10 years - ANNIVERSARY EDITION *TRAKIA JOURNAL OF SCIENCES*
Trakia Journal of Sciences, Vol. 10, No 2, pp 31-35, 2012

Available online at:
http://www.uni-sz.bg

ISSN 1313-7050 (print)
ISSN 1313-3551 (online)

Original Contribution

DETERMINATION OF HEAVY METALS (Pb, Zn, Cd and Ni) IN EGGPLANT

L. Dospatliev [1]*, K. Kostadinov[2], G. Mihaylova[3], N. Katrandzhiev[4]

[1]Department of Pharmacology, Animal Physiology and Physiological Chemistry, Faculty of Veterinary Medicine, Trakia University, Stara Zagora, Bulgaria
[2] Department of Horticulture, Faculty of Viticulture and Horticulture, Agricultural University, Plovdiv, Bulgaria
[3]Department of Dairy Science, Faculty of Agriculture, Trakia University, Stara Zagora, Bulgaria
[4] Department of Computer systems and technologies, Faculty of Technical sciences, University of Food Technologies, Plovdiv, Bulgaria

ABSTRACT
Heavy metals Pb, Zn, Cd and Ni were found in samples of eggplant collected in the Municipality of Plovdiv. Sample preparation was carried by microwave system Mileston 1200 MEGA. In determining the amount of heavy metals in plant samples ICP - OES were used. To check the accuracy of the method, a reference material CTA-VTL-2 (Virginia tobacco leaves) was used. It was found that the concentrations of the heavy metals determined in the tested eggplant samples were lower than the admissible ones regulated by the World Health Organization.

Key words: eggplant, ICP - OES, Microwave mineralization, heavy metals (Pb, Zn, Cd and Ni)

INTRODUCTION

One of the basic reasons for monitoring the levels of toxic metals in vegetables was the dramatically increased environmental pollution in recent years. The pollution sources are various and range from industrial to agricultural. The heavy metals poison the vegetables, thus causing serious human health risks, such as renal insufficiency, symptoms of chronic toxicity, liver damage, etc.. It is known that vegetable products require strict regulatory control regarding heavy metals content (1-4). Hence, the emphasis is concentrated towards accuracy and precision. However, the general problem of the laboratory quality control is the analyses cost price, i.e. to analyze a maximum number of components at a minimal cost maintaining the high accuracy. A number of techniques were applied for elemental analysis of a wide spectrum of matrices, including colorimetry, polarmetry, voltmetry, X-ray fluorescence analyses, neutron analyses, capillary electrophoresis, complexometry, electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma - optical emission spectrometry (ICP-OES). Recently, however, the establishment of (ICP-OES) including charge-transfer device with a detector, ensures the possibility for the development of flexibility development, consumers programmability, joint multielement capability, increasing spectral information and sample analyses. The low detection limit, high quantum yield and wide linear dynamic range made ICP-OES a viable alternative of the above stated techniques (5). At present the sample preparation remained the basic step in analytical practice, restricting the multielement capabilities of the modern ICP-OES technique.

The aim of the present study was to analyze the heavy metal content in eggplant (Solanum melongena L.) by applying microwave mineralization for sample preparation and to guarantee the quality of these products in the trade network.

***Correspondence to**: *L. Dospatliev, Department of Pharmacology, Animal Physiology and Physiological Chemistry, Faculty of Veterinary Medicine, Trakia University, Stara Zagora, Bulgaria, E-mail:lkd@abv.bg*

MATERIAL AND METHODS

Facilities

Measurements of heavy metals in plant samples were made at the Central Science Laboratory of Sofia University of Mining and Geology by means of an ICP-OES atomic emission spectrometer (model: VISTA-MPX, CCD simultaneous ICP-OES, VARIAN) with operating parameters presented in **table 1**.

