Determination of Heavy Metals in Chinese Herbal Medicines Using MP-AES and ICP-MS

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Abstract

All around the world, people use Chinese herbal medicines for their perceived medical benefits. Some are now worried that arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg) and chromium (Cr) are present in these products. The purpose was to measure these heavy metals in three types of herbal products using two methods, microwave plasma-atomic emission spectroscopy (MP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS). Data was obtained for nitric acid sample digestion by preparing and testing methods using standard values. MP-AES was not very sensitive, and its results were not consistent when determining As. By contrast, the results produced by ICP-MS were highly precise and very sensitive. For ICP-MS, using the internal standard (IS) resulted in strong calibration curves (R^2>0.9980) and improved reproducibility. What we found shows that ICP-MS is best for trace metal analysis in herbal matrices, while MP-AES appears to have some limitations for this purpose.

Keywords

Chinese herbal medicines, Heavy metal content determination, Microwave plasma-atomic emission spectroscopy, Inductively coupled plasma-mass spectrometry

Introduction

Chinese herbal medicines (CHMs) form an essential component of traditional healthcare practices, particularly in East and Southeast Asia. The Encyclopedia of Traditional Chinese Medicinal Substances documents over 5,700 herbal, mineral, and animal-based compounds used in these formulations. With rising global interest in complementary and alternative medicine, CHMs have gained traction for addressing both physical and psychological conditions. However, their safety has come under scrutiny due to repeated findings of contamination with heavy metals - most notably As, Cd, Pb, Hg, and Cr.

These toxic elements are known for their severe long-term health risks, including neurotoxicity, nephrotoxicity, reproductive harm, and carcinogenic effects [1]. In response, regulatory agencies such as the Therapeutic Goods Administration (TGA) in Australia have imposed strict limits on permissible concentrations of heavy metals in herbal products (TGO 101). The results are compared against the maximum allowable limit. These limits are: As (2.0 ppm), Cd (1.0 ppm), Pb (5.0 ppm), and Hg (0.2 ppm). Cr is also monitored due to potential toxicity at elevated levels.

Trace metal analysis in herbal matrices poses unique challenges due to the complexity of organic compounds, potential interferences, and variable extraction efficiency. MP-AES is often employed for elemental screening due to its cost-effectiveness and minimal gas consumption. However, its detection limits (~ppm) are frequently inadequate for trace-level contaminants. ICP-MS, on the other hand, offers superior sensitivity (ppt-ppb range), wide elemental coverage, and capacity for internal standard correction to minimize matrix effects [2].

The purpose of this study is as follows:

(1) Measuring heavy metal concentrations in three

CHM samples using both MPAES and ICP-MS.
(2) Validating calibration curves for both methods.
(3) Assessing instrument performance, particularly precision and sensitivity, for regulatory-grade testing of CHMs.

Materials and methods

This study analyzed three herbal samples: Radix Astragalis (sample 1), organic turmeric from Coles (sample 2), and organic turmeric from Nature's Way (sample 3). Approximately 0.1 grams of each sample was weighed and subjected to acid digestion. The digestion process involved treating each sample with 10 mL of concentrated nitric acid and heating it at 140°C for 90 minutes using a hot block digester. Once cooled, each digest was diluted to a final volume of 50 mL with deionized water and filtered to remove particulates. Prior to analysis, a ten-fold dilution was performed for both the MP-AES and ICP-MS methods.

For the MP-AES analysis, an Agilent 4200 instrument was used. Calibration standards ranged from 0.10 to 20.00 ppm. All measurements were taken on a single day, and the target analytes included arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), and chromium (Cr). For ICP-MS analysis, an Agilent 7900 ICP-MS was utilized. Calibration curves were prepared from 0.01 to 10.00 ppb, and internal standard (IS) calibration was applied to improve measurement reliability. The instrument was optimized for oxide ratio (CeO/Ce<3%), RF power, nebulizer gas flow, and sample depth. The interface cones were also cleaned, and torch alignment was performed to ensure plasma consistency.

