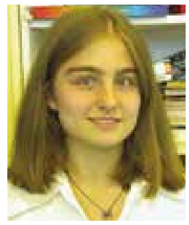
To what extent is there a difference in metal content in fruit species?

Evaluating the nutritional values of *Prunus armeniaca* L., *Prunus cerasus* L. and *Prunus spinosa* L. based on their essential metal contents using ICP-OES.

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Abstract

In the following research, the metal ion concentration of different kinds of fruits was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) which was later compared to standard nutritional values. The aim of this research was to determine the healthy, recommended amount of consumption of these fruits for a more balanced diet. The examined samples were freeze-dried apricots (Ananasnij, infected Kyoto, 4/60 hibrid, 7/1 hibrid), Fanal 3 sour cherry, D5/2 sloe and fresh Érdi bőtermő sour cherry. Element content was determined after nitric acid digestion, and results were evaluated. According to the measurement, a significant difference can be recognized in aspect of Ba, K, Mg, Mn, P, S, Sr between the different tribes of fruits. Apricots were found to be the richest sources of Al, Na and K. Ba, Mn, Sr and Zn were found in the highest concentration in sloe. Sour cherry samples were the best sources for Fe and P. Calcium and Mg concentration was almost the same in sour cherry and in sloe.

Ba, Ca, Fe, K, Mg, P, S and Sr concentrations were significantly variable in the four apricot species. Ananasnij and 4/60 hibrid were found to be the best element sources.

Fanal 3 sour cherry was by far richer than Érdi bőtermő in most cases of elements.
In conclusion, sloe is the healthiest fruit from the measured ones; however, it is a worthless, ordinary wild plant. It has no pleasant flavour; it is not consumed as a tasty fruit, but as a herb.

INTRODUCTION

This summer, we were presented with an opportunity to spend a week in the Research Centre of Natural Sciences of HAS and to use the ICP-OES technique to detect macro and trace metals in fruit samples. These kinds of elements have a huge effect on human body. Some of them are essential, while others may be poisonous or neutral to the human system. However, we were exclusively concerned about essential trace metals in the research.
The human body requires several essential metals to function, for example iron, manganese, chromium, zinc and copper. However, these requirements are not always covered by many people due to their daily diet or digestion problems. In fact, the use of dietary supplements in the US has significantly risen. In a survey from 1988 until 1994, it was found that 28% of women over 60 years took calcium (Mann, 2013). While from 2003 until 2006, survey shows that this number has risen to 61%. Furthermore, CDC (Centres for Disease Control and Prevention) reports that over half of the adult population is taking one or more supplements a day. (Mann 2011). Leading a healthy way of life is getting more wide-spread, but the problem is that using these supplements does not always benefit one's health. Most of them were not tested in laboratories, so consuming them can be really harmful. According to a study on women over 55 years old, taking dietary supplements such as "magnesium, zinc, copper, iron, vitamin B6, folic acid and other multivitamins" not only had positive effect, but had caused

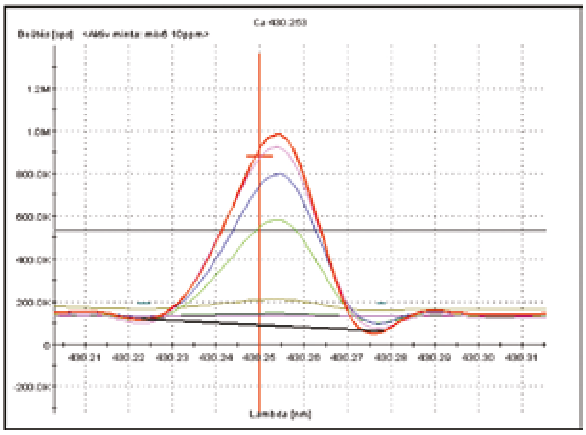


Figure 1 *Spectrum line of calcium standard solution (red line) and solutions of fruit samples. Intensity of light from fruit samples were compared to standard solutions to determine concentration.*

a slightly higher risk of death (Gann, 2011). So the best and safest way to stay healthy is to consume vitamins and essential elements by natural foods: vegetables and fruits.
Therefore, the purpose of this research was to measure the metal content of various species of fruits by ICP-OES. These fruits are all belong to the same family: the *Prunus*, however they look differently. We compared their element content, and find out, which is the best element source.

