

## Analytical, Nutritional and Clinical Methods

## Multivariate characterization of table olives according to their mineral nutrient composition

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**Abstract**

Different commercial presentations of table olives were characterized by their mineral compositions. Cu, Fe, Mn, Zn, Ca, Mg, Na, K, and P were determined. The processing of table olives affects the mineral content of commercial presentations and significant differences ( $p < 0.05$ ) were found among green (Spanish style), directly brined, and ripe olives. A predictive discriminate analysis showed that the most discriminating elements were Fe, K, Na, Mn, Cu, and P (among styles) and with Ca (among cultivars). A good classification and cross-validation was observed in the case of elaboration styles but discrimination among cultivars was less conclusive. A further analysis of the confusion matrix, according to cultivars, showed that the lower classification efficiency, in this case, was mainly due to misclassification of samples from Manzanilla and Gordal cultivars. The analysis of the confusion matrix can be useful when the assessment of its results is not obvious.

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**Keywords:** Characterization; Discriminant analysis; Mineral nutrients; Table olives**1. Introduction**

The table olive reached a total production of 1,600,000 t in the 2003/2004 season, with Spain being the main producer and exporter with about 500,000 and 250,000 t, respectively. The consumption of table olives in the Mediterranean Basin, is a widespread tradition, which is also reaching other non-producing countries (IOOC, 2005). Fresh olives, as legumes (Iqbal, Khalil, Ateeq, & Khan, 2006), fruits (Sánchez Castillo et al., 1998) or other plants (Guill Guerrero, Jiménez Martínez, & Torija Isasa, 1998) are rich in minerals (Biricik & Basoglu, 2006). However, olives must be processed before eating to remove their natural bitterness (Garrido Fernández, Fernández-Díez, & Adams, 1997). Their elaboration includes several styles (Sánchez Gómez, García García, & Rejano Navarro, 2006). 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 (Garrido Fernández et al., 1997). The different aqueous treatments may produce some changes in the mineral composition of the processed fruits. Nosti Vega, Vázquez Ladrón, and de Castro Ramos (1979) and De Castro Ramos, Nosti Vega, and Vázquez Ladrón (1979) studied the mineral content of some processed samples from the Spanish cultivars. Ünal and Nergiz (2003) studied Na, K, Ca, Fe, and Zn in Memecik (Turkish cv.). Biricik and Basoglu (2006) reported the mineral content in olive cv. Samanlı, Domat, Manzanilla and Ascolano from Turkey. However, none of these investigations used samples from marketed products.

Currently, there is a diversity of commercial presentations on the market, which, in addition to the main processing styles, also differ in their final conditioning, stuffing materials, preservation technologies and cultivars. A survey of the mineral concentration of all of them, is therefore appropriate. Such data will provide information

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on minerals to the olive industry as required by the nutritional labeling in USA (CFR, 2003), Canada (Canadian Food Inspection Agency, 2003), Europe (Council of the European Communities, 1990) or any other country. Data on mineral content in table olives may also be useful for nutritionists or consumers.

Chemometric techniques, appear to be the most powerful tools for characterizing and classifying wines (Arvanityannis, Katsota, Psarra, Soufleros, & Kallithraka, 1999), honeys (Nozal Nalda, Bernal Yagüe, Diego Calva, & Martín Gómez, 2005), dairy products (Herrera García et al., 2006), pistachios (Anderson & Smith, 2005) and beer (Alcázar, Pablos, Martín, & Gustavo González, 2002) according to their source, processing conditions, or origin. Discriminant analysis is used to find theoretical values resulting in the best possible discrimination between a priori established groups. Discrimination relies on weighting the theoretical values for each variable in such a way as to maximize between group variance with respect to within group variance. Discriminant analysis models comprise sets of equations that are linear combinations of the independent variables, resulting in the maximum possible separation between groups (Uriel & Ardás, 2005).

The aim of this work was to (i) determine the mineral composition of all marketed Spanish commercial presentations of table olives; (ii) check for possible differences in the concentration of minerals among them; (iii) evaluate the ability of discriminant analysis to classify these commercial presentations according to elaboration styles and cultivars; (iv) test these classifications with respect to those which could be obtained by chance.

## 2. Materials and methods

### 2.1. Samples

Samples belonged to the following styles, cultivars and commercial presentations:

#### 2.1.1. Green Spanish-style olives

Gordal: plain, pitted, and seasoned. Gordal stuffed with: red pepper strips, natural red pepper, almond, cucumber, onions, garlic, and jalapeño. 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 sliced 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 “alcázar”. Carrasqueña: pitted. A blend of pitted Carrasqueña olives and red pepper strips, called “salads”;

and a blend of Carrasqueña olives and capers called “alcázar”. Hojiblanca: plain, pitted, sliced. Hojiblanca olives stuffed with red pepper strips.

#### 2.1.2. Directly brined olives

Gordal: broken “seasoned” turning colour. Manzanilla: turning colour in brine alone, “seasoned” turning colour, and olives from biologic (or ecologic) production. Hojiblanca: “seasoned” turning colour. Arbequina: “seasoned” turning colour. Aloreña: green “seasoned” broken, prepared from fresh fruits and from stored olives. Verdial: green “seasoned” broken.

#### 2.1.3. Ripe olives (by alkaline oxidation)

Gordal: plain. Manzanilla: pitted. Carrasqueña: plain and pitted. Hojiblanca: plain, pitted, and sliced. Cacerena: plain, pitted, and sliced.

### 2.2. Reagents

All reagents were of analytical purity (Panreac, Barcelona, Spain). Hydrochloric acid (6 N) solution was obtained by dilution of concentrated HCl (Fluka, Buchs, Switzerland). The stock solutions of Cu, Fe, Mn, Mg, Zn, Ca, and P were obtained from Sigma. Stock solutions of Na and K were purchased from PACISA (Madrid, Spain). The standard solutions were obtained by dilution of the corresponding stock solutions and the addition of HCl in a concentration similar to that obtained in the sample solutions.

### 2.3. Cleaning of the material

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

### 2.4. Sample preparations

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 to 5 elaboration companies, according to their availability on market shelves. Producers kindly supplied those commercial presentations not available in the local markets. Average time from packing was about 3 months.

The pulp of 100 g of sample olives was separated from the pit, when it was necessary, by manual or automatic pitting machine, ground and homogenized. From the resulting paste mentioned above, 5 g olive pulp (2.5 g for ripe olives) of the diverse samples, was exactly weighted 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 calcination temperature was reached, which was maintained for ≈8–10 h. The ashes, white-grayish in colour, were slightly moistened and dissolved with three parts of

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