

Variations of chromium and nickel content during industrial processing of white asparagus

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The influence of certain industrial processing operations of white asparagus (*Asparagus officinalis*, L.) on concentrations of chromium and nickel was studied. Samples of white asparagus were taken during the following operations of the industrial processing: reception and selection of raw material (fresh asparagus), after machine-washing (washed asparagus), after peeling (peeled asparagus) and on completion of the blanching operation (blanched asparagus). Asparagus samples were selected for two varieties ('Desto' and 'Sur'), four diameters (9–11 mm, 11–14 mm, 14–19 mm and > 19 mm) and three portions of spear (tip, middle and rest). The mean concentrations found for chromium and nickel were 1.37 ± 0.94 and 5.53 ± 1.17 (mg kg⁻¹ dry weight), respectively. By means of analysis of variance, statistically significant differences ($P < 0.001$) were determined between the different processing operations for the chromium and nickel ($P < 0.05$) concentrations. Scheffé multiple range analyses ($P < 0.05$) were applied for the processing, diameters and portion factors, separately, and homogeneous groups were formed which indicated the influence of each one of these factors on the contents of chromium and nickel. © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Many studies have investigated the influence of different industrial processing operations on the mineral content of vegetables suitable for preservation (Lee *et al.*, 1982; Lopez *et al.*, 1986a,b; Hazell & Johnson, 1987; Sham & Thompson, 1987; Rincón *et al.*, 1990) or for frozen storage (Lopez & Williams, 1985; Polo *et al.*, 1992). However, there are very few works studying the mineral composition of asparagus and the influence that processing exercises on it, despite the fact that asparagus is a vegetable product of which a high percentage of its total production is destined for industrial transformation. Industrial processing involves the handling of a product from the time it is harvested until it reaches the consumer, and this can affect the product's mineral content. Washing and blanching can lead to a decrease in the trace element content, depending on the mineral content of the water used and the volume employed (Polo *et al.*, 1992).

Both green and white asparagus are vegetable products of great socioeconomic importance both for their commercialization when fresh and when they are preserved. For these reasons, it is necessary to determine their chemical composition in both states and to evaluate

what influence may be exercised on their nutritional components by different factors, including industrial processing and the storage period of the preserved vegetable. During the transformation of the fresh asparagus in the preservation process, losses of nutritional components are produced in the cutting, peeling and successive washing operations and, basically, in blanching and sterilization due to the action of heat, light, oxygen, treatment water, loss of vegetable matter, etc. (Tannenbaum, 1985; Richardson & Finley, 1985; Benages, 1990). Zurera-Cosano and Moreno-Rojas (1990) studied the effect of canning operations on the mineral content of white asparagus and observed a decrease in the levels of calcium and magnesium throughout industrial processing. Llanos *et al.* (1994) carried out a study on the chemical composition of asparagus from which they deduced that the transformation of the fresh product into a preserved one signified variations in mineral content of asparagus.

Furthermore, the determination of minerals in vegetables has assumed considerable importance in recent years, but few studies on the effect of asparagus varieties, diameters and portions on the mineral content of asparagus have been made (Zurera-Cosano & Moreno-Rojas, 1990; Zurera-Cosano *et al.*, 1990; Moreno *et al.*, 1992; Amaro-López *et al.*, 1995a,b).

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The purpose of this work was to determine whether the chromium and nickel concentrations varied when certain industrial processing operations were carried out on white asparagus classified by varieties, diameters and portions.

MATERIALS AND METHODS

Samples

The white asparagus samples were directly harvested on 1 day from the crop fields of one smallholding (Egnolac, Palma del Río, Córdoba, Spain) and processed in the pilot-plant. Samples of two varieties of white asparagus ('Desto' and 'Sur') were taken and classified into four groups on the basis of their diameters: 9–11 mm, 11–14 mm, 14–19 mm and > 19 mm. The samples were taken during the following operations of the processing of white asparagus: reception and selection of raw material (fresh asparagus), after machine-washing (washed asparagus), after peeling (peeled asparagus) and on completion of the blanching operation (blanched asparagus). All the asparagus spears were cut to a length of 21 cm and divided into three portions of 7 cm each, establishing three study portions: the apical portion or tip (contains the bud), the centre or middle portion, and the basal portion or the rest of the asparagus. Sampling was carried out in duplicate and a total of 192 samples were analysed.

