PIXE Analysis of Elemental Composition
of Food at the CENTA Laboratory*

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Abstract: We analyzed elemental composition of foods and organic foods, commonly consumed by large groups of population, using PIXE/PIGE analytical methods. The aim of this work was to measure concentrations of trace elements contained in selected crops and to compare their values for organic food and food produced in a conventional way. By following simple steps, the crops were processed into samples in the form of pressed pellets, in which yttrium was added as an internal standard. Samples were irradiated with a beam of accelerated protons with the energy of ~3 MeV, generated by an accelerator system at the laboratory of the Center for nuclear and accelerator technologies (CENTA). The measured spectra were evaluated by the GUPIXWIN software; potassium (K), calcium (Ca), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), bromine (Br), rubidium (Rb) and strontium (Sr) were included into a group of investigated elements. In the end, obtained results are discussed and compared with the results from other studies.

1. Introduction

Organic foods are generally presented as a healthier and overall better source of nutrients than just foods cultivated by conventional methods. From the chemical point of view, however, foods are made of macromolecules, such as lipids, proteins or carbohydrates, which are in fact derivates of hydrocarbons. Hence, all foods are structurally more or less the same and the term 'organic' only suggests which methods and materials are (not) used in the process of their production [1]. Although actual legal requirements on how organic foods should be produced depend strongly on the country of origin, some regulations are obligatory, e.g. refraining from the use of prohibited substances, such as synthetic fertilizers, animal feed and drugs, during the growing process [2]. Despite the general public belief that organic foods are of a better quality than non-organic variants, a study which would confirm this theory by introducing solid arguments is yet to be published.

In order to increase their production, farmers are usually forced to exploit different substances which can protect crops from various pests (pesticides) or wee-like parasitic plants (herbicides), make vegetables and fruits rich in nutrients (fertilizers), or prevent animals from getting ill (drugs). Extensive use of these materials, regardless if they are strictly natural (organic) or man-made (synthetic), can lead to potentially harmful residues to be contained in foods. Heavy metals (e.g., As, Cd, Hg, Pb) represent another group of possible food contaminants. Unlike most of the abovementioned substances based on hydrocarbons, heavy metals tend to accumulate in the environment due to very high persistence, mainly in the surface soil layer. Sources of contamination by toxic metals are

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*Dedicated to Professor Peter Prešnajder on the occasion of his 70th birthday

plentiful; they can get into the environment, for example, as a part of unintended leakages from metal producing factories, as a part of the fly-ash from coal burning, in discharges of waste waters from heavy industry or from special applications (e.g., tetraethyllead gasoline), though risk of such incidents to happen should be nowadays practically nullified, at least in the developed countries [3]. Nevertheless, governments worldwide spend non-negligible resources for composition analyses of foods to control their quality.

There are many reliable methods which are routinely used for determination of food chemical composition; selection of the right (most suitable) one depends on many factors, like analyte(s) of interest, sample size, time of analysis, required sensitivity and detection limit of the method etc. Even though less frequently employed, techniques based on principles of particle induced X-ray emission (PIXE) and particle induced -ray emission (PIGE) represent an interesting alternative to more traditional spectrometric and spectroscopic methods (e.g., ICP-MS, AAS) for analysis of elemental content in a variety of samples, including foods [4, 5]. While PIXE utilizes detection of X-rays emitted during de-excitation of inner shell electrons from target atoms ejected by incident particle impact, PIGE exploits detection of -rays from nuclei excited by bombardment with energetic particles [6–9]. With a proper detector, the former method can be used for measurements of almost all elements (Z   6), however, in the case of the latter, one typically focuses on determination of light elements only (Z   15). One of the main advantages of the PIXE/PIGE techniques is that they are non-destructive, which is especially important for samples of high cultural value, though some kind of pre-treatment is necessary for special type of samples. On the other hand, their development and optimization are, like for any other ion beam analysis (IBA) method, expensive and time-consuming.

