Heavy Metals and Mineral Elements Not Included on the Nutritional Labels in Table Olives

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The average contents, in mg/kg edible portion (e.p.), of elements not considered for nutritional labeling in Spanish table olives were as follows: aluminum, 71.1; boron, 4.41; barium, 2.77; cadmium, 0.04; cobalt, 0.12; chromium, 0.19; lithium, 6.56; nickel, 0.15; lead, 0.15; sulfur, 321; tin, 18.4; strontium, 9.71; and zirconium, 0.04. Sulfur was the most abundant element in table olives, followed by aluminum and tin (related to green olives). There were significant differences between elaboration styles, except for aluminum, tin, and sulfur. Ripe olives had significantly higher concentrations (mg/kg e.p.) of boron (5.32), barium (3.91), cadmium (0.065), cobalt (0.190), chromium (0.256), lithium (10.01), nickel (0.220), and strontium (10.21), but the levels of tin (25.55) and zirconium (0.039) were higher in green olives. The content of contaminants (cadmium, nickel, and tin) was always below the maximum limits legally established. The discriminant analysis led to an overall 86% correct classification of cases (80% after cross-validation).

INTRODUCTION

The release of hazardous pollutants into the environment persistently increases metal concentrations, thus contaminating the food supply. Metal contamination can take place during handling and processing. There is a general concern about the presence of heavy metals in foods, and tolerable daily intakes (TDIs) for some of them have been established (*1*−*3*). One of the first studies on heavy metals in food was reported by Mahaffey et al. (*4*). A survey on food contamination by metals in the European Union showed that consumer exposure to Pb, Cd, As, and Hg was superior to the TDI (*5*). An assessment of dietary exposure to As, Cd, Pb, and Hg, for which maximum limits (MLs) were established in the Commission Regulation 466/2001, showed that they were generally below MLs (*6*). A survey on the content and daily intake of Cu, Zn, Pb, Cd, and Hg from dietary supplements in México (*7*) indicated that their estimated daily intakes were lower that those recommended by the WHO (*3*) and the Institute of Medicine (*2*). A recent survey in the market basket for Pb, Cd, Cu, and Zn in Egyptian fruits and vegetables showed that they did not constitute a health hazard for consumers (*8*). The trace elements in other foodstuffs like cereals (*9*), bitter orange (*10*), or vegetables (*11*) have also been studied.

The consumption of table olives in the Mediterranean Basin is a widespread tradition, which is also reaching other nonproducing countries (*12*). Olives must be processed before eating to remove their natural bitterness (*13*). They are processed according to several styles (*14*). Green olives are treated with lye, washed, and fermented; ripe olives, darkened by oxidation after a storage period, are lye treated, washed several times, and packed; other olives are brined directly. All of them use salt in different proportions as the principal preservation agent (*13*). The different aqueous treatments may produce changes in the mineral composition of the processed fruits. Most of the studies related to the mineral content in table olives have been focused on mineral nutrients. Nosti Vega et al. (*15*) and De Castro Ramos et al. (*16*) studied processed samples from the Spanish cultivars, while Ünal and Nergiz (*17*) and Biricik and Basoglu (*18*) reported values from Turkish cultivars. Recently, the contents in Na, K, Ca, Mg, Cu, Zn, Mn, Fe, and P, all of them nutrient minerals, in Spanish table olives were published (*19*). However, information on the presence of other minerals not required for nutritional labeling in table olives is scarce. The Trade Standards Applying to Table Olives (*20*) does not have specific limits for any element not used as an additive or processing aid. The determinations of Mg, Cr, Co, Ni, Fe, Cu, Zn, Sn, Cd, and Pb in black and green olive samples from Turkey, reported by Şahan et al. (*21*), are the only available data. However, because of the diversity of commercial presentations in the market (which differ in processing styles, final conditioning, stuffing materials, preservation technologies, and

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Table 1. Overall and According to Elaboration Style Element Content (Mean ± Standard Error) in Table Olives[a]

metal	overall mean (n = 199)	green (n = 142)	directly brined (n = 27)	ripe (n = 30)	F value[b]	P value
Al	70.9 ± 2.5	71.4 ± 3.2	64.0 ± 4.6	75.9 ± 6.1	0.82	0.442
B	4.41 ± 0.12	4.34 ± 0.13	3.72 ± 0.23	5.33 ± 0.41	7.46	0.001
Ba	2.77 ± 0.10	2.78 ± 0.10	1.48 ± 0.12	3.91 ± 0.33	27.02	0.002
Cd	0.038 ± 0.002	0.034 ± 0.002	0.029 ± 0.004	0.065 ± 0.007	15.56	0.000
Co	0.119 ± 0.004	0.106 ± 0.002	0.105 ± 0.006	0.190 ± 0.016	52.90	0.000
Cr	0.195 ± 0.007	0.196 ± 0.008	0.122 ± 0.006	0.256 ± 0.025	13.92	0.000
Li	6.55 ± 0.48	5.66 ± 0.46	7.41 ± 1.25	10.01 ± 1.87	5.72	0.004
Ni	0.151 ± 0.008	0.145 ± 0.010	0.103 ± 0.010	0.220 ± 0.021	8.28	0.000
Pb	0.365 ± 0.069	0.275 ± 0.044	0.568 ± 0.294	0.609 ± 0.314	2.15	0.119
S	320 ± 10	320 ± 10	330 ± 20	330 ± 30	0.22	0.803
Sn	18.42 ± 3.02	25.55 ± 4.09	0.363 ± 0.117	0.936 ± 0.142	7.39	0.001
Sr	9.71 ± 0.20	9.85 ± 0.23	8.46 ± 0.46	10.21 ± 0.59	3.38	0.036
Zr	0.035 ± 0.002	0.039 ± 0.002	0.024 ± 0.001	0.029 ± 0.004	6.67	0.002

[a] Results of the tests of equality of the group means are also included. Values are in mg/kg e.p. [b] Degrees of freedom for *F* were 2 and 196.

cultivars), further studies for getting better knowledge on the mineral contents in table olives are necessary, especially of those elements not required for nutritional labeling. Such information should be of interest for consumers and for agencies in charge of the surveillance of the mineral and contaminant intake by consumers.

