

## Effects of Raw Materials, Ingredients, and Production Lines on Arsenic and Copper Concentrations in Confectionery Products

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The Spaniard legislation sets up maximum levels for total arsenic (As) and copper (Cu) in confectionery products at 0.1 and 5.0  $\mu\text{g g}^{-1}$ , respectively. Concentrations of these two trace elements were determined in four confectionery products: chewing gum, two licorice items, and soft candy. The effects of raw materials quality and production lines were studied. Arsenic and copper were quantified by atomic absorption spectrometry with hydride generation and slotted-tube atom trap tubes, respectively. Their levels were, in general, below the maximum limits establish by the Spaniard legislation; however, the As concentration in the licorice sticks was above this maximum limit ( $0.11 \pm 0.01 \mu\text{g g}^{-1}$ ). Statistics proved that quality of raw materials and the production lines both significantly affected As and Cu concentrations in the final products. The licorice extract and molasses were found as the common source for As and Cu pollution. The As concentration in the licorice extract was  $0.503 \pm 0.01 \mu\text{g g}^{-1}$ , and could represent a serious hazard to human health if it is used in high proportions.

**KEYWORDS:** Chewing gum; food contaminants; heavy metals; licorice; metalloids; soft candy stick; trace elements

### INTRODUCTION

The consumption of confectionery products has grown tremendously in the last two decades, especially in children and teenagers. For instance, the per capita confectionery consumption in 1997 in the U.S. was 26.7 lb (*1*). Candy currently is being retargeted as a functional food (*2*); however, in addition to beneficial properties (inclusion of functional ingredients such as vitamins, minerals, herbal remedies, etc.; and elaboration of healthy snack foods and confectionery bars), when consumed in excessive amounts, these products may be potential health hazards, for example dental cavities (*3*) and high intake of metals (*4, 5*). For this reason, potentially toxic elements in confectionery products should be documented, and allowable concentrations of essential and toxic elements should be ensured.

There are three groups of mineral elements of interest to food technologists and scientists, and nutritionists (*6*): those essential in the diets of humans (Cu, Ca, Fe, K, Mg, etc.); those essential to one or more species and plants but not currently known to be essential for humans (As, Cd, Ni, Sn, etc.); and those known only for their toxicity or therapeutic use (Al, Ba, Hg). It should be stated that “everything is toxic, only the dose makes something not toxic”. The boundary separating essentiality of an element from toxicity depends on the concentration of the

element and its quantity of dietary intake. Therefore, the ability of trace elements to cause harmful effects, both through deficiency and through excess, separates them from other known toxicants in foods and highlights the importance of the danger they present to food safety.

Since 1973, As, Cu, Cd, Fe, Hg, Pb, Sn, and Zn have been considered to be potentially toxic in the human diet by the joint FAO/WHO Codex Alimentarius Commission; with As (as arsenite) being carcinogenic (*7*).

Trace elements can easily become a component of a foodstuff; this can happen through contact with the equipment or containers and wrapping materials used during processing (secondary contaminants), or by accompanying the chemical compounds used in agriculture and livestock farming (primary contaminants) (*8*).

If the origin of the toxic element is not known, it is impossible to recommend measures for reducing the content of potentially toxic elements that do not satisfy national legislation or are rejected by stricter legislative systems. This study could be considered as a typical example of the role of a food technologist working on the minimization of food contaminants. The priority of aims for these researchers are to (a) identify the nature, levels, properties, sources, and formation of toxic substances present in foods, and (b) give recommendations to manufacturers regarding the hazard points where pollutants are being introduced (raw materials, ingredients, or industrial processing) to minimize their inputs. After this point, food toxicologists must