Table 1. *ICP-OES parameters used*

ICP-OES parameter		Value
Wavelength	Pb	220.353 nm
Wavelength	Cd	226.502 and 228.802 nm
Wavelength	Ni	231.604 nm
Wavelength	Zn	213.856 nm
Pwr		1 kW
PlasFlow		15 L/min
AuxFlow		1.5 L/min
NebPres		140.00 kPa
Replicate Time		5 s
Stab Time		10 s
ViewHeight		5 mm
Sample Uptake		22 s
Rinse Time		10 s
Pump Rate		25 rpm
Fast Pump		On

Reagents

Reagents are qualified "AR" (pa Merck & Fluka). The starting standard solutions for ICP determination of Ni, Zn, Pb, Cd at concentrations of 1000 mg / l were supplied by Merck, Darmstadt Germany. In all procedures doubly distilled water was used.

Samples

In order to check the accuracy of the method a reference material CTA-VTL-2 (Virginia tobacco leaves) was used. To assess the accuracy of assignment in conducting the experiment and the accuracy of the results obtained by different methods, three generally accepted criteria were used, as follows:

1. $D = X - X_{CRM}$, where X is the measured value and X_{CRM} is the certified value. When D is within the borders of $\pm 2\sigma$, where σ is the standard deviation from the certified value, the result is considered to be good; when it is $-3\sigma \le D \le 3\sigma$ - satisfactory, and beyond these limits the result is unsatisfactory (6).
2. $D\ \% = D/\ X_{CRM}\ .100$ – percentage difference. When the values of D % are in the limits $\pm\ 200\sigma\ /\ X_{CRM}$ the result is considered to be good, when the value is in the limits $\pm\ 200\sigma/\ X_{CRM}$ and $\pm\ 300\sigma/\ X_{CRM}$ - satisfactory, and when it is out of the limits $\pm\ 300\sigma/X_{CRM}$ the result is unsatisfactory.
3. $Z = X - X_{CRM} / \sigma$. When $Z \le 2$ the result is considered to be good, when $2 \le Z \le 3$ - satisfactory, when $Z > 3$ - unsatisfactory.
4. Results in the tables are presented as follows: the good results are marked with 2 stars (**), and satisfactory results with 1 star (*) .

For easier evaluation of the effectiveness of the different methods for sample preparation we have used R criterion showing the extent of extraction of the element in percents from the certified value.

Eggplant (Solanum melongena L.) samples were collected near Nonferrous metal processing plant – Plovdiv, Bulgaria.

The samples were prepared for the experiment in a standard way; they were dried at 65^0 C in a fan oven and stored in dark polyethylene bottles.

Sample mineralization

0.5 g. of dried and well homogenized sample material was weighed, moved into Teflon pots and 10 ml of nitric acid was added. Program mineralization included 3 stages: (I) 5 min nonpulse irradiation - 250 W; (II) 5 min pulse irradiation - 400 W and (III) 5 min pulse irradiation- 600 W. After ventilation for one minute the sample was cooled, transferred quantitatively and some water was added to a final volume of 50 ml. The samples were stored at 4 °C until analysis. The process was carried out in duplicate for each sample.

RESULTS AND DISCUSSION

The values of heavy metal contents in the certified referent material - Virginia tobacco CTA- VTA-2 are presented in **Table 2.** The results for the efficiency of microwave mineralization for Pb, Zn, Cd and Ni determination in the certified referent material - Virginia tobacco CTA- VTA-2 are displayed in **Table 3**.

It was established that the concentrations of the heavy metals determined in the tested eggplant samples were lower than the admissible ones regulated by the World Health Organization.

In a number of studies have been reported that environmental pollution with heavy metals during the recent years and the growing techniques could influence on eggplant phenol contents and mineral composition(7-9). Eggplants (Solanum melongena L.) characterize with high phenols contents with antioxidant activity, as well some minerals such as P, K, Ca and Mg. Vegetables are a significant source of antioxidants and minerals taken up by human diet. Diets with low percent vegetable content are commonly related to a higher death frequency due to cancer or cardio-vascular diseases that could be prevented by antioxidants (10-12).