EXPERIMENTAL

Materials

Fortunately, our work in the institute helped us improve our laboratory skills, such as measuring accurately very small amount of solid substances with analytical balance, and filling up a volumetric flask to the graduation mark.
Four different types of lyophilized (freeze-dried) apricot (*Prunus armeniaca* L.*),* a lyophilized and a fresh sour cherry sample *(Prunus cerasus* L.*)* and a lyophilized sloe *(Prunus spinosa* L.*)* were measured. The lyophilized fruits were collected in the Botanical Garden of Corvinus University in Soroksár, 2012 and were lyophilized in the University. The fresh sour cherry was harvested in a small suburban garden in Budapest, 2013.
Three parallel samples of each fruit were scrutinized because of the standard deviation.
0.1 g of each sample was measured into a glass for the Velp Scientifica Thermoreactor, and they were boiled for 4-5 hours on 200 °C with 4 ml nitric acid (65%). After the nitrous gases were removed, 2 ml hydrogen-peroxide was added and an extra 15 minutes of boiling was done.
All the finished samples were put into 10 ml vials, and filled with distilled water until the line.
The mass of the samples is shown in Table 1.

Method

Element content was measured by ICP-OES. The equipment used was a Spectro Genesis ICP-OES

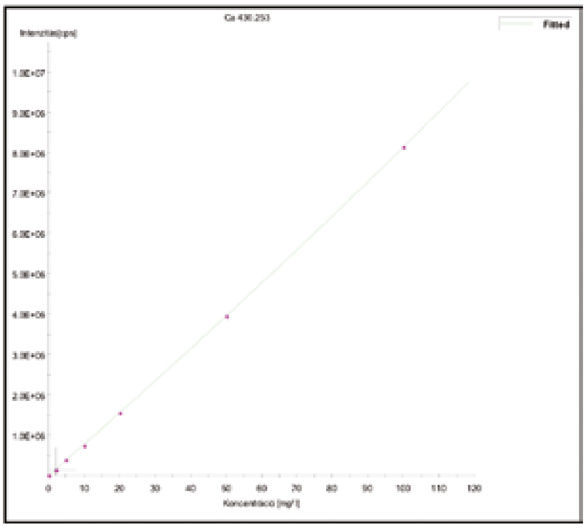


Figure 2 *Calibration curve of calcium standard solutions. The straight line, and low dispersion of data points signifies that the instrument is precisely and accurately calibrated.*

Table 1: *Mass and type of samples*

Code	Type	Mass of Sample 1 (g) ±0.0001	Mass of Sample 2 (g) ±0.0001	Mass of Sample 3 (g) ±0.0001
Apricot 1	Ananasnij	0.1012	0.1032	0.1042
Apricot 2	Infected Kyoto	0.1012	0.1003	0.0996
Apricot 3	Hibrid 4/60	0.1019	0.1008	0.1260
Apricot 4	Hibrid 7/1	0.0997	0.0996	0.0915
Sour Cherry	Fanal 3	0.1012	0.0882	0.0898
Sloe	D5/2	0.0977	0.0927	0.0923
Sour Cherry 2[1]	Érdi bőtermő	0.8598	0.8710	0.8502

[1]Non-lyophilized, fresh fruit.