In 2013, Center for Nuclear and Accelerator Technologies (CENTA) has been established at the Comenius University in Bratislava, which comprises a laboratory with an state-of-art Pelletron® accelerator (NEC, Wisconsin, USA) usable for IBA, including PIXE/PIGE, accelerator mass spectrometry and nuclear reaction analysis studies [10, 11]. Besides the accelerator, the system in the laboratory consists of two ion sources, an injection part with a double focusing 90° bending magnet, and a post-acceleration $\pm15^o$ switching magnet, followed by two end lines, one of which is equipped with a specially designed vacuum chamber for PIXE/PIGE analyses; detailed information about the PIXE/PIGE chamber have been reported elsewhere [12]. For production of proton beams, one can either use a radio frequency ion source, which works with gas hydrogen, or an ion source for solid targets, in which a cathode with pressed titanium hydride (TiH_2) can be mounted. Intensity and profile of beams can be easily adjusted by various control elements, installed along the whole system.

This paper present results of elemental composition analysis of 21 selected organic and non-organic foods, conducted with the use of the PIXE technique. Prepared sample targets, mounted on a holder of the PIXE/PIGE chamber, were bombarded with a ~3 MeV proton ion beam, produced by the tandem system of the CENTA laboratory. Due to intrinsic characteristics of the BEGe detector, installed in the chamber, we focused only on the elements with Z > 19; altogether, ten major and trace elements (from potassium to strontium) were identified to be present in samples. In most cases, we were also able to determine concentration of detected elements. Obtained results were compared with the values published in the literature and, if possible, results of quantitative analysis of organic and

non-organic foods of the same species were put in comparison as well. Finally, prepared sample targets were evaluated from the homogeneity point of view.

2. Methods

The following commercially available fruits and vegetables, both organic and non-organic, were selected for the elemental composition analysis: cabbage, cucumber, spinach, onion, parsley, carrot, potato (organic only), black bean, banana, tomato (non-organic only), and iceberg lettuce. For bananas and organic cucumber, their outer peels were processed and measured separately. Except for beans, which were chopped by a specially modified small-scale mixing instrument, all foods were first cut into pieces with a ceramic knife and dried in oven at 75 C. Afterwards, dried pieces were powdered by a mortar and sieved through 0.5 0.5 mm holes to separate the fine fraction. For each sample, approximately one gram of the fine powder was taken and mixed with the slightly acidic yttrium internal standard solution (c_{Y3+} = 1.0064 mg mL^{-1}). Then, sample powder was dried again at 35–45 C and pressed into the form of a pellet (3 15 mm), used as a thick target for PIXE.
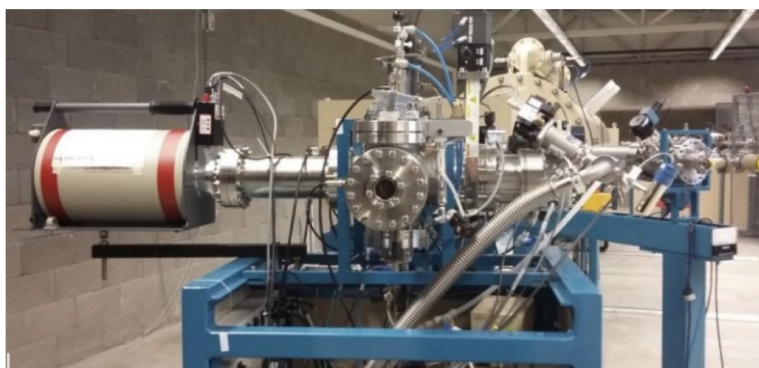

Fig. 1. PIXE/PIGE chamber with the connected BEGe detector (left) at the CENTA laboratory [13].

After mounting the target samples on the sample holder, the PIXE/PIGE chamber was evacuated to the pressure level of around 10^{-6} Torr before the measurements themselves, which usually took a few hours because of the vaporous character of samples. Proton ions for PIXE analysis were produced in the MC-SNICS ion source from the TiH_2 cathodes and accelerated to the energy of ~3 MeV. The measurements were performed with the sample holder at the 10° angle to the BEGe detector. The intensity of the ion beam was adjusted to and maintained at approximately 1 nA, and a current integrator was set to collect exactly 1 μC. To ensure high efficiency of the charge collection, spectra acquisition taking from 15 to 20 min was conducted with a secondary electron suppression electrode installed around the sample holder. With the exception of two samples, each target was measured at three individual positions (*up*, *mid* and *down*). In the end, acquired PIXE spectra were processed by the GUPIXWIN software package [14].

