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# Variation of Heavy Metal Contents in Frozen Vegetable Products

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Lead, cadmium, arsenic and mercury known as toxic minerals cause environmental pollution and their concentrations increase in time because of accumulation. If agricultural areas are close to large towns and to industrial areas agricultural products are affected by waste water irrigation or re-implementation of plant sanitation products.

In recent years, consumers have considered frozen vegetables among the most preferable products because they are easy and quick to prepare since they are semi-processed. The frozen foodstuff sector in Turkey, which has a history of 20-25 years, exports about 80% of its production. The potentiality of this sector has led to an increase in investments, and foreign investors have started to invest in this field (Anonymous 1997a; Babadogan 1998). In Turkey, fresh vegetable production is countrywide, and due to the potential increase in the frozen food sector, a system of "produce by contract" has started to gain importance. The fact that there is a probable contamination of vegetables with toxic heavy metals and that there is an absence of a related study in Turkey has necessitated a research in this field. Consequently, the aim of this study has been to determine the contents of lead, cadmium, arsenic and mercury in frozen foodstuff such as green beans, spinach and potatoes, which have a great potential for export and consumption in Turkey.

## MATERIAL AND METHODS

Green beans, spinach and potatoes provided randomly from a company producing frozen fruits and vegetables in Turkey, were used as frozen material in this study. The contents of the sample packages were homogenized in a blender with stainless steel blade without defrosting them in a polyethylene container and were analyzed immediately after weighing them.

All equipment used for sample processing and storage were cleaned thoroughly (prepared for the analyses by washing) (Jorhem 1993), and were tested for contamination by leaching them with 5% Nitric acid (Merck).

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The digestion processes were carried out using a model MLS-1200 Mega microwave unit (Milestone) and its accessories (Nöltner et al. 1990; Lautenschlaeger and Dorfer, 1992; Gawalko et al., 1997). A solution of 65 % nitric acid and 35 % hydrogen peroxide (Merck) was used for digestion. The digested samples were diluted with ultra distilled water (Milipore, Model Milli Q Plus 185) to 25 ml, and then transferred to polypropylene containers, and were stored at +8$^{o}$C until the end of the analyses.

The methods based on the Graphite Furnace Atomic Absorption Spectrometer (AAS), the Hydride Generation Technique, and the Cold Vapour Formation Technique were used for the determination of lead and cadmium (Jorhem 1993; Demirözü-Erdinç 1998); of arsenic (Hinners 1980; Hershey and Keliher 1989-90; Demirözü-Erdinç 1998); and of mercury contents (Anonymous 1987) of the samples. The Perkin-Elmer HGA-400 furnace system and the Perkin-Elmer AS 40 autosampler, combined with the Perkin-Elmer 1100 AAS; the UNICAM VP 90 hydride system combined with the ATI-UNICAM 929 AAS; and the Perkin-Elmer MHS 20 mercury/hydride system combined with the Perkin-Elmer 1100 AAS were used for this purpose, respectively.

Measurements were taken with slitwidths of 0.7, 0.7, 1.0 and 0.7 nm, at the wavelengths of 283.3, 228.8, 193.7 and 253.6 nm, using lead, cadmium, arsenic, and mercury hollow cathode lamps, respectively. Continuum Lamp Background Correction Technique was applied throughout the study and Deuterium ($D_2$) arc lamp was used for the measurements. An automatic sampler, operating in combination with the AAS devices, performed the injection of lead and cadmium samples. The standard addition method, which minimises the interference effect, was used for arsenic and mercury measurements. In arsenic and mercury determination, three solutions were prepared for each sample, and a total of six readings were taken so as to supply two readings for each solution. In lead and cadmium determination, three separate readings were performed for each sample, and the average of these figures was used for calculations of concentration. The detection limit (DL) for each metal was calculated as three times the mean value of blank determinations. At the end of the calculations the DL for lead, cadmium, arsenic and mercury were found to be 0.21, 0.02, 0.05 and 0.006 ng/g, respectively. The generalized randomized block design system was used during the statistical evaluation of the results, by using the package program of the SAS 6.12. In addition, the *Tukey* Multi-Comparision test was applied to determine any differences or similarities between products (Hinkelmann and Kempthorne 1994).

