48	1789.33 ± 184.30	4.93 ± 0.46	9.72 ± 1.18	206.64 ± 4.24	525.26 ± 24.53	382.74 ± 43.05	4.53 ± 0.95	13.26 ± 2.08
			Average	53.34 ± 4.32	935.05 ± 64.51	2.24 ± 0.26	5.78 ± 0.47	132.90 ± 5.01	101.17 ± 5.24	271.25 ± 10.85	3.25 ± 0.85	7.24 ± 1.25
Merlot	Red	8	Range	15.20 ± 1.35	124.66 ± 0.95	0.75 ± 0.01	2.37 ± 0.24	72.29 ± 2.37	72.75 ± 0.40	413.68 ± 7.35	3.77 ± 0.71	3.29 ± 0.36
				71.39 ± 4.46	979.78 ± 23.69	5.69 ± 0.06	5.78 ± 0.56	355.07 ± 6.21	388.87 ± 3.06	649.46 ± 21.61	11.50 ± 1.45	25.92 ± 1.50
			Average	32.96 ± 2.60	419.96 ± 30.16	1.83 ± 0.03	4.02 ± 0.17	156.85 ± 5.49	194.08 ± 10.19	490.14 ± 20.09	7.20 ± 0.40	14.60 ± 0.76
Shiraz	Red	4	Range	7.75 ± 1.55	121.40 ± 15.16	0.59 ± 0.10	1.46 ± 0.03	77.91 ± 4.63	99.19 ± 14.38	365.38 ± 3.68	–	–
				13.53 ± 0.20	606.07 ± 13.12	3.12 ± 0.02	13.43 ± 1.09	97.79 ± 2.69	385.50 ± 7.20	953.33 ± 15.63		
			Average	11.55 ± 0.44	277.76 ± 19.94	1.35 ± 0.03	6.71 ± 0.28	87.64 ± 5.00	225.86 ± 3.84	594.70 ± 7.72	ULOQ	ULOQ
Kalecik Karası	Red	4	Range	60.32 ± 3.42	972.72 ± 26.05	1.28 ± 0.04	6.23 ± 0.15	88.97 ± 3.56	87.61 ± 2.69	156.63 ± 8.67	–	6.65 ± 1.19
				137.80 ± 4.68	1822.21 ± 32.62	5.79 ± 0.31	11.76 ± 0.78	510.34 ± 5.05	397.62 ± 1.75	264.34 ± 7.98		9.89 ± 0.05
			Average	95.19 ± 3.33	1515.17 ± 45.46	2.55 ± 0.29	9.41 ± 0.32	302.23 ± 6.64	183.35 ± 5.12	205.66 ± 6.56	ULOQ	8.27 ± 0.48
Öküzgözü	Red	4	Range	16.77 ± 0.70	151.86 ± 10.54	0.74 ± 008	2.42 ± 0.46	68.80 ± 2.47	46.94 ± 1.19	258.66 ± 7.43	3.12 ± 0.65	2.61 ± 0.08
				66.18 ± 7.41	1556.80 ± 112.18	1.54 ± 013	10.07 ± 0.10	121.26 ± 13.19	230.03 ± 0.39	726.82 ± 4.58	5.92 ± 0.18	8.49 ± 1.36
			Average	39.13 ± 3.35	574.81.49 ± 30.58	1.07 ± 0.09	7.28 ± 0.37	97.68 ± 2.16	139.29 ± 3.13	428.25 ± 12.41	4.52 ± 0.28	5.55 ± 0.17
Boğazkere	Red	3	Range	35.44 ± 1.47	255.38 ± 16.29	0.64 ± 0.13	5.68 ± 0.66	77.30 ± 1.23	47.55 ± 0.44	224.13 ± 3.85	–	–
				86.35 ± 5.31	1576.27 ± 119.30	4.30 ± 0.17	15.31 ± 0.97	128.91 ± 2.10	152.49 ± 19.22	315.78 ± 25.83		
			Average	58.43 ± 4.06	1100.65 ± 55.12	2.26 ± 0.21	10.51 ± 0.79	107.70 ± 1.71	99.30 ± 5.56	276.22 ± 14.63	ULOQ	ULOQ
Çal Karası	Red	1	Range		–	–	–	–	–	–	–	–
			Average	15.75 ± 0.17	220.76 ± 21.12	1.43 ± 0.14	4.21 ± 0.11	86.24 ± 1.94	113.91 ± 18.08	518.32 ± 31.75	ULOQ	17.24 ± 2.38
Cinsawlt	Red	1	Range	–	–	–	–	–	–	–	–	–
			Average	54.68 ± 6.45	1901.07 ± 17.48	2.03 ± 0.22	6.88 ± 0.77	90.62 ± 5.54	95.30 ± 0.51	183.39 ± 10.98	ULOQ	ULOQ
Alikante	Red	1	Range	–	–	–	–	–	–	–	–	–
			Average	17.04 ± 1.83	200.01 ± 25.40	1.64 ± 0.19	5.78 ± 0.88	122.83 ± 2.93	64.84 ± 21.15	497.84 ± 13.42	7.42 ± 0.24	10.55 ± 0.74
Grenache	Red	1	Range	–	–	–	–	–	–	–	–	–
			Average	8.15 ± 1.44	147.09 ± 8.18	1.76 ± 0.07	2.09 ± 0.68	159.01 ± 2.22	89.75 ± 19.58	426.24 ± 15.33	5.81 ± 1.91	ULOQ
Sauvignon Blanc	White	3	Range	21.60 ± 5.40	32.89 ± 6.58	0.49 ± 0.07	9.92 ± 0.57	511.53 ± 28.90	155.15 ± 8.04	990.16 ± 31.48	–	–
				48.35 ± 7.83	80.70 ± 16.18	1.25 ± 0.11	16.53 ± 2.62	3605.65 ± 264.60	442.71 ± 8.48	5241.95 ± 98.01		
			Average	34.80 ± 7.66	56.80 ± 11.92	0.76 ± 0.08	12.95 ± 1.04	1715.54 ± 125.92	310.84 ± 7.76	2413.78 ± 57.32	ULOQ	ULOQ
Narince	White	1	Range	–	–	–	–	–	–	–	–	–
			Average	8.79 ± 1.54	139.31 ± 6.39	0.32 ± 0.07	2.14 ± 0.61	45.29 ± 1.44	139.31 ± 6.39	377.01 ± 18.09	ULOQ	ULOQ
Sultaniye	White	1	Range	–	–	–	–	–	–	–	–	–
			Average	7.23 ± 0.81	138.83 ± 4.02	0.31 ± 0.06	ULOQ	74.79 ± 6.21		397.30 ± 9.29	ULOQ	ULOQ
Chardonnay	White	1	Range	–	–	–	–	–	–	–	–	–
			Average	65.66 ± 1.77	69.25 ± 1.87	1.27 ± 0.28	10.82 ± 1.12	457.12 ± 18.28	232.23 ± 1.86	3507.11 ± 114.67	ULOQ	ULOQ
	Red Average			38.62	696.50	1.72	6.26	134.37	130.68	389.20	2.82	6.34
	White Average			29.42	101.05	0.67	0.47	573.19	158.42	2099.30	ULOQ	ULOQ

