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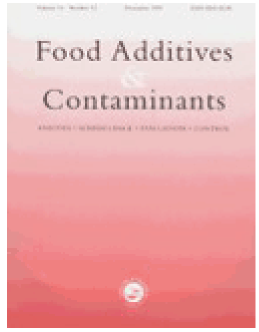
Miguel Navarro



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Copper, zinc, calcium and magnesium content of alcoholic beverages and by-products from Spain: nutritional supply

M. NAVARRO[*], C. VELASCO, A. JODRAL, C. TERRÉS, M. OLALLA, H. LOPEZ &.M.C. LOPEZ

Department of Nutrition and Food Science, School of Pharmacy, University of Granada, E-18071 Granada, Spain

* Corresponding author:

Dr. Miguel Navarro-Alarcón

Department of Nutrition and Food Science

University of Granada

18071-Granada

Spain

e-mail: nalarcon@ugr.es

Abstract

Levels of copper, zinc, calcium and magnesium were measured in alcoholic beverages (whiskies, gins, rums, liquors, brandies, wines and beers) and by-products (non-alcoholic liquors and vinegars) using flame atomic absorption spectrometry (FAAS). Mineral concentrations were found to be significantly different between the nine alcoholic and non-alcoholic by-products studied ($p < 0.001$). In distilled alcoholic beverages, concentrations measured in rums and brandies were statistically lower than those determined in gins and alcoholic liquors ($p = 0.001$). For Cu, measured concentrations were statistically different for each of the 5 groups of distilled alcoholic beverages studied ($p < 0.001$). In fermented beverages, Zn, Ca and Mg levels were significantly higher than those concentrations determined in distilled drinks ($p < 0.005$). Contrarily, Cu concentrations were statistically lower ($p < 0.001$). Wines designated as Sherry had significantly higher Ca and Mg levels ($p < 0.005$). White wines had significantly higher Ca and Zn levels ($p < 0.05$) compared to red wines and contrarily, Cu concentrations were significantly lower ($p < 0.005$). In wine samples and corresponding by-products (brandy and vinegar), statistical differences were established for all minerals analysed ($p < 0.01$). Remarkably, for Cu, the concentrations determined in brandies were statistically higher. On the basis of element levels and the official data on consumption of alcoholic beverages and by-products in Spain, their contribution to the daily dietary intake (DDI) was calculated to be 123.5 µg Cu/day and 204.5 µg Zn day^{-1}, 41.7 mg Ca day^{-1} and 20.8 mg Mg day^{-1}. From all studied elements, Cu was the one for which alcoholic beverages constitute a significant source (more than 10% of recommended daily intake). These findings are of potential use to food composition tables.

Keywords: *Copper, zinc, calcium, magnesium, alcoholic beverages and by-products, dietary intake*

Introduction

In the manufacturing process employed for most alcoholic beverages we distinguish between fermentation and distillation. In the second process, the distillate is sometimes obtained directly from a previously fermented product, which carries over the volatile compounds (water, alcohols, aromatic substances like acids, aldehides, ketones, esters, etc.) and modifies the composition previously existing in the raw product (Olivieri et al. 2003). Due to the low volatility of the four elements considered in this paper (Cu, Zn, Ca, Mg), their levels in the resulting distilled alcoholic beverages have to be lower. In the distillation process a copper still is usually employed because copper is very malleable, a good heat conductor, and resistant to corrosion, as well as playing a role as catalyser in certain chemical reactions and of complexing molecules unpleasant from the organoleptical point of view (Olivieri et al. 2003). Consequently, an increase in the Cu levels of the resulting distilled brandies would be expected. Additionally, it is known that in the ageing of brandies obtained via distillation, the activation of chemical reactions that require oxygen are probably enhanced by the existence of ions of heavy metals like Cu (Puech et al. 2003).

Vinegar is one of the oldest known wine by-products that is common in our diet. To manufacture vinegar, oak barrels fitted with aeration holes are half-filled with wine for several months so that the wine's alcohol will be transformed into acetic acid by the *Acetobacter* bacteria (Bourzeix et al. 2003). This fermentation process could influence the mineral content of the resulting vinegar.

