QUANTIFICATION OF TRACE ELEMENTS IN TEA LEAVES USING ICP-MS

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Abstract: *In recent years, the ICP-MS method has been applied to analyze biological and environmental samples. The content of several metallic elements, namely Al, Ba, Sr, Mn, Fe, Cu and Zn in green tea leaves (Camellia sinensis L.) collected from Son La province was analyzed using the ICP-MS method. The method demonstrated high sensitivity, as indicated by low values of limits of detection (LOD) and limits of quantification (LOQ). The accuracy of the method was evaluated through spiked experiments, with values ranging between 89% and 105%. The distribution of elements in the green tea samples collected from Son La followed the sequence: Mn > Al > Fe > Zn > Ba > Cu > Sr.*

Keywords: *Trace element, Son La tea leaves, ICP – MS.*

1. INTRODUCTION

Tea, derived from the leaves of Camellia sinensis L., is the second most consumed beverage worldwide, following water. Tea leaves contain a wide range of compounds, including polyphenols, alkaloids, amino acids, carbohydrates, proteins, chlorophyll, minerals, trace elements, and various other compounds (Chen et al., 2015) [3]. The elemental composition of tea leaves can be influenced by several factors, such as the plant's location, plant variety, fertilizer usage, farming methods, and storage conditions. Consumption of tea has been associated with potential benefits in combating skin cancer, prostate cancer, and lung cancer (Khan et al., 2013) [9].

Son La is a significant tea-producing region in Vietnam, particularly known for Ta Xua tea, an ancient tea variety with high economic value. Moc Chau, on the other hand, boasts a large area dedicated to tea cultivation, with tea trees that have been growing for several years. Analyzing the elemental content in tea leaves serves as a basis for assessing tea quality.

The analysis of metal content in tea samples has been conducted using various pectroscopic methods, including flame atomic absorption spectrometry (FAAS) (Podwika et al., 2018) [13], graphite furnace atomic absorption spectrophotometry (GFAAS) (Zhong et al., 2016) [20], inductively coupled plasma optical emission spectrometry (ICP OES) (Zhong et al., 2016) [20], and inductively R coupled plasma mass spectrometry (ICP-MS) (Hamza et al., 2021 [5]; Thao N. T. et al., 2018 [17]). Among these techniques, ICP-MS is widely recognized as a highly effective method for determining metal content in samples, offering exceptional detection capabilities with low detection limits, as well as superior selectivity and sensitivity. This technique allows for the simultaneous determination of multiple elements present in low concentrations within the samples (Pasvanka et al., 2021) [11].

The spectroscopic method has been applied to analyze the metal content in tea samples, such as flame atomic absorption spectrometry (FAAS) (Podwika et al., 2018) [13], graphite furnace atomic absorption spectrophotometry (GFAAS) (Zhong et al., 2016) [20], inductively coupled plasma optical emission spectrometry (ICP - OES) (Pasvanka et al., 2021) [11] and inductively coupled plasma mass spectrometry

(ICP - MS) (Hamza et al., 2021 [5]; Thao N. T. et al., 2018 [17]). ICP-MS is considered a very potent discriminant technique regarding metal content in samples since itprovides high detection power due to low detection limits as well as high selectivity and sensitivity. This technique also provides the simultaneous determination of several elements present in low concentrations in the samples (Pasvanka et al., 2021) [11].

2. MATERIALS AND METHODS

2.1. Reagents and chemicals

All chemical products were purchased from Merck and were of the highest quality. The standard stock solutions (1000 mg/L) for the ICP-MS measurements were obtained from Merck. De-ionized water (18.2 MΩ-cm) was sourced from a Milli-Q water purification system. Glassware was cleaned using a 10% HNO3 solution and rinsed several times with deionized water.

2.2. Instrumental analysis

All analyses were conducted using a NexION 2000 ICP-MS instrument (Perkin Elmer, USA) equipped with an automatic sampling system operated by a peristaltic pump. The analysis was carried out employing the Kinetic Energy Discrimination (KED) mode. The instrumental parameters for the analysis are presented in Table 1.