Chemometric techniques appear to be the most powerful tools for characterizing and classifying wines (*22*), honeys (*23*), dairy products (*24*), pistachios (*25*), and beer (*26*) according to their source, processing conditions, or origin. Among the most commonly used methods are principal component analysis (PCA) and discriminant analysis (DA), which usually include a canonical analysis. Recently, the application of multielement analysis and its chemometric study has been suggested for tracing the geographical origin of foods (*27*).

The aim of this work was to (i) determine the Al, B, Ba, Cd, Co, Cr, Li, Ni, Pb, S, Sn, Sr, and Zr contents in most relevant Spanish commercial presentations of table olives; (ii) check differences in the concentrations of such minerals due to processing styles and cultivars; and (iii) perform a chemometric study of the data to identify possible trends and to test the classification results with respect to those that could be obtained by chance.

MATERIALS AND METHODS

Samples. Samples (*n* = 199) belonged to the following styles, cultivars, and commercial presentations. Green Spanish-style olives: Gordal: plain, pitted, and seasoned; Gordal stuffed with red pepper strips, natural red pepper, almond, cucumber, onions, garlic, and jalapeño; and a blend of Gordal olives and red pepper strips called "salads". Manzanilla: plain, pitted, sliced, anchovy-flavored, and plain seasoned; Manzanilla stuffed with red pepper strips, anchovy strips, marinated anchovy strips, natural red pepper, almond, almond and red pepper, salmon strips, tuna strips, onions, capers, garlic, hazelnut, hot pepper, hot pepper strips, "piquillo" pepper, lemon paste, ham paste, orange strips, cheese, "jalapeño" strips, and garlic strips; a blend of pitted or slices of Manzanilla olives with red pepper strips called "pitted salads" and sliced "salads", respectively; a blend of Manzanilla olives with slices of carrot added called "gazpachas"; and a blend of Manzanilla olives and capers called "alcaparrado". Carrasqueña: pitted; a blend of pitted Carrasqueña olives and red pepper strips, called "salads"; and a blend of Carrasqueña olives and capers called "alcaparrado". Hojiblanca: plain, pitted, and sliced; and Hojiblanca olives stuffed with red pepper strips. Directly brined olives: Gordal: broken "seasoned" turning color. Manzanilla: turning color in brine alone, "seasoned" turning color, and olives from biologic (or organic) production. Hojiblanca: "seasoned" turning color. Arbequina: "seasoned" turning color. Aloreña: green "seasoned" broken, prepared from fresh fruits and from stored olives. Verdial: green "seasoned" broken.

Ripe olives (by alkaline oxidation): Gordal: plain. Manzanilla: pitted. Carrasqueña: plain and pitted. Hojiblanca: plain, pitted, and sliced. Cacereña: plain, pitted, and sliced.

Reagents. All reagents were of ultrapure analytical grade (Panreac, Barcelona, Spain). Hydrochloric acid (6 N) solution was obtained by dilution of concentrated HCl (Fluka, Buchs, Switzerland).

Cleaning of the Material. All glassware used for the determination of the mineral elements was immersed in 6 N HCl overnight and then rinsed several times with distilled deionized water.

Sample Preparation. Analyses were carried out in triplicate on composite samples from each commercial presentation, which were made up of 3–8 units (cans, jars, or plastic pouches), depending on their sizes, and different packing dates, from 1–5 elaboration companies, according to their availability on market shelves. Producers kindly supplied those commercial presentations not available in the local markets. The average time from packing was about 3 months.

The pulp of 100 g of olive samples was separated from the pit, when necessary, by a manual or automatic pitting machine, ground, and homogenized. From the resulting paste mentioned above, 5 g of olive pulp (2.5 g for ripe olives) of the diverse samples was weighed exactly in a quartz capsule. The capsule was put in a muffle oven and incinerated at 550 °C. At this point, the temperature was quickly brought to 100 °C and then increased slowly until the ashing temperature was reached, which was maintained about 8–10 h. The ashes, white-grayish in color, were slightly moistened and dissolved with three parts of 2 mL of 6 N ultrapure hydrochloric acid and filtered, bit by bit, through a filter paper into a 25 mL volumetric flask. After that, the filter was cleaned three times with 3 mL of deionized water, which was also added to the volumetric flask, and it was filled with deionized water until level. Dissolution was aided by slightly heating the capsule after every addition of hydrochloric acid. To ease filtration, a suction hood was used. At the same time, a blank was prepared with only the reagents.

Analytical Methods and Apparatus. The elements in sample extracts were determined by inductively coupled plasma–optical emission spectroscopy (Thermo Jarrell Ash IRIS Duo High Resolution ICP Spectrometer). A two point standardization (1 and 10 mg L^{-1}) was used to calibrate the spectrometer, except for S (20 mg L^{-1}). The standards were prepared in hydrochloric acid at the same concentration as in the samples. Interfering element correction factors were also applied to the applicable elements to compensate for any interference from Al and Fe.

Analytical Quality Control. Sample 100 (grass 94) from WEPAL-IPE Programme (*28*) was used as a Certified Reference Material (CRM), and it was analyzed in triplicate. For the elements B, Ba, Cr, Li, Ni, S, Sn, and Sr, the obtained results agreed ±5% with the certified results. For the elements Al, Cd, Co, and Pb, the obtained results agreed ±10%. There was no reported content for Zr in CRM.

Statistical Analysis. Each olive sample (object) was considered as an assembly of 13 variables represented by the Al, B, Ba, Cd, Co, Cr, Li, Ni, Pb, S, Sn, Sr, and Zr concentration in flesh (edible portion, e.p.). These variables formed a data vector, which represented an olive

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sample. Data vectors belonging to the same group (elaboration style or cultivar) were analyzed. The group was termed a category. The database from the analysis of minerals was thus arranged in a 199 × 13 (cases × variables). Elaboration styles were coded as 1 (green Spanish style), 2 (directly brined), and 3 (ripe olives); cultivars were also coded as 1 (Gordal, G), 2 (Manzanilla, M), 3 (Carrasqueña, Cr), 4 (Hojiblanca, H), 5 (Arbequina, Ar), 6 (Aloreña, Al), 7 (Verdial, Vr), and 8 (Cacereña, Cc).