Analytical procedure

For analysis of chromium and nickel contents in the white asparagus samples, the dry ashing method described by Zurera-Cosano and Moreno-Rojas (1990) was applied. The spears were first washed with deionized water to remove soil and dust from the surface. The portions of the spears were weighed separately and dried at 100°C to constant weight. Then 2 g of the homogenized and dried sample were weighed into porcelain crucibles and mineralized overnight in a furnace (460°C). The ash was extracted with 2.5 ml of a mixture of HCl–HNO₃–H₂O (deionized) at a ratio of 1:1:2 (v/v). The solution obtained was dried on a thermostatic plate and placed in a furnace (460°C) for 1 h. The resulting white ash was suspended in 5 ml of HCl–HNO₃–H₂O (deionized) (1:1:2), and the solution was placed in a 15 ml volumetric flask made up to volume with deionized water.

All glassware was washed and soaked in HNO₃ solution (15%, v/v), rinsed with distilled–deionized water and dried before use. The final sample solutions were stored in polypropylene bottles under refrigeration until their subsequent analysis by absorption spectrophotometry.

The analytical determinations of chromium and nickel were performed with a Perkin-Elmer Model 2380 atomic absorption spectrophotometer, equipped with a

Perkin-Elmer Model AS-50 autosampler, using an air–acetylene flame and single-element hollow cathode lamps. The instrument settings and other experimental conditions were in accordance with the manufacturer's specifications.

The calculation of the detection limit (3 SD) was made according to the definition and criteria established by IUPAC (Long & Winefordner, 1983; Analytical Methods Committee, 1987); the results were 0.005 mg litre⁻¹ for chromium and 0.073 mg litre⁻¹ for nickel. The concentration limits obtained (minimum detectable concentration in mg kg⁻¹ dry weight) were 0.040 and 0.549 for chromium and nickel, respectively. The precision of the method was obtained by calculating coefficients of variation according to the criteria of Barberá *et al.* (1990); the results were 6.40% for chromium and 3.32% for nickel. The sensitivities (in mg litre⁻¹) were 0.078 and 0.142 for chromium and nickel, respectively. Accuracy was evaluated by standard additions of known concentrations and by analysis of the standard reference material 'Citrus leaves' (BCR 1572; Standards Measurement and Testing, Brussels). The percentage recoveries of the standard additions were 99.4% for chromium and 99.1% for nickel. The values for chromium and nickel for the Standards Measurement and Testing, Brussels (BCR 1572), are 0.8 ± 0.2 and 0.6 ± 0.3 mg kg⁻¹, and the results found were 0.92 ± 0.10 and 0.71 ± 0.15 mg kg⁻¹, for chromium and nickel, respectively.

Statistical study

The concentration data were evaluated by descriptive statistics, analysis of variance and a Scheffé multiple range test ($P < 0.05$), which permitted the formation of homogeneous groups by an association of classes of statistically similar concentrations (Molina-Alcalá *et al.*, 1992; Piggott, 1986).

RESULTS AND DISCUSSION

The mean concentrations found for chromium and nickel (Table 1) were similar to those found in the literature for white asparagus (Amaro-López *et al.*, 1995a). The results of a four-factor analysis of variance (processing, variety, diameter, portion) indicated the existence of statistically significant differences ($P < 0.001$) between the different asparagus-processing operations for the chromium and nickel ($P < 0.05$) concentrations. The two varieties of white asparagus showed statistical differences ($P < 0.05$) for nickel content and no statistically significant differences ($P > 0.05$) for chromium content. Statistically significant differences ($P < 0.001$) were established between diameters of white asparagus for the concentrations of chromium and nickel. Finally, between the portions of asparagus spear no statistically significant differences ($P > 0.001$)

were found for chromium content, but the nickel content showed statistically significant differences ($P < 0.001$).