3. Results and discussion

Determined yttrium concentrations, added as a part of the internal standard solution during the sample processing, showed a great variance, implying that prepared targets were indeed inhomogeneous. Based on the amount of the standard Y^{3+} solution mixed with the sample material, we calculated that the concentration of yttrium was ideally supposed to be about 335±45 mg kg^{-1} for the whole sample set. However, measured yttrium content was in the range of 84–916 mg kg^{-1}, with only 10 out of 58 measurements corresponding with the expected concentration (within the relative uncertainty of 10%). Differences in the yttrium content were found not only between food species but also between positions of a single sample target, i.e. the Y concentration for e.g. non-organic onion at the position *up*, *mid* and *down* was determined to be 841 mg kg^{-1}, 354 mg kg^{-1} and 276 mg kg^{-1}, respectively. Rather poor distribution of the internal standard was probably caused by its insufficient mixing with the sample material during the target preparation. On top of that, the inhomogeneity problem was clearly apparent when we evaluated the elements of interest as well; in some cases, determined concentrations varied with a position of the interaction of protons with the target up to factor of ten. This might be explained by a specific aspect that grounding and sieving of samples produced too coarse particles, most likely substantially different in elemental composition, which created inconsistencies in the final pressed targets.

Despite the facts mentioned in the previous paragraph, we could measure some interesting results. Although the main goal of this study was to determine concentration of the elements of interest, it was impossible to obtain reasonable values for several samples, mainly due to low resolution of their respective spectra and because of high background from bremsstrahlung, example of which is shown in Fig. 2a. Therefore, only results of qualitative analysis are reported here for these samples, namely organic and non-organic carrot and parsley, organic potato (Table 1). Almost no difference was found between non-organic and organic samples of the same species, as none of the elements was detected in the non-organic sort and not detected in the organic one, or vice versa. It is important to note that results for potassium and calcium are somewhat questionable, as the used BEGe detector has unfavorable resolution and very low efficiency for determination of these two elements [15].

Tab. 1. Results of qualitative analysis of some foods (*d* = detected; *nd* = not detected; *?* = ambiguous).

Sample		K	Ca	Mn	Fe	Cu	Zn	Se	Br	Rb	Sr
						Element					
Non-organic	Carrot	*d*	*?*	*nd*	*d*	*d*	*d*	*d*	*?*	*?*	*?*
	Parsley	*nd*	*nd*	*nd*	*d*	*d*	*d*	*nd*	*nd*	*?*	*?*
Organic	Carrot	*d*	*nd*	*nd*	*d*	*d*	*d*	*d*	*nd*	*?*	*?*
	Parsley	*?*	*nd*	*?*	*d*	*d*	*d*	*d*	*nd*	*nd*	*?*
	Potato	*?*	*nd*	*?*	*d*	*d*	*d*	*d*	*nd*	*?*	*nd*

In the case of samples, which spectra were measured with satisfactory resolved peaks, we were not only able to determine whether the elements were present in the sample material
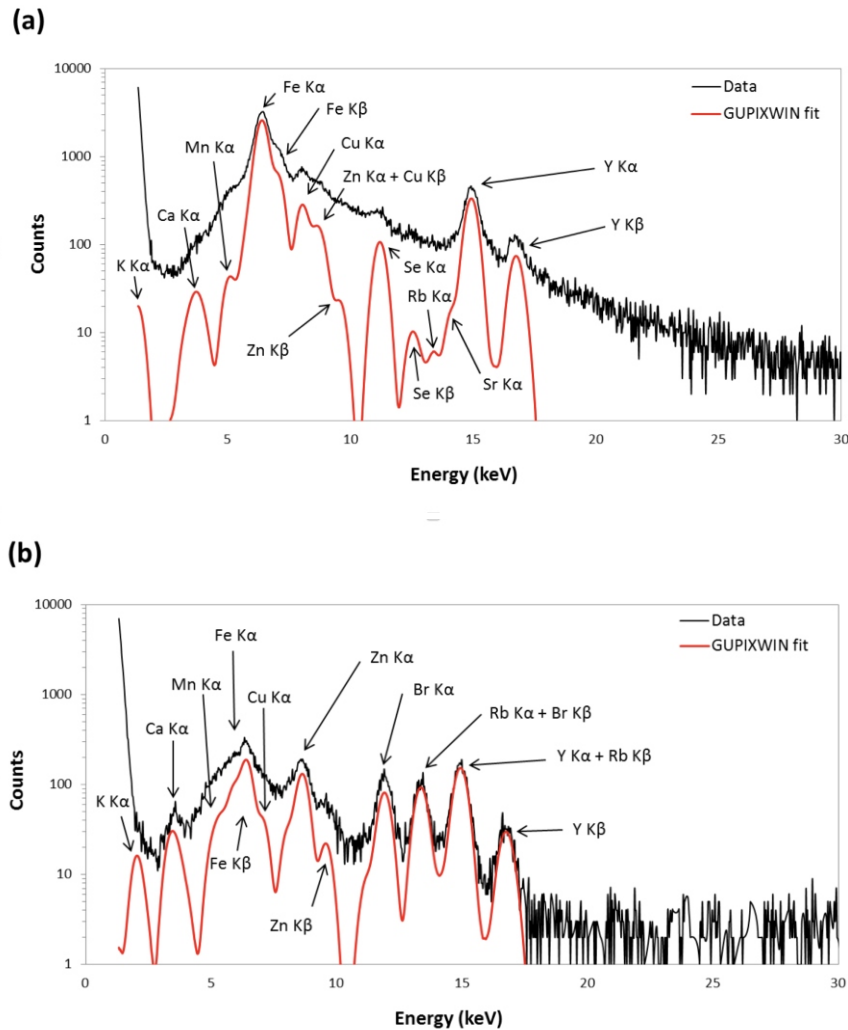
(a)

