Romanian Reports in Physics, Vol. 63, No. 4, P. 997–1008, 2011

PIXE ANALYSIS OF SOME VEGETABLE SPECIES*

ANA PANTELICA[1], ANTOANETA ENE[2], M. GUGIU[1], C. CIORTEA[1], O. CONSTANTINESCU[1]

[1] "Horia Hulubei" National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH), P.O.B. MG-6, 30 Reactorului St., 077125 Magurele, jud. Ilfov, Romania, E-mail: apantel@nipne.ro
[2] "Dunărea de Jos" University of Galati, Faculty of Sciences and Environment, Department of Chemistry, Physics and Environment, 47 Domneasca St, 800008 Galati, Romania

Received November 3, 2010

Abstract. Proton-Induced X-ray Emission (PIXE) technique was applied to determine major, minor and trace elements in some vegetable species (tomato, cabbage, pepper, and parsnip) collected from agricultural zones in Romania with no specific type of pollution. Proton beam of 3 MeV, generated by the 9 MV FN-type Van de Graaff Tandem particle accelerator of the National Institute of Physics and Nuclear Engineering "Horia Hulubei" (IFIN-HH) in Magurele, was used for PIXE analysis. Thin targets were prepared by pipetting on Mylar foils a chemically mineralized plant solution, with yttrium added as internal standard. The targets were mounted at 45° with respect to the proton beam and X-ray detector (Si(Li) energy dispersive Ortec type of 180 eV energy resolution at 5.9 keV). The GUPIX program and appropriate Certified Reference Materials (CRMs), prepared in a similar way with the investigated samples, were used for a quantitative analysis. The elements determined were Al, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Br, Rb, Sr, and Pb. This paper was supported in part by the Programme PNCDI II of the Education, Research and Youth Ministry in Romania, Project number 72-172/2008.

Key words: trace elements, PIXE, vegetables, tomato, cabbage, pepper, parsnip.

1. INTRODUCTION

Metallic trace elements, or micronutrients, play an important role in the metabolic pathways during the growth and development of plants. Food contamination is an increasingly important public health issue and governments all over the world are intensifying their efforts to improve food safety.

Analysis by atomic and nuclear methods, such as neutron activation analysis (NAA) [1-8], proton-induced X-ray emission (PIXE) [5, 9-14], and X-ray fluorescence (XRF) [2,4,6,15], has been extensively employed in the life sciences, in particular environmental field, due to their capabilities to measure a wide range of elements with an adequate sensitivity.

* Paper presented at the National Conference on Physics, 23–25 September 2010, Iaşi, Romania.

PIXE analytical technique with 3 MeV protons is most sensitive for middle-Z elements, due to the relatively high ionization cross-sections, lower intensity background traceable to the bremsstrahlung of secondary electrons, and high detection efficiency. Its sensitivity is decreasing both for lower- and higher-Z elements. For heavy elements, characterized by smaller ionization cross-sections and lower detection efficiency, PIXE can be completed by NAA [7, 8]. Elements with atomic numbers lower than 15 can be analyzed with a good sensitivity by PIGE [11].

Thick and thin target PIXE was applied at the Van de Graff Tandem Accelerator of the Horia Hulubei National Institute for R&D in Physics and Nuclear Engineering (IFIN-HH) for different interdisciplinary researches, *e.g.* in the environmental science [16-21], materials science [20-22], biology and biomedicine [23-27], archaeometry [28].

This paper presents an application of thin target PIXE to determine concentrations of major, minor, and trace elements in some vegetable samples (tomato, cabbage, pepper, and parsnip) collected from two rural areas with no specific type of pollution in Romania (Crevedia and Magurele).

The GUPIX (Guelph PIXE) program [29] and Certified Reference Materials (CRMs) prepared in a similar way with the investigated samples, with yttrium added as internal standard were used for a quantitative analysis.

The concentration results obtained by us were compared with literature data and Romanian norms.

This study is part of a larger investigation of possible foodstuff contamination with toxic elements originated from industrial activities [8], in the frame of the on-going National Plan of Research, Developing and Innovation (PNCDI II, Project 72-172/2008). The project is focused on the environmental pollution control in South, South-East and Central regions in Romania by high precision and sensitivity methods, including nuclear and nuclear related analytical methods.

2. EXPERIMENT

2.1. SAMPLE CONDITIONING AND PREPARATION

The vegetable samples investigated were collected from Crevedia (Dambovita County) and Magurele (Ilfov County) agriculture sites with no specific type of pollution, situated at 26 km NW, and 13 km SW to Bucharest, respectively. Cabbage (*Brassica oleracea*) and tomato (*Lycopersicon esculentum*) species were sampled from both localities, while pimiento and green pepper (*Capsicum annuum)* were collected from Crevedia, and parsnip (*Pastinaca sativa*) root from Magurele.

The cleaning of samples was carefully performed with distilled and deionized water to remove the external contamination with soil and dust particles [30].

