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Trace element contamination in fruits and vegetables grown in low nutrient availability soil environment by using inductively coupled plasma mass spectrometry

N. Swathi [1], P. Padmavathi[1] and N.V.S. Venugopal[2*]

Department of Chemistry, GITAM University, Visakhapatnam, A.P, India

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ABSTRACT

The major concern of the people in the world is food safety and food quality. The significant aspect of food quality and food safety in general is the state of trace element contamination in fruits and vegetables. In this communication the concentration of different elements were determined by using Inductively coupled plasma mass spectrometry (ICP-MS). The various vegetables such as Brinjol (*Solanum melongena*), carrot (*Daucuscarota* subsp. sativus), Tamoto (*Solanum lycopersicum)* cucumber (*Cucumis sativus*) etc and fruits like orange (*Citrus X sinensis*), grape (*Vitis*), apple (*Malus domestica*) and kiwi (*Apteryx)* were grown in low nutrient available soil environment and procured from varied agricultural farms. At low concentration toxic metals can be very harmful when ingested over a long time period. About twenty seven elements were recorded in various fruits and vegetables by using ICP-MS. after microwave digestion, employing only nitric acid in this step. Trace element determination is important for the prevention of different diseases occurred due to the excessive presence in fruits and vegetables.

Key words*: Trace elements, Absorption spectrometry, Fruits, Vegetables*

Introduction

Vegetables are part of daily diets in many households forming an important source of vitamins and minerals required for human health. They are made up of chiefly cellulose, hemi-cellulose and pectin substances that give them their texture and firmness (Abdulla, 1990). Consumers demands for better quality vegetables are increasing. The perceptions of what is regarded as 'better quality' are however subjective. Some consumers consider undamaged, dark green and big leaves as characteristics of good quality leafy vegetables.

However, the external morphology of vegetables cannot guarantee safety from contamination.

Heavy metals ranks high amongst the chief contaminants of leafy vegetables (Ward, 1995; Rajeshkumar Sarma, 2004; Jeffieries, 2009; Sobukala, 2007; Mapanda, 2007). The intake of heavy metals can lead to altering of humans and animals healthiness state. Thus, the carcinogenic effects generated by continuous consumption of fruits and vegetables loaded with heavy metals such as Cadmium, Lead or even Copper and Zinc are known. There are already published works related to the incidence of gastrointestinal cancer (Tricopoulas, 1997; Turkdogan, 2002) and cancer of the pancreas, urinary bladder or prostate (Waalkes, 1994). Heavy metal contamination of the food items is one of the most important aspects of food quality. Heavy metal contamination of vegetables cannot be under-

([1]Research scholar)

estimated as these foodstuffs are important components of human diet. Vegetables are rich sources of vitamins, minerals, and fibers, and also have beneficial anti oxidative effects. However, intake of heavy metal-contaminated vegetables may pose a risk to the human health. Rapid and unorganized urban and industrial developments have contributed to the elevated levels of heavy metals in the urban environment of developing countries. The aim of this study is to measure the levels of metal ions found in selected fruits and vegetables using Inductively coupled plasma-mass spectrometry (ICP-MS) technique. It is used to determine various elements in fruits and vegetables. This technique offer multi element capabilities. Numerous studies have quantified levels of toxic metal ions in common foodstuffs and in some cases these results have been extended by statistical analyses to generate 'target hazard quotients' (THQ) for a limited number of foodstuffs relating to individual and combinations of metals (Chien, 2002; Wang, 2005; Liu, 2006; Chien, 2006; Zheng, 2007).

Rapid and unorganized urban and industrial developments have contributed to the elevated levels of heavy metals in the urban environment of developing countries. Heavy metals are found everywhere in nature, and cannot be degraded or destroyed. While some metals like selenium, copper and zinc are essential to our diet at trace levels, but any metal in our food is toxic at high levels. The most notorious heavy metal contaminants are mercury, lead, and cadmium. They tend to be dangerous because they bioaccumulation in animal tissues over time. Heavy metal contamination usually originates from polluted water supplies. Fish are most susceptible to heavy metal contamination. The most widely used analytical methods for determination of heavy metals in food are graphite furnace atomic absorption spectrometry (GFAAS) and Inductively Coupled Plasma (ICP).

