

NON-DESTRUCTIVE ANALYSIS OF THE CONTENT OF MINERAL COMPONENTS OF CHICORY TO INCREASE ITS ENVIRONMENTAL SAFETY

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The content of heavy metals both in plants and in soils for growing agricultural crops steadily changes the state of ecological safety of the corresponding biocenosis. An increased amount of trace elements and compounds of heavy metals causes metabolic disorders in plant tissues. As a result, there is an accumulation of toxic elements in the crops, which disrupts the biocenosis in the system for both farm animals and humans. Therefore, the contamination of plant raw materials, in particular chicory, for the food industry with ions of heavy and toxic metals is a significant environmental problem. The results of studies of the content of trace elements and their interaction with carbohydrates of vegetable inulin-containing raw materials are presented. X-ray fluorescence analysis was used to determine the content of 20 macro- and microelements in chicory roots. The regularity of changes in the content of microelements depending on heat treatment, in particular in harsh conditions, has been proven. The method of non-destructive analysis of the content of mineral components of plant raw materials using carbohydrates as a matrix for measurements has been developed. At the same time, it practically does not affect the course of the study of the appropriate type of carbohydrates to determine this or that mineral component. According to the results of the experiments, a group of samples was recommended for the determination of such elements as Cd, Zn, Pb and Hg, and the corresponding calibration curves were constructed.

Keywords: ecology, inulin, carbohydrates, trace elements

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Introduction

The root part of chicory contains such unique components as inulin, beta-carotene, thiamine, pyridoxine, riboflavin, folic acid, as well as a diverse set of vitamins. However, many structural elements of chicory constitute a certain environmental hazard, the concentration of which depends mainly on the characteristics of the area where this plant is grown (Marangu, 2020; Zavadzka et al., 2023). Dumping and burial of waste from agro-industrial complex production lead to anthropogenic pollution of air, water and, accordingly, soil. Environmentally hazardous compounds include metal cations, various harmful trace elements, as well as heavy and toxic metals that tend to accumulate in the structure of plants, human and animal organisms. Among the most dangerous heavy metals, according to the World Health Organization, lead, mercury and cadmium. Lead leads to significant inhibition of growth and disruption of iron supply to cells, causing chlorosis (Haider et al., 2021). Its permissible concentration in crops for food products is 1-5 mg/kg of dry matter, for vegetable and

grain crops - 0.3 mg/kg, for fodder - up to 10 mg/kg. Cadmium, due to its similarity in chemical properties with zinc, can replace it in many biochemical processes, disrupting the work of enzymes and causing chlorosis of leaves, stems and petioles. This leads to zinc deficiency, inhibition of plant growth and death. The permissible concentration of cadmium in food is 70 m/kg per day for adults, and it is generally unacceptable for children (Steiner et al., 2018; Komar et al., 2021).

When exceeding the maximum allowable zinc concentration of more than 200-400 mg/kg of dry weight of plants, its phytotoxicity is manifested, which causes a change in color and death of leaf tissues. Exposure to manganese leads to the development of chlorosis between the veins of young leaves, their coloring in a yellow or whitish shade with dark brown or almost white necrotic spots. Similar symptoms are characteristic of the effects of magnesium, potassium, and calcium. If there is an unacceptable concentration of cobalt, phosphorus and calcium between the veins of some plants, necrosis also develops (Hamouda et al., 2018). All the presented elements are contained in chicory and can potentially be considered ecologically dangerous. Along with such a negative content of valuable cultivated plants in the food industry, a trend is developing towards the production of functional products enriched with valuable mineral components and biologically active compounds. Therefore, attention is drawn to the use of plants with a diverse carbohydrate composition, among which chicory occupies a special place, both for the high content of inulin and for the presence of a significant number of other biologically active compounds and the manufacturability of the products of further processing in food technologies (Maslova et al., 2019).

Data on the chemical composition of chicory given in the literature require additional research for the development of effective technologies. At the same time, the study of the peculiarities of the interaction of inulin and its structural constituent units with mineral and organic components of plant materials, which affects the release of inulin from chicory and the subsequent hydrolysis process, gains importance. The search for optimal conditions for the transformation of chicory inulin into fructose-oligosaccharide products requires careful study of both the chemical composition of chicory roots and the interaction between the components. The last factor leads to the release of inulin from plant material; ensures the stability of the initial, intermediate and end products of inulin hydrolysis; and significantly affects the further course of its fragmentation (Xu et al., 2016; Derevianko et al., 2022).

