

REDUCE CONTAMINATION WITH HEAVY METALS OF SPECIES BY VEGETABLE PROCESSING

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Abstract

Heavy metals are very stable chemical elements which do not thermally or chemically degrade, but according to their binding in the plant tissue may migrate.

The materials used in experiments, vegetable species taken from polluted and unpolluted areas, were subjected to the specific technological operations for obtaining products preserved both in glass jars and metallic cans.

The determination of the heavy metals content was performed by standardized mineralization methods, followed by the atomic absorption analysis (F-AAS, GF-AAS).

The research results have revealed the following aspects:

- phases of the technological process of treating horticultural products where the composition is altered in microelements, including heavy metals, are: cleaning, washing, breaking, infusion, sterilization.

- after the sterilization operation, some of the polluting substances, especially heavy metals contained in the solid phase, diffuse in the liquid phase (filling liquid).

Taking on account the toxic effects of heavy metals on the human body, in order to ensure the consumer's protection, it is recommended, in the case of using raw materials with a high content of heavy metals, not to use their coverage liquid from cans in the actual food preparing.

Keywords: heavy metals, vegetables, diffusion, technological operations

1. INTRODUCTION

The presence of heavy metals in vegetable and fruit products, with all the economic implications, regarding especially the health ones, is currently dealt with by the specialists in the area and the control authorities.

The use of raw materials in the industrialization process, fruit and vegetables contaminated with heavy metals, leads to obtaining products with a certain content of polluting elements.

The affinity for sulphur compounds and insolubility of formed compounds confer to heavy metals a cumulative character and determine their toxicity. Heavy metals are very stable chemical elements which do not thermally or chemically degrade, but according to their binding in the plant tissue they may migrate.

The presence of heavy metals in food products is the main area of interest for toxicologists. There are more than 20 heavy metals, but four of them have special influence upon human

health: lead (Pb), cadmium (Cd), mercury (Hg) and inorganic combinations of arsenic (As) as well. These four heavy metals present four of the most important six risks existing in the sites of toxic waste material. They are extremely toxic and may cause damaging effects, even in very small concentrations. They have the tendency to get accumulated in the food chain and in the body and they may get accumulated in soft tissues (for example in kidneys) and hard ones (for example in bones).

Heavy metals are trace metals which have a density of at least five times higher than water. As such, they are stable elements (meaning they cannot be metabolized by the body) and *bio-accumulating* (they get into the human body by food chain).

These include: mercury, nickel, lead, arsenic, cadmium, aluminium.

Heavy metals get into body by inhalation, ingestion and skin absorption. If heavy metals enter and are stocked into the body tissues faster than the body detoxifying capacity, then

a gradual accumulation of these toxins takes place. It is not necessary for the body tissues to be exposed at high concentration to cause a toxicity state, but in time they may reach levels of toxic concentration.

The increase of heavy metals level has as effect:

- decrease of nitrogen monoxide level, a compound known under the name of “endothelial relaxing factor” in the walls of coronal arteries, without this substance the blood normal circulation is braked, increasing the risk of vascular blockage;
- reduction of hormones quantity produced by adrenal glands, leading to precocious ageing, the stress decreases sexual energy and aggravates the menopause symptoms;
- lack of any reaction of diabetics’ to medication;
- appearance of neurological diseases, such as depression and decrease of intellectual capacity;
- aggravation of osteoporosis and hypothyroidism.

From obvious reasons, the elimination of heavy metals from the body under safe conditions has been a real concern for doctors for many years.

The environment contamination and exposure to heavy metals such as mercury, cadmium and lead represent a serious problem which importance is getting greater and greater all over the world. Human body exposure to heavy metals has increased dramatically in the last 50 years, as a result of exponential increase of using heavy metals in industrial processing and products.

Some metals may be found naturally in the body and are essential for human health. Iron, for example, prevents anaemia, and zinc is a co participant in over 100 enzyme reactions. Magnesium and copper are other necessary metals which in very small quantities help the good functioning of metabolism. They normally occur in low concentrations and are known as trace metals; for example, a high level of zinc may lead to a copper deficit, which is another metal needed by the body.

Toxic effect seriousness depends on:

- nature, quantity and chemical form of the metal found in food product;
- share held by the contaminated product in environment;
- body strength;
- synergic or antagonic effect with other chemical contaminants.

An important characteristic which determines toxicity degree for the body is metals’ and metallic compounds’ solubility.

Their affinities for sulphur compounds, with which they form insoluble sulphides, confer to heavy metals a cumulative character and determine their toxicity.

Gastric juice, intestinal juice and blood contain salts, acids, bases, fats situation in which metallic compounds solubility may differ from solubility in water.