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**Table 1.** Total Concentrations of Arsenic and Copper in Different Commercially Available Confectionery Products

product	arsenic ( $\mu\text{g g}^{-1}$ )	copper ( $\mu\text{g g}^{-1}$ )
licorice wheel	$0.04 \pm 0.01$ a <sup>a</sup>	$2.9 \pm 0.1$ b
licorice stick	$0.11 \pm 0.01$ b	$2.4 \pm 0.1$ b
strawberry chewing gum (1) <sup>b</sup>	$0.02 \pm 0.01$ a	$1.4 \pm 0.1$ a
strawberry chewing gum (2) <sup>b</sup>	$0.02 \pm 0.01$ a	$1.6 \pm 0.1$ a
cola chewing gum	$0.05 \pm 0.01$ a	$1.6 \pm 0.1$ a
orange soft candy stick	$0.04 \pm 0.01$ a	$2.1 \pm 0.2$ ab
strawberry soft candy stick	$0.05 \pm 0.01$ a	$2.5 \pm 0.1$ b
peach soft candy stick	$0.04 \pm 0.01$ a	$2.6 \pm 0.1$ b

<sup>a</sup> Data in this table are mean values of 12 replicates for each product; the  $\pm$  values indicate the standard error of the mean. In a column, values followed by the same letter are not significantly different ( $p < 0.001$ ), LSD–Fisher multiple range test. <sup>b</sup> Two different trademarks of strawberry chewing gum from the same company were studied.

try to understand the nature and magnitude of the danger the contaminants represent to humans and animals (7). Thus, the main objectives of this study were to (a) establish background levels of arsenic and copper in two licorice items (licorice wheels and licorice sticks), chewing gums, and soft candy sticks; (b) quantify the contribution of raw materials; and (c) study the effects of the industrial manufacture and the addition of essential and optional ingredients.

The Spaniard legislation (9) sets up maximum levels for only three elements, As, Cu, and Pb, in confectionery products. In this particular experiment, we have concentrated on the first two for the following reasons: (a) they are in our area of expertise, (b) the different nature of As (not essential for humans) and Cu (essential for humans), (c) the fact that more research has focused on lead toxicity compared to that of the other two elements (4, 5), and (d) the company supporting this study was concerned with As contents in several confectionery products. The maximum established concentrations for total As and Cu are 0.1 and 5.0  $\mu\text{g g}^{-1}$ , respectively. The products considered in this particular study were the main products manufactured by the company cooperating in this study.

The information provided by this study will assist confectionery manufacturers in reducing pollution of their final products through a better quality control of raw materials, ingredients, and production lines, and ensure their products meet the requirements of international legislation and consumer demands for quality and innocuousness.

## MATERIALS AND METHODS

**Experimental Design.** To have sufficient data for obtaining an appropriate statistical design, 12 replicates of each product were analyzed. All products were kindly provided by an anonymous confectionery company, which distributes to a wide market in Eastern Spain. Two licorice items (wheels and sticks), chewing gums, and soft candy sticks were the products selected for this study. The following raw materials were analyzed for licorice items: sugar, flour, molasses, licorice extract, isosweet syrup, caramel color, salt, and glucose syrup. For chewing gums and soft candy sticks we analyzed sugar, base gum, and glucose.

The raw materials provided by the confectionery company accounted for approximately 98% of the total content of the final products; the other 2% was constituted by colorants and flavors, which the company did not want to reveal for competitive reasons. The percentage in which each raw material is mixed in order to get the final product has been used to estimate the index contribution to the final content, CFC, and is shown in **Tables 2–5**.

**Reagents.** Deionized water, 18.2 M $\Omega$  cm, was used for the preparation of reagents and standards; this water quality was obtained