## RESULTS AND DISCUSSION

In this study, the frozen vegetables, green beans, spinach, and potatoes were analyzed for their lead, cadmium, arsenic and mercury contents. But no amount of mercury was detected in the samples.

The lead, cadmium and arsenic contents of frozen vegetables are given in Table 1.

**Table 1.** The lead, cadmium and arsenic contents of all samples (ng/g-wet weight)

| Element | Number of Treatment | Green bean | Spinach | Potato |
|---|---|---|---|---|
| Pb | 1 | 12.32±2.39 | 73.82±12.02 | 13.19±1.16 |
| | 2 | 17.47±0.66 | 33.61±5.32 | 10.10±0.26 |
| | 3 | 13.48±0.64 | 56.61±0.54 | 9.08±0.14 |
| | 4 | 11.19±0.24 | 68.05±2.75 | 10.77±0.86 |
| | 5 | 12.31±0.39 | 67.47±28.05 | 12.10±0.16 |
| | Average | 13.35±2.46 | 59.91±18.28 | 11.05±1.61 |
| Cd | 1 | 4.57±1.46 | 31.49±1.24 | 32.43±3.70 |
| | 2 | 4.39±0.31 | 18.58±0.78 | 29.72±0.76 |
| | 3 | 2.22±0.67 | 24.13±1.55 | 20.05±0.10 |
| | 4 | 1.63±0.29 | 44.77±3.92 | 22.24±2.09 |
| | 5 | 2.36±0.30 | 39.33±1.535 | 25.70±0.60 |
| | Average | 3.36±1.39 | 31.66±10.21 | 26.03±5.04 |
| As | 1 | 60.45±0.77 | 52.88±0.32 | 69.03±0.78 |
| | 2 | 58.59±0.16 | 65.93±0.52 | 87.34±0.25 |
| | 3 | 71.35±1.47 | 62.49±3.39 | 70.35±0.71 |
| | 4 | 53.70±7.08 | 56.24±0.69 | 80.76±2.30 |
| | 5 | 73.97±2.34 | 68.77±0.33 | 97.75±0.35 |
| | Average | 63.61±8.56 | 61.26±6.35 | 81.05±11.36 |

As shown in the table, the lead contents were found to be between 11.19 and 17.47 ng/g for green bean, 33.61 and 73.82 ng/g for spinach and 9.08 and 13.19 ng/g for potato samples. The potato samples had the least lead content while it was higher in green beans, and the spinach samples contained the highest amount of lead.

It has been reported that green vegetables are among the substantial sources of lead although all nutritional foodstuff has a particular lead content (Anonymous 1994, 1995). Determination of the highest lead content in spinach among the other examined frozen vegetables has accorded with this finding. Another study states that the most common source of lead causing lead contamination in vegetable products is the lead contained in gasoline. Hence, the machinery and equipment as well as the packaging materials used in food industry also play an important role in lead contamination (Anonymous 1994, 1995). Yet, in industry, no significant change in product structure is in question during freezing process. The machinery and equipment used during the process are made with stainless steel material. Therefore, the results obtained reflect that the lead contents are caused by the raw materials rather than the contamination during process. The raw materials used in the frozen fruit and vegetable industry are provided from the local market and such factors as the distance from the production points to the motorways, the quality of irrigation water used, and the type of fertilizers affect the amount of lead contamination. Moreover, it may not be possible to homogenize the entire product (depending on the technology applied during the process) therefore results can vary even among different packages of the same lot. However the results obtained from our experiments with green bean and potato samples were quite similar, while the results obtained from experiments with spinach samples varied considerably. It is estimated that this variation may have originated from the reasons stated above. Apart from these, spinach is a hard-to-clean vegetable, whose leaves can fail to be cleaned thoroughly, and may still contain some trace of soil despite the washing process.

The statistical evaluation shows that the variation in the results is insignificant ($p>0.05$). Besides this, the results obtained from the green bean and potato samples were further verified by the *Tukey* Multi-Comparison test, and found to be similar.

