

Determination of Toxic Elements in Chilli Powder using Shimadzu ICPMS-2050

Amol Ramishte, Mangesh Pawar, Saroj Mataprasad, Amol Shinde, Sampada Khopkar, Jitendra Kelkar, Pratap Rasam
Shimadzu Analytical (India) Pvt. Ltd., 5th Floor, ABR Emerald, Plot No. D-8, Street no. 16, MIDC, Andheri (E), Mumbai-400093, Maharashtra, India.

1. Overview

Spices, particularly red chillies, are essential and integral part of cuisines, offering not only distinctive flavour and aroma but also provides nutritional and preservative benefits. However, the growing concern of heavy metal contamination in chillies presents a significant threat to food safety, public health, and international trade. Effective monitoring and stringent quality control are essential to safeguard consumer well-being and maintain economic stability



Figure 1 *Red Chilli powder*

2. Introduction

This study details a precise ICPMS method for quantifying toxic elements in chilli powder, developed in strict adherence to Food Safety and Standards Authority of India (FSSAI)¹ regulations. The complex matrix of chilli powder presents significant analytical challenges for the accurate and efficient recovery of trace heavy metal elements. The presence of diverse organic compounds and high oil content can interfere with standard digestion procedures, leading to suboptimal extraction efficiencies and compromised analytical recovery of critical elements such as lead, cadmium and arsenic.

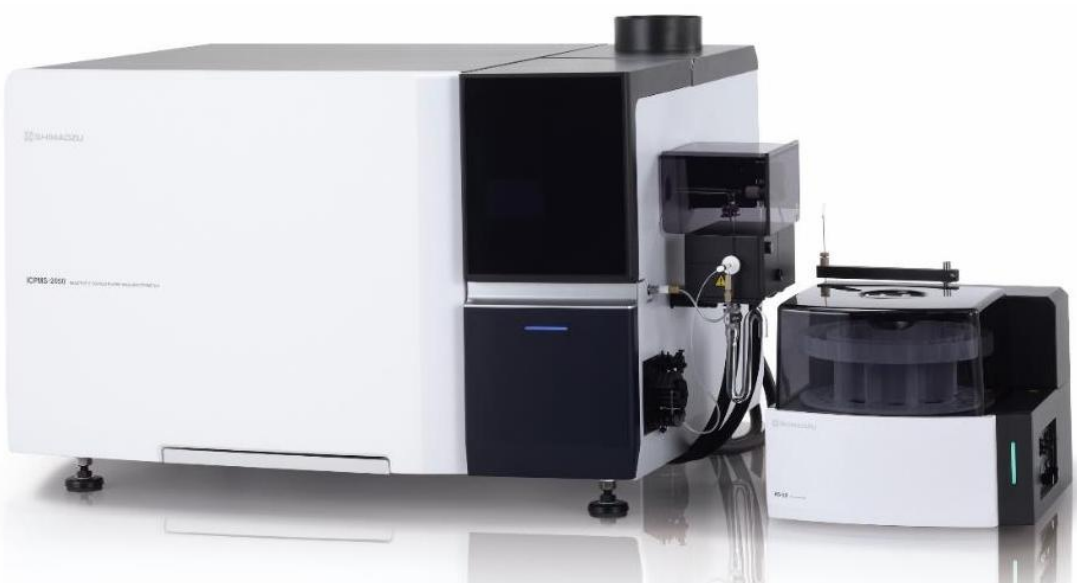


Figure 2 *ICPMS-2050*

3. Materials and methods

For this study, NIST traceable standards of elements were used for quantitation. Chilli samples were purchased from local market of two different brands (Brand 1 & Brand 2) and utilized for analysis. Ultrapure grade acids and water were used for digestion and dilution respectively, to avoid elemental contamination.

3-1. Method

An optimized sample preparation method involving microwave digestion (Make: Preekem) with nitric acid was developed and validated. Precision study and spike recoveries were analysed for both brands of chilli sample.

