ACCUMULATION OF MANGANESE AND IRON IN CITRUS FRUITS

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The aim of this work is to determine the metal contents from different components of a fruit (pulp, film and peel). The determinations of metal's traces are very important because they are involved in biological cycles and indicate high toxicity. Analyses were performed using the flame atomic absorption spectrometry (Shimadzu AA 6200), after the chemical mineralization of the sample with a Digesdahl device. The obtained values are in good agreement with the literature data.

Introduction

Plants can accumulate trace elements, especially heavy metals, in or on their tissues due to their great ability to adapt to variable chemical effects of the environment, thus plants are intermediate reservoirs for trace elements originated from the lithosphere, hydrosphere or the atmosphere.

In general heavy metals produce their toxicity by forming complexes or "ligands" with organic compounds. These modified biological molecules lose their ability to function properly, and result in malfunction or death of the affected cells. The most common groups involved in ligand's formation are oxygen, sulfur, and nitrogen. When metals bind to these groups they may inactive important enzyme systems, or affect protein structure [1].

Manganese (Mn) is a plant micronutrient that, depending on its content in the soil and on factors that control its availability such as pH, organic matter and microbial activity, can achieve levels which are toxic for the plants [2]. The critical level of foliar Mn concentration in plants to produce toxicity symptoms varies among species and even cultivars [3, 4].

Iron is closely concerned with chlorophyll formation but is not a constituent of it. Its role appears in connection to be that of a catalyst.

A point of great importance in connection with iron is its relative immobility in plant tissues. Its mobility seems to be affected by several factors, such as the presence of

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manganese, potassium deficiency and high light intensity. There is evidence that the amount of chlorophyll is related to "active" (readily soluble) iron in plants. It will be seen that so-called iron deficiency in the plant may in fact usually mean iron immobility. Lack of mobility may also account for the fact that iron deficiency is first shown in the younger tissues.

In the last years a large number of analytical techniques for metal determination in plants have been reported, such as ICP-AES [5], X-ray fluorescence spectrometry [6,7], flame atomic absorption spectrometry [8], atomic absorption spectroscopy (GFAAS) [9], flow injection spectrometry [10] and ICP-MS [11].

Experimental

Reagents and solutions

All metal stock solutions (1000 mg/L) were prepared by dissolving the appropriate amounts of the spectral pure metals in dilute acids (1:1) and then diluting them with deionized water. The working solutions were prepared by diluting the stock solutions to appropriate volumes. The nitric acid 65% and hydrogen peroxide 25% solutions used were of ultra pure grade, purchased from Merck. All reagents were of analytical-reagent grade and all solutions were prepared using deionized water.

Sample preparation

The pulp, the film and the peel of oranges, lemons and grapefruits were investigated. The samples were washed with deionized water, dried and homogenized. 0.5-0.9 grams of each dry sample was submitted digestion with 8 mL HNO_3 and 10 mL H_2O_2 at 170^oC in a Digesdhal device provided by Hach Company [12]. After the complete digestion the samples solution were filtered, made up to 50 mL in volumetric flask with deionized water.

Sample analysis

Metals were determined by FAAS in air/acetylene flame using an aqueous standard calibration curve. Analyses were made in triplicate and the mean values are reported.

A Shimadzu atomic absorption spectrometer (Model AA 6200) equipped with air-acetylene flame was used for the determination of metals (Mn and Fe) in citrus fruits. Acetylene of 99.99% purity at a flow rate of 1.8-2.0 L/min was utilized as a fuel gas and also as a carrier gas for introducing aerosols. Metals were measured using monoelement hollow cathode lamps.

Results and discussion

The metals content is reglementate by international law.

In table1 are presented the maximum admissible concentrations in fruits according to Food Surveillance Information Sheet No.131 [13].

Table 1. The maximum admissible concentrations in fruits

No	Metal	The maximum admissible concentrations (mg/kg)
1	Mn	2
2	Fe	2.7

The characteristics of metal calibration are presented in table 2.

Table 2. Characteristics of metal calibration curves

No	Metal	λ, nm	Concentration range (ppm)	Correlation coefficient
1	Mn	279.5	0.008-1.600	0.9984
2	Fe	248.3	0.020-4.000	0.9976

The content of metals in citrus fresh fruits was determined by FAAS technique.