Several techniques have been employed for the determination of minerals in wines and beverages: inductively coupled plasma mass spectrometry (ICP-MS) using a double-focusing sector fields; AAS with flame or electro thermal atomization; or electro analytical methods such as differential pulse anodic stripping voltammetry (DPASV) (Gonzalez and Pena-Mendez 2000, Mikkelsen and Schroder 2002, Olalla et al. 2002, Kokkinofta et al. 2003, Freire and Kubota 2004). In the available food composition and nutrition tables from Spain and other countries, the levels of the essential minerals studied, especially those for the trace elements Cu and Zn, are not usually collected. Therefore, the aim of this study was first to determine the Cu, Zn, Ca and Mg content of 124 alcoholic beverages most commonly produced and consumed in Spain (whiskies, gins, rums, liquors, brandies, wines and beers) and by-products (non-alcoholic liquors and vinegars) using the FAAS technique. Consequently, a common mineralization procedure for the analytical determination of the four elements in the referred samples was developed. We also studied the possible influence of the manufacturing process of alcoholic beverages and by-products on their element levels, as well as the evaluation of the existing relationships among these elements in the different samples analysed.

Additionally, we also hypothesised that the manufacturing process followed to obtain white or red wines could influence mineral content. Finally, taking into consideration the mean consumption of alcoholic beverages tested per person per day in Spain (Ministry of Agriculture, Fisheries and Food 2001), we have also calculated the supply from this source to the DDI of these elements per healthy adult in Spain. The results obtained will also prove very useful for compiling food composition tables, having noted the lack of data for these elements in existing tables.

Materials and methods

Apparatus

A Perkin-Elmer 1110B double beam atomic absorption spectrophotometer (Perkin-Elemer corp., CT) was used at a slit width of 0.7 nm, with a 5-mA (for Cu), 3-mA for Zn and 10-mA (for Ca and Mg) hollow cathode lamps for mineral measurements by FAAS. Samples were atomized for Cu, Zn, Ca and Mg determination at 324.7, 213.9, 285.2 and 422.7 nm, respectively. All analyses were performed in peak height mode to calculate absorbance values.
Wet digestion was carried out in a thermostated multi-place digestion block (Selecta S.A, Barcelona, Spain) for analytical samples (whisky, gin, rum, liquors, wines, beers and vinegars).

Reagents

All solutions were prepared from analytical reagent grade reagents: HNO_3 (65%), $HClO_4$ (60%), HCl (25%), V_2O_5 (Merck Suprapur). Commercially available 1,000 µg/mL Cu [prepared from $Cu(NO_3)_2.3H_2O$ in 0.5 M HNO_3], Zn [prepared from $Zn(NO_3)_2$ in 0.5 M HNO_3], and Ca and Mg dissolutions [prepared from $Mg(NO_3)_2.6H_2O$ and $Ca(NO_3)_2.4H_2O$ in 0.5 M HNO_3, respectively] (Tritisol Merck) were used. The water employed for preparing the standards for calibration and dilutions was ultra pure water with a specific resistivity of 18 mΩ cm^{-1} obtained by filtering double-distilled water through a Milli-Q purifier (Millipore, Waters, Mildford, MA) immediately before use. The $LaCl_3$ solution used was prepared by dissolving 1.17 g La_2O_3 in 5 ml HCl and adding water to 100 ml (1% w/v).

Sampling

The samples of alcoholic beverages and by-products analysed in the present study (n = 124) were purchased in local supermarkets in Granada (a city in south-eastern Spain). Distilled alcoholic beverages (n = 52) as well as by-products (n = 62) and beers (n = 10) were selected from the most popluar brands consumed by the local inhabitants taking into consideration their food habits. With this aim, a previous questionnaire of food consumption by individuals was prepared. The wines sampled correspond to the designations of origin of Sherry (n = 21), Rioja (n = 11) and la Mancha (n = 10). All vinegars considered (n = 10) were manufactured from wines. The samples were brought to the laboratory of the Department of Nutrition and Food Science where they were stored at –18ºC until analysed.