Studies of the dynamics of changes in the content of minerals and other components in the chemical composition of chicory roots containing heavy or toxic metals require in-depth analysis. Such structural elements of chicory are important nutrients that take an active part in the transformations of organic components through complex formation at the intermediate stages of the studied processes.

The author of the scientific paper (Tereshchenko et al., 2022) claims that the content of mobile forms of metals determines the level of their toxicity. Therefore, it is advisable to use the gross content of heavy metals in plants to assess the potential danger of soils.

Based on the findings of the study conducted by the researchers of the scientific article (Carter et al., 2019), it was proved that such mobile compounds hurt the soil biocenosis. According to the results of experimental research by the authors (Ilyas et al., 2019), it was established that the maximum permissible content of copper, zinc and nickel in plants ranges from 100, 50 and 300 mg per 1 kg of dry matter; and the authors of the article (Zheplinska et al., 2021) claim that the maximum allowable content of copper, zinc and nickel in plants varies between 50, 4 and 23. Much lower concentrations are regulated for such elements as beryllium: 0.1 mg/kg; cadmium: 0.015 - 0.5;

chromium: 0.2 - 1.0; mercury: 0.05 - 0.1; fluorine: 0.3 - 0.4; lead: 0.06; selenium: 0.2 - 2.0; tin: 0.8 – 6.0 (Tkach et al., 2022).

Over the last decade, there has been intensive growth in the production of sugar substitutes, especially the carbohydrate group, in particular, glucose-fructose syrups and high-fructose syrups (Zheplinska et al., 2022). With a global sugar production of about 130 million tons, the total number of sugar substitutes is about 15-20 million tons of sugar equivalent (Shevchuk et al., 2022). Inulin-containing plants with a high content of polysaccharide, which is a natural polymer of fructose, in particular Jerusalem artichokes and chicory, pay special attention to the developers of methods for obtaining high-fructose syrups (Langenaeken et al., 2019).

Materials and Methods

A qualitative determination of the content of chemical elements in fresh roots of chicory was carried out. Place of origin and processing of root crops, Khmelnytskyi region, Ukraine. The studies were carried out on an Elvatex X-ray fluorescence spectrometer-analyzer (Elva X software) in automatic mode to search for 60 elements that were considered the most probable.

Material samples were previously dried and ground. Qualitative detection was carried out in two modes of X-ray tube operation - with an X-ray tube current of 15 μA and 35 μA . The elemental composition of above-ground (leaves, stems) and underground parts (roots) of chicory was also compared in order to study the distribution of micro- and macro-elements in the functional parts of the chicory plant. For the study, six samples of root crops and leaves were selected, which were grown in different areas in Khmelnytsky Region. To assess the effect of heat treatment on the content of mineral components, the elemental composition of dried samples was compared with the composition of similar ashed samples.

Analysis of the elemental composition of hydrocarbon-containing raw materials was carried out by the X-ray fluorescence method.

To study the influence of the matrix (carbohydrate) on the results of the analysis, some chemically pure carbohydrates, the most common in chicory plant material, were taken: monosaccharides - glucose, fructose, disaccharides - sucrose, polysaccharides - dextrin, as well as inulin in the amount of 1.0 or 1.5 g variable amounts of cadmium, zinc, mercury and lead salts, namely from $0.1 \cdot 10^{-5}$ to $4.0 \cdot 10^{-5}$ mol of the corresponding salt.

The intensity of the X-ray fluorescent radiation was adjusted relative to the ratio of the number of moles of the element to the mass of the carbohydrate. This made it possible to determine the content of trace elements directly in the sample at the next stage of research, during the analysis of plant samples.

Results and Discussion

The spectrophotometric analysis of coloured compounds relies on the simultaneous application of the law of mass action Table 1 displays the identified elements and their respective proportions, expressed a percentage of the overall content of mineral components, based on average data compiled from observations over several years.