It was established, on the basis of the results in **Table 3**, that the extent of elements uptake toward the certified value was satisfactory. The analyses of the results obtained by the laboratories participated in FAPAS (Food Analysis Performance Assessment Scheme) during the period 1991 - 2000 Rose et al. (13), showed 30 -100 % satisfactory results, depending on the material, the mineralization method, and the measuring technique. The comparison between 5 methods for samples digestion displayed that the application of sealed pressure vessels gave good analytical results.

Poykio et al. (14) have made similar conclusions based on a comparison between a few methods for dissolving of some certified plant materials for multielemental analysis. However, according to the author microwave digestion combined with ICP-OES or ICP-MS was the most rapid method for agricultural production analyses. It is obvious, that samples mineralization for analytical purposes is the critical stage for obtaining correct data in respect of the heavy metals quantity. The latter is especially essential as in most of the cases agriculture production samples analyzed are not sufficiently homogeneous and usually contain unstable matrices.

Table 2. *Heavy metal content in Virginia Tobacco-CTA-VTA-2 certified reference material*

Certifying marerial Tobacco-CTA-VTA-2	Element, mg / kg			
	Pb	Cd	Ni	Zn
	22.1 ± 1.2	1.52 ± 0.17	198 ± 0.21	43.3 ± 2.1

Table 3. *Effectiveness of microwave mineralization in the determination of Pb, Zn, Cd and Ni in Virginia Tobacco-CTA-VTA-2 certified reference material*

Element, mg / kg	X , mg/kg	σ_{x} , mg/kg	D	D, %	Z	R
Ni	192.3	11.2	-5.7	-2.87	-0.51**	97.1
Zn	42.4	1.8	- 0.9	-2.1	-0.43**	97.2
Pb	23.0	0.8	0.9	4.1	0.75**	104
Cd	1.55	0.07	0.03	2.0	0.18**	102

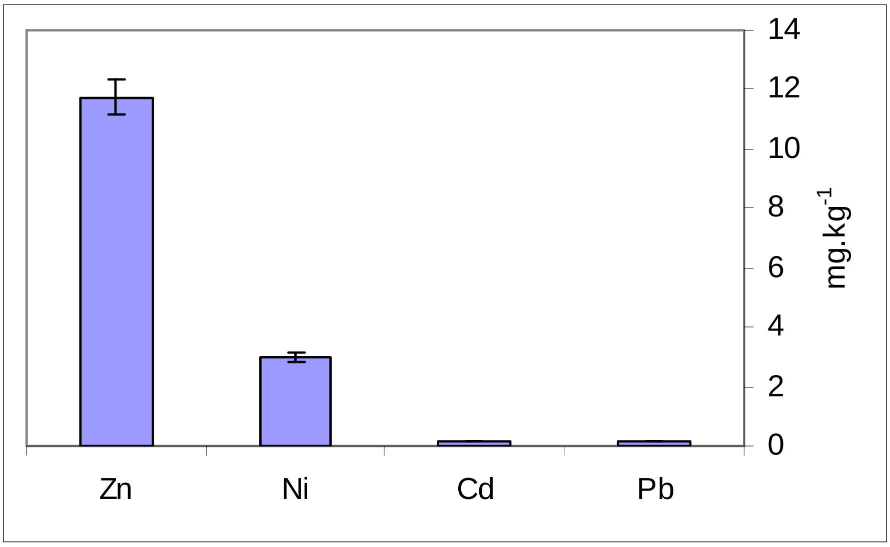

Fig. 1. The content of heavy metals Pb, Zn, Cd and Ni in samples of eggplant

CONCLUSIONS

The pollution of soils and agricultural production with heavy metals is a problem of national scale. In Bulgaria the agricultural land with a soil concentration of heavy metals and metalloids surpassing the allowable limit are above 250 000 da. They are located in Sofia, Vratsa, Montana, Pazardzhik, Haskovo Municipalities and the Rhodopes mining and metallurgical basin. Most of them are contaminated with Pb and Cd. The extent of soil pollution with heavy metals unconditionally impacts seriously the agricultural products grown on them. Therein lays the inevitable risk to human health as a real consumer. It is well known that the pollution from the large industrial enterprises is one of the main threats to human health. Heavy metals are involved in the biological cycle in very low concentrations. So even at minimal increases, they could cause severe damages to human and other living organisms, thus systematic investigations and control are required.