It has been underlined the existence of an important intensifying synergism between copper and zinc, copper and arsenic, copper and tin, arsenic and zinc as well as some antagonism between these elements and lead. It is considered that the effect of concomitant action depends on the administration dose and duration of substances. Thus, while small quantities of zinc and copper have synergic effects, in higher doses they act antagonically.

Polluting sources by heavy metals (Cu, Cd, Pb, Zn) of food products are numerous. Some of them are further presented [1].

Copper occurs in food products:

- as a result of phyto sanitary treatments by pesticides containing copper ;
- from corrosion processes of equipments made from copper or alloys;
- accidental sources.

Cadmium occurs in significant concentrations in food products as a result of:

- using residual water polluted by Cd for irrigation;
- using fertilizers containing Cd (super phosphate contains 15-21 µg Cd/kg);
- atmosphere (industrial areas, mining areas and non-ferrous metals processing areas);
- using containers, packages made from plastic materials having Cd salts as stabilizers or enamelled containers coloured by Cd-based pigments;

- accidental sources (releases of chemical substances containing Cd into air, water, soil)

Lead contamination sources of food products are:

- treatments by insecticides (fruit growing, viticulture);
- atmosphere (industrial areas, non-ferrous metal processing areas, intense traffic areas (tetraethyl lead from petrol);
- using lead or lead and tin- plated recipients and pipes ;
- accidental sources.

Food products may contain high quantities of zinc from the following sources:

- treatments by pesticides containing Zn;
- atmosphere (industrial areas, non-ferrous metal processing areas);
- pipes, recipients or tools made from plated tin;
- accidental sources.

Industrial processing of foods includes mechanical operations (sorting, cleaning, washing and breaking) and thermal ones (heating, infusion, pasteurization sterilization).

Potentially toxic metals (Pb, Cd, Zn, Cu) are very stable chemical elements which do not thermally or chemically degrade, but according to their binding in the plant tissue may migrate. Phases of the technological process of treating horticultural products where the composition is altered in microelements, including heavy metals are: cleaning, washing, barking, infusion, sterilization. [2].

During infusion, the diffusion of mineral elements of variable concentrations into the infusion medium takes place, as well as of heavy metals.

After sterilization by diffusion and solubility, mineral elements from vegetable tissue may be found in different proportions in the filling liquid of cans.

The factors influencing diffusion in this case [3]:

- division degree of vegetables and fruit;
- nature of mineral element (mobility, solubility in water);
- sterilization parameters (temperature, time);
- heat agent (water, steam).

2. MATERIALS AND METHODS

The researches were carried out in order to:

- establish the accumulation level of heavy metals (Pb, Cd, Zn, Cu) in the tissues of some vegetable species taken from industrially polluted areas;
- focus on how their content changes all along the processing operations (infusion, pasteurization, sterilization);
- study the possibilities by which fresh vegetable species with high content of heavy metals (exceeding LMA) should be used in the canning industry under conditions of full security for consumers.

Vegetable species largely used in preparing ranges of cans, either industrially or home made have been analyzed leafy vegetables (spinach, orach) for which the study of changes occurred in heavy metal content of these raw materials during the processing operations is opportune.

Experiments were made using more vegetable species, of which, two species were selected to be presented in this paper, spinach and orach. The vegetables were cropped from polluted and unpolluted areas in Romania. The vegetable species underwent technological operations specific to obtaining of preserved products: "Spinach leaves in water", "Orach leaves in water" according to product record.

The determining of heavy metal content (lead, cadmium, copper, and zinc) was achieved within the laboratories by atomic absorption spectrophotometry, using Aanalyst 400 flame absorption and Aanalyst 600 graphite furnace spectrophotometers from Perkin Elmer Company. The samples were mineralized by calcination at 450 – 500 °C and ash dissolving by diluted hydrochloric acid.

The content of heavy metals of the vegetable species used as raw materials in canning industry (carrots, parsnip, parsley, tomatoes, aubergines, cucumbers, green peppers, sweet peppers etc) is different depending on the areas where they are cultivated. It is noticed that raw materials taken from industrially polluted areas have a high content of heavy metals, most of the times registering exceeds of maximum

limits admitted by legislation in force. The distribution of heavy metals in different organs of vegetable species presents a special interest both for the study and understanding of absorption mechanism of heavy metals and assessment of vegetables' quality.

3. RESULTS AND DISCUSSION

Researches were carried out to determine the distribution of heavy metals in organs of a few vegetable species belonging to some different families of plants and identify the accumulation zone of heavy metals in the organs studied on.