**Table 1. The concentrations of both micro and macroelements in chicory.
Cultivated chicory was studied**

Atomic number	Element	Series	Concentration, %
13	Al	K	0.698
14	Si	K	0.007
19	K	K	40.556
20	Ca	K	39.443
25	Mn	K	2.210
26	Fe	K	5.144
29	Cu	K	0.500
30	Zn	K	1.531
37	Rb	K	1.268
38	Sr	K	1.218
42	Mo	K	0.507
48	Cd	K	0.483
50	Sn	K	2.319
60	Nd	L	3.395
73	Ta	L	0.479
75	Re	L	0.501
76	Os	L	0.375
82	Pb	L	0.379
83	Bi	L	0.443
90	Th	L	0.295

As can be seen from the above data, the predominant number of classical nutrients such as Ca and K. Significant amounts contain Fe, Mn, Cu, and Sn. Less than 0.5% is the relative content of plant elements such as Pb, Cd, and Te.

Analyzing the microelement composition of chicory in recent years reveals fluctuations in the content of certain mineral components. These variations appear to be influenced by factors such as the year of harvest and the duration of shelf life. The results of our experiments showed that there is a certain dependence of the micronutrient composition on the timing of harvesting and storage of chicory roots. In particular, during the storage of roots for several months, there was an increase in the content of sulfur, which can be explained by the release of the latter due to the destruction of sulfur-containing proteins. This result allows us to offer producers recommendations for reducing the processing time of fresh chicory roots to preserve the protein composition of plants.

We noticed an interesting pattern of changes in the content of trace elements depending on the heat treatment, in particular in harsh conditions. In Figure 1 shows diagrams showing changes in the content of nutrients (ie those necessary for the normal functioning of the human body) elements in different parts of the chicory plant. In all cases, there was an accumulation of such elements during heat treatment.

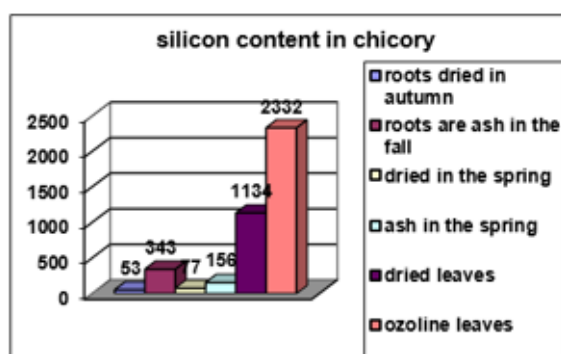
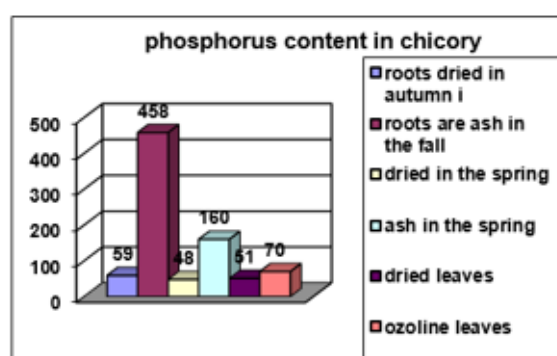
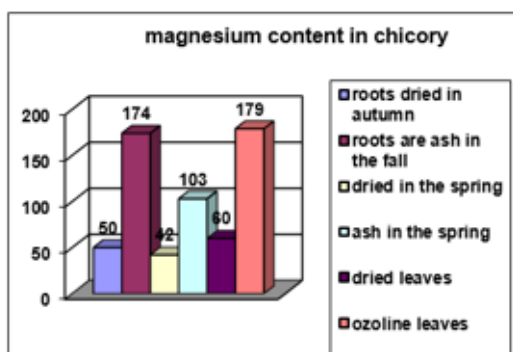
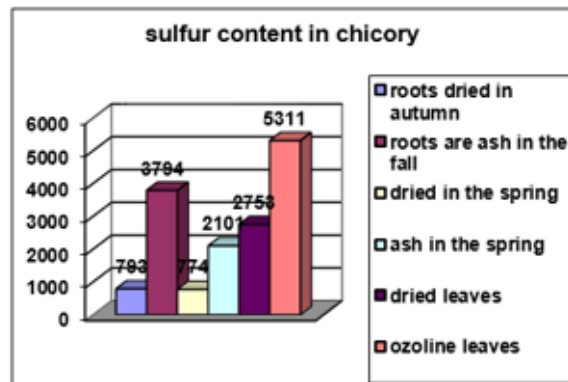
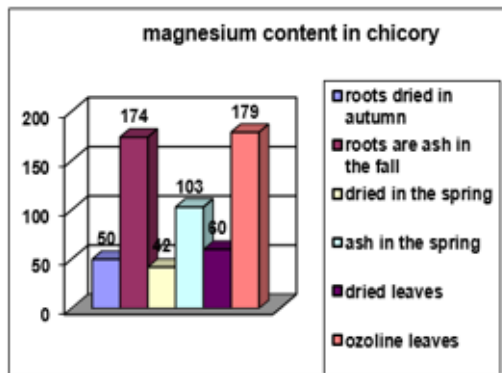


