The influence of the harvesting area on the quality of the vegetal products preserved by refrigeration.
Part I – Smardan Area, Galati County

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Abstract
The vegetal products that undergo a process of preservation by refrigeration must have superior qualities in order to have their properties in the finite product. In order that the vegetal products should meet the quality requirements necessary for this type of preservation, first of all, the area where they are collected should not be exposed as much as possible to polluting factors. For the making of this experiment we have used a batch of carrots harvested from the Smardan area, Galati County, grown near the Siderurgical Factory of Galati. There has been determined the content of heavy metals in the raw carrot, after which it has been frozen. In order to see the evolution of the content of heavy metals the calculations were repeated also on the frozen carrots.

Keywords carrots, quality, polluting factors, freezing, heavy metals

1. Introduction
The quality of a product is determined by the sum of its physical, chemical and technological properties, properties which determine its degree of utility, i.e the ability to satisfy the demands of consumption. But in order to satisfy these demands of consumption, we use products, in our case vegetables and fruit which have to meet certain quality requirements. These quality requirements with fruit and vegetables become more complex because besides the physical and chemical characteristics the quality requirement includes the degree of inocuity. Thus, the definition of quality with these food products has a dynamic character, depending also on the destination of the product: immediate consumption as fresh vegetables, preserved - stored for a longer time.

The global effect of the pollution process is seen in the drop in fertility of the soils and the fact that the nutrition conditions for the plants are getting worse. As a result, there are disturbances in the mineral nutrition of plants (the increase in the acidity of soils, the decrease of phosphorus in soil, in the content of calcium and magnesium in the plant) as well as the passive absorption of polluting factors from the air and soil which have a toxic effect on the vegetal tissue.

In vegetal food products, due to the contamination or pollution processes, there can be accumulated considerable amounts of heavy metals and pesticides.

The presence of heavy metals in food products, even in small amounts, can change the taste, the colour, leads to the degradation of its vitamins and of its structural and texture firmness. In certain amounts, metals can be harmful for the body.

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In the category of the heavy metals there are a series of chemical elements which are highly toxic for the living organisms. The toxic effect is manifested when a certain quantity is reached, quantity under which some metals (Co, Cu, Fe, Ni, Zn) may even be essential components of certain proteins involved in different metabolic processes. Thus, if food products would be completely deprived of metals, there would appear nutritional deficiencies (Lee, Susan, 1990).

The heavy metals are found in different concentrations in soil, air, water, vegetal food products, according to various factors that determine their pollution.

The air can be a source of contamination representing a way of transporting the heavy metals and depositing them on the soil, on the plants (for example the lead emission from vehicles). The contamination of the air with heavy metals is the result of numerous anthropogenic activities: the production of steel, cement, from installations of residual gases purification, accumulation and cremation of residual materials etc.

The sources of metals in soil can be: the use of fertilizers, pesticides which contain metals (fungicides which contain mercury, copper, arsen, zinc etc). It is obvious that according to the type of soil and its geographic location, it can contain high quantities of heavy metals or it can be deficient.

The concentration level of heavy metals in uncontaminated dry soils that are mentioned in literature are: chromium 50 µg/g, cobalt 8 µg/g, copper 12 µg/g, lead 15 µg/g, magnesium 450 µg/g, molybdenum 1.5 µg/g, nickel 25 µg/g, vanadium 90 µg/g, cadmium 0.4 µg/g, mercury 0.06 µg/g, zinc 40 µg/g (Lee, Susan, 1990). High levels can naturally occur in soil as a result of geological processes, but mostly it results from agricultural and industrial activities.

Water can also be an important source of contamination, as a result of spilling, of the activities of purification and pre-purification stations, overflowing of sewage water and household waste waters. The hardness of the water and its content of organic compounds may determine its enrichment with lead from the water pipes. (Banu, C. 1982). Also, an important source of heavy metal contamination of plants may be the contact with various processing machines, installations and equipment, keeping the preserves in metal cans.

The toxic effect of metal at vegetal tissue and cell level varies depending on the concentration. In high concentrations, the whole growth and development process of a plant can be inhibited, while in smaller concentrations the effects are reduced or even absent.

When these elements are carried into the plant, they have to pass first of all the barrier of cellular membranes. It has been proved that some metals can cause modifications in the membrane permeability, with a loss of potassium ions.

The heavy metals show a great affinity for the carboxyl and sulphhidryl groups, depending on the latter’s physical and chemical properties.

Thus, the oxidation and disulphuric bridges being formed by the sulphhydril groups of the membrane proteins from the erythrocytes, plays an important role in the mechanism of cell destruction and the subsequent hemolysis caused by copper.

The forming of active free radicals (H₂O₂ hydrogen peroxide, O₂⁻ super oxide anion, OH⁻ hydroxyl radical) in aerobe cells occurs in small proportions. The heavy metals determine the increase in speed with which these free radicals are formed, resulting in starting a process of per oxidation of lipids, which leads to the alteration of the functioning of the biomembranes.
An important effect highlighted in the case of some metals like mercury, cobalt, cadmium, zinc is the inhibition of the synthesis of chlorophyll pigments. Several of the enzymes of the Calvin cycle are affected directly by the heavy metals. It seems that a first effect of the cadmium ions at the level of leaves is the closing of stomatitidis and respectively the inhibition of the CO$_2$ fixed at the level of chloroplasts (spinach).

The accumulation of heavy metals in vegetal products. The contamination with heavy metals of the vegetal food products happens in the soil and atmosphere, especially when the crops are near factories, residual waters from towns, intensely circulated roads, etc.