Data are means ± SD. Results are expressed as μg/L, except for Fe, as mg/L. ULOQ: under the limit of quantitation. *n* = number of samples. All analyses were repeated 6 times (2 subsamples of each wine in triplicate).

Table 3
Distribution of heavy metals by winemaker.

Winemaker	*n*		Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Doluca	26	Range	7.23 ± 0.83	121.40 ± 15.71	0.49 ± 0.05	2.42 ± 0.08	45.29 ± 1.44	46.94 ± 1.17	183.40 ± 11.18	3.12 ± 0.09	1.60 ± 0.04
			60.35 ± 0.07	1901.07 ± 115.91	4.30 ± 1.42	16.53 ± 2.07	1519.04 ± 165.12	334.67 ± 1.67	1009.22 ± 32.49	11.50 ± 1.45	18.96 ± 6.22
		Average	28.70 ± 2.26	318.35 ± 16.72	0.97 ± 0.09	6.50 ± 0.94	110.25 ± 5.75	144.65 ± 1.33	364.69 ± 13.81	5.60 ± 0.28	13.70 ± 0.71
Büyülübağ	6	Range	63.44 ± 2.02	500.69 ± 16.50	2.01 ± 0.02	2.30 ± 0.30	72.29 ± 2.38	72.75 ± 0.40	299.66 ± 20.18	–	–
			175.01 ± 3.50	979.78 ± 23.50	4.93 ± 0.74	4.97 ± 0.23	160.39 ± 6.03	514.66 ± 7.71	953.33 ± 15.24		
		Average	75.12 ± 2.67	733.90 ± 21.58	3.60 ± 0.11	4.71 ± 0.28	111.18 ± 5.42	237.69 ± 5.65	613.63 ± 15.96	ULOQ	ULOQ
Bak Bağcılık	7	Range	60.32 ± 3.36	1556.80 ± 121.36	1.28 ± 0.13	6.23 ± 0.09	88.97 ± 3.56	87.61 ± 2.69	156.63 ± 8.64	–	2.61 ± 0.64
			99.68 ± 2.88	1822.21 ± 32.78	5.79 ± 0.34	15.33 ± 0.98	258.22 ± 5.32	230.03 ± 0.40	315.78 ± 25.89		16.49 ± 3.79
		Average	78.37 ± 2.91	1668.39 ± 57.43	2.75 ± 0.24	9.80 ± 0.76	158.02 ± 4.83	140.99 ± 3.41	226.51 ± 13.85	ULOQ	6.50 ± 1.05
Umurbey	4	Range	15.20 ± 1.32	69.25 ± 1.87	1.25 ± 0.02	3.54 ± 0.08	355.67 ± 6.21	232.23 ± 1.99	649.46 ± 21.46	–	–
			76.43 ± 7.24	212.62 ± 25.01	3.27 ± 0.05	12.82 ± 1.32	3605.65 ± 264.6	525.26 ± 24.51	5241.95 ± 98.00		
		Average	54.56 ± 3.62	134.14 ± 18.86	1.98 ± 0.05	10.15 ± 1.01	544.10 ± 21.76	397.26 ± 17.86	3132.84 ± 65.47	ULOQ	ULOQ