(b)

Fig. 2. Spectra acquired with X-ray K- and L-lines distinguished for respective elements in the case of organic parsley (a) and non-organic spinach (b). Experimental data was fitted using the GUPIXWIN software [14].

but also their overall content. Again, results for potassium and calcium should be considered as preliminary at best, for the same reason as mentioned above, thus are discussed only partially. Excluding varying values for banana samples, the highest concentrations of potassium (429 ± 42 mg kg^{-1}) and calcium (359 ± 33 mg kg^{-1}) of was found in the tomato and non-organic cabbage sample, respectively, which are one to two orders of magnitude lower than reported values [4]. On the other hand, concentrations of other elements in e.g. non-organic cabbage are in good agreement with the literature values. While content of manganese (27 ± 3 mg kg^{-1}), copper (21 ± 1 mg kg^{-1}) and zinc (30 ± 1 mg kg^{-1}) in this sample are

comparable with the results from the study where analyses were done by PIXE as well [4], concentration of iron (127±2 mg kg^{-1}) was determined to be by a factor of about three higher, though in concordance with the value given in other work [16]. Content of strontium (41±6 mg kg^{-1}) for the same sample was close to the reported value, unlike rubidium (85±3 mg kg^{-1}) which was found to be one order of magnitude higher [4]. Additionally, bromine was undetected in the non-organic cabbage sample which agrees with the result from already cited publication [4].

Examples of partial incoherence of our data with the literature were observed not just for the sample of non-organic cabbage, however, as we investigated a relatively wide spectrum of samples and elements (ten elements in 21 samples), we could not find papers dealing with a set of a similar scope. Because of this, we decided to focus on a mutual comparison of organic and non-organic food species in the next section. Furthermore, several studies [16, 17] showed that foods may contain heavy metals, such as mercury, cadmium or arsenic, whose determination can be important from the toxicological point of view. In our case, no heavy metals were measured above their limit of detection, neither in non-organic nor organic food samples.

Comparison of elemental content in organic and non-organic food species is depicted in Fig. 3 and 4. Results for K and Ca are omitted, for the same reason as discussed above. We can see that concentration of manganese was higher for five out of eight organic samples, although difference is almost negligible in the case of bean. Content of iron and copper was determined to be higher in case of four and six organic species, respectively, though Cu concentration for two remaining organic foods is only slightly lower. The amounts of zinc for five organic samples, similarly to manganese, were larger than for their non-organic variants, though the difference in the case of cucumbers was lower than 4 mg kg^{-1}. Except for iceberg lettuce, cabbage and spinach, where its concentration values for both types were on the level of uncertainty (<3 mg kg^{-1}), selenium was found higher for all organic foods. Bromine was not detected for four conventionally cultivated foods (cabbage, bean, banana's pulp, cucumber) and two organic species (banana's pulp, onion), while being more abundant in the case of other five organic and two non-organic food samples. Content of rubidium, same as for Fe, was determined to be lower for exactly fifty percent of the non-organic sample set. Lastly, strontium concentration values were comparable in the case of bananas (both peel and pulp), beans and cucumbers with the differences of less than 6 mg kg^{-1}; for the rest of the samples, the only organic food with significantly higher content of Sr was spinach.