Figure 1. The content of nutrients in the chicory plant

Determining the content of mineral components largely determines the quality of plant raw materials, in particular inulin. The contamination of vegetable raw materials for the food industry with heavy and toxic metal ions poses a significant concern. All currently used methods for determining the content of trace elements are destructive, such as burning the sample, analysis of the emitted gases, extraction with many solvents, and requiring significant time for analysis.

Using the acquired data, we formulated a set of standard samples for determining elements such as Cd, Zn, Pb, and Hg, and developed corresponding calibration curves. Figure 2 illustrates an example of a calibration curve designed for determining the lead content in vegetable raw materials



Figure 2. Determination of zinc content by X-ray fluorescence analysis using carbohydrates

As reported in the literature (Bulygin et al., 2020), the utilization of X-ray fluorescence analysis for assessing heavy metals in vegetable raw materials through α -correction, involving theoretical coefficients accounting for factors like fluorescent angles, voltage, window thickness, the sum of measured elements, etc., is acknowledged for its high accuracy. However, it necessitates the application of a complex mathematical framework for both preliminary calculations and final result computations. This complexity arises from the scarcity of standard samples with a plant composition, underscoring the challenges associated with this approach.

Therefore, we have attempted to resolve this issue in this way. First, it was necessary to study the degree of influence of the matrix on the results of the analysis (hereinafter the matrix will be called a carbohydrate, against which the trace element is determined because the bulk of plants contains a significant amount of various carbohydrates). To perform this task, it was necessary to take many carbohydrates (mono-, di- and polysaccharides) of the same fixed mass with variable amounts of salts of the respective metals. If the type of matrix (carbohydrate) does not affect the quantification of the trace element, you can solve the second part of the problem - by making a series of standard samples to determine each element.

Some physical and chemical properties of inulin were studied by scientists at the National University of Food Technologies (Kyiv), in particular dispersion, and physical and mechanical characteristics. The structure of inulin extracted from Jerusalem artichoke was studied by spectroscopic methods using isotopic H/D exchange (Luo et al., 2019).

The authors from the Netherlands (Lv et al., 2019, Rahim et al., 2021) expressed the opinion that polymer degradation occurs in most transformations of inulin. And elucidating the mechanisms of such degradation requires information about the molecular structure of both inulin itself and its polymer homologs and its influence on the physicochemical properties and transformation of the biopolymer.

One of the aspects of such research is the structural analysis of inulin and its structural constituent units (fructose, ketose, nystose, sucrose) by the NMR method on deuterium nuclei. The

authors carried out both experimental studies of the mentioned compounds and computer modelling of NMR spectral characteristics, which demonstrated a good agreement with the results.

The data we obtained made it possible to clarify the methods of combining monosaccharide units and their mutual location in the polysaccharide molecule and its lower polymer homologs, which undoubtedly affects the transformation of these biopolymers.

Conclusions

A significant problem is the contamination of plant raw materials for the food industry with ions of heavy and toxic metals, among which cadmium, tin, and lead can be noted, the concentrations of which in chicory are 0.483, respectively; 0.379; 2.319%. X-ray fluorescence analysis was used to determine the content of 20 macro- and microelements in chicory roots. The method of non-destructive analysis of the content of mineral components of plant raw materials using carbohydrates as a matrix for measurements has been developed. Chemical-analytical methods were used to investigate the complexation of the components of chicory plant material, namely inulin polysaccharide and its structural units with calcium ions.

Conflict of interest

The authors state no conflict of interest.

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