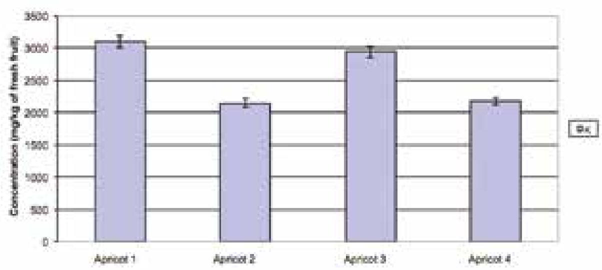


Figure 3.1

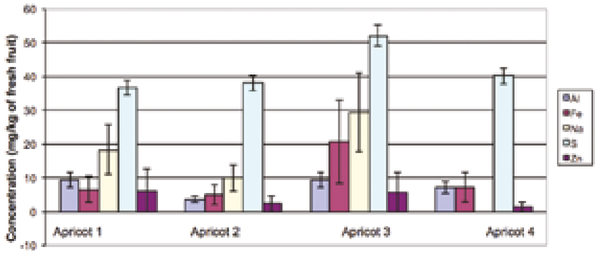


Figure 3.3

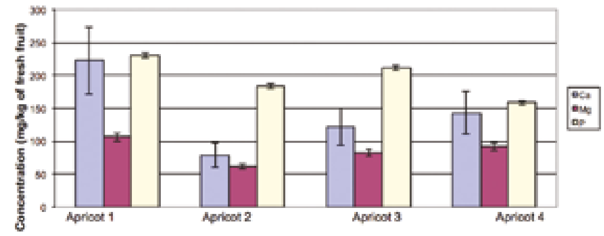


Figure 3.2

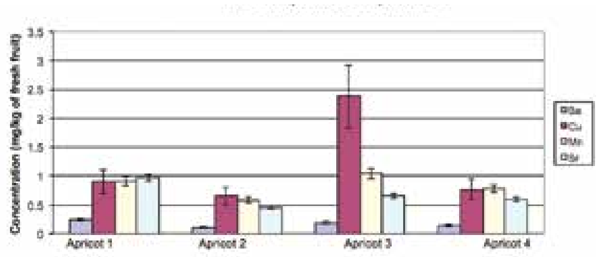


Figure 3.4

Figures 3.1-3.4 *Metal concentration of P. armeniaca samples 1-4. Different graphs were used due to extremely large differences between values. Error bars based on standard deviation.*

(Kleve, Germany) with axial plasma observation. It has CCD detectors; the wavelength range expands from 175 nm to 777 nm allowing complete spectrum capture within 3 seconds.

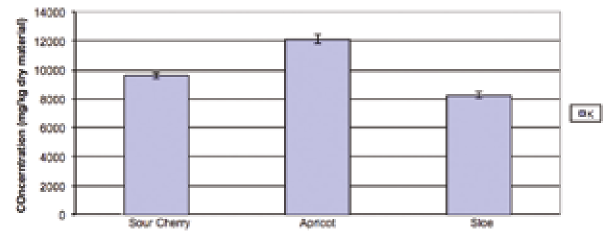
The digested solution sample was taken by a peristaltic pump, and introduced directly inside the argon plasma producing excited atoms and ions. These atoms and ions emit electromagnetic radiation that can be detected optically. Elements are identified by wavelength (Figure 1) and intensity is proportional to the concentration (Figure 2).

Results

Firstly, the four varieties of apricot, then sloe, sour cherry and apricot samples, finally the sour cherry samples were compared to each other (Figures 3.1-3.4; 4.1.-4.4; 5.1-5.4).

Results of the measurement reports that even varieties from the same kind of fruit could represent differences in element content. The origin of the fruit, the weather, the quality of the soil, the whole environment and many other factors can significantly influence the results.

One prominent example with the incident of copper must be mentioned. In general these kinds of fruits do not contain high amount of copper, but our samples had. We suspect that pesticides consisting of copper compounds could be the main reason of this.



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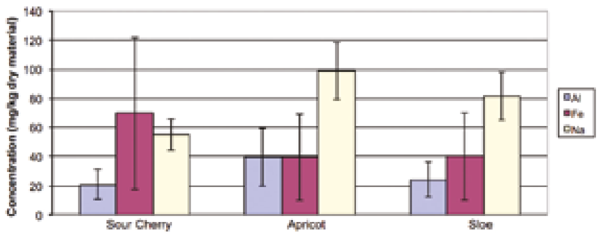


Figure 4.3

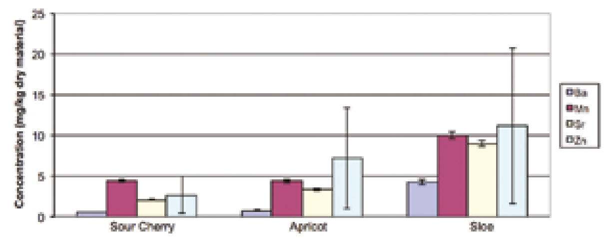


Figure 4.2

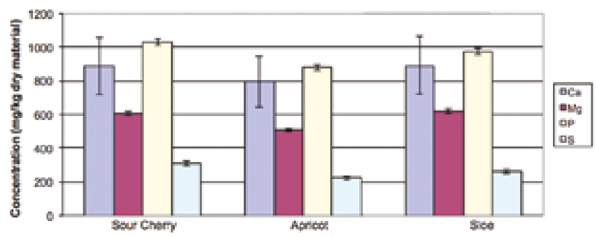


Figure 4.4

Figures 4.1-4.4 *Metal concentration of P. cerasus, P. armeniaca and P. spinosa. Different graphs were used due to extremely large differences between values. Error bars based on standard deviation.*