Data are means ± SD. Results are expressed as μg/L, except for Fe, expressed as mg/L. ULOQ: under the limit of quantitation. *n* = number of samples. All analyses were repeated 6 times (2 subsamples of each wine in triplicate).

Table 4
Heavy metal content of the grapes grown in four regions.

Region	*n*		Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
Aegean region	15	Range	7.23 ± 0.77	121.40 ± 15.76	0.54 ± 0.12	2.30 ± 0.44	73.30 ± 1.12	29.17 ± 4.16	210.02 ± 2.08	3.77 ± 0.11	1.60 ± 0.40
			175.01 ± 3.50	1470.30 ± 25.88	5.69 ± 0.71	16.53 ± 0.24	120.39 ± 6.03	385.50 ± 10.02	515.46 ± 35.54	7.42 ± 0.26	25.92 ± 1.50
		Average	48.16 ± 6.78	541.97 ± 34.41	2.37 ± 0.54	5.02 ± 0.49	102.21 ± 4.45	207.71 ± 6.31	440.75 ± 21.06	5.70 ± 0.50	17.90 ± 1.80
Marmara region	17	Range	8.15 ± 1.44	124.66 ± 0.94	0.54 ± 0.06	2.09 ± 0.06	77.91 ± 4.60	44.81 ± 0.80	143.16 ± 4.86	1.96 ± 0.58	3.29 ± 1.08
			76.43 ± 8.25	424.20 ± 9.75	3.27 ± 3.29	12.40 ± 0.31	3605.65 ± 264.6	525.26 ± 24.51	5241.95 ± 98.01	9.53 ± 0.22	18.96 ± 0.19
		Average	31.45 ± 2.46	210.63 ± 11.78	1.38 ± 0.37	6.02 ± 0.50	427.64 ± 18.60	188.33 ± 9.71	397.93 ± 17.23	5.90 ± 0.53	11.84 ± 2.48
Central Anatolia region	6	Range	8.80 ± 1.55	972.72 ± 26.05	0.32 ± 0.04	6.23 ± 0.08	45.29 ± 1.44	61.42 ± 10.68	156.63 ± 8.64	–	6.65 ± 1.13
			137.80 ± 4.70	1872.21 ± 32.78	5.79 ± 0.07	11.76 ± 0.78	351.38 ± 6.32	397.62 ± 1.75	1156.94 ± 21.96		9.89 ± 0.05
		Average	79.42 ± 6.15	1719.32 ± 27.49	1.65 ± 0.14	9.21 ± 0.57	189.90 ± 4.57	115.89 ± 6.01	391.63 ± 14.96	ULOQ	7.80 ± 0.61
Eastern Anatolia region	5	Range	16.77 ± 0.65	151.86 ± 10.04	0.87 ± 0.09	2.42 ± 0.72	68.80 ± 2.48	46.94 ± 1.15	258.66 ± 21.96	3.12 ± 0.94	2.61 ± 0.10
			86.35 ± 5.31	1576.27 ± 119.30	4.30 ± 0.54	15.33 ± 0.97	128.91 ± 2.06	230.03 ± 3.90	726.82 ± 4.57	4.46 ± 1.40	16.49 ± 3.27
		Average	56.00 ± 2.28	774.52 ± 45.28	1.50 ± 0.34	11.52 ± 0.56	118.60 ± 5.18	160.20 ± 6.92	407.86 ± 16.72	3.79 ± 1.16	9.20 ± 1.74

Data are means ± SD. Results are expressed as μg/L, except for Fe, expressed as mg/L. ULOQ: under the limit of quantitation. *n* = number of samples. All analyses were repeated 6 times (2 subsamples of each wine in triplicate).

4. Conclusion

In conclusion, recovery values were found in between 96% and 107%. These recovery values showed that the results are reliable. As the main goal of this study was determination of trace elements and heavy metal levels in Turkish wines, no comparison was made between the results.

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