Moisture

Statistically significant differences ($P < 0.001$) were established between the processing operations for moisture content, and it was found that the moisture levels slightly increased throughout processing (Fig. 1), as demonstrated by the Scheffé homogeneous groups ($P < 0.05$) formed (Table 1). The moisture values in the tip of the spear were lower than those of the middle and the rest (Table 1 and Fig. 1(A)) with statistically significant differences ($P < 0.001$) established for the three portions. These differences were corroborated by the formation of three different Scheffé groups ($P < 0.05$), one for each portion analysed, and the rest of the spear gave a higher percentage of moisture (Table 1), coinciding with that reported by Sánchez *et al.* (1992), who determined higher levels of moisture in the basal portion or stem of the asparagus compared to the apical portion or bud (3 cm from the tip). There were no variations in moisture content as a function of the diameter of the spear (Fig. 1(B)) since the differences between the diameters were non-significant ($P > 0.05$). The two varieties studied displayed a similar evolution during processing and there were no statistically significant differences ($P > 0.05$) in moisture percentage. It was only during the blanching process that certain differences were observed, with an increase in moisture in the 'Desto' variety (Fig. 1(C)).

Chromium

A Scheffé multiple range analysis ($P < 0.05$) established a single homogeneous group for the fresh spear in which the highest concentrations of chromium appeared, whilst the three remaining stages of the processing constituted a different homogeneous group (Table 1). In general, the chromium content underwent a notable diminution in the washing operation, but showed a stable, uniform evolution in the later stages in which the chromium levels were similar (Table 1 and Fig. 2).

The evolution of the three spear portions of white asparagus was very similar throughout the different industrial processing operations to that described for the process in general (Fig. 2(A)) and there were no statistically significant differences between them ($P > 0.05$) as already mentioned (Table 1). However, when only two portions were analysed, the apical portion (7 cm from the tip) and the basal portion (remaining 14 cm of the spear), statistically significant differences ($P < 0.001$) were established in the chromium content, and it was the apical portion that contained the highest concentrations of the element (Amaro-López *et al.*, 1995a). These alterations in the mineral composition of the asparagus as a function of the spear portion analysed have also been reported in previous studies (Zurera-Cosano & Moreno-Rojas, 1990; Zurera-Cosano *et al.*, 1990; Moreno *et al.*, 1992; Amaro-López *et al.*, 1995b).

A Scheffé multiple range analysis ($P < 0.05$) established a homogeneous group of the narrow diameter spears (9–11 mm), another different homogeneous group of the 11–14 mm and > 19 mm diameter spears,

Table 1. Moisture content (%) and mean concentrations of chromium and nickel (mg kg^{-1} dry weight) of white asparagus classified according to processing operation, portion, diameter and variety

