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Application News

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ICPMS-2030

Determination of toxic elements in milk powder using Shimadzu ICPMS 2030

❑ Introduction

Milk is a complex matrix composed of several organic constituents like carbohydrates, proteins and fats as well as inorganic constituents like calcium and phosphorus. Several processed milk products are consumed daily in India as well as world wide. In addition to nutritional values, these products can also have toxic elements like As, Cd, Pb and Hg. They can get transferred from contaminated soil to plants and then into grass, causing accumulation of these toxic metals in cattle, but also in human consuming milk. Milk processing may also cause contamination of milk products with these toxic elements. India is the largest milk producer as well as consumer in the world. Several dairy products are exported from India to all over the word. These products include cheese, paneer, milk powder etc. The regulating agencies like Food Safety And Standard Authority Of India (FSSAI) and Export Inspection Council (EIC) have laid down stringent specifications for Maximum Residue Limits (MRL) in milk and milk products[1-2]. These milk products has to meet the specifications laid by FSSAI/EIC in order to export them to Europe, USA or any other international market and to sell them in Indian market.

In the present study, one milk powder sample was analyzed using Shimadzu ICPMS 2030. The milk powder was tested to meet the specifications of FSSAI.

❑ Experimental

The calibration standards of As, Cd, Hg, Pb, Cu, Sn, and Zn were prepared form NIST traceable 1000 ppm Merck standards. All calibration standard were prepared in 16 % nitric acid. The linearity was performed from 10 to 250 % of the maximum residue limit (MRL) laid down by FSSAI. The elements Ce, Y, Ge and Sc were used as internal standard in the present study. The concentration of internal standard was kept at 20 ppb.

The milk powder sample was purchased form local market. The sample was weighed to 500 mg and transferred to PTFE vessels of microwave digestion system (MWD). To the vessel, 4 ml suprapure nitric acid and 1 ml water was added and the vessel was kept for heating as per MWD program given in Table 1.

After the digestion was complete, samples were quantitatively transferred to 25 ml volumetric flasks and diluted upto the mark with ultrapure water.

Table 1. MWD program for milk powder sample.

Ramp (min)	Temperature (°C)	Hold (min)
10	120	5
10	180	20

❑ Analytical conditions

The Shimadzu ICPMS 2030 featuring newly developed collision cell and fitted with standard sample introduction system (Micromist glass concentric nebuliser, a quartz peltier cooled spray chamber and quartz mini torch) was used for the analysis. The instrument was tuned before the analysis to maintain the oxide ratio and doubly charged ratio below 2 %. For polyatomic interference removal, the He with a flow rate of 6 ml per min was used.

The instrument operating conditions are summarised in Table 2.

Table 2. Instrumental conditions used in present study

Instrument	ICPMS 2030
RF Power (kW)	1.2
Sampling Depth (mm)	5.0
Plasma gas (L/min)	10.0
Auxiliary gas (L/min)	1.10
Carrier gas (L/min)	0.72
Cell gas (mL/min)	6.0
Chamber temperature (°C)	5
Profile integration time	Mid
Number of scan	10
Integration time (s)	2

The sample aspiration was performed using online internal addition kit. The internal standard is constantly nebulised and is mixed with the sample prior to nebulisation.

❑ Online internal standard addition kit

The online internal standard addition kit designed by the Shimadzu has following advantages

- It saves the time required for addition of internal standard in each sample and standard , thereby increasing the throughput
- As internal standard is constantly pumped to nebuliser, any change in sample introduction system or impact of matrix on analyte signal can be compensated without any ambiguity.

The calibration was performed from 10 % of the MRL to 250 % of the MRL. The MRLs are given in Table 3.

Table 3. MRL for toxic elements as per FSSAI

Element	MRL as per FSSAI (ppm)
As	1.1
Cd	1.5
Hg	1
Pb	0.02
Cu	30
Sn	250
Zn	50

Memory effect for mercury was minimized through the addition of 100 ppb gold solution in all standards and sample solutions. Continuous calibration verification standards were run periodically during the sequence to check the instrumental drift.

❑ Results and discussion

The results showed good linear response (figure 1) with correlation coefficient ≥ 0.999. The values obtained along with 3s (LOD) & 10s (LOQ) values are given in Table 4. The results obtained for given milk powder sample are shown in Table 5.

Table 4 Details of the calibration curve

Element	Correlation coefficient	3s	10s
As	0.99999	0.0001	0.0003
Cd	0.99988	0.001	0.005
Hg	0.99989	0.006	0.020
Pb	0.99987	0.0008	0.002
Cu	0.99995	0.013	0.045
Sn	0.99986	0.046	0.155
Zn	0.99994	0.026	0.087