3-2. Sample, spike and standard preparation

• Standard preparation

An intermediate mix elemental stock of 0.5 ppm was prepared using NIST traceable 1000 ppm standards of As, Cd, Hg and Pb. The linearity standards of concentration level 0.5, 1.0, 2.5, 5.0, 10 & 20 ppb were prepared.

• Sample Preparation

Transferred 0.1 g red chilli powder sample in PTFE vessels, added 4 mL of suprapure nitric acid and 2 mL suprapure hydrogen peroxide in it. The solution was kept as it is for pre-digestion for 10 mins. Further the solutions were heated in microwave digestion as per program in Table 1.

Table 1: Microwave digestor program

Ramp (min)	Hold temperature (°C)	Hold time (min)
10	120	2
5	160	2
10	190	30

After digestion, the content was cooled and quantitatively transferred to 50 mL polypropylene volumetric flask containing 0.5 mL of 10 ppm gold (Au) as matrix modifier and diluted up to the mark with ultrapure water. Filtered the solution with 0.45 um of nylon syringe filter. This is the sample test solution. The samples were prepared in six replicates

• Spike Preparation (0.25 ppm)

Transferred 0.1 g red chilli powder sample in PTFE vessels, added 0.05 mL of 0.5 ppm mix elemental standard stock solution. Further added 4 mL of suprapure nitric acid and 2 mL suprapure hydrogen peroxide in it. The solution was kept as it is for pre-digestion for 10 mins. Further the solutions were heated in microwave digestion as per program in Table 1.

After digestion, the content was cooled and quantitatively transferred to 50 mL polypropylene volumetric flask containing 0.5 mL of 10 ppm gold (Au) as matrix modifier and diluted up to the mark with ultrapure water. Filtered the solution with 0.45 um of nylon syringe filter. This is the sample test solution. The spike samples were prepared in six replicates.

0.1 ppm of internal standards was measured by using online internal standard kit. All blank, standard & sample solutions consist of 0.1 ppm of gold solution.

Table 2: LOQ summary

Elements	FSSAI Limits (ppm)	Targeted LOQ at 25% of FSSAI limit (ppm)	LOQ achieved (ppm)
As	1.1	0.275	0.250
Cd	1.5	0.375	0.250
Hg	1.0	0.250	0.250
Pb	2.5	0.625	0.250

Spike recoveries achieved were 4 times or lower of FSSAI limits for individual elements.

3-3. Analytical Conditions

Table 3: Instrumental parameters

Plasma condition	Set value
RF Power	1.2 Kw
Sampling depth	5 mm
Plasma gas (Ar)	9.0 L/min
Auxiliary gas (Ar)	1.10 L/min
Carrier gas (Ar)	0.85 L/min
Collision cell gas (He)	6 mL/min
Cyclone chamber temp.	5 °C
Replicates	3