Processing operation	Portion			Diameter (mm)				Variety		Total
	Tip	Middle	Remainder	9–11	11–14	14–19	> 19	'Desto'	'Sur'	
<i>Moisture</i>										
Fresh	92.2 ± 1.02	94.8 ± 0.30	95.2 ± 0.50	94.3 ± 1.21	94.2 ± 1.36	94.1 ± 1.47	93.7 ± 1.89	93.8 ± 1.52	94.3 ± 1.42	94.1 ± 1.48 ^c
Washing	92.6 ± 0.58	94.5 ± 1.23	95.2 ± 0.58	94.4 ± 0.95	93.7 ± 1.43	94.0 ± 1.53	94.3 ± 1.52	94.2 ± 1.15	94.0 ± 1.57	94.1 ± 1.34 ^{b,c}
Peeling	92.9 ± 0.39	95.2 ± 0.18	95.2 ± 0.45	94.4 ± 1.15	94.3 ± 1.41	94.5 ± 0.99	94.5 ± 1.28	94.2 ± 1.19	94.6 ± 1.17	94.4 ± 1.18 ^b
Blanching	93.7 ± 0.74	95.8 ± 0.72	95.9 ± 0.72	94.8 ± 1.30	95.0 ± 1.26	95.5 ± 1.13	95.2 ± 1.29	95.8 ± 1.13	94.5 ± 1.02	95.2 ± 1.23 ^a
Total	92.9 ± 0.89 ^c	95.1 ± 0.87 ^b	95.4 ± 0.64 ^a	94.5 ± 1.14 ^a	94.3 ± 1.41 ^a	94.6 ± 1.40 ^a	94.4 ± 1.56 ^a	94.5 ± 1.44	94.4 ± 1.31	94.4 ± 1.38
<i>Chromium</i>										
Fresh	2.21 ± 0.97	1.77 ± 0.83	1.72 ± 0.86	2.58 ± 0.87	1.63 ± 0.72	2.02 ± 0.98	1.38 ± 0.54	2.00 ± 0.89	1.81 ± 0.91	1.90 ± 0.90 ^a
Washing	1.42 ± 0.61	1.01 ± 0.42	1.01 ± 0.78	1.27 ± 0.64	0.64 ± 0.10	1.28 ± 0.55	1.39 ± 0.81	1.18 ± 0.59	1.12 ± 0.70	1.15 ± 0.64 ^b
Peeling	1.21 ± 0.54	1.04 ± 0.66	1.31 ± 0.73	1.32 ± 0.71	0.95 ± 0.49	1.42 ± 0.97	1.06 ± 0.56	1.38 ± 0.41	0.99 ± 0.61	1.19 ± 1.09 ^b
Blanching	1.22 ± 1.16	1.28 ± 0.73	1.25 ± 0.82	1.78 ± 1.43	1.05 ± 0.48	1.34 ± 0.76	0.82 ± 0.27	1.32 ± 0.94	1.18 ± 0.88	1.25 ± 0.91 ^b
Total	1.52 ± 0.94 ^a	1.28 ± 0.73 ^a	1.32 ± 0.12 ^a	1.74 ± 1.07 ^a	1.07 ± 0.61 ^b	1.52 ± 0.20 ^{ab}	1.16 ± 0.61 ^b	1.47 ± 1.04	1.27 ± 0.83	1.37 ± 0.94
<i>Nickel</i>										
Fresh	6.17 ± 1.30	5.48 ± 1.18	4.90 ± 1.14	5.09 ± 1.68	5.28 ± 1.18	5.46 ± 1.20	6.23 ± 0.817	4.64 ± 1.17	6.39 ± 0.67	5.52 ± 1.29 ^a
Washing	6.18 ± 1.23	5.28 ± 0.62	4.68 ± 0.85	5.27 ± 0.86	4.47 ± 0.87	5.91 ± 0.66	5.87 ± 1.36	5.32 ± 1.48	5.44 ± 0.55	5.38 ± 1.11 ^a
Peeling	6.34 ± 0.90	5.85 ± 0.55	5.17 ± 1.03	6.26 ± 1.10	5.52 ± 0.61	6.09 ± 0.84	5.28 ± 0.99	6.07 ± 1.03	5.50 ± 0.82	5.79 ± 0.96 ^a
Blanching	5.40 ± 0.83	5.73 ± 0.94	5.20 ± 1.35	4.85 ± 0.48	5.32 ± 1.09	6.55 ± 0.89	5.06 ± 0.85	5.74 ± 0.69	5.15 ± 1.29	5.44 ± 1.06 ^a
Total	6.03 ± 1.12 ^a	5.58 ± 0.87 ^b	4.99 ± 1.10 ^c	5.37 ± 1.21 ^b	5.15 ± 1.02 ^b	6.00 ± 0.97 ^a	5.61 ± 1.10 ^{ab}	5.44 ± 1.23	5.62 ± 0.98	5.53 ± 1.12

^{a,b,c}Homogeneous groups by Scheffé multiple range test ($P < 0.05$).

and an intermediate group, between the other two groups, of the 14–19 mm diameter spears (Table 1). The initial differences in the chromium concentration between diameters lessened during the washing operation, and the levels of the element remained very similar during the two remaining processing operations (Fig. 2(B)). When the diameters investigated were reduced to two groups (<11 mm and >14 mm), no statistically significant differences ($P > 0.05$) were fixed for chromium content (Amaro-López *et al.*, 1995a). Nevertheless, the factor diameter signified a variation in the composition of the mineral macronutrients and micronutrients in asparagus, as shown in the work of Zurera-Cosano *et al.* (1990), Moreno *et al.* (1992) and Amaro-López *et al.* (1995b).

With regard to the varieties of white asparagus studied, Fig. 2(C) shows that the evolution of the chromium content is similar for both varieties, confirming the general tendency for the concentration to diminish during the washing stage but to be maintained during the subsequent operations (Table 1).