Sample treatment

The analytical procedures employed for the mineralization and determination of the Zn, Ca and Mg levels by the FAAS technique are similar to those previously optimised and published by our research group (Terres et al. 2001, Jodral-Segado et al. 2003). For the beverages and by-products studied, a 1-mL aliquot sample was placed in a glass tube and mineralized by addition of 5.0 ml of concentrated HNO_3, 10 µg of V_2O_5, and heating at 60^{o}C for 20 min in a multiplace mineralization block. Another 5.0 ml of 4:1 mixture of HNO_3 and $HClO_4$ was added and heated continuously at 90^{o}C for 45 min. Finally the temperature was raised to 120ºC and kept until sample was completely mineralized. Then, the digest was cooled and the resulting solution diluted with ultra pure water depending on the expected Zn, Ca and Mg concentrations. The adding of 0.2 ml of $LaCl_3$ solution as matrix modifier in order to avoid the phosphate interferences (De la Fuente et al. 1996, Moreno-Torres et al. 2000) was done for the Ca and Mg measurements (Jodral-Segado et al. 2003). Zn, Ca and Mg determinations were carried out by direct aspiration into the flame atomic absorption spectrophotometer.

For the chemical analysis of Cu in alcoholic beverages and by-products another 1-ml aliquot was taken. The only difference with the previously described analytical procedure was that the final temperature selected in the digestion method was 125ºC, which was maintained until the digest became transparent.

The presence of matrix interferences was checked by comparing the slopes of the calibration graph and the standard addition methods applied to different samples from all groups of alcoholic beverages and by-products considered (data not shown). The existence of interference was observed only for Ca. Therefore, for this element, the samples were analysed by the standard addition method adding amounts of Ca ranging from 0.00 to 0.250 µg to 6 aliquots of the same sample. All Mg determinations were carried out by the linear calibration method. All samples and blanks were mineralized and diluted using the same procedure. The data were corrected for blank values which were usually very low for this method.

Analytical characteristics

The accuracy and precision were tested in 10 replicate assays with 2 CRM-certified reference materials (CRM 063R powered skimmed milk and CRM 278 mussel tissue) and 1 NIST-standard reference material (SRM 1572 citrus leaves) using the procedures previously described (Diaz-Alarcon et al. 1996, Delgado-Andrade et al. 2003). Mineral concentrations found in the reference materials assayed were not significantly different from certified levels ($p > 0.05$, table I).

Statistical analysis

For interpreting the obtained data the statistical package *SPSS 12.0 for Windows* program was employed. Results are expressed as arithmetic mean and standard deviation. They were analysed in order to evaluate the existence of statistical differences according to the category of alcoholic beverages and corresponding by-products. The normal distribution of variables and the homogeneity of variances were checked by the Kolmogorov-Smirnov and Bartlett's tests, respectively. The comparisons were done using the Student's *t*-test when the variable fulfilled parametric conditions, and the Kruskall-Wallis test when conditions were non-parametric. Linear regression analyses among all mineral concentrations determined were also made.

Results and discussion

Levels of measured minerals (Cu, Zn, Ca and Mg) in alcoholic beverages and by-products from Spain are shown in table II. A high variability in the concentrations of the four elements analysed can be noted. This finding can be related to the drink type and manufacturing process, and also to the strong influence of the soil type and agricultural practices on the content of these elements in the wine grape (Olalla et al. 2004). The mineral levels measured in alcoholic beverages and by-products were significantly different for the four elements studied ($p < 0.001$, table II). Additionally, from our regression analysis of the mineral levels in the alcoholic beverages, significant linear interrelationships ($p \leq 0.001$) between Mg and Zn ($r = -0.419$) and between Cu and Ca ($r = -0.365$), were observed.

Drinks of high alcoholic content

Cu, Zn, Ca and Mg levels in the whisky, gin, rum, liquor, and brandy samples analysed are summarized in table II, where a broad variation can be observed among the different samples. The variability is even more pronounced in the case of Cu. Mean Zn levels for alcoholic beverages found in previous research by other countries show only a trace or very low Zn concentrations (table III). In drinks of high alcoholic content, mean Ca and Mg concentrations determined in the present study are considerably higher in whisky samples (table II). In liquors, although Ca contents measured by us are higher than those shown in table IV, mean Mg concentrations were lower than that indicated by Favier et al. (1995). It is interesting to note that many of the food composition and nutrition tables included in table IV contain measurements of mineral content for spirits, although they only colect trace or 0.00 μg g^{-1} levels for Ca and Mg.