The samples were cut in small pieces using plastic or stainless steel knife, dried in an electric oven at 45–75°C, then ground and homogenized using porcelain mortars. The dried samples were put in polyethylene vials and kept in a desiccator. Wet/dry ratios were determined by using small portions of each plant material.

For the plant sample digestion, an amount of ~30 mg dry sample was introduced in a mixture of 2 mL high purity HNO_3 (65%), 100 µL H_2O_2 and 20 µL HF. The digestion was performed in closed Teflon or polypropylene vessels at 65^0C for about 3 days. An aliquot of 250 µL mineralized solution was diluted with 500 µL ultrapure water (resistivity of 18.2 MΩ·cm), then yttrium internal standard was added (100 µL, from Y_2O_3 nitric solution of 160.78 µg Y·mL^{-1}). Thin targets of about 0.5–1 mg sample/cm^2 were obtained by pipetting volumes of 100 µL diluted solution on Mylar foil (thickness of 2.5 µm). They were dried under electric bulb (~ 40 °C), then fixed on aluminum frames (2 × 3 cm^2).

The same procedure of target preparation was applied for appropriate CRMs considered as calibration standards (mass of ~ 100 mg dry matter).

2.2. EXPERIMENTAL SET-UP

A 3 MeV proton beam, generated by the 9 MV HVEC-FN type Van de Graaff Tandem accelerator of IFIN-HH in Magurele was used for the present PIXE application on vegetal samples chemically prepared as thin targets. The target was placed in the centre of the irradiation chamber at an angle of 45^0 with respect to the incident beam and X-ray detector [21]. The proton beam current on the target was around 0.5 nA, and the collimated beam spot was about 2×2 mm^2. The beam transport tubes and target chamber were maintained in a high vacuum (10^{-5} mbar) during irradiation.

Main characteristics of the X-ray detector used (Si(Li) Ortec type) are: active diameter 10 mm, sensitive depth 5.63 mm, detector to window distance 7 mm, silicon dead layer 0.1 µm, beryllium window 25.4 µm, and energy resolution of 180 eV at 5.9 keV of Mn-K_α (^{55}Fe radioactive source, EC decay type). The spectrometric chain included Canberra S100 multichannel analyzer based on PC.

Aluminum X-ray absorber of 10 µ thickness was put in front of the detector to reduce the high intensity low-energy X-rays in the spectra due to K and Ca (K_α and K_β lines), and thus to improve the analytical sensitivity for higher Z elements (lower pile-up effects).

2.3. X-RAY SPECTRA PROCESSING

GUPIX software [29] was used for the quantitative analysis of the X-ray spectra. Calibration and analytical quality control for the PIXE method were performed by means of appropriate reference materials of certified elemental

concentrations, prepared in a similar way with the investigated samples: IAEA-359 (Cabbage), IAEA-V10 (Hay), INCT-MPH2 (Mixed Polish Herbs, Institute of Nuclear Chemistry and Technology, Warsaw, Poland), P-ALFALFA (Lucerne, Institute of Radioecology and Applied Nuclear Techniques, Košice, Slovakia). Yttrium internal standard was used as proton beam flux monitor both for samples and calibration standards.

Spectral interferences by escape and summing effects in the X-ray spectra, significant in the case of vegetal samples with relatively high K and Ca contents, could be automatically resolved by GUPIX. The K and Ca escape peaks in Si(Li) detector interfere with X-ray lines of Al, P, and S; K and Ca summing peaks could interfere with X-ray lines of Fe, Ni and Cu. In addition, a spectral interference of Y (L lines) and P (K_α) could exist.

3. RESULTS AND DISCUSSION

A typical PIXE spectrum obtained with Si(Li) detector and details of the GUPIX fit for a pepper sample are given in Fig. 1; the calculated fit residues are expressed in units of one standard deviation [29].

Tables 1-3 present the concentrations of S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, and Pb (15 elements) ($mg \cdot kg^{-1}$ dry weight) determined in vegetables (four species) collected from Magurele (M) and Crevedia (C) control sites in Romania. These tables also contain wet/dry ratios measured for each sample, and literature data for vegetable crops cultivated in some regions of the world in various conditions (control and polluted sites; soils irrigated with clean or polluted water; industrial, semirural or rural sites).

The concentration results for K, Ca, Ti, Mn, Fe, Cu, and Zn are comparatively shown in Fig. 2.

In addition, the elements Al in all the samples and Co, As, Se in some of them were qualitatively determined.

The limits of detection (LD), corresponding to 3σ of the background under the characteristic peaks in the spectra, are of the order of $mg \cdot kg^{-1}$ for most of the elements investigated (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb), tens of $mg \cdot kg^{-1}$ for Ca, hundreds for Al and S, and thousands for Cl. The LD values for different elements reflect the general characteristics of the PIXE spectra (background dominated at lower energies by the bremsstrahlung of the secondary electrons, as well as by X- and gamma-ray scattering at higher energies), and the experimental conditions (detection efficiency and attenuation in absorbents for a specific counting set-up, sample matrix and thickness, pile-up effects).