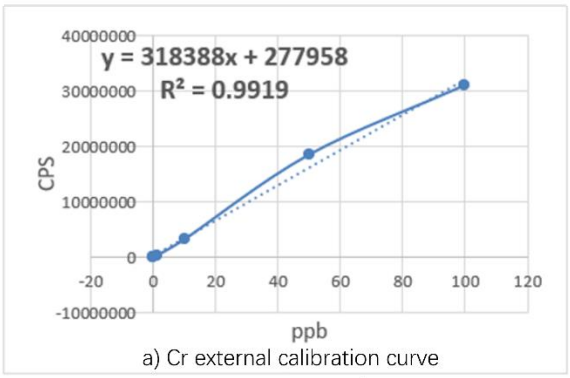
Validation criteria included linearity (R^2>0.9980), determination of limits of detection (LOD) and quantification (LOQ), and precision studies. Intraday and interday repeatability were assessed by calculating the relative standard deviation (RSD), with targets of <10% for intraday and <20% for interday.

Results and discussion

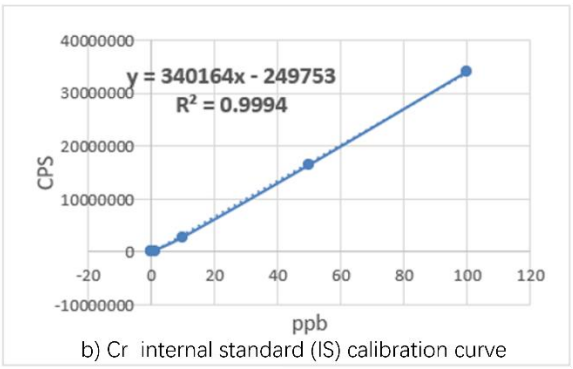
Comparison of MP-AES and ICP-MS analytical performance

The MP-AES method produced highly limited and inconsistent results across all three herbal samples. Among the five heavy metals tested - As, Cd, Pb, Hg, and Cr. Only As was detected, and even that detection was poorly reproducible. The As calibration curve yielded a low R^2 value of 0.7700, indicating poor linearity and significant instrumental or matrix-related noise. Signal intensities fluctuated markedly between replicates, resulting in relative standard deviations (RSDs) well above the acceptable intraday threshold of 10%. Probable causes for these shortcomings include the inherently low sensitivity of MP-AES at subppb levels, matrix interference from complex organic compounds (particularly from turmeric), sample introduction issues such as torch misalignment or nebulizer malfunction, and potential carry-over contamination between samples. These limitations are consistent with previous literature, which has demonstrated MP-AES's inadequacy for trace-level analysis in complex biological matrices like herbal medicines [3]. Consequently, ICP-MS was selected as the primary method for metal quantification in this study.

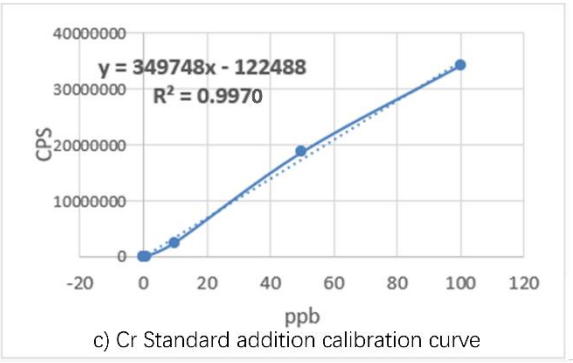
In contrast, ICP-MS provided highly reliable and precise results. To determine the most effective calibration approach, three methods were evaluated: external calibration, internal standard (IS) calibration, and standard addition calibration. Calibration curves for Cr, shown in Figure 1, exemplify the relative performance of these strategies. While all methods demonstrated strong linearity, the internal standard approach achieved the highest R^2 value (0.9994) and offered the most consistent results. This method confirms its superiority in trace element quantification within complex sample matrices.



a) Cr external calibration curve



b) Cr internal standard (IS) calibration curve



c) Cr Standard addition calibration curve

Figure 1. Calibration curves through three different methods for the analysis of Cr. a) Cr external calibration curve, b) Cr internal standard (IS) calibration curve, c) Cr Standard addition calibration curve.

Table 1 presents a comprehensive comparison of calibration parameters - including R^2 values, limits of detection (LOD), and limits of quantification (LOQ) - for all five elements across the three methods. The internal standard method consistently produced the lowest LODs and LOQs and demonstrated robust quantification in the presence of complex sample matrices. These findings align with Parvathy, who emphasized the advantages of internal standard correction in mitigating matrix effects and instrumental drift in ICP-MS workflows [4].