2.3. Sample collection

Fourteen green tea samples were collected from various tea plantations in Son La province, Vietnam. The tea samples were obtained in the form of fresh leaves, including buds and two young leaves. The tea leaves were first washed with tap water, followed by a rinse with distilled water, and then dried at 80°C until a constant weight was achieved. Subsequently, the dried tea leaves were ground into a powder and stored at a low temperature.

Table 1. Operating conditions for the ICP-MS instrument

Parameters	Value
Sample aspiration rate	300 µL/min
Mist chamber (Quartz) temperature	25^{o}C
Mode	Kinetic Energy Discrimination (KED)
Heli gas flow	5.5 mL/min
RF power	1600W
Plasma gas flow	15L/min
Auxiliary gas flow	1.2L/min
Nebulizer gas	1L/min
Nebulizer	PFA
Spray chamber	Glass cyclonic
Sample cone	Nickel sample cone
Cell entrance voltage	-7 V
Cell exit voltage	-32 V
Monitored ion	Sn^{+} (m/z 118)
Measurement mode	Peak hopping
Dwell time	50 ms
Analytical masses (amu)	^{27}Al, ^{55}Mn, ^{56}Fe, ^{65}Cu, ^{66}Zn, ^{88}Sr, ^{138}Ba

2.4. Sample preparation analysis with acid digestion

The tea samples underwent acid digestion prior to analysis. 250 mg of tea sample was transferred into a 100 mL beaker, followed by the addition of 5.0 mL of 65% HNO3 solution and 5.0 mL of 70-72% HClO4 solution. The mixture was gently heated until complete decomposition of the sample, resulting in a moist white salt. After cooling to room temperature, the sample was dissolved, filtered through a 0.45 µm filter paper, and brought up

to a final volume of 25 mL using 1% HNO3 solution. A blank sample was prepared in a similar manner, replacing 250 mg of tea with 250 mL of doubly deionized water.

3. RESULT AND DISCUSSION

3.1. Data analytical methods results

To construct a calibration curve, a series of standard solutions with concentrations of 1 g/L, 5 µg/L, 10 g/L, 25 g/L, and 50 µg/L were analyzed. The accuracy of the analytical method was validated by performing quality control using the standard substances. The Limit of Detection (LOD) and Limit of Quantification (LOQ) were calculated using the formulas LOD = 3.3σ/S and LOD = 10σ/S, respectively, where σ represents the standard deviation of the response and S denotes the slope of the calibration curve.

The results from Table 2 show that, the LODs value from 0.42 to 5.88 µg/L, the LOQs value from 4.29 to 17.82 µg/L.

Table 2. Analytical methods results

Element	Slope	Intercept	LOD (µg/L)	LOQ (µg/L)	R^2
Al	14.72	32.69	5.88	17.82	0,993
Mn	518.43	201.72	1.48	4.29	0.999
Fe	1314.70	59.99	2.02	6.12	0.999
Cu	1811.90	329.53	0.87	2.64	0.999
Zn	359.90	1599.30	5.22	15.81	0.994
Sr	383.09	– 43.18	1.74	5.27	0.999
Ba	2622.50	41.14	0.42	1.27	1,000

3.2. Recovery

The validity of the proposed procedure was assessed using the standard addition method on the MC2 tea sample. Known amounts of trace elements were added to 250 mg of the tea sample and subjected to digestion. The recovery of the added trace elements was calculated using formula (3.1), and the obtained recoveries ranged from 89% to 105% (Table 3). The recovery performance met the satisfactory criteria set by AOAC.

$$\text{Recovery (\%)} = \frac{100(C_f - C_u)}{C_a} \quad (3.1)$$

where C_f: the concentration of fortified samples, C_u: the concentration of unfortified samples, and C_a: the concentration of analyte added to the test sample.

3.3. Sample analysis

The quantification of total elements in tea leaves was performed using ICP-MS, employing the operational parameters specified in Table 1. The distribution pattern of labile elements analyzed in all green tea leaves followed the sequence: Mn > Al > Fe > Zn > Ba > Cu > Sr. This trend aligns with findings reported by previous authors (Karak et al., 2010 [8]; Zhang et al., 2018 [19]). The results are presented in Table 4.