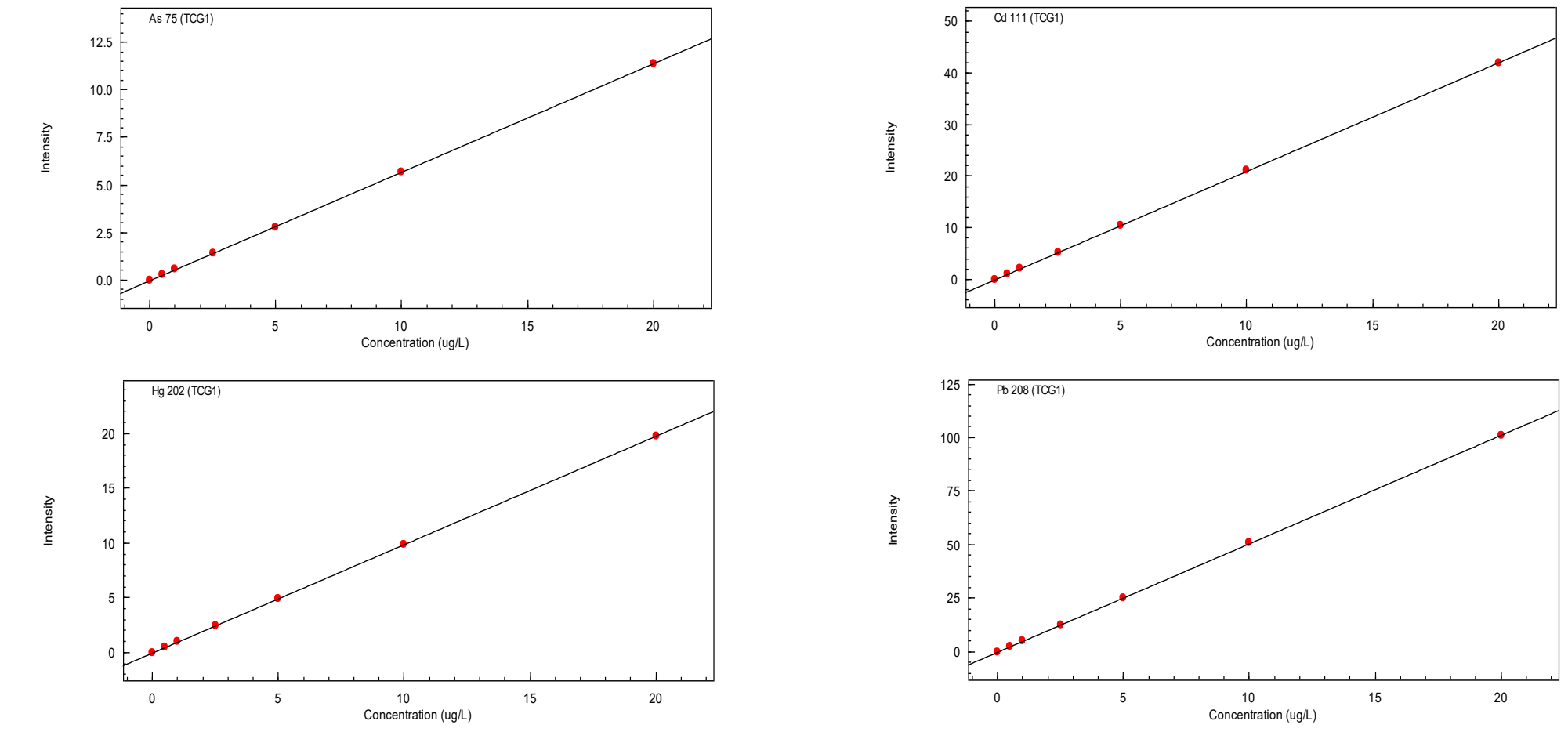


Figure 3 *Calibration Curves*

Table 4: R value, Instrument LOD & LOQ

Element	Mass	r	LOD/3S (ppb)	LOQ/10S (ppb)
As	75	0.99997	0.0314	0.1047
Cd	111	1.00000	0.0086	0.0286
Hg	202	1.00000	0.0025	0.0085
Pb	208	1.00000	0.0015	0.0051

Table 5: Recovery % at 0.250 ppm spiked in sample (Method LOQ)

Exp. No.	Sample	As	Cd	Hg	Pb
Day 1	Brand 1	98.5	95.5	112.4	94.6
	Brand 2	103.5	99.9	109.3	110.3
Day 2	Brand 1	89.2	84.9	84.7	84.9
	Brand 2	105.3	94.4	98.2	93.4

Table 6: RSD_r for precision study at 0.250 ppm spiked in sample (3 replicates/aspiration)