On the basis of the results obtained, it could be concluded that microwave digestion combined with ICP-OES or ICP-MS, is the most rapid method for agricultural production analyses applied by the food industry. .

REFERENCES

1. Flick, G.J., Burnette, F.S., Aung, L.H., Ory, R.L., Angelo, A. Chemical

composition and biochemical properties of mirlitons (Sechium edule) and purple, green, and white eggplants (Solanum melongena). Journal of Agricultural and Food Chemistry, 26: 1000–1005, 1978.
2. Ernst, E. Toxic heavy metals and undeclared drugs in Asian herbal medicines, Trends Pharmacological Sciences, 23:136-139, 2002.
3. Gosslim, R.E., Smith, R.P., Hodge, H.C., Braddock, L.E. Determination of heavy metals for the quality control in argentinian herbal medicines by ETAAS and ICP-OES, Food and Chemical Toxicology, 45:1060-1064, 2007.
4. Raigon, M., Prohens, J., Julio,E., Nuez, F. Comparison of eggplant landraces and commercial varieties for fruit content of phenolics, minerals, dry matter and protein, Journal of Food Composition and Analysis, 21:370– 376, 2008.
5. www.ecn.nl/docs/society/horizontal/hor_desk_18_annex2.pdf. Comparison of the quantities of trace elements extracted from sludges with aqua regia (EN 13346) and with hydrofluoric and perchloric acids (AFNOR NF X 31-147) Information provided by Henri Ciesielski, INRA - Laboratoire d'Analyses des Sols, France.
6. ISO/DIS 13528. Statistical methods for use in proficiency testing by interlaboratory comparisons. International Standardisation Organisation, Geneva, Switzerland , 2002 .
7. Hanson, P.M., Yang, R.Y., Tsou, S.C.S., Ledesma, D., Engle, L., Lee, T.C. Diversity in eggplant (Solanum melongena) for superoxide scavenging activity, total phenolics, and ascorbic acid. Journal of Food Composition and Analysis, 19: 594–600, 2006.
8. Stommel, J.R., Whitaker, B.D. Phenolic acid composition of eggplant fruit in a germplasm core subset. Journal of the American Society for Horticultural Science, 128: 704–710, 2003.
9. Chun, O.K., Kim, D.O., Smith, N., Schroeder, D., Han, J.T., Lee, C.Y. Daily consumption of phenolics and antioxidant capacity from fruit and vegetables in the American diet. Journal of the Science of Food and Agriculture, 85: 1715–1724, 2005.
10. Whitaker, B.D., Stommel, J.R. Distribution of hydroxycinnamic acid conjugates in fruit of commercial eggplant (Solanum melongena L.) cultivars. Journal of Agricultural and Food Chemistry, 51: 3448–3454, 2003.
11. Prohens, J., Rodrıŕguez-Burruezo, A., Raigoŕ n, M.D., Nuez, F. Total phenolic concentration and browning susceptibility in a collection of different varietal types and hybrids of eggplant: implications for higher nutritional quality and reduced browning. Journal of the American Society for Horticultural Science,132: 638–646, 2007.
12. Bravo, L. Polyphenols: chemistry, dietary sources, metabolism and nutritional significance. Nutrition Reviews, 56: 317–333, 1998.
13. Rose, M., Knaggs, M., Owen, L., Baxter M. A review of analytical methods for lead, cadmium, mercury, arsenic and tin determination used in proficiency resting, JAAS, 28 March 2001.
14. Poykio, R., Torvela, H., Peramaki, P., Kuokkanen, T., Ronkkomaki, H.. Comparison of dissolution methods for multi-element analysis of some plant materials used as bioindicator of sulphur and heavy metal deposition determined by ICP-AES and ICP-MS, Analusis, 28: 850-854, 2000.