Various researchers deal with determination of metals in fruits and vegetables at trace, ultra-trace levels using spectrometric, electrometric techniques and inductively coupled plasma mass spectrometer (ICP-MS). ICP technique has become more popular since the early 1990s. Although the use of AAS (flame, graphite furnace, hydride generation and cold vapour) has declined during the same period, it is still the most widely used technique (Rose, 2001).

Materials and Method

All samples of the fruits and vegetables were procured from varied agricultural farms. All the samples, divided in skin and pulp, were oven-dried at 75°C until constant weight and ground to a fine powder by a Fritsch pulverisette 6 with an agate pocket. All precautions taken to prevent element contamination.

Sample Preparation

Vegetables, fruit, crop and plant samples were thoroughly washed to remove all adhered soil particles. Samples were cut into small pieces, air-dried for 2 days and finally dried at 100 ± 1°C in a hot-air oven for 3 h. The samples were ground in warm condition and passed through 1 mm sieve. Digestion of these samples (2 g each) was carried out using 10 ml nitric acid, according to the procedure used for soil samples. Well-mixed milk samples of 250 ml each were taken in 500 ml glass beakers and digested in 24 ml of aqua regia on a sand bath for 3 days. After evaporation to a lesser volume, the samples were filtered and diluted to 50 mL with distilled water.

Acid digestion

Digestion procedures are regularly carried out with either open vessels using acid, acid mixture or basic reagents on hot plates or open- and closed-vessel microwave ovens. The decomposition in open system is hard, time consuming and prone to systematic error sources, i.e. contamination or analyte losses. In case of using microwave radiation, the high cost of instrumentation and dilution of the sample can be considered as disadvantages in the microwave assisted digestion system. Although the amount of sample in vessels is limited due to the generation of gaseous reaction products that can increase of pressure, the use of closed high-pressure vessels is appropriate for efficient sample digestion. On the other hand, in the use of open-focused microwave ovens, the advantages are decreasing the risk to the operator, possible introduction of reagents, During procedure, opportunity to digest larger amounts of sample and low cooling time (Sant'Ana, 2007).

Dry ashing

In general, ashing methods may provide lower analyte recovery and exhibit poorer accuracy com-

pared to acid digestion methods. Although dry ashing procedures are effective, they are time consuming and can often result in loss of analyte species that could occur during the preparation of the sample.

Multi element Analysis

The different conditions of ICP-MS are shown in Table 1

Table 1. ICP-MS Instrumental (PerkinElmer) Conditions

Nebulizer	Quartz Concentric
Spray chamber	Quartz Cyclonic
RF power	1500 W
Integration time	1000 ms (per analyte)
Replicates	3
Cell gas mode	Helium

Results and Discussion

Soil pollution and contamination is indeed a serious problem. Vegetables and fruits are part of daily diets in many households forming an important source of vitamins and minerals required for human health. They are grown in different varieties of soil environments. Before preceding the assessment of trace element contamination in vegetables and fruits, it is customary to know the quality of precious resource soil applied for growth. Poor soil always reduces nutrient mineralization, microbial biomass and activity. Soil health has direct relation with the type of food nutrition they capitulate. The soil map of study area is shown in Fig. 1.

Soil analysis

Soil samples were collected in different sites without undergoing any industrial exposure in and around Visakhapatnam district, Andhra Pradesh, India. Soil samples were dried two days and grind by using mortar and pestle. Filtered through stainless steel sieve (0.2-2 mm). Parameters such as temperature, Electrical conductivity (EC), pH, soil moisture, organic carbon, NPK were determined by using standard procedures and the status is shown in Table 2.

Fig. 1. Soil map of study area

About twenty seven elements were recorded in various fruits and vegetables by using ICP-MS after microwave digestion, employing only nitric acid in this step. Potassium was not found in many fruit and vegetables. The method has been validated by using both an oil reference material and recovery experiments over different fruits and vegetable samples, obtaining satisfactory results in all cases. The mean (±SD) concentrations were calculated for each trace metal in all kind of fruits and vegetables. Based on the average concentration and the average consumption of edible vegetables, estimates of the amount of each trace metal consumed were calcu-

Table 2. Preliminary properties

Parameter	Sample1	Sample1	Sample1	Sample1
Temperature ^{0}C	26	26.8	26.5	27.1
pH	6.8	7.9	6.85	7.1
Electrical conductivity(S/m)	220	217	238	241
Organic carbon/Kg	2.2	2.95	2.43	3.1
Moisture (%)	1.8	2.4	5.2	3.7
N kg/Ha	142.2	167.5	141.8	179
P kg/Ha	28	31	26	29.5
K kg/Ha	302	341	298	352