R^2 values, LODs, LOQs, and sample concentrations are presented for arsenic (As), lead (Pb), mercury (Hg), chromium (Cr), and cadmium (Cd) using external calibration, internal standard, and standard addition methods. ND = not detected. NA = not analyzed.

For instance, Table 1 shows that As and Cd exhibited LODs of 0.01 ppb and 0.02 ppb, respectively, when analyzed using the internal standard method. These values are 7-fold and 4.5-fold lower than those derived from external calibration. Notably, for Pb in complex herbal sample matrices (which contain abundant plant fibers and secondary metabolites), the LOQ of the external calibration method increased by 15% due to matrix interference. In contrast, the internal standard method maintained stable quantification performance without such deviations [5].

Table 1. Comparison of ICP-MS calibration methods for five elements.

Method	Element	R^2	LOD (ppd)	LOQ (ppd)	Sample 1 (ppm)	Sample 2 (ppm)	Sample 3 (ppm)
External	As	0.9978	0.01	0.04	0.020	0.020	0.020
External	Pb	0.9953	0.00	0.01	ND	ND	ND
External	Hg	1.0000	0.01	0.04	5.000	5.100	4.200
External	Cr	0.9919	0.00	0.01	ND	ND	ND
External	Cd	0.9962	0.01	0.02	ND	ND	ND
Internal	As	0.9990	0.00	0.01	0.430	0.010	1.400
Internal	Pb	0.9988	0.00	0.01	26.800	17.900	23.400
Internal	Hg	0.9996	0.01	0.03	1.890	2.300	0.100

Method	Element	R^2	LOD (ppd)	LOQ (ppd)	Sample 1 (ppm)	Sample 2 (ppm)	Sample 3 (ppm)
Internal	Cr	0.9994	0.00	0.01	9.500	18.200	22.800
Internal	Cd	0.9992	0.00	0.01	1.420	1.280	1.450
Std Add	As	0.9978	0.07	0.02	0.040	NA	NA
Std Add	Pb	0.9976	0.00	0.01	0.460	NA	NA
Std Add	Hg	0.9988	0.08	0.25	0.280	NA	NA
Std Add	Cr	0.9970	0.00	0.01	0.003	NA	NA
Std Add	Cd	0.9966	0.02	0.07	0.060	NA	NA

Since internal standard calibration performed well, it was used for all further quantification steps. Over the three days, the results for all five elements consistently showed strong linearity (R^2 was greater than 0.9980) in calibration. All samples showed that chromium (Cr) had the most reliable and consistent results and its RSD was always much lower than 10%. Lead (Pb) and arsenic (As) exhibited a moderate range of variations, but mercury (Hg) and cadmium (Cd) varied a lot more, especially in turmeric samples. Such inconsistencies may occur because of persistent matrix effects or unstable sample digestion efficiency. As seen in Table 2, the internal standard method is reliable because it has good R^2 values, LODs, LOQs, sample concentrations and RSDs for each metal.

Table 2. Intraday calibration and quantification results for ICP-MS using internal standard method.

Element	Day	R^2	LOD (ppd)	LOQ (ppd)	Sample 1 (ppm)	RSD (%)	Sample 2 (ppm)	RSD (%)	Sample 3 (ppm)	RSD (%)
Cr	Day1	0.9984	0.05	0.15	9.50	8.9	18.20	10.5	22.80	7.4
	Day2	0.9990	0.07	0.21	8.50	9.9	20.00	11.0	19.60	6.3
	Day3	0.9999	0.03	0.09	11.40	5.5	24.50	6.8	18.10	5.4
Pb	Day1	0.9970	0.18	0.54	26.80	8.3	17.90	7.6	23.40	9.2
	Day2	0.9976	0.12	0.36	30.20	6.2	24.09	9.2	22.06	7.5
	Day3	0.9984	0.15	0.45	27.71	8.2	27.94	7.0	28.68	8.1
Cd	Day1	0.9979	0.12	0.36	1.42	13.0	1.28	8.0	1.45	6.2
	Day2	0.9990	0.14	0.42	0.98	19.4	1.45	9.9	1.28	3.7
	Day3	0.9995	0.01	0.20	1.19	8.6	1.37	6.7	1.21	13.5
As	Day1	0.9989	0.13	0.39	0.43	11.3	ND	NA	1.40	5.9
	Day2	0.9992	0.10	0.30	0.69	13.6	1.12	12.3	2.30	5.7
	Day3	0.9996	0.08	0.23	1.68	12.1	1.42	14.6	1.90	13.2
Hg	Day1	0.9986	0.13	0.39	1.89	14.3	2.30	27.0	0.10	9.8
	Day2	0.9994	0.10	0.30	0.69	16.4	1.45	15.3	0.45	21.0
	Day3	0.9997	0.09	0.26	2.28	9.1	1.21	8.9	0.89	14.6