The results presented in Tables 1-3 and Fig. 2 indicate differences among the vegetable species regarding their elemental contents, due to the plant capabilities to absorb and accumulate micronutrients.

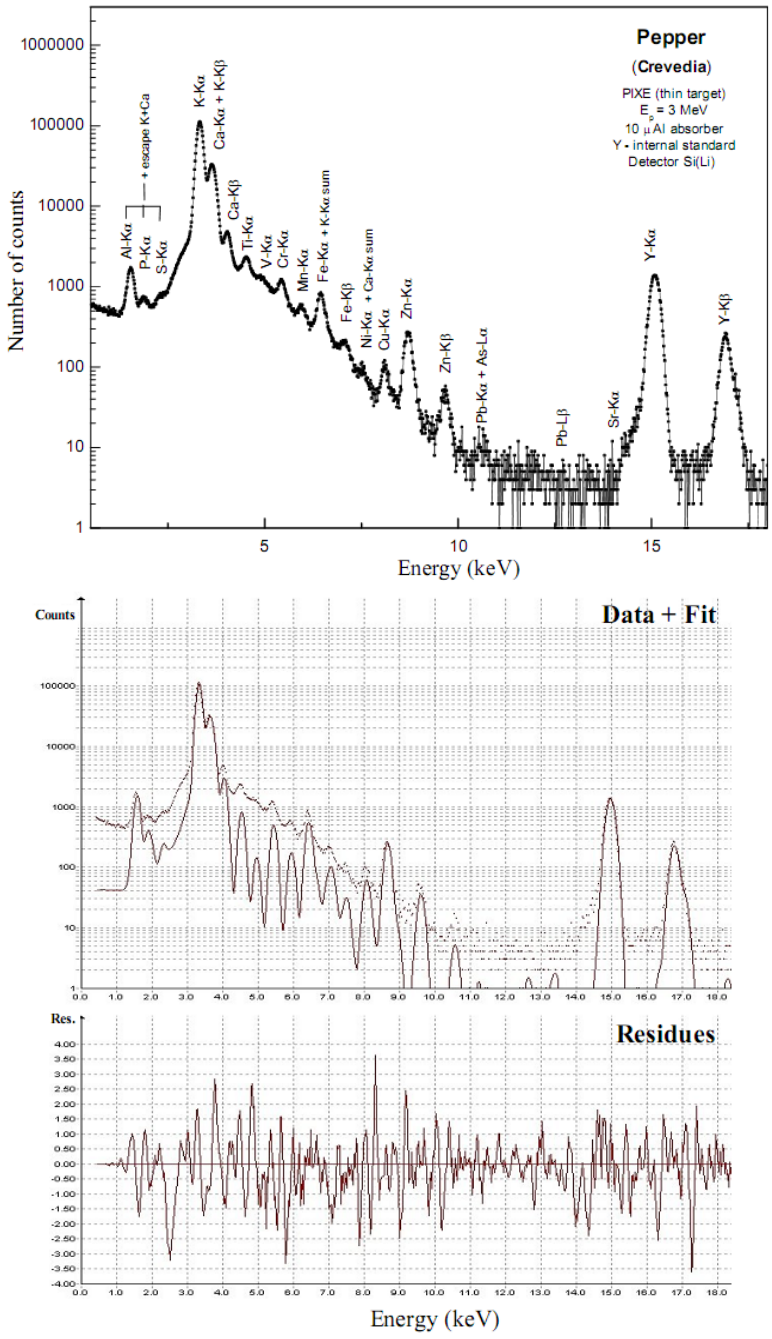

Fig. 1 – PIXE spectrum of a vegetable sample (pepper) irradiated with 3 MeV protons (top) and examples of GUPIX fit (middle) and residues (bottom).

Sulphur concentration was found to be much higher in cabbage compared with the other examined vegetables (ratios 3-12). Relatively higher concentration values (range of ratios, in parentheses) were also determined in cabbage for Ca (1.6-4.4) and Mn (1.2-6.5), as well as in tomatoes for Cl (1.8-4.0), Fe (1.4-4.0), Ni (4-22), and Cu (1.2-3.1).