Table 1. Average content of heavy metals in different organs in some vegetables

Crt. No.	Species	Organ	Content of heavy metals (mg/kg)			
			Cu	Cd	Pb	Zn
1	Spinach	root	3,18	0,13	1,08	6,17
		stem	3,62	0,14	1,48	8,94
		petiole	4,87	0,20	2,08	10,08
		“young” leaves	6,15	0,27	2,18	14,34
		“mature” leaves	7,90	0,41	3,22	17,85
2	Orach	root	2,87	0,10	1,00	6,56
		stem	3,08	0,11	1,58	9,10
		petiole	4,25	0,17	1,67	10,45
		“young” leaves	5,24	0,23	1,90	14,58
		“mature” leaves	7,64	0,35	3,10	17,80

One may notice that the highest accumulation level of the four metals is present in the leaves of the studied vegetable species. In the case of leafy vegetables the concentration of heavy metals is higher in “mature” leaves than in the “young” ones.

The accumulation level of heavy metals in diverse anatomic parts of these ones presents the following variation:

leaves > petiole > stem > root > fruit

In the case of spinach and orach, the concentration of heavy metals is 2,2 higher in leaves as compared to that in roots. Since in the case of these species, the leaves represent the comestible part a rigorous control of their content of heavy metals is compulsory needed. Table 2 show maximum admitted limits of heavy metals in fresh and processed vegetables

(Order no. 351/2007) (Commission Reg no. 1881/2006/CE) (Commission Reg. no. 333/2007/CE regarding testing and analyzing methods for the official control of inorganic Pb, Cd, Hg, Sn level in food products) [4].

Table 2. Maximum admitted limits of heavy metals in fresh and processed vegetables

Food	Content of heavy metals (mg/kg)			
	Cd	Pb	Zn	Cu
Fresh vegetables , excepting leaf vegetables	0,1	0,2	-	-
Leaf vegetables	0,2	0,3	-	-

In the case of spinach and orach we had in view the way in which the time and nature of the infusion medium influences the decrease of heavy metals quantity. The infusion time was of 2-6 minutes and water at the temperature of 85 – 90⁰C and a citric acid solution 2% (AC 2%), at the temperature 85 – 90⁰C were used as infusion media. The results obtained with regard to dried substance are shown in table 3.

Table 3. Decrease of heavy metals concentration in leafy vegetables during infusion operation

Species	Infusion time (min)	Infusion medium	Content of heavy metals (mg/kg s.u.)			
			Cu	Cd	Pb	Zn
Spinach	0	water	76,47	3,53	34,11	194,11
	2	water	69,12	3,25	29,06	184,90
	4	water	60,52	2,93	24,25	176,80
	6	water	54,50	2,78	21,20	170,50
	0	AC 2%	76,47	3,53	34,11	194,11
	2	AC 2%	66,55	3,17	27,10	182,65
	4	AC 2%	58,15	2,83	22,40	174,75
	6	AC 2%	51,75	2,60	20,65	167,80
	Orach	0	water	70,84	2,90	32,05
2		water	62,59	2,70	27,25	180,35
4		water	53,50	2,48	22,10	172,35
6		water	46,90	2,35	18,10	163,10
0		AC 2%	70,84	2,90	32,05	189,54
2		AC 2%	59,50	2,57	25,00	178,50
4		AC 2%	51,20	2,37	20,50	170,85
6		AC 2%	44,20	2,20	16,65	162,00

The concentrations of heavy metals in spinach and orach preserved by thermo sterilization are shown in table 4.

Table 4. Content of heavy metals in spinach and orach cans

Crt.No.	Product	Content of heavy metals (mg/kg)			
		Cu	Cd	Pb	Zn
1	Spinach leaves in water	2,34	0,1	0,86	7,24
2	Orach leaves in water	2,13	0,09	0,77	7,11