**Table 2.** Total Concentrations of Arsenic and Copper in the Raw Materials Used for the Elaboration of Licorice Wheels and the Proportion of Each Raw Material in the Final Product

product	proportion (%)	arsenic		copper	
		concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )
sugar	7.0	$0.02 \pm 0.01$ a <sup>b</sup>	<0.01	$1.2 \pm 0.2$ b	0.1
flour	31.4	$0.01 \pm 0.01$ a	<0.01	$2.9 \pm 0.2$ c	0.9
molasses	38.0	$0.08 \pm 0.01$ b	0.03	$4.7 \pm 0.2$ d	1.8
licorice extract	0.9	$0.50 \pm 0.01$ c	0.01	$2.7 \pm 0.3$ c	<0.1
isosweet syrup	6.8	$0.04 \pm 0.01$ a	<0.01	$0.5 \pm 0.1$ a	<0.1
caramel color	7.0	$0.03 \pm 0.01$ a	<0.01	$0.1 \pm 0.1$ a	<0.1
salt	0.3	$0.02 \pm 0.01$ a	<0.01	$0.2 \pm 0.1$ a	<0.1
glucose syrup	6.6	< $0.01 \pm 0.01$ a	<0.01	$0.3 \pm 0.1$ a	<0.1
total (theoretical)			0.04		2.9
total (experimental)			0.04		2.9

<sup>a</sup> Contribution to the final content, CFC ( $\mu\text{g g}^{-1}$  final product) = {[proportion (%)]/100}  $\times$  concentration ( $\mu\text{g g}^{-1}$  raw material). <sup>b</sup> Data in this table are mean values of 12 replicates for each product; the  $\pm$  values indicate the standard error of the mean. In a column, values followed by the same letter are not significantly different ( $p < 0.001$ ), LSD–Fisher multiple range test.

**Table 3.** Total Concentrations of Arsenic and Copper in the Raw Materials Used for the Elaboration of Licorice Sticks and the Proportion of Each Raw Material in the Final Product

product	proportion (%)	arsenic		copper	
		concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )
sugar	5.0	$0.03 \pm 0.01$ a <sup>b</sup>	<0.01	$1.4 \pm 0.1$ c	0.1
flour	40.0	$0.02 \pm 0.01$ a	0.01	$1.3 \pm 0.1$ c	0.5
molasses	44.0	$0.07 \pm 0.01$ b	0.03	$3.6 \pm 0.2$ e	1.6
licorice extract	1.0	$0.50 \pm 0.01$ c	0.01	$2.7 \pm 0.3$ d	<0.1
isosweet syrup	2.5	$0.04 \pm 0.01$ a	<0.01	$0.5 \pm 0.1$ b	<0.1
caramel color	2.6	$0.03 \pm 0.01$ a	<0.01	$0.1 \pm 0.1$ a	<0.1
salt	0.4	$0.02 \pm 0.01$ a	<0.01	$0.2 \pm 0.1$ a	<0.1
glucose syrup	2.5	< $0.01 \pm 0.01$ a	<0.01	$0.3 \pm 0.1$ ab	<0.1
total (theoretical)			0.05		2.2
total (experimental)			0.11		2.4

<sup>a</sup> Contribution to the final content, CFC ( $\mu\text{g g}^{-1}$  final product) = {[proportion (%)]/100}  $\times$  concentration ( $\mu\text{g g}^{-1}$  raw material). <sup>b</sup> Data in this table are mean values of 12 replicates for each product; the  $\pm$  values indicate the standard error of the mean. In a column, values followed by the same letter are not significantly different ( $p < 0.001$ ), LSD–Fisher multiple range test.

**Table 4.** Total Concentrations of Arsenic and Copper in the Raw Materials Used for the Elaboration of Chewing Gums and the Proportion of Each Raw Material in the Final Product

product	proportion (%)	arsenic		copper	
		concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )
sugar	32	$0.07 \pm 0.01$ b <sup>b</sup>	0.02	$1.3 \pm 0.1$ a	0.4
base gum	33	$0.05 \pm 0.01$ ab	0.01	$1.1 \pm 0.1$ a	0.4
glucose	33	$0.03 \pm 0.01$ a	0.01	$2.4 \pm 0.2$ b	0.8
total (theoretical)			0.04		1.6
total (experimental)			0.03		1.5