Discussion/Analysis:

In this project, the element content of the fruit samples was successfully determined. Significant differences were shown by several metals by a statistical method. Between the four apricot samples, concentrations of Ba, Ca, Fe, K, Mg, P, S and Sr were significantly different. Between the sour cherry samples, concentrations of Ba, Ca, Cu, K, Mg, Mn, P and S also had significant differences. This shows that it does not only matter which fruit one eats, but also the origin of the fruit, because different places have different nutritional values. This can be seen in figures 3.1-3.4, in which apricot hibrid 4/60 has significantly high amounts of sulphur and copper while Ananasnij apricot is shown to have higher amounts of potassium, magnesium and strontium. It can also be seen between the two cherry samples, Fanal 3 seemed to have higher concentrations of almost every metal elements measured than Érdi bőtermő.
Furthermore, there were also significant differences between the species of fruits. In fact, sour cherry, apricot and sloe samples showed significant differences in the contents of Ba, K, Mg, Mn, P, S and Sr. In figures 4.1-4.4, sloe has notably higher amounts of barium, manganese and strontium. Apricot has the highest potassium concentration and cherry has the biggest amount of phosphorus. In Figure 6, it is evident that sloe excels in the following elements: lithium, barium, calcium, zinc, aluminium, and sodium. Thus making it the most nutritious fruits in terms of essential metals tested in this research.

Table 2 shows the calculated percentage coverage of the RDA (Recommended Dietary Allowances) of the average values for all apricot and cherry samples. It indicates that both fruits seem to be good sources of copper and potassium.
Overall, one can conclude that different species of fruit contain significantly different metal contents. Furthermore, it is also shown that the origin of the fruit also plays an important role as differences were measured within species of fruits. However due to the variation of metal contents observed, it is hard to generalize which is the most nutritious fruit. As mentioned above, that Table 2 indicates that sour cherry (Fanal 3) seem to excel in terms of metal contents. Upon averaging all values with the same species, differences in the data are much smaller.

Limitations

The experiment was successful, in terms of determining a significant difference among fruits samples. One can see from figures 2 – 5 that some elements, such as zinc and iron have large error bars. As the error bars are based on standard deviation between the parallel trials, it can be said that there was random error present in the experiment. This could be caused by the fact that the mass of fruit samples were not close enough (see Table 1). One can see in Table 1 that apricot 1 and 3 had a slightly higher average mass than apricots 2 and 4. This is reflected on the measurements as apricots 1 and 3 also had slightly higher metal contents than 2 and 4. This could mean that in

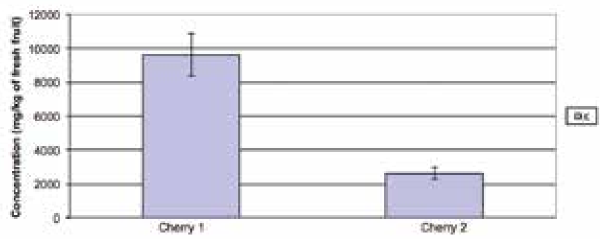


Figure 5.1

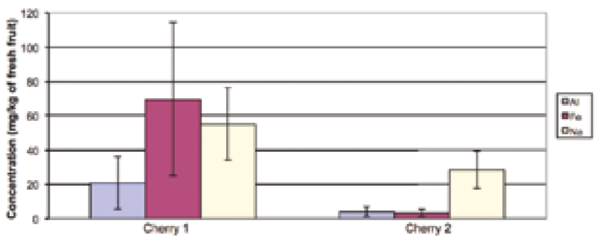
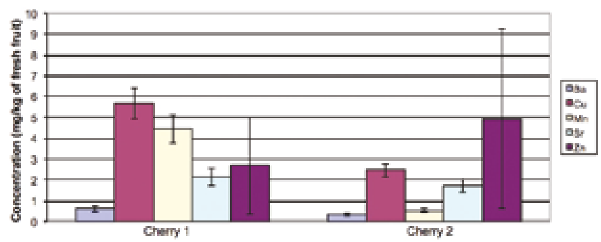


Figure 5.3



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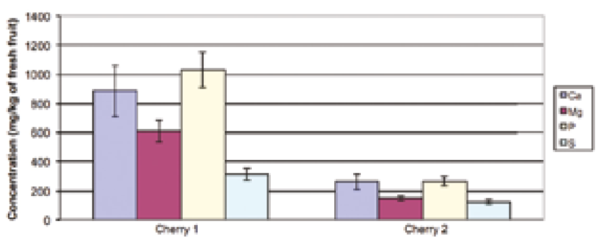

Figure 5.4

Figures 5.1-5.4 *Metal concentration of P. cerasus 1 and 2. Different graphs were used due to extremely large differences between values. Error bars based on standard deviation.*

Table 2 Averaged metal consumption (based on 200 g of fresh fruit) of the two fruit species compared to RDA values.