Numerous studies have been carried out to determine the lead contents in green vegetables consumed. The lead contents have been found as 9 ng/g in potatoes in the U.S.A. (Wolnik et al. 1983), and 7.8-21.9 ng/g and 13.3-34.3 ng/g in potatoes and green beans, in Canada (Dabeca and McKenzie 1992), while it was 48 ng/g and 209 ng/g in potatoes and green beans in Spain (Cabrera et al 1994), respectively. When the above values are compared with those obtained from the frozen vegetables, the results (9.08-13.19 ng/g and 11.19-17.47 ng/g) obtained from potatoes and green beans were lower than those obtained in Spain, and were similar to those in the USA and Canada, respectively. The lead contents in frozen spinach (33.61-73.82 ng/g) was higher than that in Japan (<0.05ng/g in all samples)(Anonymous 1997b), but were analogous (56ng/g) to that in Spain (Anonymous 1997c).

The cadmium intake takes place primarily via respiration but the foodstuffs consumed have also a considerable role. Thus vegetables are among particularly important sources of cadmium (Dunnic and Fowler 1988; Robards and Worsfold 1991). It has been also reported that vegetables with leaves such as spinach and lettuce contain more cadmium than root vegetables such as potatoes and onions (Anonymous 1994). The results obtained from fifty experimental samples were consistent with this report and the values of the spinach and potato samples in other experiments were close to each other (Table 1).
As a result of this study it has been determined that the spinach and potato samples were the groups having a higher level of cadmium than green bean

samples. In addition, it was observed that each group contained different contents of cadmium. This was verified by the *Tukey* Multi-Comparasion Test.

The statistical evaluation shows that these variations between experiments were significant ($p<0.05$), which may be due to the raw material obtained from different areas and improper homogenization.

It has been reported that the pH of the soil and the fertilizer used play a substantial role in cadmium contamination of vegetable products (Merian 1990; Robards and Worsfold 1991; Jones 1993). During spinach and potato cultivation, soil contact is more than that in the cultivation of green beans. In addition, the fertilizers containing phosphate are commonly used in this type of vegetable agriculture, and as stated in literature, these fertilizers are rich in cadmium (Robards and Worsfold 1991; Cabrera et al. 1992; Gavi et al. 1997). These factors may well be the reason for the higher cadmium content in spinach and potato samples in comparison with green bean samples.

The cadmium contents obtained from the frozen green bean samples (1.63-4.57 ng/g) were nearly the same as those in fresh green beans in Canada (1.90-4.01 ng/g), but were much higher than those in Spain (average 0.235 ng/g) (Dabeca and McKenzie 1992;Cabrera et al. 1992). The cadmium content obtained from the frozen potato samples (20.05-32.43 ng/g), on the other hand, were higher than those in fresh potatoes obtained by Wolnik et al. (1983) and Cabrera et al. (1994) (average 3 ng/g and 0.18 ng/g, respectively). The values obtained from the frozen spinach samples (18.58-44.77 ng/g) were higher than those found in Japan (<50 ng/g in all samples)(Anonymous 1997b).

As can be seen in Table 1, the arsenic contents of all frozen vegetable samples were determined to be between 52.88 to 97.75 ng/g. In the packages analyzed in the same experiment for each product group, the values of cadmium content in general were determined to be close to each other while each experiment with the sample group gave different results from the others. The statistical evaluation of the results showed that this variation among experiments was quite significant ($p<0.05$). The results obtained from the green bean and spinach samples were close whereas those of the potato samples were different, as verified by the *Tukey* Multi-Comparison Tests.

It has been reported that the arsenic contents in plants are variable, depending on the type of plant, and on arsenic contamination in soil caused by the kind of irrigation water and fertilizer (Anonymous 1982; Arnold 1988).

The comparison of arsenic contents of frozen vegetables obtained in this study with those in the literature, i.e. arsenic contents of fresh vegetables in other countries, gave different results. They have been found as <0.1 to 11.0 ng/g in Canada, 78.0 to 167.0 ng/ and 59.0 to 73.0 ng/g in Spain for potatoes as and green beans, respectively (Navarro et al. 1992; Debeca et al. 1993). The values obtained in this study were higher than those in Canada but analogous to that in Spain.

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