Due to the different manufacturing processes used to produce the liquors and complex brandies [simple brandies redistilled with vegetable matter and then aged (Olalla-Herrera and Lopez-Martínez (2005)], we performed a statistical study to see their influence on Cu, Zn, Ca and Mg concentrations. We discovered that mean Cu levels measured in liquors were statistically lower than those found in the group of complex brandies ($p < 0.001$) (table II). This result could be related to the use of copper stills for complex brandies (whiskies, rums and brandies) which increases Cu concentrations. Contrarily, mean Mg concentrations found in liquors were significantly higher ($p < 0.005$) than mean levels measured in complex brandies.

Distilled and fermented drinks

When a comparison was made between the mineral content of distilled products (whisky, gin, rum and alcoholic liquors) and fermented products (wine, beer and vinegar), significant differences were observed for all four minerals ($p < 0.005$). Specifically, the Zn, Mg and Ca concentrations in distilled drinks were statistically lower. That is to say that in a still, the volatilization process favors the transfer of alcohol, other aromatic and low molecular weight compounds through the condensation coils, and tends to leave behind the heavier metals (Zn, Ca and Mg). Therefore the final Zn, Ca, and Mg concentrations present would be significantly lower in distilled products. Conversely, for fermentation products, Zn, Ca and Mg transfer from the grape (Maria 2002, Cabanis 2003) and barley grain is largely conserved.

Wines and by-products

The mean mineral contents measured in our study for wines, brandies and vinegars (table II) differ from those provided by the food composition tables for several countries (tables III and IV). Mineral levels for the different types of samples analysed (wine, brandy and vinegar are included in table II. Their statistical study in three sample groups demonstrated the existence of significant differences among them ($p < 0.001$). Specifically, Cu levels found in brandy samples (8.01 ± 1.58 μg ml^{-1}) were significantly higher ($p < 0.001$). This finding is related with the distillation process necessary for their manufacturing. Contrarily for Zn, Ca and Mg mean concentrations found in wines were higher than those found in brandy and vinegar (table II). For Zn, mean levels found in vinegar samples were statistically lower ($p < 0.001$).

Mean Ca concentrations determined in brandy samples were significantly lower. Finally, mean Mg concentrations were statistically different among the three groups of samples considered. Specifically, Mg levels in wines were significantly higher. These findings underline that the main source of Ca and Mg in wines and by-products is the grape itself. The presence of these minerals in the grapes (as with all vegetables) is derived from the soil (Kokkinofta et al. 2003, De Lima et al. 2003, Salvo et al. 2003) from which the available fractions of both elements are obtained by the plants. These minerals as cations are present in the grape juice and persist in the wine normally in lower concentrations due to their insolubility during the fermentation and ageing process (Olivieri et al. 2003).

In white wines analysed, mean Zn and Ca levels (1.386 ± 0.630 and 150.0 ± 51.7 µg ml^{-1}, respectively) were significantly higher to those found in the red wines ($p < 0.05$, table V). Contrarily, Cu concentrations were statistically lower (0.349 ± 0.149 *vs.* 0.464 ± 0.124 µg ml^{-1}). Olalla et al. (2004) measured Zn and Cu levels in white and red grapes (0.455 ± 0.147 and 0.525 ± 0.270 µg g^{-1}; and 0.479 ± 0.611 and 0.491 ± 0.137 µg g^{-1}; respectively) from the most popular commercial brands in Spain. They did not find a significant difference between the two types of grapes.

Salvo et al. (2003) noted that when organic pesticides are used on the grapes, a significant enhancement in mineral content is produced in the wine. These findings established that the type of soil, climatic, agronomic and agrochemical treatments influence the total mineral content in wines and are related with the high variability existing in Cu and Zn levels in wines from different countries and regions (Salvo et al. 2003; Gremaud et al. 2004).