Nickel

In spite of having determined statistically significant differences, albeit with a low degree of significance ($P < 0.05$), the Scheffé multiple range analysis ($P < 0.05$) indicated the formation of a single homogeneous group which covered all the processing operations (Table 1). In the peeling stage, a small increase in nickel levels was noted (Fig. 3), possibly related to the removal of the cortical surface of the spear. In order to verify the effect of the peeling operation on the mineral content of white asparagus, a statistical test of homogeneity of means was applied which permitted comparison of the mineral concentrations in the cortical surface or external peel of the spear with the concentrations found in the same peeled spear. Statistically significant differences ($P < 0.05$) were determined between the nickel levels in the peelings and those of the peeled spear itself, and it was shown that, as has been previously mentioned, the nickel content exhibited a certain increase after the peeling operation (Fig. 3). As the spear peelings showed a lower concentration

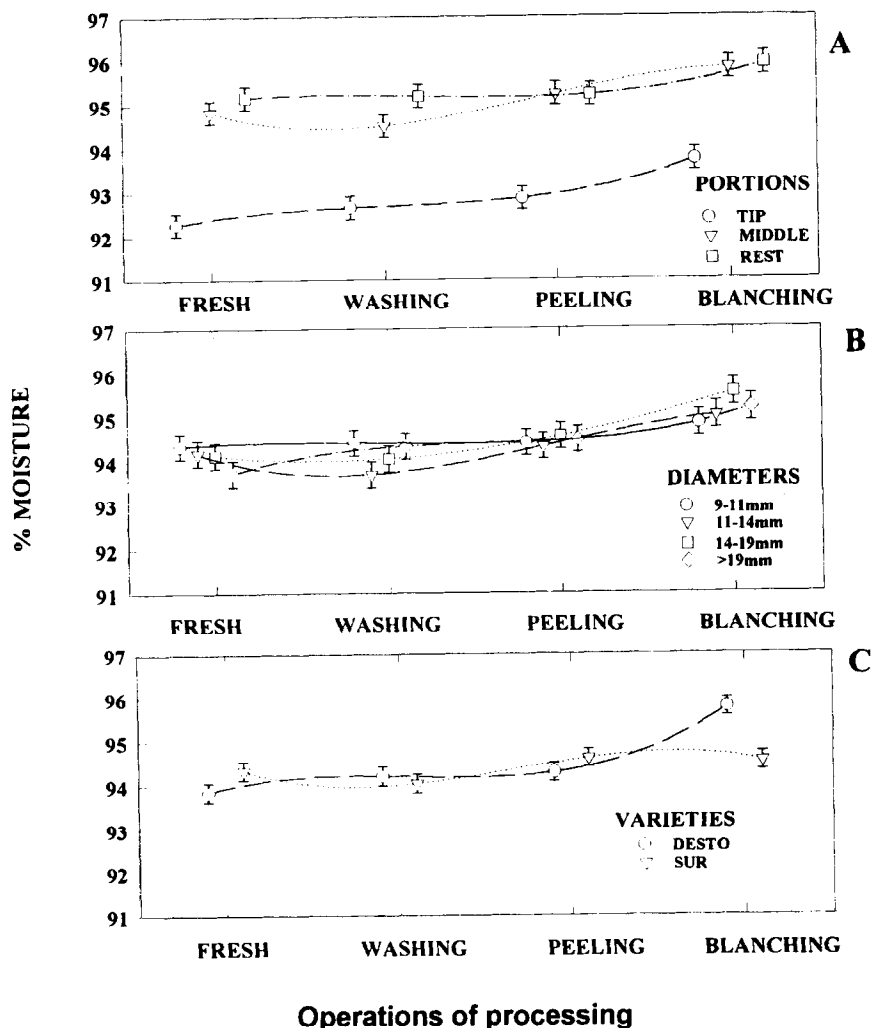


Fig. 1. Evolution of moisture content during processing of white asparagus, according to portion (A), diameter (B) and variety (C).

(5.81 ± 0.90 mg kg⁻¹ dry weight) than those found in the peeled spear (6.51 ± 1.01 mg kg⁻¹), it is to be supposed that, on removing the peel from the asparagus, a relative increase of the nickel levels in the peeled spear occurred compared to the same unpeeled spear.