<sup>a</sup> Contribution to the final content, CFC ( $\mu\text{g g}^{-1}$  final product) = {[proportion (%)]/100}  $\times$  concentration ( $\mu\text{g g}^{-1}$  raw material). <sup>b</sup> Data in this table are mean values of 12 replicates for each product; the  $\pm$  values indicate the standard error of the mean. In a column, values followed by the same letter are not significantly different ( $p < 0.001$ ), LSD–Fisher multiple range test.

by filtering distilled water through a Milli-Q purifier (Millipore, Gif-sur-Yvette, France). All chemicals were of pro analysi quality or better. Standard solutions of pentavalent arsenic ( $1000 \pm 2$  mg L<sup>-1</sup>) and copper ( $1000 \pm 2$  mg L<sup>-1</sup>) were prepared by dilution of Titrisol standards

**Table 5.** Total Concentrations of Arsenic and Copper in the Raw Materials Used for the Elaboration of Soft Candy Sticks and the Proportion of Each Raw Material in the Final Product

product	proportion (%)	arsenic		copper	
		concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )	concentration ( $\mu\text{g g}^{-1}$ )	CFC <sup>a</sup> ( $\mu\text{g g}^{-1}$ )
sugar	16.0	$0.07 \pm 0.01$ b <sup>b</sup>	0.01	$1.3 \pm 0.1$ a	0.2
base gum	16.3	$0.05 \pm 0.01$ ab	0.01	$1.1 \pm 0.1$ a	0.2
glucose	16.7	$0.03 \pm 0.01$ a	<0.01	$2.4 \pm 0.2$ b	0.4
chewing gum	49.0	$0.04 \pm 0.01$ a	0.02	$1.3 \pm 0.1$ a	0.6
total (theoretical)			0.04		1.4
total (experimental)			0.05		2.6

<sup>a</sup> Contribution to the final content, CFC ( $\mu\text{g g}^{-1}$  final product) = {[proportion (%)]/100}  $\times$  concentration ( $\mu\text{g g}^{-1}$  raw material). <sup>b</sup> Data in this table are mean values of 12 replicates for each product; the  $\pm$  values indicate the standard error of the mean. In a column, values followed by the same letter are not significantly different ( $p < 0.001$ ), LSD–Fisher multiple range test.

(Merck, Darmstadt, Germany). Potassium iodide, sodium borohydride, sodium hydroxide, nitric acid, and hydrochloric acid were all from Panreac.

All glassware was treated with 10% v/v  $\text{HNO}_3$  for 24 h, and then rinsed three times with deionized water before being used.

**Sample Digestion.** A multi-place digestion block, Selecta Block Digest 20 (Barcelona, Spain), was used for sample mineralization. Candy samples were frozen with liquid nitrogen and then homogenized by using a meat grinder. A 0.250-g portion of homogenized sample was treated with 5 mL of 65% (w/v)  $\text{HNO}_3$  in Pyrex tubes, placed in the digestion block, and heated at 60 °C for 60 min and at 130 °C for 120 min (10). A maximum temperature below 140 °C was set up in order to avoid arsenic volatilization (11). Solutions were left to cool to room temperature, transferred to a volumetric flask, and diluted to a final volume of 25 mL with ultrahigh-purity deionized water.

**Total Arsenic and Copper Analyses.** *Arsenic.* Determination of total arsenic in previously acid-mineralized samples was performed with a Unicam Solaar 969 atomic absorption spectrometer equipped with a continuous hydride generator (Unicam Solaar VP90).

A mixture containing 5% m/v KI and 5% m/v ascorbic acid was employed as a prereducing solution for all the samples before the quantification of total arsenic. The  $\text{NaBH}_4$  was prepared daily and filtered through Whatman no. 42 paper.