Zn concentrations found in white and red wines (1.386 ± 0.630 and 0.878 ± 0.238 µg ml^{-1}, respectively) were lower than those shown in the food composition and nutrition tables (table III). Mean Ca contents measured by us in white and red wine samples (table V) are higher than those shown in the most commonly used food composition and nutrition tables considered (table IV) with the exception of levels indicated in Danish white wines (Food Informatics 2005) which were similar. For Mg we found that the data shown by most of the tables are nearly in agreement with our study (table V). In wines, it is important to know the exact levels of Ca in order to avoid the precipitation as Ca titrate. On the order hand, the Mg is a main component of chlorophyll.

When mineral levels determined in wines are compared taking into account their place of origin (Sherry, Rioja and la Mancha; Commission of the European Communities, 2006) no significant differences were observed for Mg and Cu concentrations ($p > 0.05$) (table VI). For Ca, levels measured in sherry wines were significantly higher ($p < 0.005$) than those found in Rioja wines. This finding is similar to that established for Slovakian, Bohemian and European wines (Korenovska and Suhaj 2005, Sperkova and Suchanek 2005) for which these researchers found that Ca and Mg contents are the best markers that can be used for the identification of the wine region. For Zn, levels in sherry wines were significantly higher than Rioja and la Mancha wines. Similarly to the results of others (Camean et al. 2000) the content of these metals was higher in Sherry wines than in Sherry brandies (table II), with the exception of Cu .

For wine vinegars, Cu and Zn levels determined in the present study (0.321 ± 0.132 μg ml^{-1} and 0.723 ± 0.108 μg ml^{-1}) were higher than those published by the Danish Institute for Food and Veterinary Research [0.100 μg g^{-1}, (Food Informatics 2005)], the USDA Agricultural Research Service (2005) [0.067 and 0.667 μg g-1, respectively,] and those included in the Spanish food composition tables [1 μg g^{-1}, (Farran et al. 2004)]. Mean Ca and Mg levels in vinegar are included in the Danish [120 and 220 μg g^{-1}, respectively; (Food Informatics 2005)], American [66.7 μg g^{-1}, (USDA Agricultural Research Service 2005)], Spanish [150 and 200 μg g^{-1}, respectively; Farran et al. 2004] and Peruvian [70 μg g^{-1} only for Ca, (Zavaleta Martinez 1996)] food composition and nutrition tables. However, not all these data indicated the source of the vinegar samples.

Beers

The mean Cu, Zn, Ca and Mg contents in analysed beer samples are shown in table II. Mg was the mineral for which a lower variation was observed. The British food composition and nutrition tables (Holland et al. 2001) showed more different types of beer and gave a more precise and complete mean Cu (0.467 μg ml^{-1}), Zn (0.183 μg ml^{-1}), Ca (82.9 μg ml^{-1}) and Mg (97.1 μg ml^{-1}) levels.

Estimation of DDI of Cu, Zn, Ca and Mg

Taking into account the element concentrations in alcoholic beverages and by-products (table II), their contribution to the mean daily mineral intake in the Spanish diet was calculated by multiplying the mean element content of each drink by its mean consumption in Andalusia (Southern Spain) per person per day as collected in the foodstuff consumption tables in Spain (Olalla et al. 2004). On the basis of results obtained, the daily dietary intake of every element for each drink could be estimated. Thusly, a daily dietary intake of 123.5 µg Cu, 204.5 µg Zn, 41.7 mg Ca and 20.8 mg Mg per day per person in the Spanish diet was calculated (table VII). Specifically, beer represents the alcoholic beverage which supplies more than 45% of Cu, Ca and Mg intakes in the daily diet (table VII). For Zn, wine constitutes the main source, with a DDI of 55%, followed by beer (40%). These findings are due to the higher beer and wine consumption in the daily diet, and to their higher Ca and Mg content, when compared with distilled alcoholic beverages and liquors.