With regard to the portions, three homogeneous groups were formed (Table 1). It was generally the tip portion that showed higher levels of nickel, in agreement with Amaro-López *et al.* (1995a), who determined statistically significant differences ($P < 0.001$) in nickel contents between different portions of asparagus, with higher levels in the apical portion. In addition, the results obtained confirmed the greater capacity of the apical portion of the asparagus to concentrate minerals, a fact which has already been established in various studies (Zurera-Cosano & Moreno-Rojas, 1990; Zurera-Cosano *et al.*, 1990; Moreno *et al.*, 1992; Amaro-López *et al.*, 1995b), and is possibly related to a greater enzymatic activity in the tip in which there is a greater growth and cellular development compared to the rest of the asparagus. Initially, the nickel concentrations were clearly different in the three portions, but changed during the course of processing such that the nickel

contents were similar in all three portions during the blanching operation (Fig. 3(A)).

Using a Scheffé multiple range analysis ($P < 0.05$) for the diameter factor (Table 1), a homogeneous group was formed for the narrow diameter spears (9–11 mm and 11–14 mm), and the spears with a diameter of 14–19 mm formed another homogeneous group in which the highest nickel concentrations were determined. The > 19 mm diameter spears were included in an intermediate group between the other two groups. The effect of the processing on each diameter, although signifying various changes, did not cause any significant modifications in the nickel content in any of the diameters considered (Fig. 3(B)). However, the narrowest diameters were those that displayed most changes in the course of the various industrial processing operations. The influence of the spear diameter on the mineral composition of the asparagus did not correlate with any established model, but it signified variable alterations in mineral content as a function of the element and the diameter studied (Zurera-Cosano & Moreno-Rojas, 1990; Zurera-Cosano *et al.*, 1990; Moreno *et al.*, 1992; Amaro-López *et al.*, 1995a,b).

