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Inductively Coupled Plasma Optical-Emission Spectroscopy Determination of Major and Minor Elements in Vinegar

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Abstract

This study characterizes the mineral content of vinegar samples. The concentrations of Na, K, Ca, Mg and P (major elements) as well as Fe, Mn, Sn, Cu, Ni, Zn, Pb and Cd (minor elements) were determined in 35 commercial vinegar samples using inductively coupled plasma optical-emission spectrometry (ICP-OES). The elements with the highest concentrations were K, Na, Ca, Mg and P. The concentrations of heavy metals in the vinegar samples, including Cd, Ni, Sn and Pb, were not considered a health risk.

Keywords: mineral elements, vinegar, inductively coupled plasma-optical emission spectroscopy

Introduction

Minerals play an important role in human nutrition, because they are not synthesized in the body. They can be divided into the following groups: macro-minerals (major elements), such as sodium, potassium, magnesium, calcium and phosphorus, micro-minerals (minor/trace elements) such as iron, copper, zinc and manganese; and ultra-trace elements, such as aluminum, bromine and cadmium. Some elements such as lead, cadmium and mercury, can produce toxic effects at high concentrations. Therefore, in recent years, there has been increasing interest in evaluating the macro- and micro- elements in a variety of food samples (DiSilvestro, 2005; Belitz *et al.,* 2009).

Vinegar, an astringent product, has been used for thousands of years as both a condiment and a preservative (Solieri and Giudici, 2009). In folk medicine traditions, it has been used to promote recovery from exhaustion, regulate blood glucose and blood pressure, aid digestion, stimulate the appetite, and promote calcium absorption (Ebihara and Nakajima, 1988; Adams, 1998; Liljeberg and Bjorck, 1998; Kishi *et al.,* 1999; Fushimi *et al.,* 2001; Kondo *et al.,* 2001). Vinegar is produced by alcoholic fermentation followed by acetic fermentation of any raw material that is rich in carbohydrates. Starting material may be derived from wine, molasses, dates, sorghum, apples, whey or various other agricultural materials. Another method of production is chemical synthesis from natural gas and petroleum derivatives, resulting in a highly concentrated acetic acid solution (Adams, 1998). Vinegars flavored with tarragon, basil, garlic, lemon, and raspberry are used as a seasoning in vinaigrette dressings or mayonnaise. Furthermore, they are used in cooking meat and fish as well as in the manufacturing of canned foods (Nobuhara *et al.,* 1986; Guerrero *et al.,* 1994, 1997; Horiuchi *et al.,* 1999, 2000; Parrondo *et al.,* 2003; Giudici *et al.,* 2006).

Quantification of the mineral elements present in vinegars is important due to the roles of metals in metabolism, the potential toxicity of certain metals the detection of adulteration of the product and and the characterization of the vinegar (Artiles *et al.,* 1993; Akbas and Cabaroglu, 2010). High concentrations of certain elements may induce undesirable properties, such as precipitation, color changes and turbidity (González and Chozas 1988; Guerrero *et al.,* 1994; Joshi and Sharma, 2009). The mineral composition of vinegar depends on the natural composition of the raw materials, the constituents formed during fermentation, contact with production and storage equipment, contamination of the production environment and, sometimes, the substances formed during the aging process (Solieri and Giudici, 2009). For this reason, it is logical to suppose that vinegars may be characterized and differentiated by the analysis of their mineral components. Data on the mineral content in vinegars have been extensively studied and reported due to their implications in organoleptic, hygienic and dietetic characteristics as well as their toxicological implications (Artiles *et al.,* 1993; Guerrero *et al.,* 1996; Da Silva *et al.,* 2007). The most commonly used techniques for qualitative and quantitative determination of minerals in food samples are inductively coupled plasma optical/atomic emission spectroscopy (ICP-OES/ICP-AES) and atomic absorption spectrometry (AAS) (Dolan and Capar, 2002; Dean and Ma, 2008).

Information on the metal content in vinegar is important to evaluate the potential human health risks of vinegar consumption, and the quantification of these elements can serve as a tool to characterize vinegar quality and authenticity. Therefore this paper aims to determine

the concentrations of major- and minor- elements in wine, apple cider, rice, sour-cherry and balsamic vinegar samples using ICP-OES analyses.

Materials and methods

Vinegar samples

Thirty-five vinegar samples, representing the common types of vinegars readily available to consumers, were obtained from retail stores. Sixteen samples of wine vinegar, five samples of apple cider vinegar, three samples of rice vinegar, three samples of sour-cherry vinegar, three samples of date vinegar and five samples of balsamic vinegar (of different brands) were analyzed. The majority of the vinegars were in glass bottles; however, several were in plastic bottles. Sample containers were (500 ml) and an identification code was assigned for each sample: WV for wine vinegar, ACV for apple cider vinegar, RV for rice vinegar, SCV for sour-cherry vinegar, DV for date vinegar and BV for balsamic vinegar. The samples were stored at 4±1°C prior to analysis. Sample selection was completed in two stages: (1) one sample of each product was obtained from the supermarkets; and (2) after one month, a second visit was made to the same supermarkets to obtain a second sample. This procedure was utilized to include different batches of each product. The numbers of samples of each product depended on the numbers of brands available in the market.