Table 1

Elemental concentrations determined by PIXE in tomato samples, compared with literature data ($mg \cdot kg^{-1}$; $*g \cdot kg^{-1}$, dry weight)

Elem.	Tomato (Crevedia) this work	Tomato (Magurele) this work	Tomato (municipal markets, Ghana) [7]	Tomato (industrial/ semirural/ rural sites, India) [36]	Tomato[a] (industrial polluted sites, Romania) [35]	Tomato[b] (tannery industry pollution, Nigeria) [32]	Tomato[b] (clear/waste water irrigation, India) [33]	Tomato[b] (tannery industry pollution, Nigeria) [34]	Tomato[b] (agrarian fields, India) [37]
S*	< 1.94	2.48 ± 0.74							
Cl*	22.6 ± 6.9	10.2 ± 4.3							
K*	33.8 ± 1.6	69.0 ± 3.3	1.44-10.7						
Ca*	3.24 ± 0.12	2.79 ± 0.12	0.01-0.16						
Ti	88 ± 12	113 ± 15							
Cr	37.3 ± 8.6	10.1 ± 2.7				3-12	1.5/ 11.9	10.1-14.9	
Mn	15.6 ± 2.1	20.0 ± 1.9	27.2-65.1			1-6			
Fe	85.4 ± 3.0	92.5 ± 3.1				2-10			246.3
Ni	33.8 ± 11.4	24.2 ± 8.1		2.2/ 2.62/ 1.53		1.55-5.67	0.7/ 18.4		1. 90
Cu	24.3 ± 2.0	16.6 ± 1.5		1.9/ 5.9/ 2.5	0.6-0.75	0.34-2.23	3.2/ 8.3		2.76
Zn	46.2 ± 2.1	34.9 ± 1.6		16.5/ 32/ 20.0	3-5.5	2-6	4.3/ 8.0		9.82
Br	13.0 ± 8.3	< 8.3	15.3-37.9						
Rb	< 5.2	7.1 ± 2.4							
Sr	23.7 ± 8.6	< 12.0							
Pb	4.0 ± 1.5	3.0 ± 1.1		3.55/ 1.72/ 0.88	0.5	2-6.66	0.9-14.6	3.92 - 19.4	0.335
Ratio (wet/ dry)	**13.8**	**17.3**							

[a] fresh weight; [b] fresh weight (not explicitly mentioned).

Table 2

Elemental concentrations determined by PIXE in cabbage samples, compared with literature data (mg·kg^{-1}; *g·kg^{-1}, dry weight)

Elem.	Cabbage Crevedia this work	Cabbage Magurele this work	Cabbage external leaves Crevedia this work	Cabbage (market, Nigeria) [39]	Cabbage (phyto-remed. study, Poland) [40]	Cabbage[a] (two sites, no specific pollution, Australia) [38]	Cabbage[b] (tannery industry pollution, Nigeria) [32]	Cabbage[b] (clear/ waste water irrigation, India) [33]	Cabbage[b] (waste water irrigation, Pakistan) [41]
S*	18.5 ± 2.8	10.2 ± 1.6	20.8 ± 3.2						
Cl*	< 5.7	5.6 ± 2.8	18.7 ± 6.1						
K*	41.2 ± 2.0	33.5 ± 1.6	33.0 ± 1.6						
Ca*	5.04 ± 0.18	5.52 ± 0.19	23.4 ± 0.8						
Ti	57.6 ± 7.8	59.1 ± 8.3	65.5 ± 9.0						
Cr	40.5 ± 9.2	6.8 ± 2.1	36.1 ± 8.3				0.21-3.22	0.7/ 7.8	0.34
Mn	44.2 ± 2.1	24.0 ± 1.9	70.5 ± 3.4				1.54-2.43		
Fe	43.3 ± 1.5	37.9 ± 1.6	56.6 ± 2.3				1.22-4.33		
Ni	5.9 ± 2.0	2.5 ± 1.2	< 1.0	0.13-0.19			2-5.33	0.4/ 15.5	
Cu	9.2 ± 0.8	14.3 ± 1.3	5.2 ± 1.0	0.068-0.070		0.356/ 6.27	0.12-0.66	2.4/ 3.2	0.25
Zn	30.3 ± 1.2	20.3 ± 1.1	19.8 ± 1.0	0.032-0.064		2.97/ 8.13	0.33-3.11	4.9/ 20.5	0.78
Br	< 4.4	< 9.5	24.4 ± 11.8						
Rb	4.9 ± 1.3	5.7 ± 2.4	5.2 ± 1.9						
Sr	13.4 ± 5.5	38.8 ± 7.8	202 ± 23						
Pb	0.87 ± 0.47	2.6 ± 1.2	< 1.4	0.09-0.17	3.1	<0.02/ 0.041	0.54-2.11	0.3/10.5	1.921
Ratio (wet/ dry)	**11.96**	**15.26**	**8.47**						

[a] fresh weight; [b] fresh weight (not explicitly mentioned)

By a comparison of the vegetable samples collected from two control sites (tomato and cabbage), higher concentrations in tomatoes were found for Cl, Cr, As, Br, Sr, and Pb at Crevedia, and for Al, S, K, and Rb at Magurele, while higher concentrations in cabbage were found for S, Cr, Mn, Co, Ni, and Zn at Crevedia, and for Cl, Se, Sr, and Pb at Magurele.