Average values for cultivars within elaboration styles were obtained by the general linear model technique (nested analysis of variance, ANOVA). Data were also studied by multiple ANOVA (MANOVA) to test overall differences between groups across the different variable. These tests were carried out using original data. Diverse pattern recognition tools were used in this work.

Variables were also autoscaled (*29*) according to:

$$y_{mj} = \frac{(x_{mj} - \bar{x}_m)}{s_m}$$

where y_{mj} is the value j for the variable m after scaling, x_{mj} is the value j of the variable m before scaling, $\bar{x}_m$ is the mean of the variable m, and s_m is the standard deviation for the variable m. The results were variables with zero mean and a unit standard deviation, which were later used for the chemometric study.

PCA is a standard tool in chemometrics for data compression to capture the main features in the multivariate data sets and to extract information from them (*30*). The analysis was carried out on the basis of the backward stepwise option. The values of probability to enter or to remove were fixed at 0.05 and 0.1, respectively. The number of steps was fixed at 100, the minimum tolerance was set at 0.01, and no variable was forced to enter in any model (*31*).

Linear discriminant analysis (LDA) is a supervised technique that provides a classification model characterized by a linear dependence of the classification scores with respect to the descriptors (groups previously defined) (*32*). Two very distinct purposes and procedures for conducting DA exist as follows: discriminant predictive analysis (derivation of the linear discriminant functions) and discriminant classification analysis (to evaluate the previous linear functions to classify current and future samples). To measure the classification power of the analytical data, the percentage of individuals correctly predicted to belong to the assigned group is calculated, considering that prior probabilities are proportional to the number of samples in each group.

In this work, a leaving-one-out cross-validation procedure was performed for assessing the performance of the classification rule. In this procedure, the sample data minus one observation was used for the estimation of the discriminant functions, and then, the omitted sample was classified from them. The procedure was repeated for all samples. Consequently, each sample was classified by discriminate functions, which were estimated without its contribution (*33*).

The calculation of the confusion matrix has traditionally been the final step in the DA. However, the confusion matrix, when viewed as a contingency table, may be subject to further analysis, specifically with respect to the observed correct classification (*34*). In this work, we applied tests for overall classification, group classification (individual rows), and individual cells to compare the predicted classification using the model to that expected from chance alone.

The overall classification may be accomplished by the conventional χ^2 test for a contingency table, in which

$$\chi^2 = \sum_i \sum_j \frac{(o_{ij} - e_{ij})^2}{e_{ij}}$$

where o_{ij} is the observed number of samples classified in the cell ij; e_{ij} = $(n_{i\cdot} \cdot n_{\cdot j})/n$ with $n_{i\cdot}$ equal to the number of samples classified in row i, $n_{\cdot j}$ equal to the number of samples classified in column j, and n equal to the total number of samples. As usual, the number of degree of freedom is $(i - 1)(j - 1)$.

The tests of group differences were achieved according to the Morrison (*35*) likelihood analysis, which provides a criterion that may be used to compare the proportion of correctly classified observations with the proportion expected by chance. The proportion expected by

Table 2. Element Content (Mean ± Standard Error) in Green Spanish Style Olives, According to Cultivars[a]

metal	Gordal n = 32	Manzanilla n = 90	Carrasqueña n = 9	Hojiblanca n = 11
Al	85.89 ± 9.11	66.95 ± 3.50	83.67 ± 4.86	55.76 ± 7.90
B	4.371 ± 0.312	4.20 ± 0.14	3.83 ± 0.43	5.84 ± 0.42
Ba	2.38 ± 0.19	2.86 ± 0.13	2.80 ± 0.18	3.27 ± 0.41
Cd	0.037 ± 0.005	0.035 ± 0.003	0.027 ± 0.010	0.031 ± 0.007
Co	0.109 ± 0.005	0.107 ± 0.002	0.093 ± 0.011	0.099 ± 0.009
Cr	0.189 ± 0.020	0.207 ± 0.010	0.122 ± 0.009	0.178 ± 0.024
Li	8.66 ± 1.31	4.38 ± 0.40	10.56 ± 2.69	3.47 ± 0.71
Ni	0.112 ± 0.011	0.161 ± 0.014	0.103 ± 0.023	0.154 ± 0.041
Pb	0.262 ± 0.082	0.283 ± 0.062	0.331 ± 0.093	0.201 ± 0.022
S	370 ± 20	290 ± 10	250 ± 20	450 ± 30
Sn	0.307 ± 0.103	40.01 ± 5.940	0.123 ± 0.015	1.390 ± 0.279
Sr	10.35 ± 0.42	9.29 ± 0.28	12.76 ± 1.27	10.58 ± 0.58
Zr	0.031 ± 0.003	0.039 ± 0.003	0.032 ± 0.003	0.062 ± 0.009

[a] Values are in mg/kg e.p.

chance, designated the proportional chance criteria, is expressed as c_{pro} = $p \cdot \alpha + (1 - p)(1 - \alpha)$, where p = the true proportion of each style (or cultivar) in the total sample, and α = the proportion of each style (cultivar) in the whole sample categorized in that style (cultivar) by the model. This relationship between chance and observed proportions can be tested using a Z statistic of the form:

$$Z = \frac{p_{cc} - c_{pro}}{\sqrt{\dfrac{c_{pro}(1 - c_{pro})}{n}}}$$

where p_{cc} is the overall percent observations correctly classified in the sample.

The classification and misclassification within groups (cells in the confusion matrix), applied to determine the source of deviation, was conducted using the maximum chance criterion, c_{max}, defined as the minimum expected correct classification for a select group of interest; the calculation of c_{max} is based on the assumption that all observations are categorized as coming from that group (*35*). A Z statistic is used to test this relationship:

$$Z_{ij} = \frac{o_{cc} - c_{max}}{\sqrt{\dfrac{c_{max}(1 - c_{max})}{n}}}$$

where o_{cc} stands for observed correct (incorrect) classification of the specific cell. The test may be conducted for all of the cells in the confusion matrix. The different statistical techniques used in this work were implemented using STATISTICA, release 6.0 (*36*), and SYSTAT, release 10.2 (*31*).