The toxicity of the heavy metals is influenced by the solubility of the metal and its metallic components. On the other hand there has been observed a synergism that increases their potential between Cu and Zn, Cu and As, Cu and Sn, Zn and As, but also an antagonism between these elements and Pb. However, the synergic or antagonist effect depends on the quantity of the substances and period they are applied (Catana Luminita, 2002).

2. Materials and methods

Samples preparation. The heavy metals content from carrots samples were analyzed after dry burning of 10 g in the quartz capsules at 6500°C for 4 hours. After complete burning a nitric acid 0.5 N solution was added up to 50 mL. The solutions obtained were used for total heavy metals contents determination by flame atomic absorption spectrometry (FASS).

Reagents. The standard solutions (1000 mg/L) were analytical grade from Riedel de Haen (Germany). The nitric acid 65% solution was of ultra pure grade (Merck, Germany). All solutions were prepared using deionized water.

Metals content determination Analysis of metals content was made with ContrAA-300, Analytik-Jena device, by flame atomic absorption spectrometry (FASS) in air/acetylene flame. The device working parameters (air, acetylene, optics and electronics) were adjusted for maximum absorption for each element.

Acetylene was of 99.99 % purity. Under the optimum established parameters, standard calibration curves for metals were constructed by plotting absorbency against concentration. In a definite range for each metal a good linearity was observed. The correlation coefficient for the calibration curves ($r^2$) ranged between 0.9745 -0.9891. All analyses were made in triplicate and the mean values were reported. All the values obtained for metals contents in analysed samples were calculated in mg/kg carrots(ppm).

Statistical interpretation of data obtained using multivariate analyses was performed with Statistica-6 software.

4. Results and discussion

As a result of the research there has been established the content of micro and macro-elements from the fresh carrot (TS), the carrot frozen once (AS1), the carrot frozen twice (AS2), the one frozen three times (AS3). The obtained values are presented in table 1.

By comparing the results obtained with the maximum limits of heavy metals admitted in fresh vegetables according to Order no. 1/Jan 2002, related to the security and quality conditions for vegetables we have obtained the graphic in fig. 1.

According to fig. 1 it can be observed that the toxic metals that are over the admitted limits are Zn, Pb, Cu, Cd.

Taking into account the area where the carrot was harvested we can say that Pb combined with Zn comes from the industrial area of the Siderurgical Factory in Galati, and Cd comes from the inadequate use of the fertilizer concentration used by the producer.
4. Conclusions

The pollution of the soil is found in the vegetables that grow on such a soil. The tests run on the carrot in the Smardan area, near the Siderurgical Factory of Galati show high levels of metals with toxic potential (lead, copper, zinc).

Although they do not significantly alter the qualities of the carrot (structure, color, taste), by consumption, in time they can accumulate in the human body in quantities that may produce various diseases (abotions, decrease in the learning ability in children, it can affect children’s behavior, compulsive behavior, etc.).

### Figure 1 – The variation of the heavy metals content

#### Tabel - The heavy metals content

<table>
<thead>
<tr>
<th>Probaj ppm</th>
<th>Cu</th>
<th>Zn</th>
<th>Mn</th>
<th>Fe</th>
<th>Cr</th>
<th>Co</th>
<th>Ni</th>
<th>Cd</th>
<th>Pb</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
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<tr>
<td>PO</td>
<td>-</td>
<td>-</td>
<td>0.0076</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total Content</td>
<td>PM</td>
<td>0.440</td>
<td>0.6751</td>
<td>0.2147</td>
<td>2.709</td>
<td>0.025</td>
<td>0.017</td>
<td>0.025</td>
<td>0.0071</td>
<td>8.145</td>
<td>10.0</td>
<td>8.339</td>
<td>4.082</td>
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<tr>
<td></td>
<td>PA1</td>
<td>0.026</td>
<td>0.6782</td>
<td>0.1221</td>
<td>1.465</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>7.857</td>
<td>7.886</td>
<td>4.969</td>
<td>3.629</td>
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<tr>
<td></td>
<td>PA2</td>
<td>0.219</td>
<td>0.4477</td>
<td>0.1334</td>
<td>2.328</td>
<td>0.025</td>
<td>0.0041</td>
<td>0.025</td>
<td>0.025</td>
<td>7.912</td>
<td>9.069</td>
<td>6.444</td>
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<tr>
<td></td>
<td>PA3</td>
<td>0.025</td>
<td>0.5155</td>
<td>0.0750</td>
<td>1.606</td>
<td>0.025</td>
<td>0.0004</td>
<td>0.025</td>
<td>0.025</td>
<td>7.714</td>
<td>8.835</td>
<td>6.529</td>
<td>3.653</td>
</tr>
<tr>
<td>Extraction HNO₃, 0.5N (12h)</td>
<td>PM</td>
<td>0.025</td>
<td>0.0279</td>
<td>0.025</td>
<td>0.0003</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
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<td>8.140</td>
<td>7.510</td>
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<td>0.0873</td>
<td>0.0036</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
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<td>0.0152</td>
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<td>0.025</td>
<td>0.025</td>
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<td>5.557</td>
<td>6.066</td>
<td>2.407</td>
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<td>0.025</td>
<td>0.0085</td>
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<td>0.025</td>
<td>0.013</td>
<td>0.053</td>
<td>0.025</td>
<td>0.0013</td>
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<td>5.557</td>
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<td>1.505</td>
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<tr>
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<td>0.025</td>
<td>0.066</td>
<td>0.0026</td>
<td>0.0063</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>0.025</td>
<td>5.652</td>
<td>6.715</td>
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<td>0.003</td>
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<td>5.052</td>
<td>5.969</td>
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<td>6.240</td>
<td>6.041</td>
<td>1.712</td>
<td>1.328</td>
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