Apparatus

Elemental analysis was carried out on an OPTIMA™ 2100 DV inductively coupled plasma-optical emission spectrometer (Dual View, Perkin Elmer Life and Analytical Sciences, USA). Tab. 1 shows the analytical lines used for each element, and the instrument settings.

Reagents and solutions

Standard solutions were prepared by dilution of each pure element standards obtained from Merck (Darmstadt, Germany). Analytical grade nitric acid (65% Merck) was used for the mineralization of the samples. All aqueous solutions and dilutions were prepared with ultrapure water (Milli-Q, Millipore, Bedford, MA).

Analysis of mineral elements

Prior to analysis, the samples were thoroughly mixed and analyzed directly, without a previous digestion treatment, using ICP-OES. The vinegar samples were diluted 1:1 with 0.2% (v/v) HNO_3 and centrifuged for 20 min at 2 000 rpm (Hettich Universal 30F, Tuttlingen, Germany). All sample vials, sample cups, and glass-ware were cleaned by soaking in 10% (v/v) HNO_3 and rised with de-ionized water prior to use. The appropriate standards for each element were made within the concentration range of the elements in the samples. The results were obtained from triplicate measurements.

Tab. 1. Operating parameters for ICP-OES

Nebulization gas flow rate	0.55 l min^{-1}
Auxiliary gas flow rate	0.2 l min^{-1}
Plasma gas flow rate	17 l min^{-1}
Sample flow rate	1.5 ml min^{-1}
Operating power	1 450 W
View	Axial
Interface	Shear gas
Sample uptake rate	1.0 ml min^{-1}
Spray chamber	Cyclonic
Nebuliser type	Meinhard
Nebuliser set up	Instant
Replicates	3
Detection wavelengths (λ/nm)	
P	214.914
Na	589.592
K	766.490
Ca	393.366
Mg	279.553
Fe	259.940
Cu	324.754
Zn	213.857
Mn	257.610
Ni	221.647
Pb	220.353
Sn	235.485
Cd	214.440

Statistical analyses

All obtained data were subjected to statistical analysis that was performed by using Tarist, a statistical software (Tarist, 1994), and the correlation coefficients (r) were determined.

Results and discussion

Elemental concentrations (including standard deviations) in vinegar samples determined by ICP-OES are listed in Tab. 2.

The results of the mineral analysis of commercial vinegars showed a high variability when compared with those described in the literature (Tab. 2). Of the elements present in the highest concentrations (K, Na, Ca, P and Mg), potassium was the mineral element with the highest concentration in all vinegar types. Wine and apple cider vinegar samples from Spain and Germany were analysed by Artiles *et al.* (1993) and, compared to the present study showed similar levels for K, but slightly lower levels for Na. The high concentrations of potassium and sodium may be

Tab. 2. Major- and minor- element composition (mg l^{-1}) of different vinegar samples (mean ± standard deviation)

	WV *(n:16)*	ACV *(n:5)*	RV *(n:3)*	DV *(n:3)*	SCV *(n:3)*	BV *(n:5)*	Interval[a] (mg l^{-1})
P	74.72±24.869	48.06±17.044	0.22±0.020	70.32±36.123	63.14±11.078	182.60±50.577	-
Na	475.90±1157.325	360.21±250.380	*nd*	181.40±25.787	303.20±38.562	264.96±26.766	-
K	710.19±310.659	802.24±1146.647	0.43±0.056	1384.93±132.745	1058.93±103.502	1557.73±416.841	26.70-1800
Ca	113.84±43.023	104.75±28.695	*nd*	1136.00±105.112	670.80±30.811	188.28±46.997	9.60-200
Mg	81.83±34.086	65.60±7.565	*nd*	195.60±22.235	142.60±46.711	127.04±18.470	4.20-130
Fe	4.25±1.946	1.31±0.585	0.62±0.103	10.44±2.526	10.68±0.591	6.94±1.498	1.95-10.50
Cu	0.13±0.019	0.03±0.032	0.17±0.018	0.11±0.004	0.35±0.028	0.42±0.153	0.02 -0.35
Zn	0.10±0.019	*nd*	*nd*	0.02±0.024	0.32±0.013	0.36±0.162	0.01-7.90
Mn	0.78±0.434	0.18±0.130	0.22±0.011	0.28±0.018	0.67±0.009	1.31±0.180	0.10-9.83
Ni	0.05±0.027	0.01±0.013	0.01±0.003	0.16±0.008	0.12±0.008	0.03±0.019	-
Pb	0.02±0.024	0.01±0.008	0.01±0.012	*nd*	0.02±0.001	0.02±0.025	0.013-0.265
Sn	0.46±0.060	0.48±0.033	0.34±0.155	0.51±0.015	0.50±0.005	1.33±0.268	-
Cd	*nd*	0.01±0.004	*nd*	*nd*	*nd*	0.02±0.005	-