Table 3. Recovery efficiency of the analytical procedure

Element	Added (µg/L)	Total (µg/L)	Recovery (%)
Al	-	28.24	-
	5	32.84	92
	10	38.05	98
Mn	-	23.59*	-

	5	28.68	102
	10	33.39	98
Fe	-	17.03	-
	5	21.83	96
	10	27.13	101
Cu	-	16.39	-
	5	21.04	93
	10	26.29	99
Zn	-	22.39	-
	5	27.64	105
	10	32.09	97
Sr	-	14.38	-
	5	23.38	90
	10	23.88	95
Ba	-	8.72	-
	5	13.17	89
	10	17.82	91

***** Samples for analysis of Manganese content were diluted 5 times

Table 4. Analysis of content element in tea leaves (mg/kg)

Samples	Mn	Al	Fe	Zn	Cu	Ba	Sr
MC1	741.92	260.22	61.88	31.85	13.64	13.04	14.95
MC2	1179.39	282.44	85.14	33.58	16.39	4.36	7.19
MC3	1239.37	273.67	86.60	34.69	15.23	11.97	8.40
MC4	923.03	281.94	81.48	31.28	15.58	6.10	7.61
MC5	918.55	201.70	67.41	39.79	14.62	7.04	9.14
MC6	613.33	189.20	65.76	27.67	14.55	12.12	10.56
MC7	576.47	171.43	65.47	35.83	13.04	12.57	6.99
MC8	558.81	185.02	66.17	31.62	14.93	8.00	7.39
BY1	762.75	562.71	61.47	23.99	13.01	26.75	15.50
BY2	554.34	296.06	98.34	31.78	13.68	22.22	11.09
BY3	499.58	206.73	59.37	26.40	14.39	12.60	9.11
BY4	603.27	398.04	72.33	29.45	15.17	22.90	14.92
BY5	629.64	793.67	52.55	20.65	14.28	37.28	34.68
BY6	871.07	433.18	125.32	26.01	12.74	13.26	9.37
Mean	**762.25**	**324.00**	**74.95**	**30.33**	**14.38**	**15.02**	**11.92**

The manganese content in the 14 green tea samples collected from Son La province exhibited a range of 499.58 to 1239.39 mg/kg, with an average value of 762.25 mg/kg. These findings are consistent with the results published by Brzezicha et al. (Brzezicha et al., 2016) [2], who reported manganese concentrations ranging from 390 to 1260 mg/kg in 41 samples of various tea types. However, higher manganese concentrations were reported by Podwida et al. (Podwika et al., 2018) [13], with values ranging from 2210 to 3475 mg/kg in 27 samples of different tea types.

The aluminium content in green tea from Son La ranged from 171.43 to 793.67 mg/kg. N. T. Thao et al. reported that the aluminium

content in 10 samples of green tea from Yen Bai, Vietnam, ranged from 456.97 to 2454.48 mg/kg, and in 9 samples from Tuyen Quang, Vietnam, it ranged from 241.23 to 739.61 mg/kg (Thao N. T., 2018) [17]. The aluminium content in Son La tea samples was similar to that of Tuyen Quang, Vietnam, and lower than that of Yen Bai, Vietnam. In the study conducted by R. Street et al., the aluminium content in 29 tea samples from the Czech Republic was higher than the aluminium content found in this study (Street et al., 2007) [15].

Iron content in 14 tea samples from Son La province ranged from 52.55 to 125.32 mg/kg. The iron content observed in this study was lower than that reported by R. Street et al., which ranged from 103 to 523 mg/kg (Street et al., 2006) [16]. However, the iron levels in this study were higher compared to other publications (Jalbani et al., 2007) [7]. Similar findings were reported by Thao N. T. et al. for 10 tea samples from Yen Bai province, Vietnam, with a range of 47.99 to 75.36 mg/kg, and 9 tea samples from Tuyen Quang province, Vietnam, with a range of 64.98 to 112.48 mg/kg (Thao N. T. et al., 2018) [17].

Zinc is a crucial trace element that plays a vital role in numerous structural proteins, enzymatic processes, and transcription factors. It is involved in various functions, including cell-mediated immunity, bone formation, tissue growth, brain function, as well as the growth of the fetus and child (Bagherani et al., 2016) [1]. In this study, the zinc content ranged from 20.65 to 39.79 mg/kg, which was higher than the zinc content reported in six Japanese green teas by Islam et al. (range 14.7 – 26.4 mg/kg) (Islam et al., 2012) [6]. Similar zinc content was also reported by H. Deka et al. in Indian tea samples, with a range of 20.2 – 35.1 mg/kg and a mean of 26.79 mg/kg (Deka et al., 2021) [4].