RESULTS AND DISCUSSION

Concentration of Minerals in Table Olives. The overall means (**Table 1**) as well as averages according to styles (**Table 1**) and cultivars within styles (**Tables 2−4**) in table olives were obtained using a nested ANOVA, which showed significant differences among styles for some elements (**Figure 1**). The most abundant elements were S and Al, followed, at a marked distance, by Sn, Sr, Li, B, and Ba; the remaining elements were in concentrations below 1 mg/kg e.p. (**Table 1**). The content of S ranged from 567 mg/kg e.p. in green Manzanilla olive stuffed with onion to 109 mg/kg e.p. in directly brined "seasoned" Hojiblanca, while the overall average was 320 mg/kg e.p. Differences among elaboration styles were not significant. The average S contents according to cultivars within elaboration styles are shown in **Tables 2−4**. The concentrations found in table olives were similar to those reported by Anderson et al. (*37*) in diverse vegetables. Aluminum contents, with an overall average of 71 mg/kg e.p., ranged from 204 mg/kg e.p. in plain

Table 3. Element Content (Mean ± Standard Error) in Directly Brined Olives, According to Cultivars[a]

metal	Gordal $n = 3$	Manzanilla $n = 10$	Hojiblanca $n = 2$	Arbequina $n = 3$	Aloreña $n = 6$	Verdial $n = 3$
Al	74.90 ± 5.32	64.30 ± 9.04	67.80 ± 37.20	49.37 ± 5.00	71.93 ± 7.95	48.10 ± 8.16
B	3.15 ± 0.34	4.21 ± 0.27	1.57 ± 0.25	3.22 ± 0.24	4.37 ± 0.60	3.27 ± 0.44
Ba	1.30 ± 0.23	1.63 ± 0.23	1.86 ± 0.78	1.11 ± 0.13	1.35 ± 0.31	1.58 ± 0.17
Cd	0.042 ± 0.004	0.025 ± 0.005	0.016 ± 0.016	0.045 ± 0.003	0.034 ± 0.015	0.014 ± 0.005
Co	0.121 ± 0.002	0.108 ± 0.011	0.085 ± 0.041	0.126 ± 0.004	0.099 ± 0.019	0.088 ± 0.010
Cr	0.144 ± 0.006	0.128 ± 0.009	0.090 ± 0.012	0.162 ± 0.017	0.103 ± 0.011	0.100 ± 0.007
Li	9.71 ± 3.77	5.99 ± 2.20	8.95 ± 6.86	12.21 ± 4.67	8.00 ± 2.34	2.84 ± 0.97
Ni	0.164 ± 0.065	0.112 ± 0.009	0.048 ± 0.006	0.105 ± 0.020	0.087 ± 0.16	0.75 ± 0.002
Pb	0.276 ± 0.034	0.320 ± 0.067	0.181 ± 0.031	0.257 ± 0.034	0.239 ± 0.028	0.294 ± 0.026
S	300 ± 26	270 ± 20	150 ± 50	390 ± 20	410 ± 20	430 ± 10
Sn	0.825 ± 0.773	0.303 ± 0.110	0.110 ± 0.034	1.088 ± 0.581	0.105 ± 0.015	0.060 ± 0.011
Sr	7.09 ± 0.92	7.01 ± 0.70	8.47 ± 2.54	9.06 ± 0.71	11.17 ± 0.69	8.64 ± 0.29
Zr	0.017 ± 0.003	0.029 ± 0.005	0.012 ± 0.005	0.009 ± 0.003	0.029 ± 0.004	0.026 ± 0.004

[a] Values are in mg/kg e.p.

Table 4. Element Content (Mean ± Standard Error) in Ripe Olives, According to Cultivars[a]