The instrumental conditions used for arsenic determination by HGAAS were as follows: reducing agent, 1.0% (m/v)  $\text{NaBH}_4$  in 0.1%  $\text{NaOH}$ , 5 mL  $\text{min}^{-1}$ ; HCl solution, 10% (v/v), 10 mL  $\text{min}^{-1}$ ; carrier gas, argon, 250 mL  $\text{min}^{-1}$  flow rate; and for atomic absorption spectrometry, wavelength 193.7 nm; spectral band-pass 0.5 nm; hollow cathode lamp current setting 8 mA; and air/acetylene flame with a fuel flow rate of 0.8 L  $\text{min}^{-1}$ .

The detection limit of this method was 0.25  $\mu\text{g L}^{-1}$ . The detection limit was translated into the limit of quantification (LOQ, smallest arsenic concentration in the original specimen that could be measured) based on the amount of sample taken for digestion and other procedural data, such as dilutions made. The LOQ value for arsenic was 8  $\mu\text{g kg}^{-1}$ .

*Copper.* Determination of total copper in previously acid-mineralized samples was performed with a Unicam Solaar 969 atomic absorption spectrometer equipped with slotted-tube atom trap (STAT) tubes. These tubes allow for a longer interaction between the light ray from the hollow cathode lamp and the copper atoms, which results in a lower detection limit and a better sensitivity of the technique.

The instrumental conditions used for copper determination by AAS were as follows: wavelength, 324.8 nm; spectral band-pass, 0.5 nm; hollow cathode lamp current setting, 7.5 mA; air/acetylene flame with a fuel flow rate of 1.1 L  $\text{min}^{-1}$ .

The detection limit and LOQ of this method were 10  $\mu\text{g L}^{-1}$  and 0.25 mg  $\text{kg}^{-1}$ , respectively.

**Analytical Quality Control.** All instruments were calibrated using matrix-matched standards. In each analytical batch, at least two reagent blanks, one internationally certified reference material (CRM) and one

spike were included to assess precision and accuracy for chemical analysis. The certified materials selected for the current experiment were GBW07603 (bush, branches and leaves) and SRM1548a (typical diet: proximates and trace elements), which have certified values for arsenic of 1.25  $\mu\text{g g}^{-1}$  and 0.20  $\mu\text{g g}^{-1}$ , and for copper 6.6  $\mu\text{g g}^{-1}$  and 2.32  $\mu\text{g g}^{-1}$ , respectively. These certified reference materials were provided by LGC Deselaers S. L. (Barcelona, Spain) and produced by the Institute of Geophysical and Geochemical Exploration of China (GBW07603) and the U.S. National Institute of Standards and Technology (SRM1548a).

## RESULTS AND DISCUSSION

**Analytical Quality Control.** Quality control data for analysis of As were quite good. The mean recoveries for the arsenic present in the reference materials GBW07603 and SRM1548a were 92.0%  $\pm$  1.8% ( $n = 10$ ) and 90.1%  $\pm$  2.0% ( $n = 10$ ), respectively. The spikes recoveries were 95.6%  $\pm$  1.1% ( $n = 10$ , 5 for GBW07603 and 5 for SRM1548a) and 96.8%  $\pm$  1.7% ( $n = 10$ , 5 for GBW07603 and 5 for SRM1548a), for arsenite and arsenate, respectively. These spike recoveries were carried out using both reference materials because of the different nature of the samples analyzed. Some of the candy samples were also analyzed by a different analytical technique: dry ashing in a muffle furnace with addition of ashing aid suspension 20% (w/v)  $\text{Mg}(\text{NO}_3)_2$  and 2% (w/v)  $\text{MgO}$  (12) and the results were consistent with those previously reported; the mean recovery for the reference materials was 95.8%  $\pm$  1.3 ( $n = 6$ , 3 for GBW07603 and 3 for SRM1548a). No problem at all was experienced with the recovery of copper from the reference materials studied and spikes, with recovery values of 99.3%  $\pm$  0.7 ( $n = 20$ ) for reference materials and 98.7%  $\pm$  1.2 ( $n = 20$ ) for spikes.