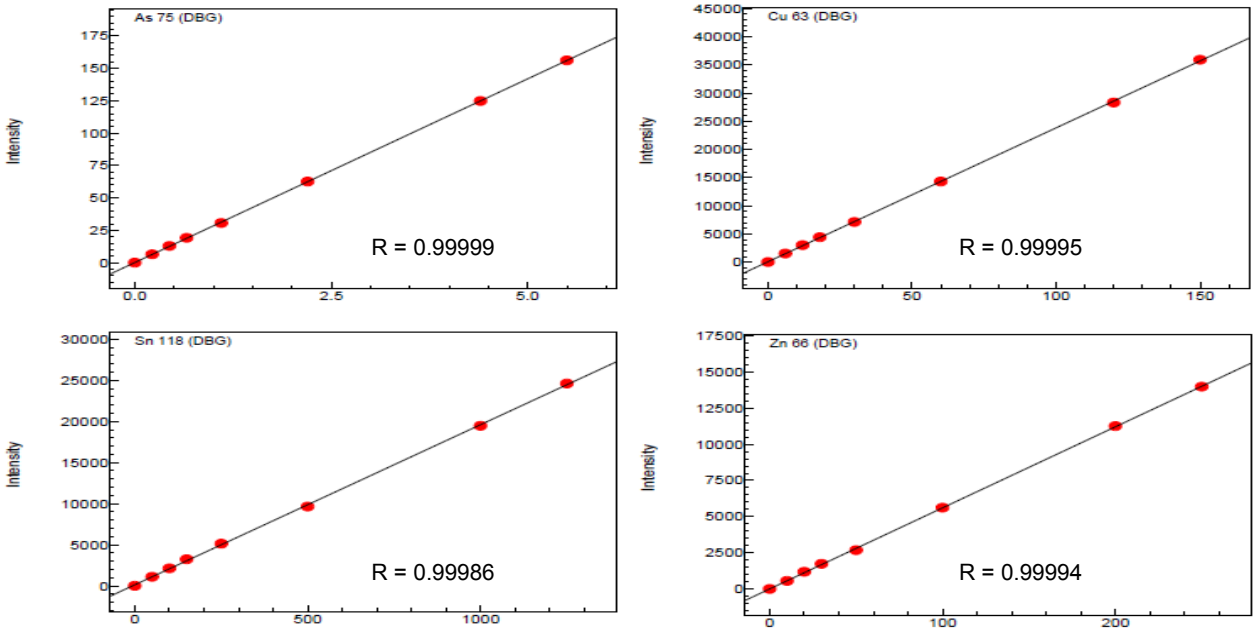

Fig 1 Typical calibration curves obtained during analysis of milk powder

The element Zn was found to be present in the sample, this presence can be attributed to the fact that some elements are fortified in the food matrices to increase their nutritional value. The precision and recovery of the method was tested by aspirating 4 replicates of spike recoveries at 20 % and 200 % of the MRLs. The results of recovery are given in Table 6. It can ne seen that % RSD was less than 10 % showing good repeatability of the developed method. The % recoveries were between 70 to 120 %, which is in good accordance with the AOAC[3] guidelines.

In order to check drift and robustness of the plasma conditions and uptake of sample throughout the sequence, Quality control check (QC Check) samples were run in between the sequence. The initial calibration verification check (ICV) were run just after completion of the calibration, the continuous calibration verification checks (CCV) were run after running recovery samples. Their % recoveries are given in Table 7. The recovery ICVs was between 90-110 %, which is in good acceptance with AOAC. The recovery of CCVs was between 85-115.

The stability of the response of CCVs for complete run of the sequence demonstrated the robustness of the plasma generated using a plasma gas flow of 10 L/min.

Conclusion

Trace metals in milk powder sample were analysed following FSSAI guideline using ICPMS-2030 combined with online internal standard addition kit. Highly sensitive, selective & accurate ICPMS method was developed for milk powder. The repeatability and reproducibility achieved in the present method ensures that the use of lower plasma flow does not compromise the sensitivity and precision required to analyze food matrices like milk powder.

Table 5. Measured concentrations of the elements in milk powder sample

Element	As	Cd	Hg	Pb	Cu	Sn	Zn
Concentration in ppm	Below LOQ	Below LOQ	Below LOQ	Below LOQ	Below LOQ	Below LOQ	23
LOQ In ppm	0.22	0.30	0.20	0.004	6	50	10

Table 6. The % recoveries and precision obtained in the present study

Element	Day 1				Day 2			
	20 % of MRL		200 % of MRL		20 % of MRL		200 % of MRL	
	Average	% RSD	Average	% RSD	Average	% RSD	Average	% RSD
As	119.7	1.4	117.0	3.5	113.8	0.5	113.7	1.6
Cd	104.0	0.8	94.8	1.8	97.3	3.2	97.4	1.3
Hg	112.8	0.9	115.9	3.0	96.3	2.0	98.5	1.6
Pb	107.9	4.8	109.0	3.4	95.4	6.9	99.3	2.5
Cu	105.1	2.6	106.0	4.5	105.4	1.2	105.7	1.2
Sn	116.8	1.5	107.9	3.9	114.3	1.5	106.8	1.4
Zn	97.6	7.3	109.6	4.3	104.7	6.2	106.7	4.3

Table 7. The % variations in the QC checks

Element	DAY 1			DAY 2		
	ICV	CCV 1	CCV 2	ICV	CCV1	CCV2
As	96.8	99.3	99.5	104.5	101.1	101.1
Cd	98.2	93.5	85.5	102.8	103.3	101.5
Hg	100.0	102.8	113.3	98.0	95.5	99.5
Pb	100.0	103.6	109.5	100.6	97.9	103.9
Cu	96.7	96.7	99.5	104.2	103.3	103.5
Sn	105.0	102.0	102.4	108.0	107.0	109.0
Zn	99.0	98.5	103.0	104.0	98.0	101.0

References

[1] Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2011
[2] Food Safety and Standards (Contaminants, Toxins and Residues) Third Amendment Regulations, 2016
[3] AOAC Official Method 2015.01, Heavy Metals in Food

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