The dietary reference intake tables for the measured elements included the recommended dietary allowances (RDA) for Cu, Zn, Ca and Mg in different life stage groups (Institute of Medicine 1997, 2002). For male and female healthy adults these RDAs are 900 µg Cu day^{-1}, 11 and 8 mg Zn day^{-1}y, 1000 mg Ca day^{-1} and 400-420 and 310-320 mg Mg day^{-1}. Taking into consideration the daily dietary intakes measured for studied minerals (table VII), the percentages that they would cover of the established RDAs are 13.84%, 1.76 and 2.42%, 4.03%, and 4.84 and 6.31%, respectively. It is interesting to note that the only one element for which alcoholic beverages would constitute an important source is the Cu.

However, only a small portion of the minerals ingested through alcoholic beverages in the daily diet is absorbed and transformed into a biologically active form (Azenha and Vasconcelos 2000). Consequently, future research will be needed in order to understand how specific factors, such as the manufacturing process and/or components of alcoholic beverages can influence the bioavailability of those mineral in the human gastrointestinal tract.

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Table I. Accuracy of the spectrometric determination of Cu, Zn, Ca and Mg in reference materials (n = 10)

Reference material	Cu µg g^{-1} (dry weight)		Zn µg g^{-1} (dry weight)		Ca mg g^{-1} (dry weight)		Mg µg g^{-1} (dry weight)	
	Certified (mean ± SD)	Measured (mean ± SD)	Certified (mean ± SD)	Measured (mean ± SD)	Certified (mean ± SD)	Measured (mean ± SD)	Certified (mean ± SD)	Measured (mean ± SD)
CBR CRM 063R	0.60 ± 0.02	0.57 ± 0.07	49.0 ± 0.60	48.50 ± 2.32	13.49 ± 0.10	13.21 ± 0.05	1262.5 ± 24.00	1258.0 ± 42.10
CBR CRM 278	9.60 ± 0.16	9.26 ± 0.26	136.6 ± 2.9	138.6 ± 2.10	1.07 ± 0.04	1.14 ± 0.05	1.38 ± 0.02	1.33 ± 0.09
NIST SRM 1572	16.5 ± 1.0	16.38 ± 0.55	29.0 ± 2.0	27 6 ± 2.80	31.5 ± 1.00	31.1 ± 1.30	5.80 ± 0.30	5.34 ± 0.25

[a,b,c,d] $p > 0.05$

Table II. Cu, Zn, Ca and Mg contents in alcoholic beverages and by-products from Spain

Sample	*n*	Mean Cu ± SD[a] (μg ml^{-1})	Mean Zn ± SD[b] (μg ml^{-1})	Mean Ca ± SD[c] (μg/ ml^{-1})	Mean Mg ± SD[d] (μg ml^{-1})
Drinks of high alcoholic content	52	2.77 ± 3.18	0.80 ± 0.42	100.1 ± 57.8	36.2 ± 32.1
Whisky	10	1.01 ± 0.15	0.67 ± 0.47	105.1 ± 51.8	34.8 ± 43.4
Gin	10	0.10 ± 0.23	0.55 ± 0.13	135.0 ± 53.7	64.8 ± 27.6
Rum	10	2.34 ± 0.94	0.62 ± 0.30	84.7 ± 44.4	11.4 ± 5.28
Liquor	12	0.59 ± 0.29	0.93 ± 0.47	125.0 ± 77.0	60.4 ± 30.5
Brandy	10	8.01 ± 1.58	1.03 ± 0.40	65.7 ± 20.4	18.4 ± 8.8
Fermented alcoholic drinks	52	0.39 ± 0.15	1.08 ± 0.58	145.9 ± 54.0	93.2 ± 21.9
Wine	42	0.39 ± 0.15	1.20 ± 0.58	136.5 ± 48.1	97.5 ± 26.6
Beer	10	0.40 ± 0.15	0.55 ± 0.20	185.2 ± 62.4	74.9 ± 11.5
By-products	20	0.40 ± 0.18	0.67 ± 0.11	84.3 ± 31.8	45.3 ± 29.3
Non alcoholic liquors	10	0.48 ± 0.18	0.68 ± 0.09	64.8 ± 21.7	27.3± 13.5
Wine vinegars	10	0.32 ± 0.13	0.72 ± 0.11	103.8 ± 28.6	63.4 ± 30.1

[a]$p < 0.001$. Cu concentrations measured in brandies were significantly higher to the remaining groups of samples; in rums, found Cu levels were also significantly higher to the other sample groups with the exception of brandies; in samples of whisky, Cu concentrations were significantly higher than those measured in the other groups with the exception of brandies and rums; and finally Cu levels measured in gin samples were significantly lower to the other samples groups.