	Sample Name	As	Cd	Hg	Pb
Day 1	Brand1 – 1	5.67	2.67	1.13	1.21
	Brand1 – 2	6.59	6.89	1.2	1.24
	Brand1 – 3	2.66	8.36	3.8	1.5
	Brand1 – 4	8.3	2.11	1.88	0.92
	Brand1 – 5	1.87	4.79	0.91	0.82
	Brand1 – 6	15.64	4.11	2.32	0.86
	Brand2 - 1	4.15	1.64	0.53	0.57
	Brand2 – 2	9.37	3.92	2.62	0.76
	Brand2 – 3	6.71	5.1	2.52	0.77
	Brand2 – 4	10.17	1.41	1.41	1.58
	Brand2 – 5	2.3	4.04	2	0.83
	Brand2 – 6	2.17	7.37	3.24	0.68
Day 2	Brand1 – 1	12.71	5.29	2.85	0.93
	Brand1 – 2	2.23	4.96	2.61	0.7
	Brand1 – 3	13.06	3.88	0.7	0.97
	Brand1 – 4	4.57	6.52	0.8	1.55
	Brand1 – 5	7.05	0.81	2.66	1.78
	Brand1 – 6	8.09	6.04	1.97	0.81
Day 2	Brand2 - 1	5.1	5.9	1.92	0.85
	Brand2 – 2	15.98	6.92	1.12	0.17
	Brand2 – 3	13.07	2.85	2.07	0.65
	Brand2 – 4	11.85	5.47	2.47	0.52
	Brand2 – 5	8.83	4.47	2.68	0.9
	Brand2 – 6	7.51	4.97	0.06	0.75

Table 7: RSD_R for precision study at 0.25 ppm spiked in sample (6 separate preparations)

Exp. No.	Sample	As (%)	Cd (%)	Hg (%)	Pb (%)
Day 1	Brand 1	9.09	4.98	5.18	5.33
	Brand 2	3.86	2.89	1.65	1.54
Day 2	Brand 1	8.77	6.29	7.49	5.44
	Brand 2	4.81	2.83	3.46	3.79

Table 8: %recovery in QC checks performed by aspirating 5 ppb standard solution

Exp. No.	QC Check	As (%)	Cd (%)	Hg (%)	Pb (%)
Day 1	ICV	98.2	101.8	101.0	100.6
	CCV 1	96.8	96.6	98.2	99.6
	CCV 2	100.4	97.6	98.4	100.8
Day 2	ICV	99.2	97.8	99.0	100.2
	CCV 1	99.4	101.0	98.6	100.0
	CCV 2	102.0	95.6	93.8	99.6

ICV – Initial calibration verification, CCV – Continuous calibration verification

4. Results

Quantitation results for As, Cd, Hg & Pb in chilli samples found to be BLOQ. Validation parameters like linearity, recovery and precision were studied to establish LOQs. This method successfully achieved LOQ of 0.250 ppm in sample. The summary results and system stability are shown in Table 4, 5, 6, 7 & 8 respectively. As per FSSAI guideline.

BLOQ – Below limit of quantitation, LOQ – Limit of quantitation

4-1. Linearity

NIST traceable calibration standards were used for linearity study and quantification of spiked samples. Six level calibrations curve was plotted for 0.5, 1.0, 2.5, 5.0, 10 & 20 ppb concentration levels. For all calibration standards accuracy was found within 80 to 120 % range.

4-2. Recovery

Recovery was studied at 0.250 ppm spiked samples against calibration curve. Six preparations for each brand of samples were prepared. Mean recoveries were found to be within 80 -120 % at LOQ level (Refer Table 5).

4-3. Precision

For precision, repeatability and within-laboratory reproducibility studies were carried out. **RSD_r**: The % RSD for 3 replicates of each sample aspiration at LOQ (0.250 ppm) levels was found to be less than 20 % (Refer Table 6). **RSD_R**: Reproducibility experiment for recoveries was performed on 6 different spiked samples at 0.250 ppm concentration levels. The % RSD of 6 spiked samples at their respective LOQ level was found to be less than 10 % (Refer Table 7).

5. Conclusion

- This study demonstrates that the Shimadzu ICPMS system is a reliable and effective instrument for quantifying toxic elements in chilli powder samples.
- Because of the complex nature of chilli powder, higher dilution factor needed to be applied in conjunction with Shimadzu's Octa-plate Collision Cell technology to minimizes spectral interferences for achieving lower LOQs.
- The Shimadzu ICPMS enables trace-level detection in samples, contributing to enhanced method ruggedness and ensuring consistent, reproducible analyte detection.
- The combination of a highly sensitive instrument and a robust analytical method makes it well-suited for use in testing laboratories for the analysis of toxic elements in chilli powder.

6. Reference

- Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2011.