**Confectionery Products and Production Lines.** Finely-ground calcium carbonate and talc are used as optional ingredients in confectionery products such as chewing gums. Because these minerals can be contaminated naturally with arsenic, as suggested by the candy company cooperating in this study, the total content of this metalloid should be quantified in manufactured products. Sometimes, improper use of the equipment or the use of undesirable metals in parts of it may cause contamination in the foods being elaborated. For instance, metallic and ceramic vessels and utensils may give off Cu, Cd, Cr, Sn, Pb, Fe, and Al (7). For all of the above factors, among others, the Spanish legislation (9) sets up maximum levels for total As and Cu in confectionery products at 0.1 and 5.0  $\mu\text{g g}^{-1}$ , respectively. However, no such limits exist for raw materials or essential or optional ingredients.

The arsenic concentrations in the products studied ranged from  $0.02 \pm 0.01 \mu\text{g g}^{-1}$ , in strawberry chewing gums (mean value of 12 replicates  $\pm$  standard error of the mean), up to  $0.11 \pm 0.01 \mu\text{g g}^{-1}$ , in licorice sticks. In this way, licorice sticks were the only candy with an “illegal” arsenic content, independently of its health hazard; its arsenic content was 10% greater than the maximum limit established by the Spaniard legislation. However, to evaluate the risk that consumption of licorice sticks entails to human health, it is necessary to know their contribution to the total intake of this metalloid. No problem at all was detected in relation to the copper content in the manufactured products studied and its content ranged from  $1.4 \pm 0.1 \mu\text{g g}^{-1}$  (strawberry chewing gums) to  $2.9 \pm 0.1 \mu\text{g g}^{-1}$  (licorice wheels).

Applying the Cochran–Bartlett test to check the statistical normality of the individual data of arsenic or copper (in the final products, Table 1, and raw materials, Tables 2–5), it was found that the data did not fit a normal distribution. Hence, the

Kruskal–Wallis test was selected, and it indicated that statistically significant differences at  $p < 0.001$  existed among the means of As and Cu contents in the confectionery products groups. These statistical analyses indicated that both the raw materials and the industrial processing were having a significant effect on the concentrations of As and Cu in the final products. Similar results were obtained when the LSD–Fisher and the Bonferroni multiple range tests were used.

The next step in this study is to quantify the contribution of the industrial processing and quality of raw materials and ingredients to the final concentrations of the two chemical elements studied, especially in the products where high arsenic or copper contents were detected.

**Licorice Wheels and Sticks.** Trace elements can easily become components of a foodstuff. This can happen through contact with the equipment or containers used during processing, or by accompanying the chemical compounds used in agriculture and livestock farming (such as the use of arsenical fungicides, herbicides, etc.). A clear example of the effect of chemical compounds used in agriculture on food pollution is illustrated in **Tables 2** and **3**. The licorice extract used in the preparation of licorice wheels and sticks had the highest arsenic concentration,  $0.50 \pm 0.01 \mu\text{g g}^{-1}$ , of all the raw materials studied.

Uptake of As by plants depends on many factors, including plant species and As concentration in the soil solution (13–15). Upon As absorption, usually plants accumulate As mainly in the root system, with intermediate levels found in the vegetative tops, and the lowest residues being found in fruits and edible seeds (13–15). Therefore, the As pollution found in the licorice extract is not surprising because the licorice extract is produced after extracting the roots of the licorice plant. However, this situation does not imply that all the extracts obtained from roots necessarily present high concentrations of As, only those from plants grown on polluted soils.

The effect of the industrial processing on the concentrations of trace elements in the manufactured products is visible in **Tables 2** and **3**. The same raw materials and ingredients are used in the preparation of licorice wheels and sticks, although they are mixed in slightly different proportions. However, the total arsenic concentration in the final products is significantly different: this concentration was well below the statutory maximum ( $0.10 \mu\text{g g}^{-1}$ ) in licorice wheels,  $0.04 \pm 0.01 \mu\text{g g}^{-1}$ , and above this maximum limit in licorice sticks,  $0.11 \pm 0.01 \mu\text{g g}^{-1}$ .