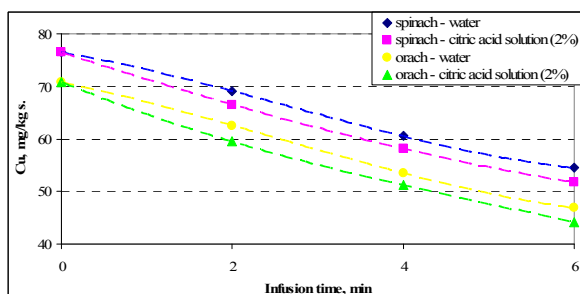


Figure 1. Leafy vegetables - Copper content vs. Infusion time

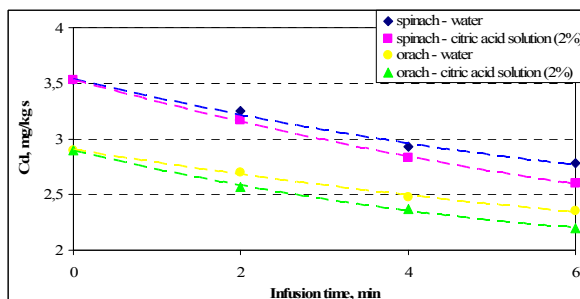


Figure 2. Leafy vegetables - Cadmium content vs. Infusion time

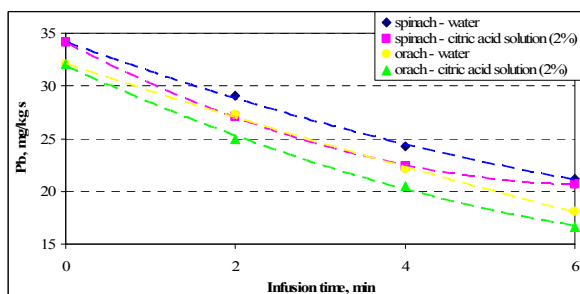


Figure 3. Leafy vegetables - Lead content vs. Infusion time

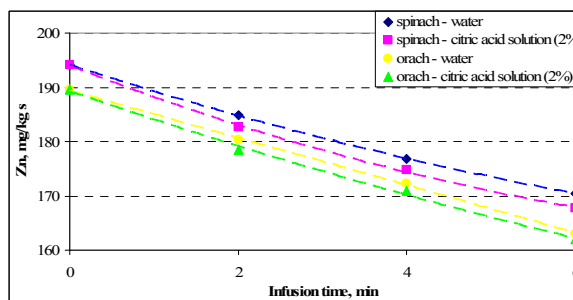


Figure 4. Leafy vegetables - Zinc content vs. Infusion time

From the data presented in table 4 and graphs of figures 1 - 4 it results that:

- the most significant decreases of concentrations of heavy metals occur when using citric acid solution 2% at the temperature of 85-90°C as infusion medium.
- in the case of orach the migration process of heavy metals to the infusion medium is more prominent as compared to spinach.
- when preserving leaf vegetables in recipients due to the filling liquid, the concentration of heavy metals decreases.
- also, after sterilization some of the polluting substances (heavy metals, nitrates), contained in the solid phase diffuse in the liquid phase (filling liquid)

One may notice from the results obtained that the two products subscribe to the maximum admitted limits regarding Cu, Cd and Zn content, the limit for Pb content being exceeded.

Although processing treatments determine decreases of the content of heavy metals, lead high concentration from the raw material used (of appreciatively 5 times higher than the maximum admitted value for fresh leafy vegetables) did not allow to obtain finished products with lower lead content than the maximum admitted value for vegetable cans in water.

4. CONCLUSIONS

1. The accumulation potential of heavy metals (lead, cadmium, copper, zinc) in species of

leafy vegetables varies as follows: spinach > orach

2. Within vegetable species the accumulation potential of heavy metals (lead, cadmium, copper, and zinc) varies in different anatomic parts of these ones as follows:

leaves > petiole > stem > root > fruit

3. Heavy metals are very stable chemical elements which do not thermally or chemically degrade, but according to their binding in the plant tissue may migrate.

4. Phases of the technological process of treating horticultural products where the composition is altered in microelements, including heavy metals are: cleaning, washing, barking, infusion, sterilization.

5. Leafy vegetables during infusion operation present a differentiated decrease of heavy metals content depending on infusion time and medium nature, water temperature at 85 – 90⁰C, and citric acid solution 2% respectively at temperature 85 – 90⁰C, the most significant decreases of heavy metals content being registered when using citric acid solution 2% at the temperature of 85 – 90⁰C. In the case of orach the migration process of heavy metals into the infusion medium is more intense as compared to spinach.

6. Finished products made from vegetables cropped from polluted areas by heavy metals, exceed in differentiate way the maximum admitted limits for heavy metals content (lead, cadmium, copper and zinc). Spinach leaves in water and orach leaves in water exceed LMA for lead content;

7. Although heat processing treatments (washing, infusion) determine decreases of heavy metals content, the raw materials taken from intensely polluted areas which exceed several times the maximum limits admitted by legislation in force regarding heavy metals content, do not always allow to obtain finished products subscribing to OMS stipulations and represent a risk for consumers' health.

8. Taking into consideration the toxic effects of heavy metals upon human body, it is strongly recommended for consumers' protection safety that filling liquid of cans made from raw materials with high content of heavy metals should not be used at their preparation.

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