Table 3. Trace elements in vegetables determined by Inductively coupled plasma-mass spectrometry

Analyte	Cell gas mode; Helium		Concentration; microgram per litre	
	BRINJOL µg L^{-1}	CARROT µg L^{-1}	TOMATO µg L^{-1}	CUCUMBER µg L^{-1}
Na	162957.924	418336.559	58197.041	S
Mg	167728.203	149077.305	89505.283	1077778.53
Al	1192.118	71478.474	2970.597	13130.186
Si	122800.202	62684.303	11601.634	171372.718
K	S	S	S	687421.06
Ca	218589.478	359213.563	68265.649	1325244.174
V	249.694	692.642	220.257	476.922
Cr	111.900	267.612	117.245	462.883
Mn	1143.617	3831.361	721.555	1923.889
Fe	3074.207	42076.326	3049.325	11653.478
Ni	399.438	361.889	267.907	951.185
Co	11.162	89.108	11.298	46.967
Cu	797.314	879.350	390.685	2276.666
Zn	2916.913	1620.642	1363.559	5707.169
As	104.312	281.066	133.543	843.105
Se	7.343	-4.441	3.841	-11.907
Rb	383.620	2124.950	2198.879	5350.073
Sr	1184.871	2414.766	614.699	15976.091
Mo	18.784	20.555	18.072	314.418
Ag	8.786	10.035	12.494	20.070
Cd	2.997	1.125	4.891	8.599
Sb	1.490	1.861	1.518	3.048
Ba	959.165	4724.498	477.951	3856.353
Tl	0.027	0.655	0.035	0.046
Pb	56.596	69.086	76.439	108.391
U	1.708	2.378	0.718	2.540

S - Beyond detection (Over saturated)

Table 4. Trace elements in fruits determined by Inductively coupled plasma-mass spectrometry

ANALYTE	Cell gas mode; Helium		Concentration ; microgram per litre	
	ORANGE µg L^{-1}	GRAPES µg L^{-1}	APPLE µg L^{-1}	KIWI µg L^{-1}
Na	311099.157	14858.646	145442.216	137251.951
Mg	309052.734	19953.586	70932.983	96694.948
Al	1393.29	1678.014	2578.263	3996.808
Si	105708.537	8639.017	80865.670	112768.234
K	S	S	S	S
Ca	1636550.440	32239.319	101444.128	250210.138
V	286.726	302.120	265.712	256.342
Cr	73.782	102.225	134.135	96.781
Mn	1060.928	425.685	245.302	391.169
Fe	6433.767	1926.157	2183.239	2624.397
Ni	273.257	1144.834	160.968	257.314
Co	11.654	5.598	38.069	13.066
Cu	313.782	171.380	127.746	663.476
Zn	1698.208	731.695	1411.135	1900.260
As	1503.823	143.570	167.119	260.239
Se	28.414	3.862	4.416	0.845

Table 4. *Continued ...*

ANALYTE	Cell gas mode; Helium		Concentration ; microgram per litre	
	ORANGE	GRAPES	APPLE	KIWI
	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
Rb	352.278	484.866	157.193	524.060
Sr	23418.949	222.025	799.751	1801.222
Mo	12.537	7.767	14.468	11.058
Ag	11.535	13.191	5.561	11.605
Cd	1.099	1.127	0.989	1.279
Sb	2.048	1.052	1.369	1.919
Ba	8890.318	170.539	756.155	2026.063
Tl	0.233	0.060	0.043	0.055
Pb	56.631	79.055	69.929	67.894
U	1.820	0.674	1.435	1.587

S - Beyond detection (Over saturated)

lated. The results of trace elements in vegetables and fruits were given in Table 3 and 4.

Conclusion

The intake of heavy metals can lead to altering of humans and animals healthiness state. The aim of this study was to determine the concentrations of trace metals in selected edible fruits and vegetables. ICP-MS has excellent analytical features such as simultaneous multielement capability, extremely high sensitivity, and wide linear dynamic range for most metal elements. Therefore the method has been validated by using both an oil reference material and recovery experiments over different fruits and vegetable samples, obtaining satisfactory results in all cases.

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