The amounts of an element that should be found in the manufactured products according to the concentrations found in the raw materials and the proportion of each raw material in the final product (contribution to the final content, CFC) are included in **Tables 2–5**. According to these data, it can be observed that the contribution from the manufacturing process (difference between the arsenic and copper concentrations experimentally found and their concentrations assuming no additional contamination took place during the production) of the licorice sticks to the final total arsenic concentration is significant, implying a nondefined source for arsenic pollution in this production line.

However, from the data of this particular study it is impossible to recommend modifications of the manufacture process because the candy company provided only samples from the very beginning and end of the production lines. Now that it is known that there is some pollution being generated through the processing of the licorice sticks, samples from each of the

processing steps should be taken and individually studied in order to isolate the hazard point or points responsible for the pollution.

Besides, this difference could also be due, at least in part, to pollution caused by the 2% of raw materials not analyzed in this experiment.

On the other hand, it must be pointed out that studying the individual total concentrations of trace elements could be distracting because in some cases the raw materials or ingredients with the highest levels of As or Cu are mixed in the lowest proportion. Therefore, and considering the values of the index CFC, which combines the concentration of the trace elements in each raw material and the mixing proportion of the raw materials, the molasses is the main raw material to control in both licorice items and for both arsenic and copper (**Tables 2** and **3**).

Copper concentrations in the two licorice items and their raw materials were significantly below the statutory maximum for copper in confectionery products,  $5.0 \mu\text{g g}^{-1}$ . The only raw material with copper concentrations close to this limit was molasses. Also, no significant effect of the processing method was observed for these two licorice products; the amounts of copper that should be found in the final product, assuming no additional contamination occurred during the manufacture, agreed quite well with the experimentally found concentrations (**Tables 2** and **3**).

**Chewing Gum and Soft Candy Stick.** Concentrations of arsenic and copper in the manufactured products, chewing gums and soft candy sticks of different flavors, and in the raw materials studied were always below the statutory limits set by the Spaniard legislation for the content of arsenic and copper in confectionery products (**Tables 4** and **5**).

When considering the index CFC, the sugar appears to be the raw material with the highest contribution to the arsenic pollution; however, the glucose seems to be the main source of copper in both types of candies.

The amount of copper that theoretically should be present in the final soft candy sticks, according to the concentrations found in the raw materials and the proportion of each raw material in the final product, was significantly lower than the experimental one. This difference implied that some extra pollution occurred that was due to the production line or to the 2% of raw materials not analyzed in this experiment.

The differential effect due to the optional ingredients on the final concentrations of arsenic was only visible in the case of chewing gums (**Table 1**). Arsenic concentrations in strawberry and cola chewing gums were  $0.02 \pm 0.01$  and  $0.05 \pm 0.01 \mu\text{g g}^{-1}$ , respectively. Therefore, it seems that optional ingredients added to this product to provide the cola taste and aroma were, at least in part, responsible for the increase in the arsenic concentration compared to that of the strawberry chewing gum.

## CONCLUSIONS

The first objective achieved in this study was the development of precise, accurate, sensitive, fast, and automated methodologies for the simultaneous detection and quantification of total contents of arsenic (volatile element) and copper (nonvolatile element) in confectionery products and their raw materials and ingredients. Atomic absorption spectrometry with the help of hydride generation and STAT tubes for arsenic and copper, respectively, provided analytical data of reliable quality in widely consumed confectionery products.

After quantifying the contribution of the different raw materials and ingredients, our recommendations are to strictly

control the quality of the licorice extract (the raw material with the highest concentration of As) and molasses (the raw material with the highest proportion in the final product) because these raw materials seem to be the main sources for arsenic and copper pollution.

A more detailed study dealing with the licorice sticks production line is required because some arsenic input is occurring but could not be localized in this study (no intermediate samples were analyzed).

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