nd; not determined; [a]Reported values (González and Chozas, 1988; Artiles *et al*., 1993; Guerrero *et al*., 1997; Rizzon and Miele, 1998; da Silva *et al*., 2007; Akbas and Cabaroglu, 2010)

related with to the raw material (i.e. grapes, apples and other fruits) used in the production. Ca, Mg and P were also present, though in minor concentrations, in the raw materials. The values of K and Mg may be also indicative of the raw material authenticity because they are absorbed together with calcium by the grape-vine. The calcium and magnesium contents of date and sour-cherry vinegars were higher than values described in the literature. The presence of magnesium in wine vinegars is reported to be dependent on the natural content in grapes (Da Silva *et al.,* 2007). Rizzon and Miele (1998) have mentioned that Mg content could be a useful parameter in establishing vinegar integrity. Calcium concentrations however, should not be taken into account when determining the chemical composition of vinegars as Ca may be added during the enological process (Guerrero *et al.,* 1996). The rice vinegar samples, although different brands, presented similar mineral contents. However, the values obtained were greater than the values described in the literature (Da Silva *et al.,* 2007).

Interest in microelements has recently increased because they can be used as an index of processes that affect the properties and healthy aspects of vinegars, such as the production process, environmental pollution, sanitary conditions and the quality of the raw material. In this respect, elements such as Ni, Cd, Pb and Sn are of particular importance because of their correlation with environmental pollution, and other such as Cd, Cu and Fe for their release from metal alloys of the equipment used for vinegar production. The overall concentrations of Ni and Pb were <1 mg l^{-1} in all samples. Sn content was <1 mg l^{-1} in all cases except in balsamic vinegar. Ndung'u *et al.* (2004) determined the lead concentrations of 59 different types of vinegars (15-307 μg l^{-1} in balsamic vinegars and 36-50 μg l^{-1} in wine vinegars) using both inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS). According to the Turkish Food Codex (2002), the content of Pb found in the samples exceeds the maximum permissible concentration for vinegar, 1 mg l^{-1}. However, the contents of Ni, Cd and Sn were not reported.

According to the Codex Alimentarius (2000) and the Turkish Food Codex (2002), the total zinc plus copper and iron concentrations have been designated as 'contaminants' and their levels must not exceed 10 mg l^{-1}. All of the vinegar samples had copper plus zinc and iron contents below this limit. The iron concentrations in the present study are in agreement with the values reported by Artiles *et al.* (1993), González and Chozas (1988) and Akbas and Cabaroglu (2010), with the exception of the date and sour-cherry vinegars, mainly due to the mineral composition of the raw material's. Excess iron (10-15 mg l^{-1}) can give vinegar a dark and cloudy aspect. The contents of copper, zinc and iron are directly related to the development of undesirable precipitates or other negative phenomena, such as the growth of acetic acid bacteria (González and Chozas, 1988). The presence of copper in vinegar may be due to corrosion of the tanks and metallic pipes by the acetic acid and from the sulfate treatment to which grapes are submitted. In 40 samples of wine vinegars derived from both slow and quick elaboration methods, Guerrero *et al.* (1997) determined the average contents of copper plus zinc (1.7-6.4 mg l^{-1}) for slow elaboration, rather than quick. These values were significantly higher than present study, indicating that the metal content is closely related to the elaboration process and could be a suitable tool for vinegar characterization.

A correlation analysis was performed to investigate the relationships between the element concentrations in vinegar samples. The data were subjected to statistical analysis, and Tab. 3 reports the correlation matrix (*r*) between major- and minor-elements for 13 variables. All variables show significant correlation with at least one other vari-

Tab. 3. Correlation coefficient between major- and minor- element concentrations in vinegar samples

	P	Na	K	Ca	Mg	Fe	Cu	Zn	Mn	Ni	Pb	Sn
Na												
K	0.897***	-0.284*										
Ca			0.438***									
Mg	0.622***		0.842***	0.702***								
Fe	0.339**		0.556***	0.605***	0.590***							
Cu	0.613***		0.596***		0.384**	0.301*						
Zn	0.653***		0.625***		0.419**	0.322*	0.814***					
Mn	0.691***	-0.239*	0.668***		0.381**	0.459***	0.453***	0.625***				
Ni				0.577***	0.304*	0.743***						
Pb	0.228*						0.609***	0.460***				
Sn	0.857***		0.756***		0.462***	0.399**	0.625***	0.573***	0.618***			
Cd	0.712***		0.564***				0.485***	0.596***	0.606***	-0.407**		0.789***

*(p<0.05); **(p<0.01); ***(p<0.001)

able. There was a negative relationship between Cd and Ni content (r=-0.407, p<0.01).

Conclusions

It has been demonstrated that the use of axially viewed ICP-OES is a feasible and quick method for the quantification of multiple macro- and micro-elements in commercial vinegar samples. The elements analyzed are generally classified as essential elements for living organisms due to their activity and function in biochemical processes. However, these elements may be toxic when present in high concentrations. The concentrations of the major-and minor- elements analyzed in the commercial vinegar samples may be considered non-toxic, because the ingested quantities of these elements are significantly lower than the recommended safe dietary intake values.

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