Copper is vital for essential life processes such as energy metabolism, detoxification of reactive oxygen species, iron uptake, and signaling in eukaryotic organisms (Ruiz et al., 2021) [14]. In the Son La tea samples, the copper content ranged from 12.74 to 16.39 mg/kg, with a mean of 14.38 mg/kg. The copper content observed in this study was lower than that reported by Deka et al. (Deka et al., 2021) [4] (13.4 – 22.73 mg/kg) and Street et al. (Street et al., 2007) [15] (9.0 – 65.0 mg/kg for the group of 30 samples). A lower mean copper content of 8.18 mg/kg was published in the study conducted by Yao et al. (Yao et al., 2022) [18] for Tieguanyin Tea samples from Fujian, China.

The content of barium (Ba) in the tea samples from Son La ranged from 4.36 to 37.28 mg/kg, with a mean value of 15.02 mg/kg. The barium content in Moc Chau tea samples was lower compared to that in Bac Yen tea samples. The barium content in this study was similar to the value reported by Pinto et al., which was 16.63 mg/kg (Pinto et al., 2020) [12]. However, the barium content in this study was lower than that found in 10 samples of Yen Bai tea, Vietnam, which ranged from 13.42 to 57.66 mg/kg (Thao N. T. et al., 2018) [17].

The content of strontium (Sr) in this study ranged from 6.99 to 34.68 mg/kg, with a mean value of 11.92 mg/kg. The strontium content in the 14 samples of Son La tea was lower than that in samples consumed in Senegal, which ranged from 20 to 90 mg/kg (Mbaye et al., 2013) [10].

4. Conclusion

The ICP-MS method was utilized to simultaneously analyze the elemental composition of tea leaves collected in Son La. This method demonstrated a LOD and LOQ, along with a satisfactory recovery efficiency of 93% to 105%, meeting the requirements for trace analysis. The distribution of elements in the green tea samples followed the sequence: Mn > Al > Fe > Zn > Ba > Cu > Sr. These findings are consistent with previous publications on the subject.

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REFERENCES

1. Bagherani N. and Bruce S., 2016. An overview of zinc and its importance in dermatology- Part I: Importance and function of zinc in human beings. *Global Dermatology*. 3(5): 337-350.
2. Brzezicha C. J., Grembecka M. and Szefer P., 2016. Monitoring of essential and heavy metals in green tea from different geographical origins. *Environmental Monitoring and Assessment*, 188(3):183.
3. Chen, Z. M. and Z. Lin, 2015. Tea and human health: biomedical functions of tea active components and current issues. *J Zhejiang Univ Sci B*, 16(2):87-102.
4. Deka H., Barman T., Sarmah P. P., Devi A., Tamuly P., Karak T., 2021. Impact of processing method on selected trace elements content of green tea: Does CTC green tea infusion possess risk towards human health? *Food Chemistry: X*, 12:100173.
5. Hamza A., Bahaffi S. O., Abduljabbar T. N., and El-Shahawi M. S., 2021. Trace determination and speciation of elements in green tea. *Results in Chemistry*, 3:100081.
6. Islam M.A., Ebihara M., 2012. Elemental characterization of Japanese green tea leaves and tea infusion residue by neutron-induced prompt and delayed gamma-ray analysis. *Arabian Journal of Chemistry*.
7. Jalbani N., Tasneem G. Kazi, Bilal M. Arain, M. K. Jamali & Hassan I. Afridi, 2007. Evaluation of total contents of Al, As, Ca, Cd, Fe, K, Mg, Ni, Pb, Zn and their fractions leached to the infusions of different tea samples. A multivariate study. *Chemical Speciation and Bioavailability*, 19(4):163-173.
8. Karak T, Bhagat R. M., 2010. Trace elements in tea leaves, made tea and tea infusion: A review. *Food Research International*, 43(9):2234-2252.
9. Khan N. and Mukhtar H., 2013. Tea and health: studies in humans. *Curr Pharm Des*, 19(34):6141-6147.
10. Mbaye M., Traoré A., Ndao A, S., and Wagué A., 2013. Classification of tea consumed in Senegal using XRF techniques and chemometric based on their country of origin. *African Journal of Agricultural Research*, 8(44):5522-5529.
11. Pasvanka K., Kostakis M., Tarapoulouzi M., Nisianakis P., Thomaidis N. S. and Proestos C., 2021. ICP–MS Analysis of Multi-Elemental Profile of Greek Wines and Their Classification According to Variety, Area and Year of Production. *Separations*, 8(8):119.
12. Pinto G., Illiano A., Carpentieri A., Spinelli M., Melchiorre C., Fontanarosa C., Martino di Serio and Amoresano A., 2020. Quantification of Polyphenols and Metals in Chinese Tea Infusions by Mass Spectrometry. *Foods*, 9: 835.
13. Podwika W., K. Kleszcz, M. Krosniak and P. Zagrodzki. 2018. Copper, Manganese, Zinc, and Cadmium in Tea Leaves of Different Types and Origin. *Biol Trace Elem Res*, 183(2):389-395.
14. Ruiz H., Lina, Allan Libedinsky and Alvaro Elorza. 2021. Role of Copper on Mitochondrial Function and Metabolism. *Frontiers in Molecular Biosciences*, 8:711227.