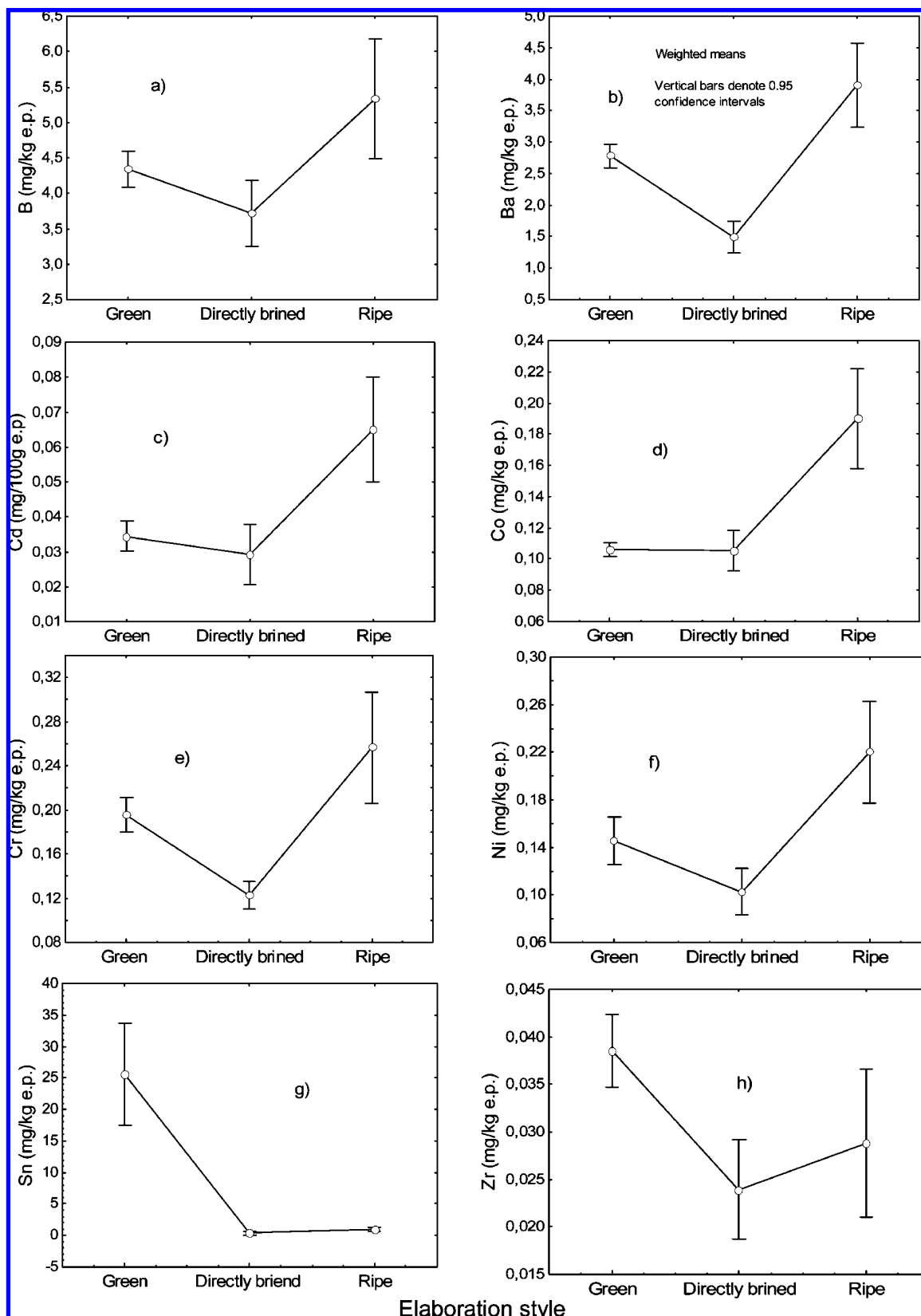| metal	Gordal $n = 3$	Manzanilla $n = 3$	Carrasqueña $n = 6$	Hojiblanca $n = 9$	Cacereña $n = 9$
Al	94.63 ± 27.85	63.80 ± 9.48	92.73 ± 21.47	70.38 ± 6.48	68.01 ± 9.20
B	2.80 ± 0.56	6.92 ± 0.18	4.20 ± 0.34	4.85 ± 0.81	6.86 ± 0.73
Ba	3.35 ± 0.51	6.36 ± 0.78	3.29 ± 0.86	3.25 ± 0.35	4.34 ± 0.64
Cd	0.064 ± 0.059	0.084 ± 0.006	0.048 ± 0.012	0.075 ± 0.009	0.060 ± 0.012
Co	0.165 ± 0.057	0.255 ± 0.010	0.147 ± 0.037	0.206 ± 0.028	0.190 ± 0.031
Cr	0.201 ± 0.044	0.279 ± 0.104	0.211 ± 0.040	0.291 ± 0.067	0.263 ± 0.026
Li	19.03 ± 0.56	5.49 ± 1.24	12.35 ± 5.88	8.49 ± 2.96	8.47 ± 3.70
Ni	0.195 ± 0.016	0.261 ± 0.051	0.163 ± 0.036	0.234 ± 0.049	0.240 ± 0.041
Pb	0.638 ± 0.239	0.317 ± 0.035	0.196 ± 0.021	0.216 ± 0.047	1.366 ± 1.036
S	260 ± 11	410 ± 40	220 ± 30	390 ± 40	320 ± 50
Sn	0.131 ± 0.027	0.538 ± 0.091	1.479 ± 0.451	1.080 ± 0.295	0.816 ± 0.086
Sr	10.93 ± 0.74	11.03 ± 0.12	9.14 ± 2.24	11.61 ± 0.80	9.00 ± 0.95
Zr	0.041 ± 0.014	0.042 ± 0.018	0.028 ± 0.005	0.030 ± 0.006	0.020 ± 0.008

[a] Values are in mg/kg e.p.

Gordal green olive to 17.5 mg/kg e.p. in Manzanilla green olives stuffed with natural pepper, but there were no significant differences among styles (which ranged from 64 to 76 mg/kg e.p.) (**Table 1**). However, differences among cultivars were significant. The lowest concentration was found in Arbequina (49 mg/kg e.p.), and the highest was found in Gordal (94 mg/kg e.p.). Levels of Al in other foods are also high. Saiyed and Yokel (*38*) reported concentrations from 1 to 27000 mg/kg in selected foods in the United States, which contained Al as an approved food additive. Shafer and Seifert (*39*) found levels between 100 and 200 mg/kg dry matter in vegetables, herbs, and spices. Legumes and nuts had 2.7−48.5 mg/kg e.p. (*40*). Aluminum is used as an additive in the food industry, and numerous pharmaceutical preparations (antacids, analgesics, antiulceratives, and phosphate binders) (*39*). The Al presence was consistently high in table olives regardless of the elaboration process, so its origin must be the same raw material; however, the contents reported by Nergiz and Engez (*41*) for fresh olives from Domat and Memecik Turkish cultivars were markedly lower (0.9−7.3 mg/kg e.p.).

The overall level (18.4 mg/kg e.p.) of Sn in Spanish table olives was mainly due to its presence in green olives, where it reached 25.5 mg/kg e.p. (**Table 1**). This is because some of these presentations are packed in microthin tin-coated cans to prevent corrosion; on the contrary, the mean contents in directly brined olives and ripe olives, which use lacquered cans, were markedly lower, 0.4 and 1 mg/kg e.p., respectively (**Table 1**). Furthermore, within green olives, the Manzanilla cultivar (average 40.0 mg/kg e.p.) was preferably packed in tin-coated cans, while Gordal, Carrasqueña, and Hojiblanca were not, as reflected by their low levels of Sn (0.31, 0.12, and 1.39, respectively) (**Table 2**). Concentrations of Sn found by Şahan

et al. (*21*) in green olives (33.3−47.6 mg/kg e.p.) were markedly higher than those found in this work for the same style but similar to the levels detected in the green Manzanilla cultivar. The level reported by this author for black olives (35.5 mg/kg e.p.) was markedly higher than that observed in directly brined olives in Spain (average 0.36 mg/kg e.p.). This may indicate the use of tin-coated cans for packing this product.

The Codex Alimentarius Commission regards tin as a priority contaminant. Food and especially canned foods represent the main source of human exposure to tin (*42*). Mean Sn values in this work were below the average reported by Wehrer (*43*) from more than 500 samples of canned food from retail sources (70 mg/kg); in this case, only 5% of the samples exceeded 250 mg/kg. The Sn concentration increased with storage time. The canned fruit or vegetable generally contained more Sn than the juice or brine in which they were packed (*43*). An average proportion of 90 mg/kg was found by Jorhem and Slorach (*44*) in fruits and vegetables packed in welded unlacquered cans. Concentrations found by Perring and Basic-Dvorzac (*45*) in diverse foodstuffs were between 58 and 113 mg/kg in fruits, between 2 and 30 mg/kg in vegetables, and especially high in beverages, 180−240 mg/kg (*45*).