[b]$p < 0.001$. Zn levels found in samples of wine were significantly higher than those measured in non-alcoholic liquors and gins; in brandies, found element concentrations were significantly higher than those determined in gin and beer samples.

[c]$p < 0.01$. Ca concentrations determined in wines and beers were significantly higher than those found in rum, non-alcoholic liquors and brandies; and in samples of vinegar, mean Ca concentrations were statistically higher than levels measured in brandies.

[d]$p < 0.01$. Mean Mg levels measured in rums, non-alcoholic liquors and brandies were significantly lower than those found in liquor, wine, vinegar and beer samples; in samples of rums and brandies the mean Mg concentrations found, were statistically lower than levels determined in gin samples; in brandies, mean Mg levels were statistically higher than those found in rums; and finally in wines the mean Mg levels measured, were significantly higher to those determined in beers and liquors.

Table III. Mean Cu and Zn contents in alcoholic beverages from the most frequently used food composition and nutrition tables from various countries

	Cu (µg g^{-1})					Zn (µg g^{-1})				
			Wine					wine		
Reference (country)	Drinks of high alcoholic content		Red	White	Beer	Drinks of high alcoholic content		red	white	beer
Souci et al. (1989, Germany)		-	0.700	0.700	0.200		-	1.55	2.30	-
Jimenez Cruz et al. [1994, 2000 Spain]	gin	0.040	0.300	0.300	0.080		-	3.00	3.00	0.200
	rum	0.500								
	whisky	0.200								
Favier et al. (1995, France)		-	-	-	-		-	-	-	-
Mataix Verdu and Carazo Martin (1995, Spain)	liquor	-	-	-	-	liquors	0.000	1.00	1.00	0.000
						whisky	6.00			
Zavaleta Martinez et al. (1996, Peru)	-	-	-	-	-		-	-	-	-
Muñoz et al. (1999, Spain)	liquor	-	-	-	-	liquor	0.000	1.00	1.00	0.200
Holland et al. (2001, United Kingdom)	spirits	trace[a]	1.200[a]	0.200[a]	0.470[a]	spirits	trace[a]	0.500[a]	0.220[a]	0.180[a]
USDA (2002, USA	liquors	0.500	0.200	0.210	0.055	liquors	0.502	0.874	0.680	0.113
	spirits	2.140				spirits	0.476			
Farran et al. (2004, Spain)	liquors	-	-	-	-	liquors	trace	1.00	1	trace
	spirits	-				spirits	trace			
Spanish Ministry of Agriculture (2004, Spain	spirits	-	-	-	-	spirits	0.000	1.30	0.700	0.200
Food Informatics (2005, Denmark)	whisky	0.200	0.400	0.400	0.066	whisky	0.100	1.20	0.600	0.083
	gin	0.000				gin	0.000			
	rum	0.700				rum	0.200			
	brandy	0.100				brandy	0.100			
Minister of Health (2005, Canada)	liquor	-	-	-	-	liquor	trace	0.787	0.787	0.293
	spirits	-	-	-	-	spirits	trace			

[a] *µg/ml*

Table IV. Ca and Mg contents in alcoholic beverages in the most frequently used food composition and nutrition tables in different countries