15. Street Renée, Ondrej Drabek, Jirina Száková and Lenka Mladkova, 2007. Total content of aluminum in tea leaves and tea infusions. *Food Chemistry*, 104(4):1662-1669.

16. Street Renée, Jirina Száková, Ondrej Drabek and Lenka Mládková, 2006. The status of micronutrients (Cu, Fe, Mn, Zn) in tea and tea infusions in selected samples imported to the Czech Republic. *Czech Journal of Food Sciences*, 24(2):62-71.

17. Thao N. T, Mai. T. T., 2018. Determination of metal content in tea leaves grown in Yen Bai and Tuyen Quang provine. *Vietnam Journal of Science and Technology*, 55(5A):143 - 150.

18. Yao Q., Minmin Huang, Yunyun Zheng, Meizhen Chen, Chongyao Huang and Qiu Lin, 2022. Prediction and Health Risk Assessment of Copper, Lead, Cadmium, Chromium, and Nickel in Tieguanyin Tea: A Case Study from Fujian, China, *Foods* 11(11): 1593.

19. Zhang J., Yang R., Chen R. ,Peng Y., Wen X., and Gao L., 2018. Accumulation of Heavy Metals in Tea Leaves and Potential Health Risk Assessment: A Case Study from Puan County, Guizhou Province, China. *Int J Environ Res Public Health*, 15(1): 133.

20. Zhong W. S., Ren T., and Zhao L. J., 2016. Determination of Pb (Lead), Cd (Cadmium), Cr (Chromium), Cu (Copper), and Ni (Nickel) in Chinese tea with high-resolution continuum source graphite furnace atomic absorption spectrometry. *J Food Drug Anal*, 24(1):46-55.

ĐỊNH LƯỢNG CÁC NGUYÊN TỐ HÀM LƯỢNG VẾT TRONG LÁ CHÈ SỬ DỤNG ICP-MS

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Tóm tắt: *Trong những năm gần đây, phương pháp ICP-MS đã được ứng dụng để phân tích các mẫu sinh học và mẫu môi trường. Hàm lượng một số nguyên tố kim loại Al, Ba, Sr, Mn, Fe, Cu và Zn trong lá chè xanh (Camellia sinensis L.) thu hái từ tỉnh Sơn La được phân tích bằng phương pháp ICP-MS. Phương pháp này thể hiện độ nhạy cao, được biểu thị bằng các giá trị giới hạn phát hiện (LOD) và giới hạn định lượng (LOQ) thấp. Độ chính xác của phương pháp được đánh giá thông qua các thí nghiệm với mẫu thêm chuẩn, với các giá trị nằm trong khoảng từ 89% đến 105%. Sự phân bố các nguyên tố trong các mẫu trà xanh thu hái tại Sơn La theo trình tự: Mn > Al > Fe > Zn > Ba > Cu > Sr.*

Từ khóa: *Nguyên tố vi lượng, lá chè Sơn La, ICP – MS.*

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