From the aforementioned comparison based on our obtained results, it is impossible to conclude which type of foods is richer in essential or non-essential trace elements, as their concentrations varied a lot. For example, looking at the bananas' pulps, we can see that the non-organic variant contained much more potassium than the organic one, however, the opposite was true for Fe and Zn. In contrast, mutual comparison of the iceberg lettuce samples showed that they had almost identical content of K, Ca, Cu, Se, Rb and Sr, while being slightly different in zinc (25 mg kg^{-1}) and significantly different in Fe, Mn and Br (43–70 mg kg^{-1}) concentration (Fig. 3). This would suggest that the lettuce sample targets were prepared fairly homogenous and the distribution of the studied elements in this particular food is probably quite uniform. However, results for other samples imply that concentration of element is dependent on its preferential absorption by specific food
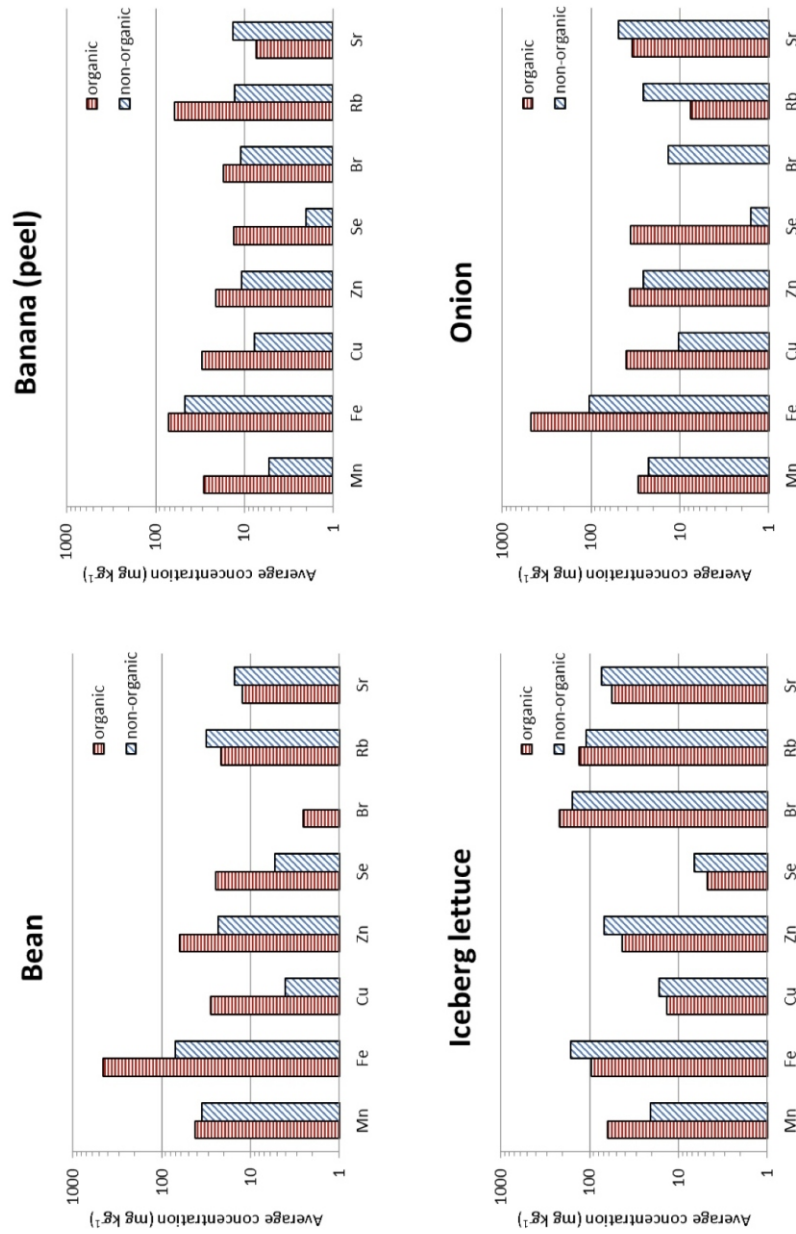
Fig. 3. Comparison of values of concentration of elements of interest determined in organic and non-organic bean, bananas peel, onion and iceberg lettuce by the PIXE method.
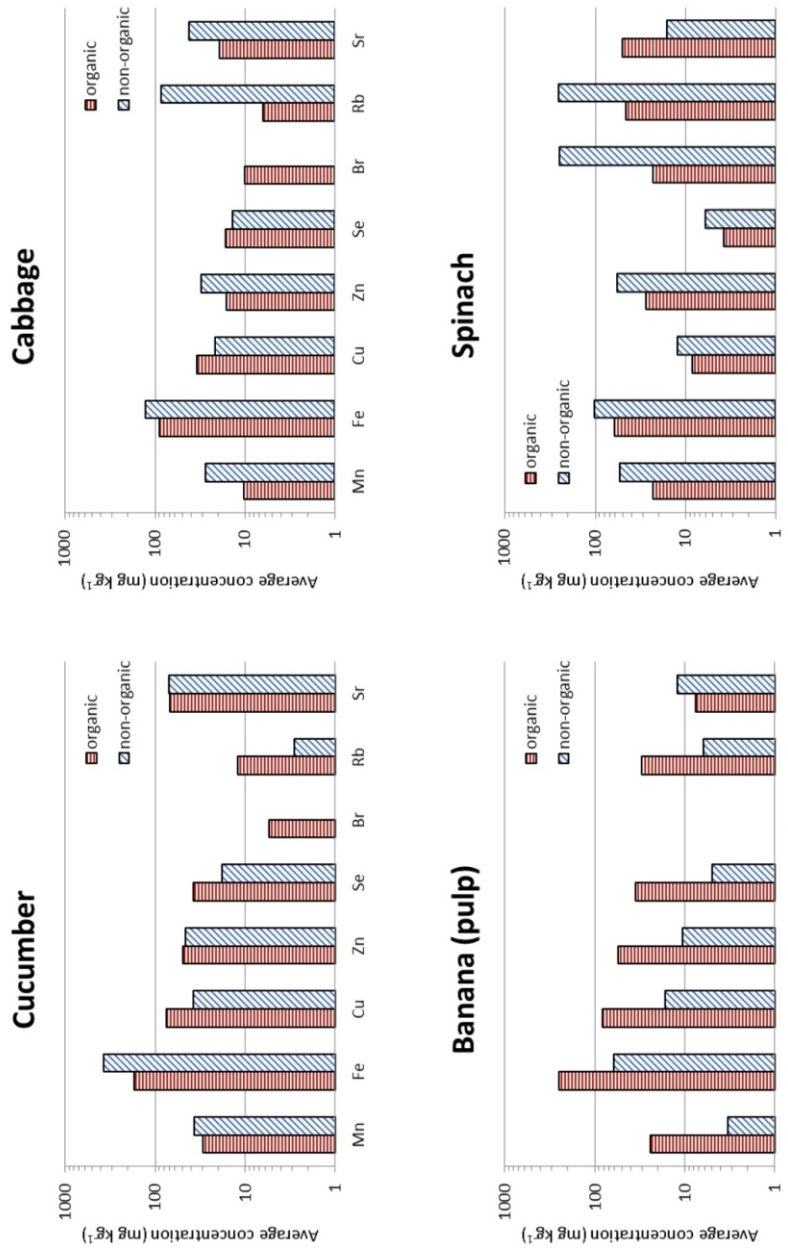
Fig. 4. Comparison of values of concentration of elements of interest determined in organic and non-organic cabbage, cucumber, spinach and banana's pulp by the PIXE method.

species, regardless whether it they are produced in a conventional or organic way. Another important factor to consider is chemical composition of soil where analyzed foods were grown, though its investigation was beyond the scope of this study.

4. Conclusions

Concentrations of macro and trace elements were determined in selected non-organic and organic foods. From eleven foods, we prepared altogether 23 thick samples which were analyzed by PIXE at the CENTA laboratory. Measurements of yttrium, used as an internal standard, and other elements showed that samples were mixed and pressed to some extent inhomogeneously, leading to varying elemental distribution in the irradiated targets, though it may be that determined elements are naturally non-uniformly distributed in examined food species. In some cases (e.g. for parsleys or carrots), low resolution of acquired spectra, allowed only qualitative analysis of the respective samples. Results of direct comparison of non-organic versus organic food species were ambiguous, presumably due to inconsistency in concentration values of the elements of interest. Toxic heavy metals, such as Cd, As or Hg, were not detected in any food sample. The homogeneity problem identified as the main source of hardly interpretable results could be eliminated by further development of the methodology, e.g. by exploiting thin targets instead of thick ones.

Acknowledgments

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