	Ca (μg g^{-1})					Mg (μg g^{-1})				
			Wine					Wine		
Reference (country)	Drinks of high alcoholic content		Red	White	Beer	Drinks of high alcoholic content		Red	White	Beer
Souci et al. (1989, Germany)	whisky	15.0	73.0	90.0	33.7	whisky	2.500	83.0	100.0	90.0
Jimenez Cruz et al.(1994, 2000, Spain)	-	-	70.0	70.0	100.0	-	-	200.0	200.0	50.0
Favier et al. (1995, France))	liquor	60.0	80.0	95.0	66.7	liquor	60.0	150.0	80.0	96.7
Mataix Verdu and Carazo Martin (1995, Spain))	liquor	0.000	87.0	87.0	80.0	liquor	0.000	80.0	80.0	50.0
Zavaleta Martinez et al. (1996, Peru)	-	-	-	-	0.000	-	-	-	-	-
Muñoz et al. (1999, Spain)	liquor	0.000	87.0	87.0	70.0	liquor	0.000	80.0	80.0	60.0
Holland et al. (2001, United Kingdom))	spirits	trace	70.0[a]	100.0[a]	82.9[a]	spirits	trace	110.0[a]	85.0[a]	97.1[a]
USDA (2005, USA)	liquors	26.2	77.7	87.4	39.5	liquors	27.6	126.2	97.1	55.0
	spirits	0.000				spirits	0.000			
Farran et al. (2004, Spain)	liquors	60.0	80.0	90.0	80.0	liquors	60.0	150.0	83.3	115.0
	spirits	trace				spirits	trace			
Spanish Ministry of Agriculture (2004, Spain)	spirits	0.000	76.0	90.0	40.0	spirits	0.000	83.0	110.0	90.0
Food Institute Informatics (2005, Denmark)	whisky	0.000	80.0	127.5	66.6	whisky	0.000	110.0	77.5	65.0
	gin	0.000				gin	0.000			
	rum	0.000				rum	0.000			
Minister of Health (2005, Canada)	liquor	0.000	80.0	88.0	49.9	liquor	-	-	-	-
	spirits	0.000				spirits	-	-	-	-

[a]μg ml^{-1}

Table V. Cu, Zn, Ca and Mg levels measured in white and red wines from Spain

Wine type	n	Mean Cu ± SD[a] (µg ml^{-1})	Mean Zn ± SD[b] (µg ml^{-1})	Mean Ca ± SD[c] (µg ml^{-1})	Mean Mg ± SD (µg ml^{-1})
White wine	27	0.35 ± 0.15	1.40 ± 0.63	150.0 ± 51.7	97.9 ± 14.9
Red wine	15	0.46 ± 0.12	0.88 ± 0.24	112.2 ± 28.5	96.9 ± 30.9

[a,b,c] $p < 0.05$

Table VI. Cu, Zn, Ca and Mg concentrations in different Spanish wines depending of their designations of origin

Designation of origin	*n*	Mean Cu ± SD (μg ml^{-1})	Mean Zn ± SD^a (μg ml^{-1})	Mean Ca ± SD^b (μg ml^{-1})	Mean Mg ± SD (μg ml^{-1})
Sherry	21	0.38 ± 0.15	1.51 ± 0.65	155.4 ± 54.1	97.0 ± 16.0
Rioja	11	0.46 ± 0.15	0.81 ± 0.22	98.8 ± 20.4	96.2 ± 35.9
La Mancha	10	0.33.± 0.13	0.99 ± 0.21	138.3 ± 31.5	100.0 ± 10.7

$^{a,b}p < 0.05$

Table VII. Contribution of alcoholic beverages to the DDI of Cu, Zn, Ca and Mg in the Spanish diet

Sample	Daily consumption (ml/person)	Edible fraction	Cu		Zn		Ca		Mg	
			Mean (μg ml^{-1})	Daily intake (μg $person^{-1}$)	Mean (μg ml^{-1})	Daily intake (μg $person^{-1}$)	Mean (μg ml^{-1})	Daily intake (mg $person^{-1}$)	Mean (μg ml^{-1})	Daily intake (mg $person^{-1}$)
Wines	83.8	100	0.390	32.7	1.20	100.6	136.5	11.4	97.5	8.2
Beer	149	100	0.403	60.0	0.552	82.2	185.2	27.6	74.9	11.2
Distilled alcoholic Beverages and liquors	13.7	100	2.330	31.9	0.769	10.5	93.3	1.28	34.5	0.473
Total intake				124.6		193.3		40.3		19.87