The overall average of Sr was moderate (9.71 mg/kg e.p.); its maximum level (19.8 mg/kg e.p.) was found in the ripe Carrasqueña cultivar, while the lowest (7.06 mg/kg e.p.) was observed in green Manzanilla stuffed with natural pepper. Data on the presence of this element in foods are scarce. A content similar to that of table olives has been reported in fruits of the elm (7.68 mg/kg) (*46*), but its level in Lithuanian honey was lower (0.15 mg/kg) (*47*). The Sr level in herbal tea products ranged from 1.5 to 212 mg/kg and from 0.08 to 2.35 mg/L in their infusions (*48*). Concentrations between 0.21 and 0.79 mg/

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Figure 1. Mean values (mg/kg e.p.) and confidence limits ($P = 0.05$) of selected mineral elements, according to processing styles: (**a**) boron, (**b**) barium, (**c**) cadmium, (**d**) cobalt, (**e**) chromium, (**f**) nickel, (**g**) tin, and (**h**) zirconium. Elements were determined by IPC-OES.

kg or 1.16 and 4.63 were found in milk products and marine smoked fish (*49*).

Li was found in an overall mean of 6.55 mg/kg e.p., but its values were variable according to processing styles and cultivars. Its highest value (36.8 mg/kg e.p.) was found in ripe Ca-rrasqueña olives, and its lowest level (0.23 mg/kg e.p.) was

found in "seasoned" green Manzanilla presentation. Data on Li in food are scarce. Nabrzyski and Gajewska (*49*) reported concentrations ranging from <0.03−0.50 and 0.03−0.58 mg/ kg for milk products and marine smoked fish, respectively.

Boron (overall average 4.41 mg/kg e.p.) was the sixth element in abundance in table olives. Its content was significantly higher

in ripe (5.33 mg/kg e.p.) with respect to directly brined olives (3.72 mg/kg e.p.), while the level in green was intermediate (4.34 mg/kg e.p.) (**Table 1**). An eventual presence of this element in NaOH solutions might be responsible for its increment as the number of NaOH treatments (green < ripe) to olives increases. Directly brined Hojiblanca had the lowest content (1.57 mg/kg e.p.), and ripe Manzanilla had the highest (6.82 mg/kg e.p.) (**Tables 2–4**). The contents of boron in other foods are 28.2 (almond), 27.7 (hazelnuts), 45.1 (raisins), and 21.1 (dried apricots) mg/kg; the same source attributes 3.5 mg/kg to olives (*50*), which is quite similar to the level found in this work. The content in Turkish hazelnuts ranged from 13.8 and 22.2 mg/kg (*51*).

The overall Ba content in table olives was 2.77 mg/kg e.p. Directly brined olives had the lowest significant proportion (1.48 mg/kg e.p.), while ripe had the highest (3.91 mg/kg e.p.) (**Table 1** and **Figure 1**). The concentration was fairly similar among cultivars within elaboration styles with the ripe Manzanilla being the presentation with the greatest content (6.36 mg/kg e.p.). Reported levels of Ba in fresh Domat and Memecit Turkish cultivars were fairly lower, 50–319 and 431–513 μg/kg (*41*). Ba in bitter orange and in their marmalades ranged from <0.001 to 9.98 mg/kg and from 0.11 to 0.70 mg/kg, respectively (*10*).

With respect to elements found in concentrations below 1 mg/kg e.p., Pb was at an average content of 0.37 mg/kg e.p. (**Table 1**), which was progressively higher in green, directly brined, and ripe olives, with ripe Cacereña (1.37 mg/kg e.p.) being the presentation with the highest level (**Tables 2–4**). Proportions of Pb were slightly lower, apart from the ripe Cacereña exception, than those reported by Şahan et al. (*21*) for Turkish green (0.56–0.86 mg/kg) and black olives (0.51–0.91 mg/kg). These concentrations are similar to those found by Madejón et al. (*52*) in the flesh of wild olives, which ranged from 0.20 to 40 mg/kg, depending on the soil and season. Apparently, the levels found in table olives may come from the fruit itself and not from any contamination during processing. However, the use of contaminated chemicals led to high levels of Pb (10–31 mg/kg) in darkened by oxidation olives (*53*). Concentrations in table olives were lower that those found by Demirezen and Aksoy (*11*) in Turkish vegetables (3.0–10.7 mg/kg), which were related to the contents in the soils, being significantly higher in urban areas. However, contents reported by Radwan and Salama (*8*) in a survey of heavy metals in Egyptian fruits (0.05–0.87 mg/kg) and vegetables (0.01–0.58 mg/kg) were of the same order as in olives.

The concentrations of Cr, Ni, and Co were at 0.20, 0.15, and 0.12 mg/kg e.p., respectively. Their proportions were significantly higher in ripe olives (**Tables 2–4** and **Figure 1**), but no specific trend was found among cultivars. These values were similar to those found by Şahan et al. (*21*) in Turkish green and black olives and comparable to those reported for fresh fruits from Turkish Domat (Cr, 75–219 μg/kg; Co, 8–15 μg/kg) and Memecit (Cr, 46–74 μg/kg) cultivars (*41*). Levels of Ni (3.30–10.50 mg/kg), Cr (0.50–1.60 mg/kg), and Co (0.85–1.45 mg/kg) in potato chips (*54*) were higher than in olives.

