Bull. Environ. Contam. Toxicol. (1993) 51:852-856

Environmental Contamination and Toxicology

Levels of Cd, Pb, and Ni in Different Types of Vinegars

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The main production of vinegar in Spain is wine vinegar. However, in the EEC countries as a whole the production is assorted (57% alcohol vinegar, 33% wine vinegar, 8% malt vinegar, 2% others) (Asociación de elaboradores y envasadores de vinagre 1988).

The inorganic ions in different types of vinegar (Na,K,Ca,Mg,Fe,Cu and Zn) are normal constituents derived from the raw materials used in its production (Acosta et al. in press). The presence of toxic metals in vinegars can be derived from residues of agrochemical products, contamination from deteriorated metallic receptacles or environmental contamination (Troncoso et al. 1988).

MATERIALS AND METHODS

Fifty-two samples of bottled vinegars were purchased from the principal supermarkets of Tenerife and Gran Canaria Island. Table 1 describes the types of vinegar samples analyzed.

The treatment of samples analyzed used a modification of the official method to obtain ash in wines and "orujo" (refuse of grapes after pressing) vinegars (Ministerio de Sanidad y Consumo 1985). A known volume (50 ml) of vinegar was carefully evaporated to dryness.

Table 1. Description of vinegar samples analyzed.

Brand	Type of vinegar	N. of samples	
A	Wine	6	Spain (M)*
B	Wine	5	Spain (M)
C	Wine	5	Spain (CI)**
D	Wine	5	Spain (M)
E	Wine	5	Spain (CI)
F	Alcohol	5	Germany
G	Aromatic-alcohol	5	Germany
F'	Apple	5	Germany
H	Apple	5	Spain (M)
I	Malt	6	England

* (M) = Mainland ** (CI) = Canary Island

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Successively, the dry extract obtained was introduced into a furnace and the temperature slowly increased (rate 25ºC each half hour) to 500 ± 25ºC. The white ash obtained was dissolved in 1:1 diluted clorhidric acid, and the resulting solutions were analyzed by atomic absorption spectrophotometry using a Varian Spectr AA-10 plus with atomization by flame air/acetylene. The resonance lines measured were 228.8 nm for Cd, 217.0 nm for Pb and 232.0 nm for Ni. The detection limits were 0.012, 0.035 and 0.047 ppm for Cd, Pb and Ni, respectively, calculated as three times the background of the blank. Six measurements per sample were made for the assay of each metal, obtaining a precision of 4.9% for Cd (0.02 ppm), 5.0% for Pb (0.5 ppm) and 5.0% for Ni (0.5 ppm).

For each type of vinegar and metal, an analysis of variance was carried out (Bent 1978).

RESULTS AND DISCUSSION

To evaluate the rates of recovery of the proposed method, we spiked a sample of vinegar with three standard solutions. We treated the vinegar with and without the standard four tines, the same way as in the samples. The recoveries obtained were: Cd (2 µg spiked) 95.0 ± 4.7%, Pb (5 µg spiked) 92.8 ± 7.8%, and Ni (5 µg spiked) 100.7 ± 4.8%. These results indicated significant losses for Cd and Pb (5 and 7% for Cd and Pb, respectively) in the process of sample treatment due to volatization in ashing. However, we considered the recoveries acceptable.

Table 2 shows the cadmium, lead and nickel concentrations in the vinegars studied. Cadmium concentration was the highest in wine vinegar and the lowest in alcohol vinegar, with 60% of these samples non detectable. No significant differences ($p<0.1$) were found between the mean values of the four types of vinegars. The majority of our data (94%) were lower than 0.04 ppm. Analysis of variance indicated no significant differences between mean values of the different brands of vinegar tested. This may have been due to the high number of samples with non detectable levels, as well as the high variability of the various brands (Fig 1.). These data are significantly higher than the values reported for Andalusian (Ureña et al. 1987) and Spanish (Fernández and Martín 1987) wines.

Lead concentrations were significantly different ($p<0.1$) between different types of vinegar (Table 2). This difference was accentuated when we considered brand ($p<0.01$). Lead concentrations in apple vinegar were significantly lower than in wine vinegar ($p<0.05$) and in malt vinegar ($p<0.001$). Furthermore there were more samples of apple vinegar with non detectable (40%) levels of lead (Fig. 1). Brand (C), corresponding to wine vinegar, had a mean value significantly ($p<0.05$) higher than the rest of the brands. This brand had no undetected values. This may be due to the type of wine used in the production of the vinegar. Fernández and Martín (1987) reported that the presence of metals in wines changes depending on the type and pH of the soil the grape is grown in the ribeness, of the grape and the general climatic conditions of the