In figure 1 are presented the average values of Mn concentrations from citrus fruits.

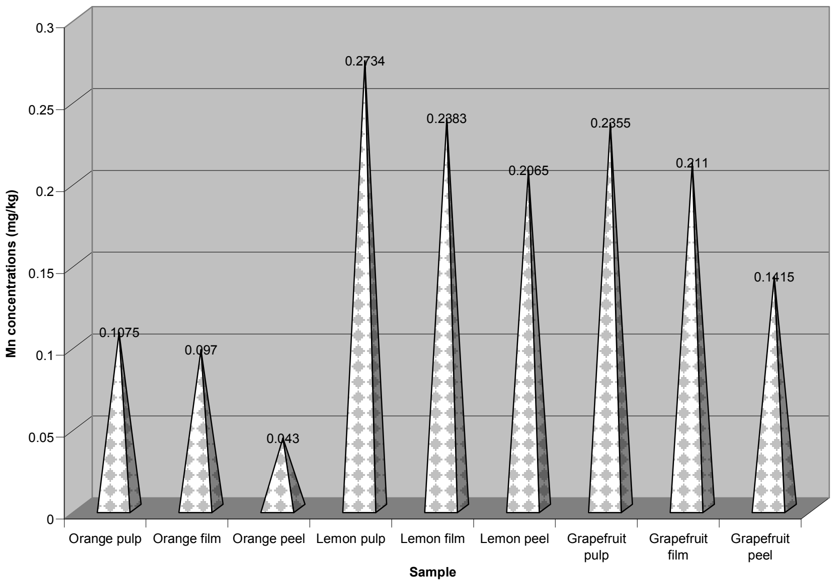

Fig. 1: *Mn concentrations in citrus fruits (mg/kg)*

We can observe that the highest value for Mn concentrations is that of lemon's pulp (0.2734 mg/kg) and the lowest is that of orange's peel (0.043 mg/kg). But it can be noticed that all values of Mn concentrations are under the maximum admissible value (2 mg/kg).

In figure 2 are presented the average values of Fe concentrations from citrus fruits.

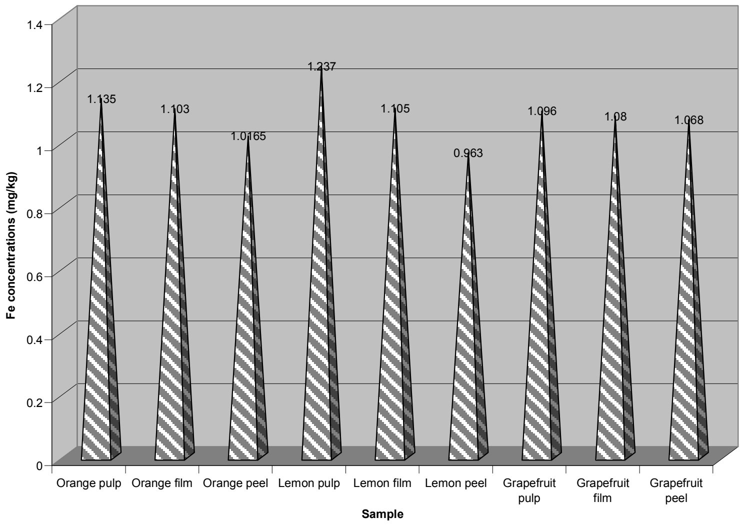

Fig. 2: *Fe concentrations in citrus fruits (mg/kg)*

All values for Fe concentrations are comparable and under the maximum admissible value (2.7 mg/kg).

Konstantin Lubenov [14].while analyzing Mn concentrations in some medicinal plants and their infusions by a kinetic spectrophotometric method find that most of the manganese in the infusions exists in a bound state, and only very low concentrations are in a free state.

Conclusions

1. This paper presents original studies concerning metals accumulation in citrus fresh fruits by FAAS.
2. It can be noticed that the highest value for Mn concentrations is that of lemon's pulp (0.2734 mg/kg) and the lowest is that of orange's peel (0.043 mg/kg).
3. All values of Fe concentrations are comparable and under the maximum admissible value.
4. The obtained concentrations of these elements in citrus fruits are situated within the limits imposed by the last regulations of the specialized international commissions such as EC's Scientific Committee for Food.

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