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Application News

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ICPMS-2030

Establishment of analytical method on Shimadzu Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) for toxic elements in fruits

Introduction

Fruits and vegetables have great importance in our diet because they have various nutrients like carbohydrates, proteins, vitamins and minerals. Sometimes they also contain elements like calcium, iron etc. which play very important role in various biological functions of human body. In addition to these important elements, some elements which do not have any role in biological functions may get accumulated in fruits and vegetables. Among these elements, toxic elements like lead, cadmium and mercury are notable.

In the last decade, the pollution caused by toxic elements has raised public awareness. The scientists all over the world are studying harmful effects caused by toxic elements. These elements may be deposited from the earth's surface and absorbed by fruits and vegetables. They are transferred from plant body to human beings. Elemental content of fruits need to be checked to assure their usage for consumption. We must have a sensitive and reliable analytical method for elemental quantitation. Here we present an ICP-MS method for determination of toxic elements in fruit sample. Table 1 shows Maximum Residual Limits (MRLs) as per FSSAI[1,2] . . Limit Of Quantifications (LOQs) were set as per commission regulation (EU) 836/2011[3] .

Table 1: FSSAI MRLs (ppm) for fruits and LOQs (ppm) achieved in present work

Elements	FSSAI MRLs (ppm)	LOQ (ppm)
Arsenic (As)	1.1	0.22
Cadmium (Cd)	1.5	0.3
Copper (Cu)	30	6
Mercury (Hg)	1.0	0.2
Lead (Pb)	0.1	0.02
Tin (Sn)	250	50
Zinc (Zn)	50	10

Experimental

Two types of fruits (Apple and Pear) were purchased from local market for this study.

Sample Preparation

About 500 mg of sample was weighed into microwave vessels. Samples were kept for pre digestion after carefully adding 2 mL high purity nitric acid and 2 mL ultrapure water. Samples were digested under controlled temperature program (Table 2). After digestion, samples were cooled to ambient temperature and transferred to 50 mL volumetric flask and diluted with ultrapure water. Pre-spiked recovery samples were prepared at LOQ & 10 x LOQ levels.

Table 2: Microwave digestion program

Steps	Ramp (min)	Temp (°C)	Hold time (min)
1	10	120	05
2	10	180	20

Calibration standard preparation

Certified reference standards of each element (1000 ppm) were used for preparation of intermediate stock solution. Calibration standard solutions were prepared by diluting intermediate stock solution to cover concentration range from 10 to 250 % of MRLs. The concentrations of linearity standards are given in Table 3.

Table 3: Concentrations of linearity standards in ppb

STD	As	Cd	Cu	Hg	Pb	Sn	Zn
BLK	0	0	0	0	0	0	0
10%	1.1	1.5	30	1	0.1	25	50
20%	2.2	3	60	2	0.2	50	100
50%	5.5	1.5	150	5	0.5	125	250
100%	11	15	300	10	1	250	500
200%	22	30	600	20	2	500	1000
250%	27.5	37.5	750	25	2.5	625	1250

Analytical Conditions

A Shimadzu ICPMS-2030 coupled with auto sampler AS-10 and quartz mini-torch plasma system (Figure 1 & 2) was used for developing method for measuring elements in Apple and Pear. The instrument configuration and operating parameters are summarized in Table 4.

Fig 1. Shimadzu ICPMS-2030 with autosampler AS-10

Continuous Calibration Verification (CCV) checks were run in between to monitor drift of the system throughout the run. Standard of LOQ concertation was run as CCV.

Table 4. Instrumental parameters

Plasma torch	Mini torch (P/N:S211-94018)
Radiofrequency	1.2 kW
Sampling depth	5 mm
Plasma gas flow rate	10 L/min
Auxiliary gas flow rate	1.1 L/min
Carrier gas flow rate	0.7 L/min
Collision gas flow rate	Helium - 6.0 mL/min

Result

The calibration standard solutions showed good linear response with correlation coefficient (r) ≥ 0.999 for all elements. Results of percentage recoveries for Apple and Pear are given in Table 5.

Fig 2. Quartz mini torch for ICPMS-2030

The percentage recoveries at LOQ and 10 x LOQ level was between 80 to120 % for all elements.

% RSD of result obtained for 4 preparation are less than 8 indicating good repeatability.

The percentage recovery of the CCVs was between 90 to 110 % for Apple and Pear sample. The results are shown in Table 6.

The content of all elements in Apple and Pear was found be below LOQ.