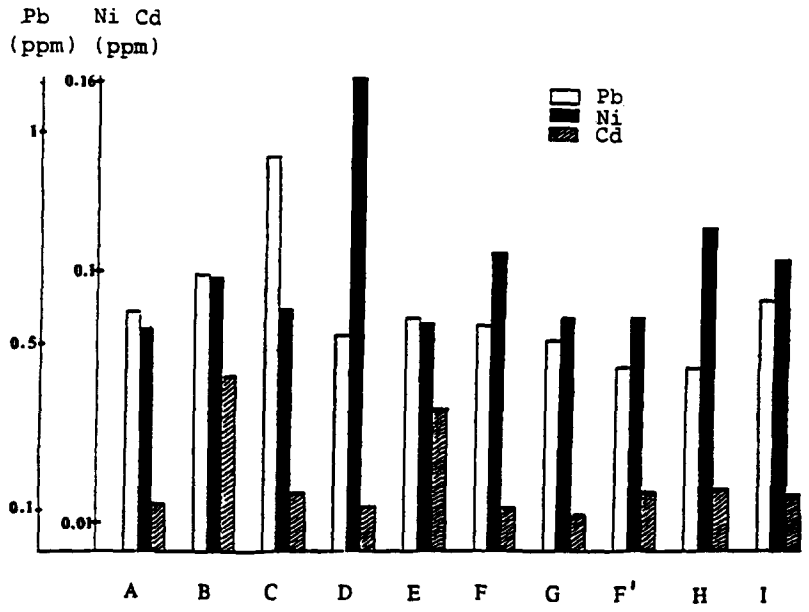

Figure 1. Average concentration of Pb, Cd and Ni of each brand of vinegar tested.

Table 2. Cadmium, lead and nickel concentrations (ppm) in different types of vinegar.

Metal		Overall (N)	Wine vinegar	Apple vinegar	Alcohol vinegar	Malt vinegar
		(52)	(26)	(10)	(10)	(6)
	X	0.028	0.035	0.022	0.014	0.020
	S.D.	0.042	0.056	0.008	0.002	0.006
Cd	M	0.245	0.245	0.037	0.017	0.025
	m(% nd)	0.012(33)	0.012(27)	0.012(20)	0.012(60)	0.012(33)
	C.V.	150	160	36	14	30
	X	0.60	0.67	0.44	0.52	0.60
	S.D.	0.22	0.27	0.08	0.12	0.08
Pb	M	1.28	1.28	0.55	0.76	0.68
	m(% nd)	0.35(19)	0.36(24)	0.35(40)	0.36(10)	0.45(0)
	C.V.	36	40	19	23	10
	X	0.102	0.105	0.100	0.092	0.104
	S.D.	0.042	0.045	0.053	0.024	0.042
Ni	M	0.206	0.205	0.201	0.119	0.171
	m(% nd)	0.047(15)	0.048(18)	0.048(20)	0.047(20)	0.057(0)
	C.V.	41	43	53	26	40

X = mean; S.D. = standard deviation; % nd = non detected percentage of samples; M = maximum value; m = minimum value; C.V. = variation coeficient.

grape growing area. Only three samples (6%) of all the samples tested exceeded the level of 1 ppm, the legal limit established in Spain for lead plus mercury plus arsenic (Millo 1975). These values are similar those reported for wine vinegar (Troncoso 1988), and wines for other regions of Spain (Ureña et al. 1987; Fernández et al. 1987; Gallego et al. 1981). López-Artíguez et al. (1990), however, reported values significantly lower than ours although they explained that they obtained low values because the wines were new and, consequently, preserved without lead foil closures.

Table 3. Average concentrations* (ppm) of metals and percent non detectable samples** in the different brands of vinegar tested.

Type of vinegar	Brand	Cd	Pb	Ni
Wine	A	0.017*(50)**	0.57(50)	0.079(33)
	B	0.063(0)	0.66(20)	0.098(20)
	C	0.021(20)	0.94(0)	0.087(20)
	D	0.016(40)	0.52(20)	0.169(0)
	E	0.051(40)	0.56(0)	0.082(0)
Alcohol	F	0.015(60)	0.54(20)	0.106(40)
	G	0.013(60)	0.51(0)	0.084(0)
Apple	F'	0.021(20)	0.44(20)	0.084(20)
	H	0.022(20)	0.44(60)	0.115(20)
Malt	I	0.020(33)	0.60(0)	0.104(0)

There were no significant differences ($p<0.1$) in nickel concentrations between the four types of vinegar. Significant differences (p) between brands however, were noted. Thus wine vinegar D was significantly higher ($p<0.05$) in Ni than the rest of the brands (Table 3). There are no available data on nickel levels in vinegars. Our nickel values were higher than those obtained ub Italian (Finoli et al. 1986) and Spanish (Fernández et al. 1987) wines, but in the same order of magnitude indicated by Cela et al. (1983).

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Received February 18, 1992; accepted May 10, 1993.