Cd and Zr were the elements found in the lowest concentrations in table olives (average ≈0.04 mg/kg e.p.). Significant differences for Cd (higher in ripe olives) and Zr (higher in green olives) were found (**Table 1** and **Figure 1**). In wild fresh olives, the Cd content was fairly low (0.01–0.54 mg/kg). On the contrary, the use of contaminating chemicals or nonauthorized darkening products has led to a high proportion of Cd (3.2–6.4 mg/kg) in darkened by oxidation Egyptian olives (*53*). Then, the highest Cd value in Spanish ripe olives may also come from
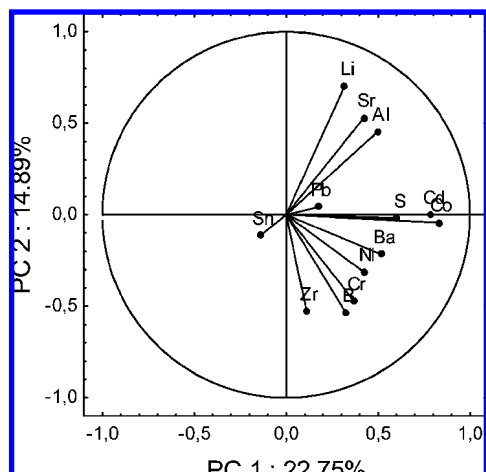
Table 5. Estimated Intake Values of Elements, Based on the Consumption of Table Olives Estimated by Cuadrado et al. (*9*)[a]

element	average daily intake from olives[b] (mg/day)	EU MLs (*10*) (mg/kg)	JECFA (*24, 25*) (mg/day)	EGVM (*14*) (mg/day)	panel on micronutrients (*39*) (mg/day)
Al	0.340		10.00[d]		
B	0.021			9.60[e]	20.00[f]
Ba	0.013				
Cd	0.0002	0.05–1.0[c]	0.07[d]		
Co	0.0006			1.40[e]	
Cr	0.0009			10.00[e]	0.025[g]
Li	0.032				
Ni	0.0007			0.26[e]	1.00[f]
Pb	0.002	0.020–1.50[c]			
S	2				
Sn	0.002–0.123[b]	50–200[c]	140.00[d]	13.00[e]	
Sr	0.047				
Zr	0.0002				

[a] When appropriate, EU established MLs, recommended daily intakes, safe upper levels, and provisional tolerable upper intakes are also included. [b] Considering that the average intake of table olives in Spain is 4.8 g/person/day (*9*). [c] Range of maximum contents in different foods. [d] Provisional TDI for a 70 kg adult individual. [e] Safe upper levels for a 60 kg adult individual. [f] Recommended daily intakes for adult individuals. [g] Tolerable upper intake levels for 60 kg adult individuals.

the chemicals used in ripe olive processing. Cd (0.24–0.94 mg/kg) in Turkish vegetables (*11*) was also greater than the levels found for olives in this work. The content of Cd in dietary supplements in México was 0.001–2.90 mg/kg (*7*). Levels of Cd in Turkish green (0.11–0.15 mg/kg) and black (0.12–0.16 mg/kg) (*21*) were above the contents found in this work, while in fresh Domat they ranged from <5 and 35 μg/kg (*41*). Information on the presence of Zr in foods is scarce. No explanation for its highest content in green olives can be deduced from this study, although it might be related to the predominant use of unlacquered cans in such style.

On the basis of the average table olive consumption in Madrid estimated by Cuadrado et al. (*9*), the daily intake of the analyzed elements in Spain was estimated (**Table 5**). The values were then compared with those limits, recommended daily intakes, or tolerable maximum levels established for some of them (**Table 5**). The average content of Cd and Sn (**Table 1**) was below the lower limits established by the EU for these elements, except the contents of Cd for ripe olives, which were slightly above this limit; then, the industry must pay attention to the purity of the chemicals used for processing them. The Pb content was always fairly close to the lowest limit and within the range established by the EU for this element. Therefore, no concern with respect to the Cd (except in ripe olives), Pb, or Sn exceeding the permitted legal limits should arise from this study. In the diet of consumers, low average daily intake of the studied elements from table olives should be expected (**Table 5**). S would be the highest contributor with about 2 mg/day. It is followed by Al (0.34 mg/day), but even in this case, its contribution would be only about 3.4% of the provisional tolerable upper daily intake (**Table 5**). Relatively high daily intakes are also for Sr or Li, although they are not of any health concern, and the Sr value is sensibly lower than the reference dose (RfD) established for this element, 36 mg/day for a 60 kg adult (*55*). The daily intake of B is far lower than the safe upper level established by EGVM (*56*) and the recommended daily intake fixed by the Panel on Micronutrients (*57*). Its contribution and that of Ba to the diet from olives are fairly low with respect to the RfD, 12 mg/day/60 kg person, established for both by the U.S. EPA (*55*). Co and Cr are a reduced proportion of the

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Figure 2. Results of the PCA. Only four eigenvalues higher than 1 were found. The first accounted for 22.75%, and the second accounted for 14.89% (accumulative variance of 59.86% of the total). The graph shows the projection (loadings) of the variables (none on labeling mineral elements) on the plane of the two first principal components.

upper safe limits from EGVM (*56*), and the latter is below the RfD 0.18 mg/day/60 kg adult as suggested by the U.S. EPA (*55*). The Ni daily intake for olives is fairly low as compared with the safe upper limit of EGVM (*56*) or the 1.2 mg/day/60 kg adult as admitted by the U.S. EPA (*55*).

Intakes from different styles may vary from the figures shown in **Table 5** due to significant differences in concentrations among them (**Table 1–4**). Some of these differences were clearly disclosed in **Figure 1**. Such effects were significant for most of the elements, except Al, Pb, and S. In general, ripe olives were richer in most of the studied elements (**Table 1** and **Figure 1**), except for Sn and Zr. The increase may be caused by the high presence of such elements in NaOH and/or other chemicals used in ripe olive processing. This circumstance can be of concern in case of intake restriction for specific elements. The higher presence of Sn in green olives was clearly associated with their packing in tin-coated cans, which can also contain Zr as a contaminant.

Chemometric Analysis. The group statistics (averages, standard errors, and *F* and *P* values for comparisons) related to elaborations styles are shown in **Table 1**. There were significant differences among styles for most of the elements, except for Al ($P = 0.442$), Pb ($P = 0.119$), and S ($P = 0.803$). The group statistics for cultivars were calculated similarly (data not shown); in this case, there were also significant differences among cultivars except for Cd ($P = 0.109$). Then, data showed appropriate characteristics to be subjected to the chemometric analysis.