Table 3

Elemental concentrations determined by PIXE in pepper and parsnip samples, compared with literature data ($mg \cdot kg^{-1}$; $*g \cdot kg^{-1}$, dry weight)

Elem.	Green pepper Crevedia this work	Pimiento Crevedia this work	Pepper polluted area, Korea [6]	Pepper (municipal markets, Ghana) [7]	Pepper (tannery industry pollution, Nigeria) [42]	Pepper (control/ polluted sites, Korea) [43]	Parsnip (Magurele) this work	Parsnip (phyto-remediation study, Poland) [40]
S*	3.24 ± 0.65	2.79 ± 0.48					1.46 ± 0.39	
Cl*	< 4.4	< 4.0					< 6.0	
K*	40.6 ± 1.9	26.2 ± 1.3		0.74-3.07			27.7 ± 1.3	
Ca*	2.52 ±0.10	1.25 ± 0.05	0.36				2.64 ± 0.10	
Ti	62.5 ± 8.6	44.8 ± 6.1					59.8 ± 8.2	
Cr	42.3 ± 9.7	38.6 ± 8.8	1.7				52.1 ± 11.8	
Mn	12.7 ± 1.5	6.8 ± 0.9		16.1-22.5			9.7 ± 1.2	
Fe	60.8 ± 2.1	48.0 ± 1.5	213				23.3 ± 1.1	
Ni	4.9 ± 1.8	4.5 ± 1.6			2.73-6.90		0.9 ± 0.6	
Cu	12.6 ± 1.1	7.8 ± 0.7	30			8.45/ 25.5	8.9 ± 0.8	
Zn	39.2 ± 1.6	21.3 ± 0.9	103		10.4-35.1	28.1/ 32.2	26.0 ± 1.1	
Br	< 5.8	2.22 ± 1.95		7.56-29.1			< 3.7	
Rb	2.6 ± 0.6	2.0 ± 0.8					13 ± 3	
Sr	< 10.4	< 9.1					11.7 ± 5.5	
Pb	1.20 ± 0.66	0.57 ± 0.33				0.38/ 1.22	0.8 ± 0.5	1.5
Ratio (wet/ dry)	**17.51**	**13.76**					**4.98**	

Comparing external and internal leaves of the cabbage head (collected from Crevedia), higher S, Cl, Ca, Cr, Mn, Fe and Sr concentrations were determined in external leaves (ratios of 2.0, 3.3, 4.2, 5.3, 2.9, 1.5, and 5.2, respectively).

Normal concentrations of K, Ca, Fe, and Cl in fresh vegetables ($mg \cdot kg^{-1}$), given by ref. [45], are: 1860 (K), 80 (Ca), and 6 (Fe) for pepper; 3800 (K), 570 (Ca), 13 (Fe), 350 (Cl) for parsnip; 3100 (K), 150 (Ca), 6 (Fe), 600 (Cl) for tomato; 4000 (K), 720 (Ca), 400 (Cl) for cabbage. These levels were exceeded in some cases: Ca in green pepper, tomato, and cabbage (external leaves) at Crevedia (1.8, 1.6, and 3.8 times, respectively); K in green pepper at Crevedia, as well as in tomato, and parsnip at Magurele (1.25, 1.29, and 1.46 times, respectively); Cl in tomato and cabbage (external leaves) at Crevedia (3.1 and 6.2 times, respectively).
Concerning Cu, Zn, and Pb toxic elements, lower concentrations than the maximum permissible levels given by the Romanian norms were found in all vegetable samples. These reference values, expressed in $mg \cdot kg^{-1}$ fresh weight, are: 5 (Cu), 15 (Zn), and 0.5 (Pb) [44].

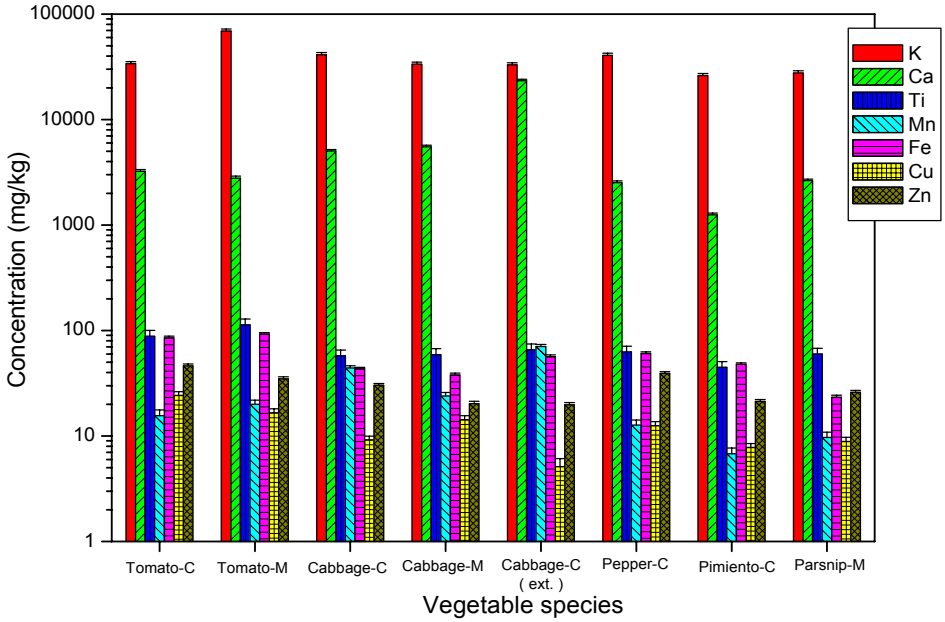

Fig. 2 – Elemental concentrations of K, Ca, Ti, Mn, Fe, Cu, and Zn determined by PIXE in four vegetable species collected from two control sites in Romania (Crevedia – C; Magurele – M).