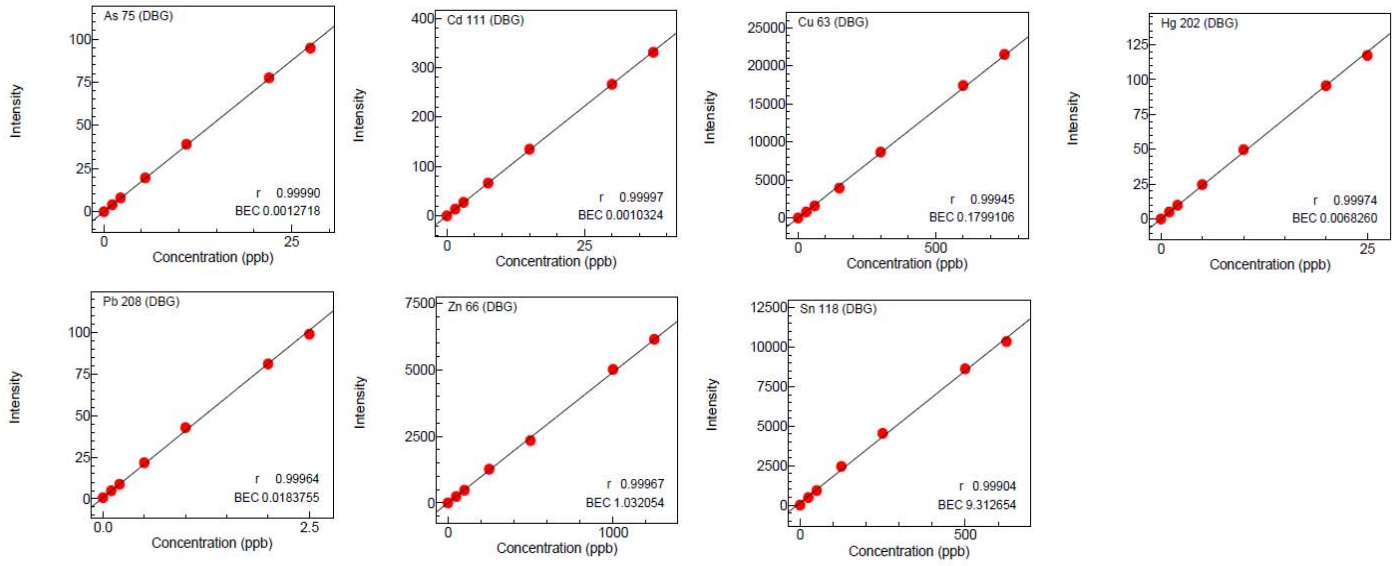

Fig 3. Typical calibration graphs obtained in present study

Table 5: Average % recovery and % RSD at LOQ, 10 x LOQ (n=4 replicates)

Elements	Apple				Pear			
	LOQ % recovery	LOQ % RSD	10 x LOQ % recovery	10 x LOQ % RSD	LOQ % recovery	LOQ % RSD	10 x LOQ % recovery	10 x LOQ % RSD
As	95.8	3.9	91.9	3.8	101.5	5.1	101.5	2.1
Cd	96.5	3.3	90.9	3.9	107.2	3.1	108.4	2.0
Cu	91.1	4.0	93.2	4.4	101.9	3.1	101.1	1.5
Hg	99.2	4.0	90.6	3.6	105.1	2.9	105.7	1.6
Pb	103.1	4.2	94.6	7.4	103.2	6.6	111.7	7.4
Sn	105.2	4.4	96.1	5.6	103.7	4.4	101.2	2.6
Zn	89.2	3.4	90.7	5.0	97.3	2.8	100.0	1.4

Table 6: % Accuracy of continuous calibration verification standards

Elements	Apple			Pear		
	CCV 1	CCV 2	CCV 3	CCV 1	CCV 2	CCV 3
As	96.4	100.5	102.3	97.7	96.4	101.4
Cd	99.0	99.0	101.0	100.7	101.3	106.3
Cu	92.0	95.3	96.7	104.2	103.2	104.8
Hg	108.5	103.5	109.0	101.0	93.0	99.0
Pb	102.5	102.0	101.5	92.0	104.5	100.0
Sn	90.0	95.6	97.0	94.0	91.0	96.4
Zn	91.4	94.6	97.2	102.0	100.0	103.0

Conclusion

A simple digestion method for determination of toxic elements in Apple and Pear by ICPMS is established. Using ICPMS-2030, excellent spike recoveries were achieved for all elements in spiked samples. Figure of merits like % recovery and % RSD shows reliability of the method. The accuracy of the CCV standards shows robustness of the plasma while analyzing different types of matrix.

References

[1] Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2011

[2] Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2006

[3] Commission regulation (EU) No 836/2011

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