The correlation matrix between elements showed that there were no strong relationships among them (coefficients ≈ 0.50 at maximum). The structure was then not prone to achieve a reduction in dimensions. The PCA showed that there were four eigenvalues higher than 1, which accounted for an accumulative variance of 59.86% of the total. The projection of the variable loadings on the plane defined by the first two PCs (**Figure 2**) allowed a visualization of the variables and their corresponding correlations, which are the cosine of the angle of their respective vectors (90° no correlation at all) (*58*). Thus, Al is related to Sr and Li, while Cd is related to S and Co; however, the relationships cannot be assigned to concrete causes. On the contrary, Sn can hardly be related to any other, as it corresponds to its specific origin from tin-coated cans. In addition, the projections (loads) of the variables on the PC1 and PC2 axes

Table 6. Confusion Matrix According to Elaboration Styles[a]

current olive style	n_i	predicted olive style			sensitivity (%)	$p_i = n/n$
		green	directly brined	ripe		
green	142	138 (134)	3 (7)	1 (1)	97.18	0.7136
directly brined	27	16 (11)	11 (8)	0 (1)	59.25	0.1357
ripe	30	8 (11)	0 (1)	22 (18)	73.33	0.1508
total (n_j)		162	14	23	$n = 199$	
specificity (%)		85.19	78.57	95.65		
$\alpha_i = n/n$		0.8141	0.0070	0.1155		

[a] The DA was based on the element contents in table olives. In parentheses, classification obtained in the cross-validation (jack-knifed matrix). Overall correct classification, 86%; overall correct classification after cross-validation, 80.4%. Sensitivity (proportion of samples correctly assigned to the group they belong) and specificity (proportion of samples correctly assigned to a group with respect to the total samples classified into it) are estimated only for the classification matrix and not for cross-validation (jack-knifed matrix).

Table 7. Analysis of the Confusion Matrix[a]

current olive style	predicted olive style			Z_i
	green	directly brined	ripe	
green	8.84 (<0.0001)	−21.60 (<0.0001)	−22.05 (<0.0001)	6.59 (<0.0001)
directly brined	18.82 (<0.0001)	2.0 (=0.0226)	−5.59 (<0.0001)	1.88 (=0.0301)
ripe	4.32 (<0.0001)	−6.06 (<0.0001)	22.48 (<0.0001)	3.02 (=0.0013)

[a] Values of Z and probability (in parentheses) for the analysis of elaboration types (Z_i), rows, and cells. Overall $\chi^2 = 180.55$ with 4, (3-1)(3-1), degree of freedom ($P < 0.0001$).

represent their contributions to them. PC1 was mainly related to Cd, Co, and S, but PC2 was more closely related to Li, Sr, Al, B, or Zr. The plot of the case scores on the plane of these two PCs did not lead to their clear separation according to styles or cultivars. Then, data were subsequently subjected to a canonical and DA.

The canonical analysis showed that the elements that most contributed to differentiate among processing styles were Co (54.99, *F* to remove; 0.616, tolerance), Ba (12.94; 0.935), S (15.91; 0.636), Cr (8.58; 0.976), and Sn (8.03; 0.960), where tolerance is a measure of the redundancy of respective variable in the model (high correlation, small tolerance). The equations of the respective standardized canonical functions using only two decimal figures were as follows:

$$\text{function}\_1 = 0.23\text{Ba} + 1.05\text{Co} + 0.31\text{Cr} - 0.66\text{S} - 0.28\text{Sn}$$

$$\text{function}\_2 = 0.75\text{Ba} - 0.54\text{Co} + 0.45\text{Cr} + 0.20\text{S} - 0.47\text{Sn}$$

A plot of the case scores vs these functions showed a fairly good separation between samples, although an overlapping between some samples belonging to green and directly brined olives was observed. The procedure reached an overall correct classification of 86% with 80% after cross-validation. The correct classification for each style is shown in **Table 6**. There was a high sensitivity for green (>97%) and ripe olives (>73%), while specificity was reversed (>85.19% for green and >95% for ripe olives). Specificity was also moderately high (78%) in directly brined olives. The main difficulty was the incorrect classification of most of the directly brined olives into green olives and some samples from ripe into green olives (**Table 7**). Then, an analysis of the results with respect to those expected by chance may be of interest. The overall correct classification observed was 86%, $(137 + 10 + 25)/199$. The calculus of the expected cases (e_{ij}) per cell and the overall χ^2 lead to a value

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of 180.55 with $P < 0.0001$ (with 4 df) (**Table 7**). So, it must be concluded that the model performance yielded a better classification into styles than those expected by chance alone.

The test based on the likelihood ratio defined by Morrison (*35*) can be applied to evaluate the expected classification of specific styles (rows). The values of p_i and $\alpha_{.j}$, necessary for the calculus of c_{pro} (expected correct classification by chance), are given in **Table 6**. The estimated c_{pro} may be compared with the overall correct classification by the Z_i score obtained for each group (style). The Z_i values for the respective styles are shown in **Table 7**. The classification obtained using the model is always significantly better ($P < 0.05$) than that expected by chance. Values in any of the confusion matrix cells may also be tested to determine whether its proportion differs from that which could be obtained by chance. The Z_{ij} values of this comparison and its associated probabilities are shown in **Table 7**. The correct classification of samples in each style (diagonal) was always higher ($P < 0.05$) than that expected by chance. The misclassification of green as directly brined and ripe olives and the misclassification of directly brined olives as ripe were significantly lower than by chance. The misclassification of directly brined into green was significantly higher than by chance, which means a bias of the model, but its misclassification as ripe was significantly lower. Misclassification of ripe into green was significantly higher than by chance, but the model was able to significantly discriminate between directly brined and ripe olives because the proportion obtained was significantly lower than that eventually obtained by chance. The chemometric analyses using cultivars as grouping variables always led to poor results (data not shown).

This work provides information on minerals that are not required for nutritional labeling in table olives. The research has included the most popular processing styles, cultivars and commercial presentations. The most abundant elements were S, Al, and Sn, although this element was closely related to a specific style and cultivar (green Manzanilla olives). Most of the elements were found in higher proportions in ripe olives. PCAs showed relationships among some elements, while LDA clearly differentiated green olives from directly brined olives or ripe olives, but these could be confused with green olives. However, directly brined olives and ripe olives were clearly different from one another.

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