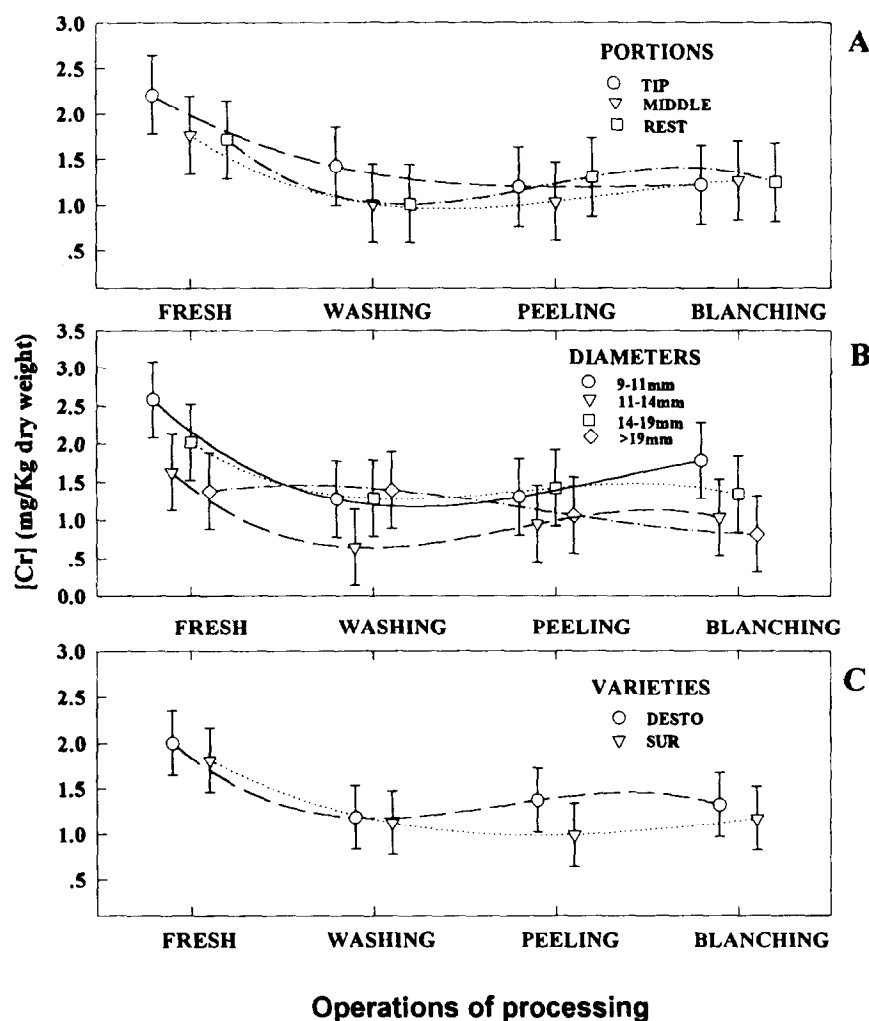


Fig. 2. Evolution of chromium content during processing of white asparagus, according to portion (A), diameter (B) and variety (C).

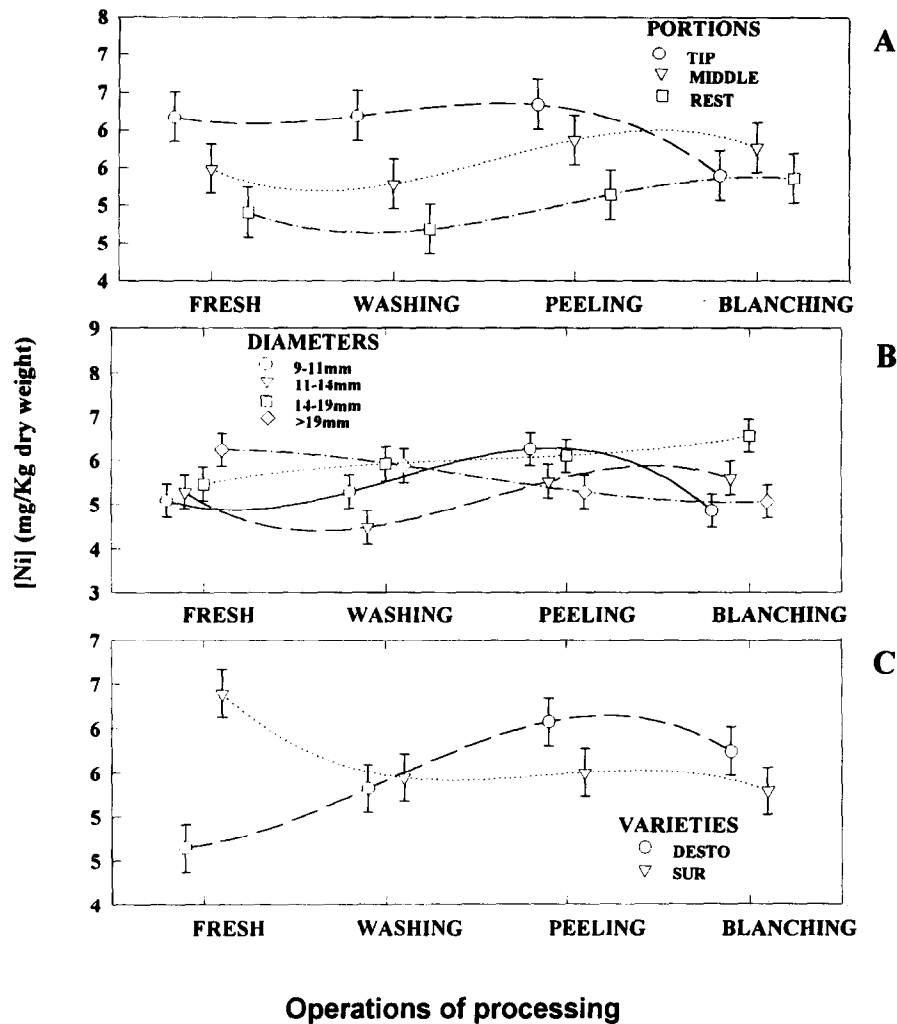


Fig. 3. Evolution of nickel content during processing of white asparagus, according to portion (A), diameter (B) and variety (C).

As occurred with the portions, the processing had a depressant effect on the initial differences in the nickel concentration between the asparagus varieties 'Desto' and 'Sur', since these differences became minimized during the washing operation (Fig. 3(C)) when the nickel contents in the two varieties became equal and subsequently had a very similar evolution.

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