The results obtained in the present work are comparable with concentration values reported in the literature for tomatoes [7, 32-37], cabbage [32, 33, 38-41], pepper [6, 7, 42, 43], and parsnip [40]. Similarly, higher Cu contents in tomato than in cabbage and other vegetables were reported [32, 33].

Similar results with those determined by using GUPIX were obtained by peak areas calculation in the X-ray spectra using the program GammaW (bremsstrahlung background), followed by corrections of spectral interferences based on mono-element standards. Certified reference materials prepared in the same way with the samples, as well as Y internal standard as proton beam monitor, were also considered for a relative standardization.

4. CONCLUSIONS

PIXE technique proved to be a reliable multi-elemental and high sensitive analytical tool. It is complementary to NAA for determination of Pb, and to the long-lived nuclides NAA, for Al, S, Cl, Ti, V, Mn, and Cu.

Biological samples, in particular plants with matrix composed from low-Z elements (H, C, N, O), undetectable by the usual X-ray spectrometers, are very suitable to trace element analysis by PIXE. Due to their relatively high K and Ca

contents, attention should be paid to the spectral interferences traceable to escape and summing peaks in the X-ray spectra. These difficulties in spectra processing could be successfully resolved by GUPIX program.

Thin-target PIXE offers the possibility to determine elemental concentrations without corrections for X-ray self-absorption and proton stopping in target as it is the case of thick-target PIXE. As disadvantage, a rather difficult target preparation in some of the cases, as well as the risk of incomplete chemical digestion and trace element contamination is to be mentioned.

Comparing the four vegetable species, higher values of Cl, Fe, Ni, and Cu in tomatoes, as well as of S, Ca, and Mn in cabbage were put in evidence.

The levels of Cu, Zn, and Pb toxic elements in these samples are lower than the maximum allowable limits given by the Romanian norms [44].

Compared with the normal levels in Romania [45], concentration values 3-6 times higher were found for Ca and Cl in cabbage (external leaves), as well as for Cl in tomato. Moreover, these levels are slightly exceeded by Ca and K in some of the tomato, pepper, and parsnip samples.

Acknowledgements. This paper was supported in part by *Project TIPSARMER 72-172, from 1/10/2008,* funded by the National Plan of Research, Developing and Innovation PNCDI II, for implementation of high precision and sensibility methods for the bio-monitoring of the environmental pollution in South, South-East and Central regions of Romania.

REFERENCES

1. E. Steinnes, *Neutron activation techniques in environmental studies*, J. Radioanal. Nucl. Chem., **243**, 235–239 (2000).
2. V. Cercasov, A. Pantelica, M. Salagean, G. Caniglia, A. Scarlat, *Comparative study of the suitability of three lichen species to trace-element air monitoring*, Environmental Pollution, **119**, *1*, 129–139 (2002).
3. A. Pantelica, C. Oprea, M.V. Frontasyeva, I.I. Georgescu, E. Pincovschi, L. Catana, *Contamination of crop vegetation with trace elements from a fertilizer plant: An INAA study*, J. Radioanal. Nucl. Chem., **262**, 111–118 (2004).
4. V. Cojocaru, A. Pantelica, E. Pincovschi, I.I. Georgescu, *EDXRF versus INAA in pollution control of soil*, J. Radioanal. Nucl. Chem., **268**, 71–78 (2006).
5. M.C. Freitas, A.M.G. Pacheco, *Elemental concentrations of aerosols near Portuguese power plants by INAA and PIXE*., J. Radioanal. Nucl. Chem., **271**, 185–189 (2007).
6. K. Y. Lee, M. K. Yang, Y. Y. Yoon, S. K. Shim, S. Y. Cho, B. K. Seo, Y. S. Chung, J. H. Lee, *Biomonitoring of environmental pollution based on studies of trace elements in soil and crops***,** J. Radioanal. Nucl. Chem., **259**, *1*, 69–74 (2004).
7. D. K. Adotey, Y. Serfor-Armah, J. R. Fianko,P.O. Yeboah, *Essential elements content in core vegetables grown and consumed in Ghana by instrumental neutron activation analysis*, Afr. J. Food Sci., **3**, *9*, 243–249 (2009).
8. A. Pantelica, O. Culicov, M. Frontasyeva, C.R. Badita, I.C. Calinescu, *Elemental concentrations in vegetable species from industrial zones in Romania determined by INAA*, 16th Radiochemical Conference, April 18–23 2010, Marianske Lazne, Czech Republic, Paper Id:210.

