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Estimation of heavy metals in processed fruit products using Shimadzu inductively coupled plasma mass spectrometry

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1. Overview

In the present work, an inductively coupled plasma mass spectrometry (ICPMS) method for elemental analysis of processed fruit products with ICPMS-2030 was developed.

2. Introduction

Commercially available fruit jams, juices and concentrates (Figure 1) contain different physiologically and nutritionally important compounds, e.g. bioactive phytochemicals (phenolic, flavonoids, carotenoids etc.) and vital nutrients (proteins, carbohydrates and vitamins).

An increased popularity and demand for these food items is due to increased awareness about healthcare and average life expectancy in society. All these reasons make fruit products very widely consumed in both developed and developing countries by different age groups. Apart from nutritional and functional compounds, fruit juices contain many major (macro elements like Ca, K, Mg etc.), minor (micro elements like Cu, Fe, Mn, Zn etc.) and trace elements (As, Cd, Cr, Pb, Hg, Se etc.).

Figure 1. Typical processed fruit items

Copper plays an important role in hemoglobin synthesis. Zinc is essential for many enzymes involved in several physiological functions such as protein synthesis and energy metabolism. Lead is highly toxic element that accumulates in biological systems and it leads to deficits in psychological functions such as intelligence and learning ability in humans. Even though macronutrients are required for many biological functions, their excess presence in human body leads to health hazards. The main sources of the elements in such samples may be water, fruit, soil, manufacturing process, container and environmental contamination due to fertilizers, pesticides, raw materials etc.

Considering the nutritional value associated with essential elements indispensable for life maintenance on one hand, and the health hazard of toxic elements on other hand, elemental analysis of these food items is of importance. It becomes particularly important for fruit products, due to high seasonal variability in their elemental composition. Their regular examination with respect to elemental content can bring valuable information about their suitability for consuming. Reliable information on the elemental content of jam, fruit juice, and concentrates can help producers to improve the overall quality of these products by identifying sources of contamination with toxic elements. It is also important for consumers in view of the nutritional value of processed fruit products.

The present work aimed to develop an ICPMS method for determination of heavy elements in jam, juice and concentrates samples as per FSSAI limits.

3. Method

Commercially available samples from local market were used for this experiment. The Maximum Residual Limits (MRL's) of elements as per Food Safety Standards Authority of India (FSSAI) guidelines are shown in Table 1. The analysis was performed on Shimadzu ICPMS-2030 (Figure 2) coupled to an autosampler.

Table 1. FSSAI limits for heavy element in processed fruit products

Element	FSSAI Limit in ppm
Arsenic (As)	0.1*
Cadmium (Cd)	0.1*
Mercury (Hg)	1
Lead (Pb)	1
Copper (Cu)	7
Tin (Sn)	250
Zinc (Zn)	5

*Due to nonavailability of FSSAI limits, they were taken arbitrarily.

Figure 2. ICPMS-2030 with auto sampler AS-10

3-1. Sample preparation

About 500 mg of sample was weighed in microwave vessels. Samples were kept for 10 minutes of pre-digestion after carefully adding 3 mL of suprapure nitric acid (HNO_3) and 2 mL of ultra pure water. The vessels were then heated in microwave digestor under controlled temperature program (Table 2).

After digestion, samples were left to cool at ambient temperature and filled up using ultra-pure water in a 50 mL volumetric flask. Pre-spiked recovery studies were carried out at limit of quantifications LOQ & 10 x LOQ levels by spiking samples with standard stock solution. The LOQ level was set as per EC 836/2011. Table 3 shows the (LOQs) which were achieved in the present study.

Table 2. Microwave digestion program used in present study

Ramp (min)	Temperature (°C)	Hold (min)
10	120	5
10	180	30

Table 3. LOQs for processed fruit products

Element	LOQ in ppm
As	0.02
Cd	0.02
Hg	0.2
Pb	0.2
Cu	1.4
Sn	50
Zn	1

3-2. Calibration standard preparation

Sigma Aldrich 1000 ppm individual certified reference standards were used for preparation of intermediate stock solution. Calibration standard solutions were prepared by diluting intermediate stock solution. Yttrium and Bismuth were used as internal standards. Internal standards were aspirated using online internal standard addition kit. The instrumental configuration and analytical conditions are given in Table 4. The concentrations of linearity standards are given in Table 5.

Table 4. Instrumental Parameters

Plasma torch	Mini torch
Radiofrequency	1.2 kW
Sampling depth	5 mm
Plasma gas flow	10 L/min
Auxiliary gas flow	1.1 L/min
Carrier gas flow	0.7 L/min
Collision gas	Helium
Collision gas flow	6.0 mL/min
Cyclone Chamber temp.	5 °C

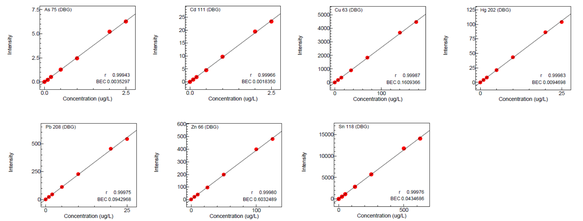

Figure 3 Linearity curves for targeted elements

The calibration standard solutions showed good linearity with correlation coefficient ≥ 0.995. The internal standards used were Bi and Y. The selection of internal standard was as follows; for Pb and Hg, Bi was used and for As, Cd, Cu, Sn and Zn, Y was used as internal standard. The concentration of internal standard was 20 ppb. The memory effect of mercury was alleviated by adding 100 ppb gold into the standards and samples.

Table 5 Concentrations (in ppb) of linearity levels used in present work

Calibration level	As	Cd	Hg	Pb	Cu	Sn	Zn
Level 1	0.1	0.1	1	1	7	25	5
Level 2	0.2	0.2	2	2	14	50	10
Level 3	0.5	0.5	5	5	35	125	25
Level 4	1.0	1.0	10	10	70	250	50
Level 5	2.0	2.0	20	20	140	500	100
Level 6	2.5	2.5	25	25	175	625	125

4. Results

The elemental content in all matrices was found to be below LOQ. Table 6 shows the results obtained for % recoveries at LOQ and 10 x LOQ level. Using ICPMS-2030, excellent spike recoveries were achieved for most of the elements in spiked samples. Recoveries were within 80 to 120 % for all elements.

Table 6. Average % recoveries obtained at LOQ and 10 X LOQ (n=4)

Elements	Jam		Juice		Concentrate	
	% Recovery at LOQ	% Recovery at 10 X LOQ	% Recovery at LOQ	% Recovery at 10 X LOQ	% Recovery at LOQ	% Recovery at 10 X LOQ
As	91.8	91.7	92.5	95.2	102.3	99.8
Cd	97.4	95.4	92.3	93.8	99.1	95.6
Hg	94.9	92.7	95.2	92.3	97.3	91.7
Pb	101	97.4	97.4	96.2	103	102.4
Cu	99.5	94.4	103.3	99.6	109.9	107.7
Sn	96.1	100.9	96.1	97.5	98.6	104.7
Zn	107.1	94	96.8	94.9	108.6	96.7

5. Conclusion

The macronutrient as well as toxic elements specified by FSSAI were measured in sub ppb to ppm range. The spiked recoveries shows reliability of the method. The results demonstrate suitability of the Shimadzu ICPMS-2030 for routine analysis of jam, juice and concentrate samples.