	Ca	Cu	Fe	K	Mg	Mn	P	Zn
RDA² **(mg/day)**	800	1	14	2000	375	2	700	10
P. cerasus (RDA %)	5.26	34.84	11.25	21.82	6.85	6.70	6.44	5.42
P. armeniaca (RDA %)	3.54	23.51	14.02	25.91	4.55	8.30	5.61	7.70

²Recommended Dietary Allowances: estimated to meet the daily intake requirement of 97-98% of healthy people. (Health Canada)

order to improve the accuracy of the results, one must have very low tolerances in the variation of mass of samples.

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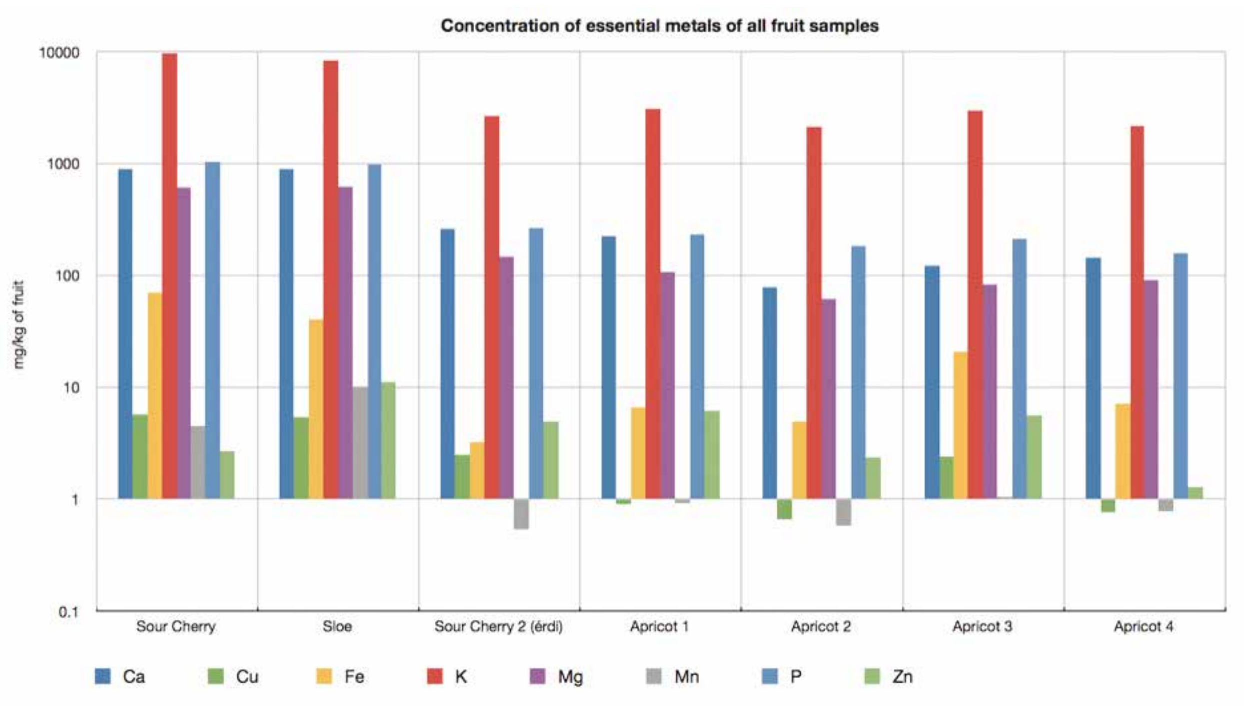

Figure 6 Concentrations of essential metals of all fruit samples were graphed on a logarithmic scale. This graph contains all samples and essential metals which are beneficial to health. It should be noted that Cherry 2 (érdi) was fresh whereas other samples were lyophilised.