9. S.A.E. Johansson, T.B. Johansson, *Analytical applications of particle induced X-ray emission*, Nucl. Instr. and Meth., **137**, 473–516 (1976).
10. S. Szymczyk, J. Kajfosz, A.Z. Hrynkiewicz and J. Curzydło, *PIXE studies of pollutants in plants*, Nucl. Instr. and Meth., **181**, *1–3*, 281–284 (1981).
11. M. Bertrand, G. Weber, B. Schoefs, *Metal determination and quantification in biological material using particle-induced X-ray emission*, Trends in Analytical Chemistry, **22**, *4*, 254–262 (2003).
12. W. Maenhaut, *Recent advances in nuclear and atomic spectrometric techniques for trace element analysis. A new look at the position of PIXE*, Nucl. Instr. and Meth., **B 49**, 518–532 (1990).
13. O. Innegraeve, X. Blanchet, C. I. Muntel, I. C. Muntele, R. L. Zimmerman, L. Popa-Simil, D. Voiculescu, P. M. Racolta and D. Ila, *PIXE pollution studies across Europe*, Nucl. Instr. and Meth., **219–220**, 191–195 (2004).
14. C. Solis, A. Mireles, E. Andrade, *Environmental applications of PIXE at the Institute of Physics*, UNAM, Rev. Mexicana Fisica, **S53**, *3,* 33–37 (2007).
15. C. Stihi, I. V. Popescu, A. Gheboianu, M. Frontasyeva, A. Ene, G. Dima, O. Bute, V. Cimpoca, V. Stihi, C. Oros, S. Dinu, M. Voicu, *Mineral content of native vegetables obtained by energy dispersive X-ray fluorescence spectrometry*, J.. Sci. Arts, **9**, *2,* 331–334 (2008).
16. A. Pantelica, V. Cercasov, E. Steinnes, P. Bode, H.Th. Wolterbeek, I. Wentz, *Comparative characterisation of air pollution at six industrial sites in Romania*, EC Contract ICA1-CT-2000-70023, Report WP2 IDRANAP 79–04/2004.
17. C. Ciortea, I. Piticu, D. E. Dumitriu, Al. Enulescu, D. Fluerasu, M. M. Gugiu, A. T. Radu, L. C. Dinescu, M. Haralambie, A. Stoichioiu, *Development of analysis methodology using Particle Induced X-ray Emission (PIXE) as a complementary method to determine some heavy metals*, Report WP4 IDRANAP 51–03 / 2003, EC Contract ICA1-CT-2000-70023.
18. Z. Szanto, A. Olariu, *Air quality monitoring studies using lichens*, Report WP1 IDRANAP 09-01/2001, EC Contract ICA1-CT-2000-70023.
19. C. Stihi, A. Bancuta, I. V. Popescu, M. Virgolici, V. Cimpoca, M. Gugiu, Gh. Vlaicu, *Air pollution studies using PIXE and ICP Methods*, IoP Journal of Physics: Conference Series, **41**, 565–568 (2006).
20. A. Ene, I. V. Popescu, C. Stihi, *Applications of proton-induced X-ray emission technique in materials and environmental science*, Ovidius Univ. Ann. Chem., **20**, *1*, 35–39 (2009).
21. A. Ene, I.V. Popescu, C. Stihi, A. Gheboianu, A. Pantelica, C. Petre, *PIXE analysis of multielemental samples*, Rom. J. Phys., **55**, *7–8,* 806–814 (2010).
22. A. Ene, I.V. Popescu, T. Badica, C. Besliu, *Comparative study of PIGE, PIXE and NAA analytical techniques for the determination of minor elements in steels*, Rom. Journ. Phys., **51,** *5–6*, 595–602 (2006).
23. T. Badica, C. Ciortea, V. Cojocaru, M. Ivaşcu, A. Petrovici, A. Popa, I. Popescu, M. Salagean, S. Spiridon, *PIXE and neutron activation methods in human hair material analysis*, Nucl. Instr. and Meth., **3**, *1–3*, 288–290 (1984).
24. I. Suciu, E. A. Preoteasa, D. Gurban, E. Ionescu, D. Bodnar, *Potential of PIXE for the elemental analysis of calcium hydroxide used in dentistry*, Rom. Rep. Phys., **58**, *4,* 569–582 (2006).
25. E. Preoteasa, R. Georgescu, C. Ciortea, D. Fluerasu, L. Harangus, A. Iordan, F. Severcan, H. Boyar, E. Preoteasa, I. Piticu, D. Pantelica, V.I. Gheordunescu, *Standardless PIXE analysis of thick biomineral structures*, Anal. Bioanal. Chem., **379**, *5–6*, 825–841 (2004).
26. C. Stihi, I. V. Popescu, G. Busuioc, T. Badica, A. Olariu, G. Dima, *Particle Induced X-Ray Emission (PIXE) analysis of Basella Alba L leaves*, J. Radioanal. Nucl. Chem., **246**, *2*, 445–447 (2000).
27. E.A. Preoteasa, M. Salagean, A. Pantelica, D. Plostinaru, B. Constantinescu, St. Berceanu, *INAA and PIXE study on the complex modifications of human blood serum mineral composition in several hemopathies*, J. Radioanal. Nucl. Chem., Articles, **151**, *2*, 261–270 (1991).
28. B. Constantinescu, R. Bugoi, E. Oberländer-Târnoveanu, K. Pârvan, *Medieval silver coins analyses by PIXE and ED-XRF techniques*, Rom. Journ. Phys., **54**, *5–6*, 481–490 (2009).