Cr was the best performer when it came to interday reproducibility, since the RSDs for all three herbal samples were below 16.0%. There was a lot of variability in Hg and As from one day to the next, especially in Radix Astragalis, with RSDs over 35.0% in most cases. Although Cd was found in every sample of turmeric, it showed a high RSD of 66.0% (Coles). This means that ICP-MS can measure trace elements well, though some analytes in herbal mixtures sometimes make it hard to maintain reproducibility [6]. Table 3 gives a summary of the average concentrations and interday RSDs for every

element and each sample.

Table 3. Interday calibration summary using internal standard method.

Sample	Hg (ppm)	RSD (%)	Cd (ppm)	RSD (%)	Pb (ppm)	RSD (%)	Cr (ppm)	RSD (%)	As (ppm)	RSD (%)
Radix Astragalis	1.60	45.0	1.20	26.0	28.20	6.0	9.80	14.3	0.93	71.0
Turmeric, Coles	1.70	35.0	1.37	66.0	23.30	22.0	20.90	15.5	0.85	88.0
Turmeric, NW	0.40	39.0	1.31	9.0	24.70	14.0	20.20	12.0	1.87	24.0

Comparison with previous studies and regulatory standards

The results of our interday analysis reveal levels of heavy metal contamination in Chinese herbal medicines (CHMs) that are both concerning and consistent with findings from the literature [7-9]. For example, lead (Pb) concentrations in Radix Astragalis reached 28.20 mg/kg, with turmeric samples showing 23.30 and 24.70 mg/kg -all exceeding Australia's Therapeutic Goods Order No. 101 (TGO 101) limit of 5.00 mg/kg for Pb. This aligns with findings by Kong, who reported Pb levels up to 35.50 ± 32.00 mg/kg in CHM products [10].

Arsenic (As) was detected in all samples, with turmeric from NW showing 1.87 mg/kg, a value below the TGO 101 threshold of 2.00 mg/kg, yet relatively close to the upper limit. Wang reported As concentrations up to 3.20 mg/kg, indicating our findings fall within expected ranges for CHM products.

Mercury (Hg) also exceeded the regulatory limit of 0.20 mg/kg in all three samples, ranging from 0.40 to 1.70 mg/kg in our interday data. Liu similarly identified Hg as a persistent concern in Chinese patent medicines, reinforcing the need for strict monitoring [11].

While cadmium (Cd) and chromium (Cr) do not appear to exceed current TGO 101 limits - 1.0 mg/kg for Cd and no specific regulatory limit for Cr - the interday precision varied. Cd showed RSDs as high as 66.0%, particularly in the turmeric from Coles, which had a concentration of 1.37 mg/kg, marginally above the TGO 101 threshold. Cr concentrations were relatively high (9.80-20.90 mg/kg) but with better interday reproducibility (RSDs<16.0%), making them the most technically reliable results in the dataset.

Overall, these findings reflect a consistent pattern in CHM contamination, as described across various studies, and highlight the necessity for routine ICP-MS-based monitoring and tighter quality control in herbal product regulation.

Conclusion

The study testes the accuracy of both MP-AES and ICP-MS for finding heavy metals in Chinese herbal medicines. MP-AES doesn't detect at very low levels, whereas ICP-MS with internal standard calibration provided high sensitivity, linearity and accuracy. Both arse-nic and Cr concentrations are within Australian TGO 101 limits, yet all the CHM samples go past the permitted levels for Hg and Pb. The Cd concentration is almost at the acceptable level in single sample. Cr showed good precision from day to day in all the samples examined. The findings agree with earlier research and prove that ICP-MS is the best choice for regulatory testing. Future studies should use a broader range of CHMs, try matrix-matched calibration and put stronger quality control systems in place to keep the public safe.

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Conflicts of Interest

The authors declare no conflict of interest.

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