29. J.L.Campbell, D. Higuchi, J.A. Maxwell, W.J. Teesdale, *Quantitative PIXE microanalysis of thick specimens*, Nucl. Instr. and Meth., **B 77**, 95 (1993).
30. A. Wyttenbach, L. Tobler, *Soil contamination in plant samples and in botanical reference materials: Signature, quantification and consequences*, J. Radioanal. Nucl. Chem., **254**, *1*, 165–174 (2002).
31. B. Raith, A. Stratmann, H.R. Wilde, B. Gonsior, S. Brüggerhoff, E. Jackwerth, *PIXE analysis by means of an external proton beam*, Nucl. Instr. and Meth., **181**, 199–204 (1981).
32. J.C. Akan, F.I. Abdulrahman, V.O. Ogugbuaja and J.T. Ayodele, *Heavy metals and anion levels in some samples of vegetable grown within the vicinity of Challawa industrial area, Kano State, Nigeria*, Am. J. Appl. Sciences **6**, *3,* 534–542 (2009).
33. A. Singh, R. Kumar Sharma, M. Agrawal, F. M. Marshall, *Risk assessment of heavy metal toxicity through contaminated vegetables from waste water irrigated area of Varanasi, India*, Tropical Ecology **51,** *2S*, 375–387 (2010).
34. M. S. Abdullahi, A. Uzairu, G. F. S. Harrison, M. L Balarabe, *Trace metals screening of tomatoes and onions from irrigated farmlands on the bank of River Challawa, Kano, Nigeria*, Electronic J. Environ. Agric. Food Chem., **6**, *3*, 1869–1878 (2007).
35. R. Lacatusu, A.R. Lacatusu, *Vegetable and fruits quality within heavy metals polluted areas in Romania*, Carpath. J. Earth Environ. Sci., **3**, *2*, 115–129 (2008).
36. N. Srinivas, S. R. Rao, K. S. Kumar, *Trace metal accumulation in vegetables grown in industrial and semi-urban areas – a case study*, Appl. Ecol. Environ. Res., **7**, *2*, 131–139 (2009).
37. J.I. Nirmal Kumar, H. Soni, R. N. Kumar, I. Bhatt, *Hyperaccumulation and mobility of heavy metals in vegetable crops in India*, J. Agric. Environ. **10**, 29–38 (2009).
38. A. G. Kachenko, B. Singh, *Heavy metals contamination in vegetables grown in urban and metal smelter contaminated sites in Australia*, Water Air Soil Pollut., **169**, 101–123 (2006).
39. O. P. Sobukola, O. M. Adeniran, A. A. Odedairo and O. E. Kajihausa, *Heavy metal levels of some fruits and leafy vegetables from selected markets in Lagos, Nigeria*, Afr. J. Food Sci., **4**, *2*, 389–393 (2010).
40. A. Sekara, M. Poniedziaek, J. Ciura, E. Jedrszczyk, *Cadmium and lead accumulation and distribution in the organs of nine crops: implications for phytoremediation*, Polish J. Environ. Stud., **14**, *4*, 509–516 (2005).
41. M. Farooq, F. Anwar, U. Rashid, *Appraisal of heavy metal contents in different vegetables grown in the vicinity of an industrial area*, Pak. J. Bot., **40**, *5*, 2099–2106 (2008).
42. U.A. Awode, A. Uzairu, M.L. Balarabe, G.F.S. Harrisson and O.J. Okunola, *Assessment of peppers and soils for some heavy metals from irrigated farmlands on the bank of River Challawa, Northern Nigeria*, Pakistan J. Nutrition, **7**, *2*, 244–248 (2008).
43. M. C. Jung, *Heavy metal concentrations in soils and factors affecting metal uptake by plants in the vicinity of a Korean Cu-W mine*, Sensors, **8**, 2413–2423 (2008).
44. *** Hygienic-Sanitary Norms for Aliments, Ordinul Ministerului Sanatatii No. 975/1998, Monitorul Oficial al Romaniei No. 268/1999 (in Romanian).
45. I. Mincu, *Rational alimentation of the healthy people* (in Romanian), Editura Medicală, Bucharest, 1978.